

CYCLICS IN POLYESTER AND POLYPHOSPHATE SYSTEMS

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Doctor in Philosophy at the University of York

by

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Among ears of corn, whatever the kind,
you will not find one just like another;
but each will be marked by some distinctive
feature. The same holds good of the various
shells we see adorning the bosom of the
land where the sea with pliant ripples laps
on the thirsty sands of its winding shore.
Here, then, is proof upon proof that in the
stream of atoms likewise, since they exist
in nature and are not hand-made to a fixed
pattern, there are certain individual
differences of shape.

Lucretius, "On the Nature of Things"
(Translated by R.E. Latham).

ABSTRACT

A method is described for the extraction of the oligomeric content of poly(ethylene terephthalate). Evidence is presented that the extracts from high molecular weight polymer are mixtures of cyclic oligomers, forming a series from trimer to at least undecamer. The mixtures are analysed by gel permeation chromatography, supplemented by a mathematical treatment of the chromatographic tracings. If polymer of low initial cyclic content is heated in the melt at 270°C., the cyclic concentrations increase to those of a ring-chain equilibrium. The cyclisation equilibrium constants, in moles of cyclic/dm³, are $K_3 = 0.0317$; $K_4 = 0.0103$; $K_5 = 0.0054$; $K_6 = 0.0040$; $K_7 = 0.0028$; $K_8 = 0.0021$; $K_9 = 0.0013$; the relative uncertainties are 15% for K_3 , increasing to 40% for K_9 . The constants in the melt at 300°C. and in solution at 250°C are similar. The concentrations are diminished by heating the polymer as a solid; this is attributed to exclusion of the rings from the crystalline regions. The melt concentrations are higher than predicted by the theory of Jacobson and Stockmayer, applied in conjunction with current rotational isomeric state models of poly(ethylene terephthalate) chains. Short chains of this polymer do not conform to Gaussian statistics. It is argued that the cyclics adopt special favourable conformations.

Low molecular weight extracts obtained from prepared samples of poly(decamethylene adipate) and poly(ethylene succinate) are shown to be mixtures of cyclic oligomers. By gel permeation chromatography, the extract from the first polymer is resolved into species from monomer to pentamer, those from the second into dimer to heptamer.

The experimental concentrations of the metaphosphates in sodium phosphate melts are discussed in relation to the conformations of the polyphosphate chains. A rotational isomeric state model is set up for the chains, taking into account Coulombic and steric interactions between atoms up to eight bonds apart. Molar cyclisation equilibrium constants of the metaphosphates are calculated.

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CHAPTER 1

INTRODUCTION.

1.1 CYCLIC MOLECULES IN POLYCONDENSATION SYSTEMS

It has long been recognised that, in any system where intermolecular polycondensation reactions are proceeding, with the combination of bifunctional reactants into chains of progressively higher molecular weight, there is always a certain probability that a particular chain will instead undergo an intramolecular reaction, to a cyclic product; and further, that the relative proportions of linear and cyclic species must be determined by both the ease of formation of the rings concerned, and the extent to which the intermolecular condensations are retarded by diluting the reactants. Striking examples of such behaviour were noted at an early stage, for the polyesterification of hydroxy-carboxylic acids: depending upon the number of carbon atoms separating the hydroxyl and carboxyl groups in the acid, it will yield primarily long-chain polyesters, primarily a low molecular weight cyclic ester (monomer or dimer), or a mixture of rings and chains. Quantitative investigations of the cyclisation behaviour of these acids were first undertaken by Stoll and Rouvé¹, some forty years ago.

It became clear, also, that cyclic species could appear in polycondensates even though polymerisation had ceased, and though the linear molecules corresponding to the rings being generated were present in negligible amounts. For a variety of cases, the proper conditions of temperature and catalyst could bring about bond interchange reactions

within and between polymeric chains, leading to the formation of the cyclics. Carothers^{2,3} showed that if the ring compounds were removed as they formed (specifically, by volatilisation) then polymeric samples could be continuously converted to cyclics. On the other hand, heating the rings with catalyst would often result in their transformation to polymer.

Since the work of Stoll and Rouvé on hydroxy-acids, studies have been made of the concentrations of cyclic species in a range of polycondensation systems. Of these, the variously substituted polysiloxanes have been subject to a particularly thorough examination⁴⁻¹⁰; a recent extension of these investigations concerns a polymer in which there is an alternation of siloxane and paraffinic segments.¹¹ Polyamides of different types^{12,13,14}, a polyether¹⁵, and a polyurethane^{16,17}, have been studied. Attention has also been given to polyesters, derived from the reaction of alkane diols with both aliphatic¹⁸ and aromatic¹⁹⁻²⁵ diacids. As for inorganic polymers, the cyclic content of sulphur has been discussed²⁶, and several measurements have been made of the concentrations of the ring metaphosphates in polyphosphate melts and glasses^{27,28}.

The value of such investigations will be immediately evident, insofar as there can clearly be no full description of a polycondensation system, unless knowledge of the distribution of linear molecules according to chain length is complemented by information on the distribution of cyclic molecules according to size. Their usefulness, however, goes beyond the determination of the cyclic concentrations as mere experimental parameters; for, excepting those cases where the purely geometrical constraints of bond lengths and angles effectively

exclude its formation, a ring will be present in amounts determined largely by the conformational behaviour of the open chain from which it (at least formally) derives. The theoretical link between the ring concentration, and the chain shape, is offered in the analysis of Jacobson and Stockmayer²⁹ (as well as that of Kuhn³⁰); and it is by application of this theory to the experimental results that it might be hoped to gain insight into the conformational characteristics of the polymer chains. Such insight would be the more valuable, in that ring concentrations may be determined under a range of conditions, and corresponding to a range of chain lengths, not necessarily accessible to other methods of investigating chain conformations.

Hence, examination of the cyclic content of polycondensates may be regarded as serving two purposes: the first, to determine the ring concentrations, for their own sake; the second, to probe the conformations of the polymeric chains.

Both these aspects figure in the studies to be described in this thesis. The concern of the Chapters immediately succeeding this is an experimental investigation of the concentrations of cyclic oligomers in poly(ethylene terephthalate), and also in two polyesters derived from aliphatic diacids; since for the first system, it was possible to determine the cyclic concentrations characteristic of a state of equilibrium between the rings and the chains, it was permissible to proceed further, to the use of the Jacobson-Stockmayer theory in attempts at their interpretation. For the aliphatic polyesters, on the other hand, it proved possible to do no more than demonstrate the existence of the series of cyclic oligomers, and devise means for their analysis; it was not feasible to determine their concentrations at

equilibrium. The final Chapters concern reconciliation of the known concentrations of metaphosphates in sodium phosphate melts with available information on the structure of the polyphosphate chains.

1.2 EXPERIMENTAL DETERMINATION OF CYCLIC CONCENTRATIONS

The procedure by which the concentrations of cyclic species may be determined comprises several steps:

(a) Since in most samples, the rings are present in too small an amount to permit their proper analysis in situ, a method must be found for their quantitative extraction from the polymer. For many cases, there are convenient solvent/non-solvent systems that render this step straightforward, provided the molecular weight of the chain fraction is sufficiently high; this is so for the aliphatic polyesters studied, but not for the poly(ethylene terephthalate), for which the successful extraction of the rings is difficult.

(b) It is, of course, necessary to confirm that the extracted material is indeed a mixture of the cyclic oligomers of the polymer under consideration. This requires a thorough examination of the properties of the extracts, or of the individual components, if these are separable, and comparison with the properties of such standard compounds as may be obtained synthetically. Such tests will rarely provide absolutely conclusive evidence that every one of the components of the mixture is a cyclic oligomer; but they can nevertheless give strong support to a contention that this is the case.

(c) A technique must be available for the quantitative resolution of the overall extract into the individual ring species. In a number

of instances, notably the polysiloxanes and the polyethers, analysis of the extracts may be accomplished with facility by the method of gas chromatography. For other cases, including those to be considered here, but also those of the polyamides and polyurethanes, the low volatility of the rings prohibits the worthwhile use of this technique; then, resort must be had to different means, such as those of adsorption chromatography, or (as here) gel permeation chromatography.

If it is desired to measure concentrations of clear theoretical significance, then a further step must be introduced: the preparation of samples in which the dynamic equilibrium between rings and chains has been attained. (While it is true that some insight can be won from results obtained under the correct non-equilibrium conditions, their unambiguous theoretical interpretation is frequently difficult; see below.) Discovery of conditions of temperature and catalyst that will permit equilibration, while avoiding degradation of the polymer, may be an obstacle; and, indeed, this was so for the polyesters, both aliphatic and aromatic.

1.3 THEORETICAL INTERPRETATION OF CYCLIC CONCENTRATIONS

The discussion in this Section will reflect the studies to be described later, insofar as it will centre on the rationalisation of equilibrium cyclic concentrations, and will give relatively little attention to the treatment of situations where the concentrations are determined by non-equilibrium factors. There are two reasons why this is the case: the first may be dealt with at once, but consideration of the second will be deferred until towards the end of this Section.

The experimental results of Stoll and Rouvé¹ on the cyclisation of hydroxy-acids at high dilution in benzene were expressed in terms of a "cyclisation constant", C , for each acid; this was defined as the ratio of the rate constant for the unimolecular cyclisation, to that for the bimolecular chain polymerisation reaction³¹. Now, the value of this constant will be determined by two factors: firstly, the frequency with which the reactive ends of the hydroxy-acid approach each other; secondly, the intrinsic reactivities of the groups for intramolecular cyclisation, compared to those for intermolecular condensation. If the carbon chain between the hydroxyl and carboxyl groups in the acid is sufficiently long, the groups in a molecule will be no more nor less reactive towards each other than towards the groups in other molecules³². Therefore, for such long chains, the constant C will depend only on the concentration of one end of the chain in the region around the other end; specifically, it may be shown equal to $W(\underline{0})N_A$, where N_A is Avogadro's Number, and $W(\underline{0})$ is a quantity discussed in greater detail below, the "density of end-to-end vectors" at \underline{r} , as \underline{r} approaches $\underline{0}$. Kuhn³⁰ pointed out that this means that, for very long chains, C will diminish roughly according to the inverse three-halves power of the number of atoms in the chain.

Since the magnitude of $W(\underline{0})$ is directly dependent upon the chain conformation^{32,33}, it may seem that the link between experiment and theory has been established. For so simple an interpretation, however, several conditions must be satisfied. Firstly, it must be true that the functional groups are equally susceptible to inter- and intramolecular reactions. Secondly, the kinetic laws governing the reactions must be well understood; for instance, in the case of the

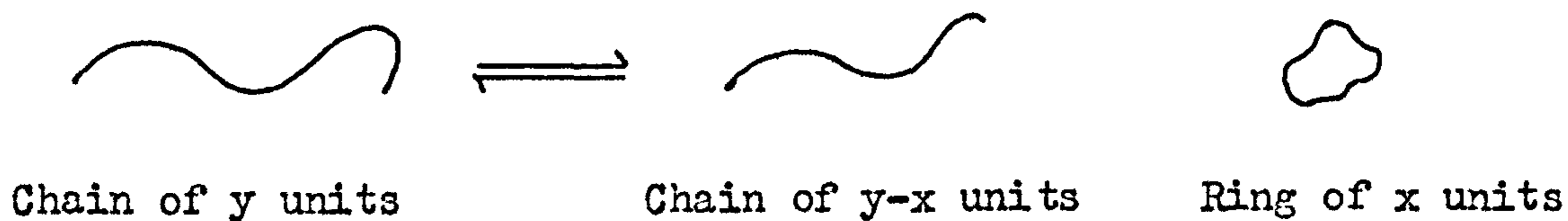
hydroxy-acids, addition of a strong acid catalyst was necessary to ensure that the cyclisation was indeed unimolecular, and the chain condensation bimolecular. Thirdly, the experimental conditions must conform to restrictive criteria. If the extent of reaction is not kept low, each of the chains that will be formed as the degree of polymerisation advances will undergo partial cyclisation; further, in some cases there will be the possibility that the cyclic products will be subject to significant back-reaction, leading to their incorporation into chains. Even if analytical methods are available for the thorough elucidation of the medley of inter- and intra- molecular reactions, the results will be hard to rationalise in the absence of powerful mathematical techniques^{16,17}.

It is true that some of these obstacles will not arise in a system where generation of the rings is by bond interchange within an already polymerised sample, with little change in the degree of polymerisation; but here the base of reference provided by the chain condensation in the work of Stoll and Rouvé would be lacking, and it would be necessary to make comparisons between the absolute rates of ring appearance and of overall bond interchange. Again, detailed information on the kinetic processes would be essential.

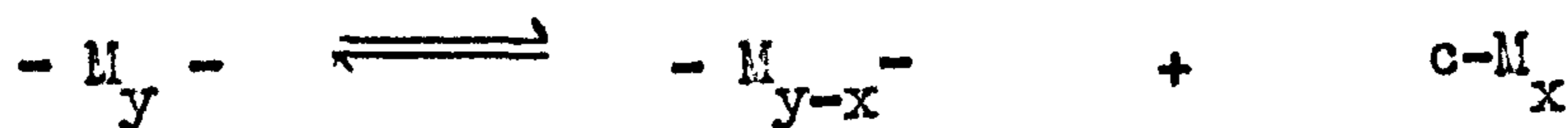
Measurement of the equilibrium concentrations presents the overwhelming advantage that, purely in principle, they are independent of the mechanism by which equilibrium has been attained, and are determined solely by the equilibrium states of the polymer and the rings themselves. Their interpretation rests upon the thermodynamic analysis of Jacobson and Stockmayer²⁹, which will now be described. Partly because it is couched in more recent notation, but also because

it introduces several valuable modifications, the account presented here will be that of Flory and Semlyen³⁴.

The equilibrium under consideration is that between a long chain (of y units, say), and a ring (of x units) together with the shortened chain ($y-x$ units);

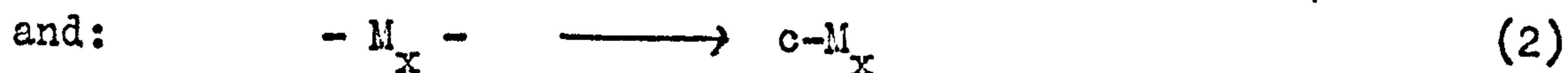


or, as it will be henceforth represented:



In the strictest terms, it should be acknowledged that for polycondensations of Flory's type ii, where there are two monomeric reactants (e.g. a diol and a diacid), the chains need not comprise integral numbers of repeat units, but can instead be made up of odd numbers of monomeric units³². The simplification that will be accepted here is that the repeat unit may be regarded as a composite monomer unit, so that the chains consist exclusively of completed repeat units. The error associated with this procedure is introduced in equation (8) below, with the ratio of the concentrations of the chains on either side of the equilibrium; provided that the monomeric reactants are present in closely equivalent amounts, and that reaction has proceeded to high molecular weight, it is found to be imperceptible. (See, also, Chapter 6.) With similar pre-conditions, the nature of the groups on the ends of the chains may also be ignored.

Since the mechanisms whereby the equilibrium is achieved are of no relevance, the reaction from left to right may be considered to consist of two steps:



where $-M_x-$ represents the open chain comprising the same number of repeat units as the cyclic.

The molar free energy change accompanying step (1) is written as:

$$\Delta G_1 = \Delta H_1 - RT \cdot \ln(4\pi V/N_A \sigma_a \cdot \delta r \cdot \delta \omega) \quad (3)$$

where N_A is again Avogadro's Number, ΔH_1 is the heat of dissociation of the bond ruptured, σ_a is the symmetry number for the acyclic species and V is the volume of the system, per mole of each species. δr is a small volume element, in which the ends of the two chains must meet for bond formation; similarly, $\delta \omega$ is a range of solid angle within which the terminal bonds must lie. Here, it is assumed that the existence of a bond between the chains demands not only that their ends are in close proximity, but also that they are at the correct mutual orientation; whereas in the absence of a bond the ends may be anywhere in the system, and at any angle to each other, with equal probability.

The intramolecular bond formed by step (2) will be equivalent to that ruptured in (1), unless the ring is so small as to be strained in

some way; hence the heat liberated upon its formation will equal that absorbed upon the breaking of the bond in the first step, i.e.

ΔH_1 . If $W_x(\underline{r})$ is the "density of end-to-end vectors"^{32,33} at a position defined by the vector \underline{r} , where the origin of the system of co-ordinates is situated at one end of the x-meric chain, then the probability that the other end lies within a volume element $\delta \underline{r}$ at that point will be $\delta \underline{r} \cdot W_x(\underline{r})$; so the probability that both ends lie within a volume $\delta \underline{r}$ and that bond formation will be possible will be given by $\delta \underline{r} \cdot W_x(\underline{0})$. For long chains, the relative orientation of the ends will be random, even when they come close to each other; therefore, the probability of fulfillment of the further condition of correct angle of approach of the termini will again be given by $(\delta \omega / 4\pi)$.

The molar free energy change for the step (2) may therefore be written as:

$$\Delta G_2 = -\Delta H_1 - RT \cdot \ln(W_x(\underline{0}) \cdot \delta \underline{r} \cdot \delta \omega \cdot \sigma_a / 4\pi \sigma_{R_x}) \quad (4)$$

(where σ_{R_x} is the symmetry number of the ring),

so that the overall free energy change for the equilibrium is:

$$\Delta G_{tot} = -RT \cdot \ln(V \cdot W_x(\underline{0}) / N_A \sigma_{R_x}) \quad (5)$$

$$\text{whence } K_x = W_x(\underline{0}) / N_A \sigma_{R_x} \quad (6)$$

K_x being the equilibrium constant for the reaction, in moles per unit volume. The relation between conformational behaviour and the cyclic concentration is completed by noting that:

$$[c-M_x] = K_x \cdot ([-M_y -] / [-M_{y-x} -]) \quad (7)$$

and that the ratio of the chain concentrations is given by the most probable distribution of Flory³² as equalling p^x , p being the "fractional extent of reaction of the functional groups"; so

$$\underline{[c-M_x] = W_x(0) \cdot p^x / N_A \sigma_{Rx}}$$

Several remarks may be made on this derivation:

(a) Whereas Jacobson and Stöckmayer treated the polymeric chains as freely-jointed, and therefore regarded the changes in conformational energy as purely entropic, in this derivation the enthalpic contribution to the conformational energy is acknowledged, in the use of the Gibbs free energy function in place of a simple entropy.

(b) The symmetry number of a chain equals the number of identical ends it possesses (e.g. two for a siloxane chain, but only one for a chain from a hydroxy-acid), while that of a ring equals the number of bonds per molecule capable of being broken to yield the open chain (e.g. $2x$, for an x -meric siloxane ring, but only x for an x -meric cyclic ester of a hydroxy-acid).

(c) The supposition that the energy for bond formation in (2) equals that for bond rupture in (1) depends not only upon the freedom of the ring from strain, but also upon the applicability of Flory's principle of equal reactivity³² to the corresponding chain. As intimated above (while discussing kinetically controlled systems) the functional groups may have different intra- and inter- molecular reactivities if

the chain is very short. Such effects will be more serious than small deviations of the high molecular weight fraction from Flory's most probable distribution, since the latter enters into the model only in the factor p^x , which will in any case often be close to unity.

(d) It will be noted that the volume element δr does not appear in the final equations (6) and (8). This does not signify, however, that for the intermediate equations the magnitude (or position) of δr is unrestricted. The derivation does not explicitly account for certain free energy changes that accompany the processes (1) and (2); it is tacitly assumed that in the overall reaction they are exactly cancelled. Specifically, the juxtaposition of the ends, their reaction once in proximity, and the relaxation of the newly-formed junction to its equilibrium condition, will all be accompanied by enthalpic and entropic changes not included in the equations (3) and (4). These changes will be equivalent for the inter- and intramolecular reactions only if there is a close similarity between both the environments within the two volume elements, and the distributions of the interacting ends within them. Indeed, this will be the case for very long chains; but it may not be so for short chains, where the overall disposition of the ends within the element during cyclisation may differ from that during the approach of two separate chains (see below), and where, even in the absence of conventional bond strain, the final conformational state in the region of the junction in the cyclic may depart from that of such a junction within a long chain. To give an example of the latter effect: the junctions in the smallest cyclics in the polysiloxane systems are found to be free from so many of the steric interactions present at the junctions within long chains that

it is necessary to carefully revise the conformational descriptions of the rings³⁵.

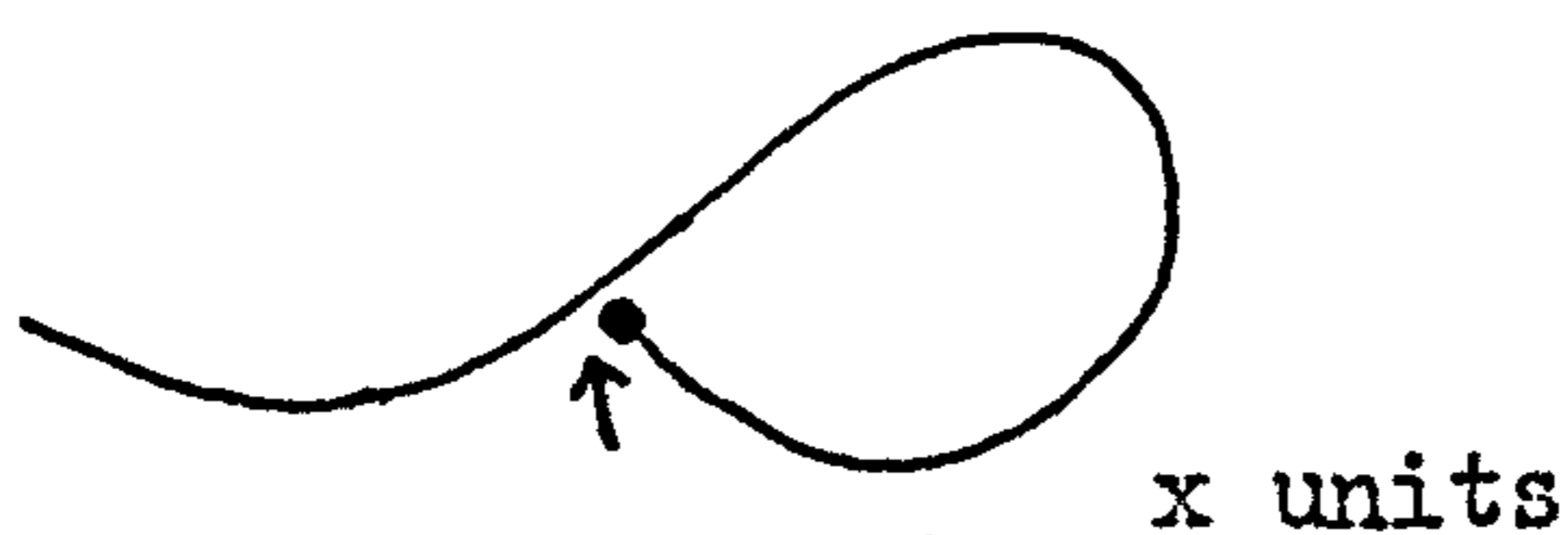
The magnitude and location of the volume element: $\delta \underline{r}$ are arbitrary, insofar as they are unrelated to any mechanistic considerations; but they are determined by the admissibility of the resulting thermodynamic cycle as a method of calculating the overall free energy change. Setting aside for the present the question of non-random angular distributions of the termini, it is plain that during the cyclisation step (2) the radial distribution of one end about the other must be sensibly uniform within the chosen element. If the element was centred on one end, but was made so large that $W_x(\underline{r})$ within it was no longer constant, but (say) diminished moving out from the centre, then there would be further changes in conformational free energy as ends moved from the peripheries into the correct juxtaposition for bonding; but the uniform concentration within the element for the intermolecular reaction would ensure that no parallel changes would occur in the step (1). Similar differences would arise if even a small element was put at a point in the system remote from the reactive end. Hence, the element should properly be considered as small and as placed at the final position, relative to one end, that will be occupied by the other. Furthermore, the volumes of the elements for the intra- and inter- molecular reactions must be considered identical; calculations³⁶ where two different volumes are employed, without accounting for the resulting discrepancies in the free energy changes, will give incorrect results.

(e) The condition that for bond formation the termini must lie within a solid angle $\delta \omega$ was an innovation by Flory and Semlyen designed

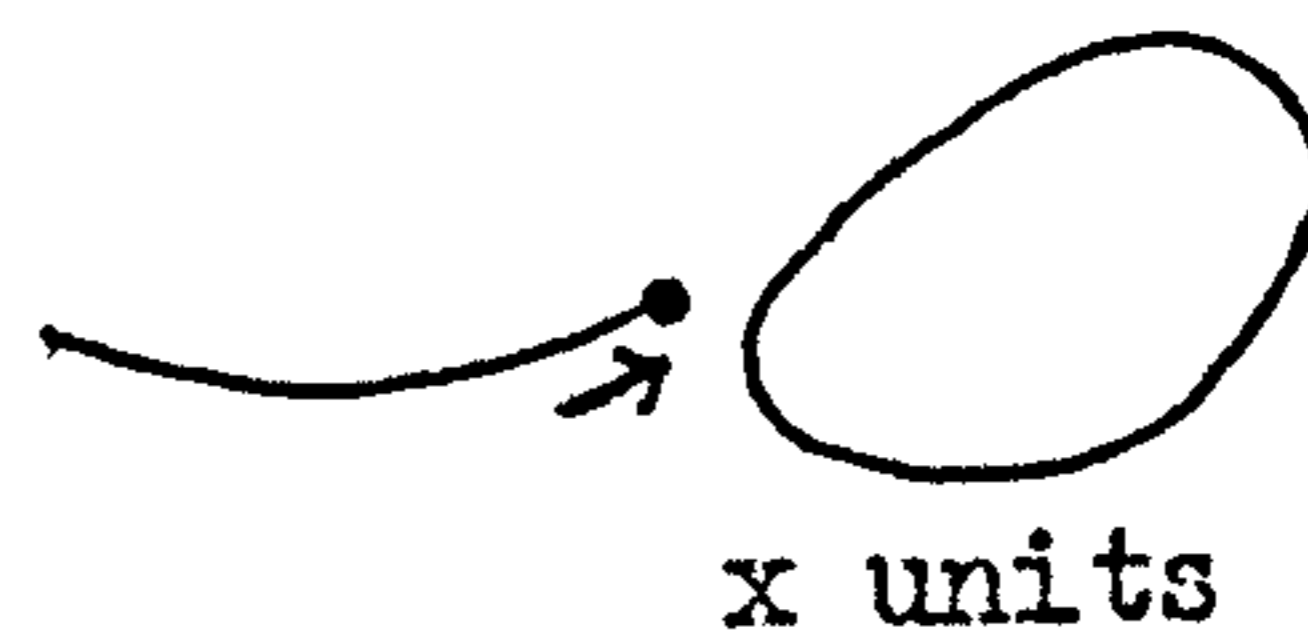
to pay formal regard to the possibility that the ends of a short chain may be non-randomly oriented with respect to each other, whereas in the intermolecular step (1) the relative orientation will always be random. (Jacobson and Stockmayer, deriving the theory for macrocyclics, were able to ignore this question.) The arguments applied here are analogous to those given in (d) above. In the final, bonded, condition, the termini will lie at a definite angle to each other. If in the cyclising step the ends within the volume element δr are non-randomly oriented, then the free energy change accompanying their adoption of the correct alignment will differ from that in the case of random orientation; expressed otherwise, the probability of the correct angle of approach will be different. It is to account for these differences that, in both steps, consideration is confined to those of the ends that lie at the correct mutual angle.

Particularly favourable angular approach for cyclisation has been put forward as a reason for the anomalously high equilibrium concentrations of the smaller cyclics in certain systems³⁴. It has not yet been possible to account for this "pointing effect" in quantitative terms, however; the angular parameters do not appear in the final equations (5), (6) and (8) above, since it was in fact necessary to restore the assumption (valid for very large rings) that the angular distribution was random. Nevertheless, there is hope that in the future it may prove possible to introduce factors that deal with the probability that the termini are correctly aligned for bond formation, in the same manner as there are at present those that account for the probability of their sufficiently close approach.

The Jacobson-Stockmayer relations can also be derived by kinetic arguments²⁹; the details of the derivation will now depend upon the mechanism(s) operating during equilibration. It might be, for instance, that ring formation is by a unimolecular bond interchange between an active end-group and a bond at an appropriate position further back down the chain, while the ring itself is continually re-absorbed into chains by similar attack upon its units:



Ring formation



Ring re-absorption

The probability that any particular chain possesses more than x units will be p^x . For such a chain, the density of the unit about to be attacked in the region of the active end will be $W_x(\underline{0})$ molecules/unit volume, or $W_x(\underline{0})/N_A$ moles/unit volume. If the molar concentration of the ends is $[E]$, and the specific rate constant for attack is k_f , then the rate of formation of the ring will be:

$$d [c-M_x] / dt = k_f [E] W_x(\underline{0}) p^x / N_A.$$

The rate of re-absorption will be given by:

$$- d [c-M_x] / dt = k_b [E] [c-M_x] \cdot \sigma_{Rx}$$

k_b being the constant for back-reaction. So, at equilibrium,

$$[c-M_x] = k_f W_x(\underline{0}) p^x / k_b \cdot N_A \cdot \sigma_{Rx}$$

or, if $(k_f / k_b) = 1$,

$$[c-M_x] = W_x(\underline{0}) p^x / N_A \cdot \sigma_{Rx}$$

which, of course, is identical to equation (8) above.

Such a treatment is adequate for large rings, and might indeed serve to clarify the thermodynamic analysis: but it lacks the adaptability of the thermodynamic approach to smaller rings, where deviations may arise. The thermodynamic treatment requires knowledge of only the initial and final states (the relative positions of the atoms, the angles between the bonds etc., for both chain and ring); but the kinetic treatment demands information on intermediate states. For instance, it would be impossible to account for non-random angular distributions of the termini during the cyclisation step. The position of the solid angle $\delta\omega$, within which the termini must approach, could be determined from the mechanism involved; but even then the correct juxtaposition and alignment will be those for a transition state, only, and yet more information would be needed for an understanding of the complete reaction. Failure to consider the full sequence of chemical processes will manifest itself as uncertainty in the ratio (k_f / k_b) ; on the other hand, the wealth of detailed mechanistic information needed for a proper calculation will necessarily be perfectly irrelevant to the final outcome.

Precisely similar argument hold for the non-equilibrium situations discussed first in this Section. Here, there would be great obstacles to the rationalisation of the concentrations of cyclics that failed to conform to the simple relation $C = W(\underline{0}) / N_A$.

It is now necessary to consider the dependence of the quantity $W_x(\underline{0})$ on the conformational characteristics of the polymer chains, and how it might be obtained for any chain. In these studies, two methods have been used for its calculations. They have in common that they both describe the chain conformations by a "Rotational Isomeric State Model" (RISM)³³. In this every bond is assumed to have open to it several discrete "rotational states", each corresponding to a specified angle of rotation (ϕ) about the bond, and each with a probability of occupancy determined by the associated energy. For many of the calculations, also, it is assumed that the energy of a bond in any state is independent of the states of the other bonds in the chain, beyond its nearest neighbours. In this case the chain may be treated as pairs of bonds, and the probability that the second member, b, of a pair is in a state q, out of n available, if the first a, is known to be in state p, out of m, can be expressed as the element (p,q) in a (m x n) "statistical weight matrix", \underline{U} :

$$\underline{U} = \begin{array}{c} \begin{array}{c} 1_a \\ 2_a \\ \vdots \\ m_a \end{array} \left| \begin{array}{cccc} 1_b & 2_b & \dots & n_b \\ d_{11} & d_{12} & \dots & d_{1n} \\ d_{21} & d_{22} & & \\ \vdots & & & \\ \vdots & & & \\ d_{m1} & & & \end{array} \right. \end{array}$$

In this matrix, the rows are indexed according to the state of the first bond in the pair, the columns according to that of the second; the elements are Boltzmann factors: $d_{pq} = \exp(-\Delta E_{pq}/RT)$, where ΔE_{pq} is the difference between the energy attributable to such a bond-pair in states p and q, and that of one where the bonds are both trans. Frequently there will be three symmetrically disposed states

for each bond: trans (t), gauche + (g+) and gauche- (g-): the convention is that the ϕ -values corresponding to these states are 0° , $+120^\circ$ and -120° , respectively. In this instance the first column of the \underline{U} -matrix will comprise elements of unity, and the whole matrix becomes thus:

$$\underline{U}_i = \begin{array}{c|ccc} & t_i & g_i^+ & g_i^- \\ \hline t_{i-1} & 1 & \sigma_i & \sigma_i \\ g_i^+ & 1 & \sigma_i \psi_i & \sigma_i \omega_i \\ g_i^- & 1 & \sigma_i \omega_i & \sigma_i \psi_i \end{array}$$

where σ_i represents the probability that the bond i is in a gauche state if $i-1$ is trans, $\sigma_i \psi_i$ that for i to be gauche if $i-1$ is in the gauche state of the same sign, $\sigma_i \omega_i$ that for i to be gauche if $i-1$ is in the gauche state of the opposite sign. To find the probability, or statistical weight, of an entire conformation, where all the bonds of a chain are in specified rotational states, it is simply necessary to proceed along the entire sequence of bonds, take them pair-wise, and multiply together the statistical weight elements corresponding to the states of each pair.

Now, Flory and Jernigan^{37,33} have devised matrix methods whereby, given the \underline{U} -matrix for each bond, together with certain structural data, the mean-square separation of the ends of a polymer chain may be calculated. Further, it may be shown that, for long chains, the distribution of end-to-end vectors is given by the Gaussian type expression:

$$W(\underline{r}) = (3/2 \pi \langle r^2 \rangle)^{3/2} \exp \left[-(3/2 \langle r^2 \rangle) r^2 \right]$$

where $W(\underline{r})$ is the density of end-to-end vectors at a point defined by the vector \underline{r} , r is the magnitude of the vector, and $\langle r^2 \rangle$ is the statistical mechanical average of the square of this magnitude (i.e., the mean-square end-to-end distance). Hence, $W(\underline{0})$ may be found:

$$\underline{W(\underline{0})} = \underline{(3/2 \pi \langle r^2 \rangle)^{3/2}}$$

This approach to $W(\underline{0})$ has been adopted in these studies. For short chains, however, certain approximations in the derivation of the Gaussian distribution may fail. There is then another method which may be used to calculate $W(\underline{0})$: to employ an electronic computer to generate all the chain conformations defined by the rotational isomeric state model, and for each assign the correct statistical weight and evaluate the end-to-end distance. The density $W(\underline{0})$ is then found by discovering the sum of the statistical weights of those conformations where one end lies within a small sphere centred upon the other, and dividing this sum by both the volume of the sphere and the total weight for all the chain conformations. So:

$$W(\underline{0}) = z_d / (Z \frac{4}{3} \pi d^3),$$

where z_d is the sum of the weights of the conformations with ends approaching to within a distance d , and Z is the total statistical weight (i.e. the conformational partition function).

This procedure, which was used extensively here, obviates reliance on the Gaussian distribution; but it may instead be sensitive to other

errors which are inherent in the basic RISM, although not greatly affecting the results when the latter is used in calculations of the chain dimensions. The assignment of somewhat inaccurate statistical weights to highly-coiled conformations will often alter the calculated value of $\langle r^2 \rangle$ negligibly, since the weights are so low that the conformations will in any case contribute little to the average; but frequently it is just such conformations that must be adopted for cyclisation to occur, and their statistical weights must be known precisely. Furthermore, the restriction of each bond to a few discrete rotational states is an approximation: at best, it is a physical approximation, reflecting high energy barriers to bond rotation; otherwise, it is a mathematical approximation, whereby an integral over all rotational angles is replaced by a sum over a few states. For small rings, especially, an approximation of either kind may fail, and it may be impossible to adequately describe the conformation of the cyclic in terms of just those rotational states allowed in the normal RISM. In certain of the calculations discussed in the final Chapter of this thesis, extra states were allocated to each bond, in order to overcome this difficulty.

CHAPTER 2.

GENERAL EXPERIMENTAL METHODS

2.1 PURIFICATION OF CHEMICALS

(a) General solvents were of laboratory grade, supplied in drums: they were distilled before use through an 18" Vigreux column, with rejection of the solvent-water azeotrope, if this formed. Solvents for equilibrations were S.L.R. grade, and were dried over calcium hydride, and distilled through a Gallenkamp fractionation apparatus; save for 1-methylnaphthalene, which was distilled under vacuum through the Vigreux column, with rejection of a large first fraction.

(b) Other chemicals were S.L.R. grade, unless otherwise stated. Where necessary they were purified by standard methods of distillation or recrystallisation.

2.2 WEIGHING

For the most precise work, by an Oertling analytical balance accurate to four decimal places; otherwise, by a balance accurate to 0.1 gm (from Eta Ltd., Watford).

2.3 VACUUM TECHNIQUES

Evacuation of apparatus was by means of a Speedivac oil-pump (Edwards High Vacuum Ltd., Crawley) used with a Vacustat gauge (from

the same makers). Except where this could lead to contamination of solvents or distillates, ground glass joints were sealed with Edwards silicone grease.

2.4 SOLVENT REMOVAL

Removal of fairly volatile solvents was effected by a Büchi rotary evaporator, used in conjunction with a filter or oil pump. An apparatus for the removal of solvents of lower volatility will be described in Chapter 5. Final drying of solids was in a Gallenkamp vacuum oven.

2.5 INFRA-RED SPECTROSCOPY

Complete spectra of solids (2000 - 15000 nm.) were obtained by the potassium bromide disc method on a Unicam SP 200 spectrophotometer; but when searching for hydroxyl or carboxyl groups, it was preferred to mull the substance with hexachlorobutadiene, and use just the Range 1 (2500 - 7500 nm.) on a Unicam SP 200G instrument. Not only was this very much more convenient, but it also removed the risk of finding spurious absorptions arising from traces of moisture picked up during preparation of a disc.

2.6 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Spectra were obtained from a Perkin-Elmer 60 Mcs. R-10 Model spectrometer. Substances were studied as solutions in deuteriochloroform or trifluoroacetic acid.

2.7 VISCOMETRY

A viscometer of the Cannon-Ubbelohde suspended level type was used, in a water-bath held at 25 (± 0.05)^oC. by a Gallenkamp mercury-bulb thermostat.

2.8 EQUILIBRATION IN AMPOULES

Ampoules were made from 45 mm. diameter medium-wall borosilicate glass. They had bodies 12 cm. long; their necks, of about the same length, and ending in a B14 ground-glass socket, were wide enough for easy entry of coarse solids into the body. Each was provided with two glass-rod bridges between neck and shoulder, so that a loop of stout copper wire might be attached, to act as a handle.⁺

The ampoules were always sealed under oil-pump vacuum. If the contents were volatile, they were frozen in an acetone/solid carbon dioxide mixture, prior to evacuation and sealing.

A special heater was constructed so that these ampoules might be safely heated.* Four heavy steel explosion tubes were embedded in an aluminium block shaped as a cylinder, 16 cm. diameter by 35 cm. high. Each tube, 6 cm. diameter by 23 cm. deep, was fitted with a heavy screw cap, this being bored with two small vents that also permitted insertion of a key, for screwing and unscrewing the cap. Two 1 kW. band heaters (Heden Heat Co., S.Woodford) were fastened around the block, and this was enclosed in a 1 cm. thick asbestos case, diameter 20 cm. into which fitted a thick asbestos lid; the space between block and case

+ Thanks are due to Mr. A. Watson for constructing these ampoules.

* Thanks are due to Mr. D. Sympson for constructing this heater.

was filled with Micanite chips. A central hole in the lid enabled a thermometer to be inserted into the block. An aluminium stand lifted the whole assembly off the bench. Temperature control was by a Variac, only: if it had been necessary, a solid-state controller could have been inserted into a hole at the base of the block; but it was found that, standing in a hood, and protected from draughts, etc., the block maintained a set temperature for many days to within 1 - 2 degrees at around 100°C., and to within 3 - 5 degrees at around 300°C. This was an adequate stability for the intended purposes.

Transfer of the ampoules to and from the heater was with a metal hook through the loop of wire fixed on the ampoule. Glass wool in the bottom of each of the explosion tubes made a soft bed for the ampoule. When handling the evacuated ampoules, most especially when just taken from the heater, all proper precautions were taken (viz., the wearing of a mask and asbestos gloves, and the wrapping of the ampoule in thick cloths).

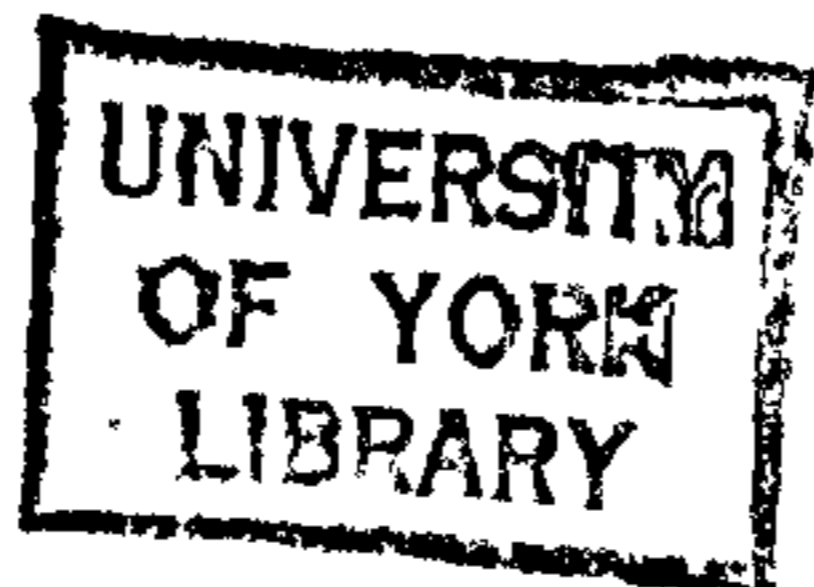
2.9 VAPOUR PRESSURE OSMOMETRY

A Model 301A osmometer from Mechrolab Inc. (Mountain View, California) was used, with chloroform as solvent.

2.10 GAS-LIQUID CHROMATOGRAPHY

A Pye Series 104 gas chromatograph, with katharometer detection, was used in conjunction with a Servoscribe RE 511.20 potentiometric recorder. 4' glass columns packed with Embacel, silanized according to

the procedure of Bohemen and co-workers³⁸, and appropriately coated, were used. The liquid phases used were 2% OV-17 (Field Instruments Co., Ltd., Richmond, Surrey) and 8% methyl silicone gum (E30, supplied by W.G. Pye and Co., Ltd.). Carrier gas was purified nitrogen at 50 ml./min. The detector oven was set at 330°; temperature conditions for the columns were variable, and often involved programmed runs. The instrument was equipped with an injection port heater, and care was taken to use only those syringes with needles of the correct length to reach to the hottest part of the heater block.



CHAPTER 3.

GEL PERMEATION CHROMATOGRAPHY

3.1 INTRODUCTION

In the closely related techniques of "gel filtration" and "gel permeation chromatography", separation of mixtures is effected by partition of the components between a stationary phase, consisting of solvent held within the sub-microscopic pores of beads, packed in a column, and a mobile phase, consisting of solvent passing through the column, and flowing round the beads. The greater the extent to which the molecular dimensions of a substance permit it to penetrate the pores, the longer it is delayed in the column, and the greater the volume of solvent that must be passed through before it will emerge; conversely, the exclusion of a component from the pores speeds its passage through the column. Separation is therefore (largely) according to molecular size.

The method of "gel filtration" is the longer established. It was initially restricted to aqueous solvents and hydrophilic beads, of which the best known are the cross-linked dextrans³⁹ marketed as Sephadex; although other similar types have been introduced⁴⁰. More recently, beads compatible with organic solvents, both polar and non-polar, have come into use: for example; in the first class, the alkylated forms of Sephadex, and lightly cross-linked poly(vinyl acetate)s⁴¹; in the second class, lightly cross-linked polystyrenes^{41,42,43}. For all these materials, the beads have an open structure, but lightly cross-linked, and are swollen by the appropriate solvents to gels featuring cavities of a suitable size range. The applications for

most, though not all, of these gels are to separating components of quite low molecular weight.

The practical upper limit to the molecular weight range covered by the gels compatible with organic solvents was determined by the technical difficulties of handling the highly-swollen beads; this reduced the usefulness of the technique, for the analysis of hydrophobic polymers, until Moore⁴⁴ introduced a modified method for the preparation of the porous beads. In his process, styrene and a bifunctional reactant, divinylbenzene, were co-polymerised in the presence of an inert diluent, During the polymerisation, the diluent precipitated as minute droplets which remained as cavities within the final bead. With a high proportion of cross-linking agent, the polymeric structure forming the walls of these pores could be made sufficiently rigid to prevent the bead from swelling in solvent. Moore described analysis using beads of this type as "gel permeation chromatography"; although the term "gel" for these beads can no longer be taken to imply that they possess the properties normally associated with gels. Such gels are now available commercially.

The potential suitability of this method for the analysis of mixtures of cyclic oligomers will be immediately evident. Indeed, there are other techniques equally effective in separating chemically similar materials according to their molecular size. Gas liquid chromatography has been used for the analysis of the oligomers of polysiloxanes^{6,7,8,10} and polyethers^{15,45}, with considerable success; but the cyclic oligomers of polyesters are insufficiently volatile for this method to be of comparable usefulness in their case. For the aliphatic polyesters, the first two, or perhaps three, rings, may

be detected (Chapter 8); for poly(ethylene terephthalate) (Chapter 4) it is barely possible to detect the trimer (the smallest cyclic present in sensible amount under equilibrium conditions). Adsorption chromatography, also, has been employed, with a certain success²³.

There are precedents for the application of either variant of the gel exclusion method to the analysis of cyclic species. "Gel filtration", with both Sephadex, and cross-linked polystyrenes, has been extensively used by Zahn and his co-workers to resolve cyclic extracts from polyamides and polyesters²², as well as to purify oligomers obtained by synthesis⁴⁶. By "gel permeation chromatography", it has been possible to determine the molecular weight distributions of samples of cyclic dimethylsiloxanes where there are up to several hundred bonds in each molecule^{6,9}.

The chemical nature of the gel to be employed will obviously depend upon that of the solvent; selection of the solvent is governed by several factors. Not only must it dissolve the substances to be analysed to the necessary extent (about 1%) but it must also permit their detection: if (as here) differential refractometry is the means of detection, there must be a sufficient difference between the refractive indices of solute and solvent. Bearing in mind the large volumes of solvent required, it will also be advantageous if it is non-toxic, inexpensive, and easily recovered after use.

For analysis of the cyclic oligomers of aliphatic and aromatic polyesters, chloroform proved to be an adequate solvent. In conjunction with this solvent, the most suitable gels were the cross-linked polystyrenes. Both types, i.e. rigid and non-rigid, were essayed; the rigid beads were found not to serve the purpose, and their use was

abandoned in favour of the non-rigid. It is true, therefore, that the technique finally adopted lay closer to the original "gel filtration", than to the more recently innovated "gel permeation chromatography"; but no such fine distinction in terminology will be attempted in what follows, where the methods used will be uniformly described as gel permeation chromatography, g.p.c..

3.2 THE GEL PERMEATION CHROMATOGRAPH*

The design of the gel permeation chromatograph is best described with reference to the flow diagram in Figure 3.1. The component parts, fabricated throughout from stainless steel, are:

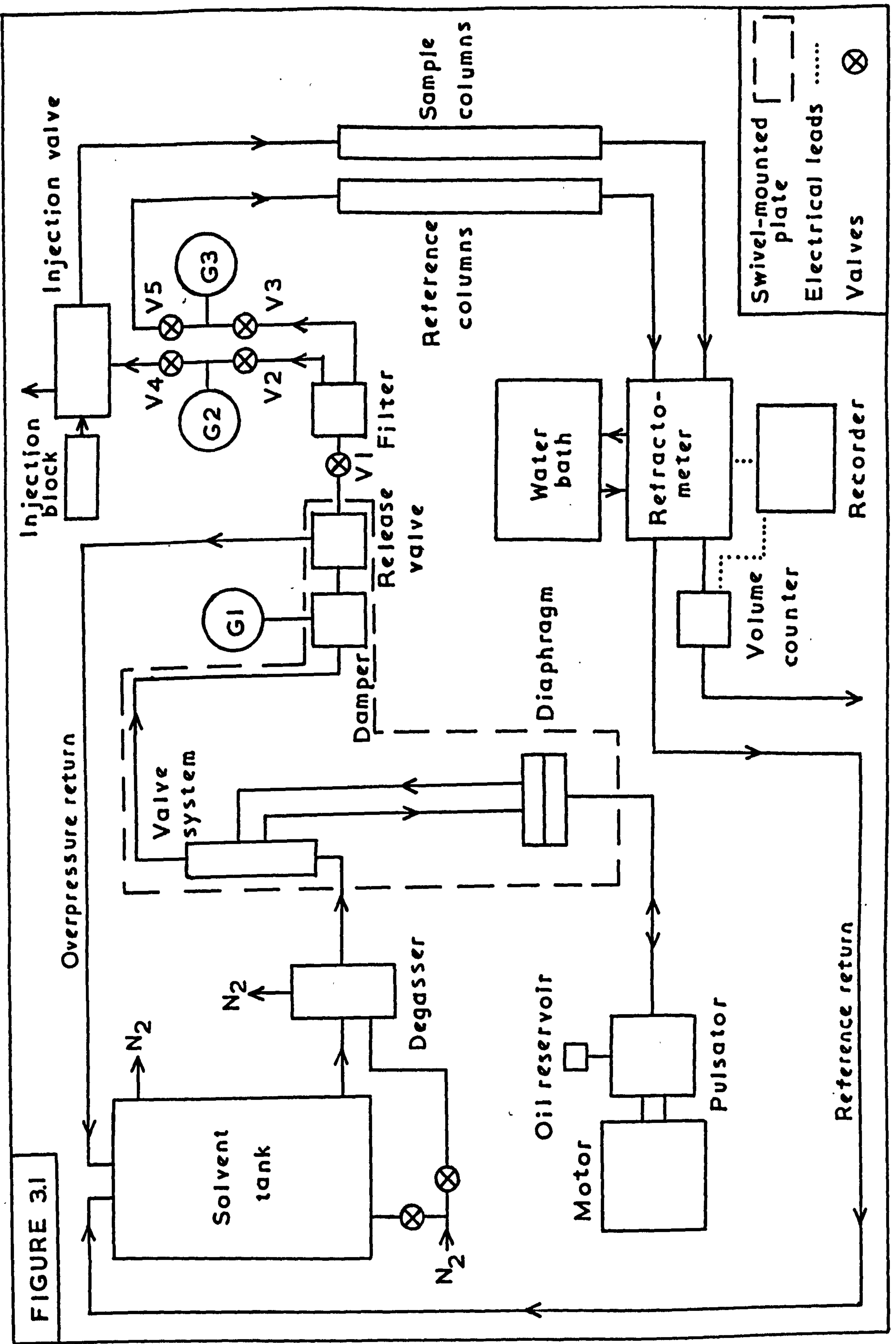
(a) Solvent tank. A 16 litre drum, contained in an insulated box, with provision for pre-heating the solvent. An inlet at the base of the tank permitted nitrogen to be bubbled through the solvent.

(b) Degasser. This is shown in detail in Figure 3.2: It was designed for a flow path ensuring that all the solvent came in proper contact with the heated block, which was maintained at the required temperature by means of a "Minitherm" controller (Temperature Controls Ltd., Manchester). There was an inlet for nitrogen in the base of the block. The glass tube extended up to a height of six feet; it served as an indicator of the level of solvent in the tank.

(c) Oil pulsator. This consisted of a spring returned reciprocating shaft acting upon the column of hydraulic fluid leading to the near side of the diaphragm. (Shaft diameter: $\frac{1}{8}$ " ; stroke: 0.2".) It was powered by a 96 r.p.m. motor (Parvalux, of Bournemouth).

* Special thanks are due to Mr. D. Sympson, of the Chemistry Department, for undertaking the design and construction of this instrument.

FIGURE 3.1



(d) Diaphragm. The pulses in the oil were transmitted to the solvent through a 0.0025" corrugated diaphragm, of 3 sq.in. working area. (The physical separation of the solvent and the reciprocating part prevented the contamination of the solvent, common with metering pumps).

(e) Valve system. Two valve units, each in itself consisting of two $\frac{1}{8}$ " diameter sapphire balls, lightly spring-loaded, against stainless steel seatings, controlled the flow of solvent from degasser to diaphragm, and from diaphragm to pulsation damper, respectively.

(f) Pulsation damper. This consisted of a 0.2 sq.in. working area bellows, maintained under pressure by a spring, itself controlled by a screw projecting from the main body of the damper.

(g) Pump pressure gauge (G1). A Budenburg diaphragm type gauge, maximum reading 300 p.s.i., to indicate the pressure generated by the pumping system.

(h) Over-pressure release valve. This is shown in detail in Figure 3.3. Deflection of the diaphragm by a solvent pressure in excess of that applied by the spring momentarily opened the valve and allowed solvent to flow out and return to the solvent tank. A sight glass permitted the return flow to be observed.

(i) Shut-off valve (V1). A Hoke needle valve.

(j) Filter and flow splitter. The solvent was filtered through a Carlson-Ford asbestos filter supported on a $1\frac{1}{8}$ " diameter by $\frac{1}{8}$ " thick stainless steel sinter (BSA Sintered Components, Ltd., Birmingham).

(k) Needle valves (V2, V3). These were Hoke valves, intended to provide fine control over the solvent pressure on either set of columns, and so enable the flow-rates to be accurately adjusted.

(l) Gauges (G2,G3). Of the same type as the pump pressure gauge G1, these indicated the pressures applied to the sample and reference column sets, respectively.

(m) Control valves (V4,V5). These were valves of the same type as the valve V1, and were used to interrupt the flow to either set of columns without disturbing the fine control valves.

(n) Sample injection block. A cylindrical block of aluminium, bored to permit the insertion of a 10 ml. syringe, and equipped with a Luer centre-lock fitting, to connect the syringe to the sample injection valve. There was provision for maintaining the block at temperatures above ambient.

(o) Sample injection valve. This was an 8-port column switching valve (Waters Associates, Framingham, Massachusetts), adapted to its present purpose by introducing an appropriate connection between the 4 ports on one level and the 4 on the other. (See Figure 3.4.) The sample loop consisted of a suitable length of capillary piping; its capacity was 1.25 ml.

(p) Column sets. These will be described separately.

(q) Differential refractometer. A Waters Associates Model R4, capable of detecting differences in refractive index of 10^{-7} units. The cell capacity was 0.07 ml.

(r) Thermostatic bath and circulator. A Tempunit, from Techne, Cambridge, stable to at least 0.1°C .

(s) Volume counter. This was constructed on a rocker principle (Figure 3.5). The solvent ran into compartment A until its weight caused the rocker to swing over, emptying the contents of A into the receiving bottle, and placing instead compartment B under the flow. The

FIGURE 3.2

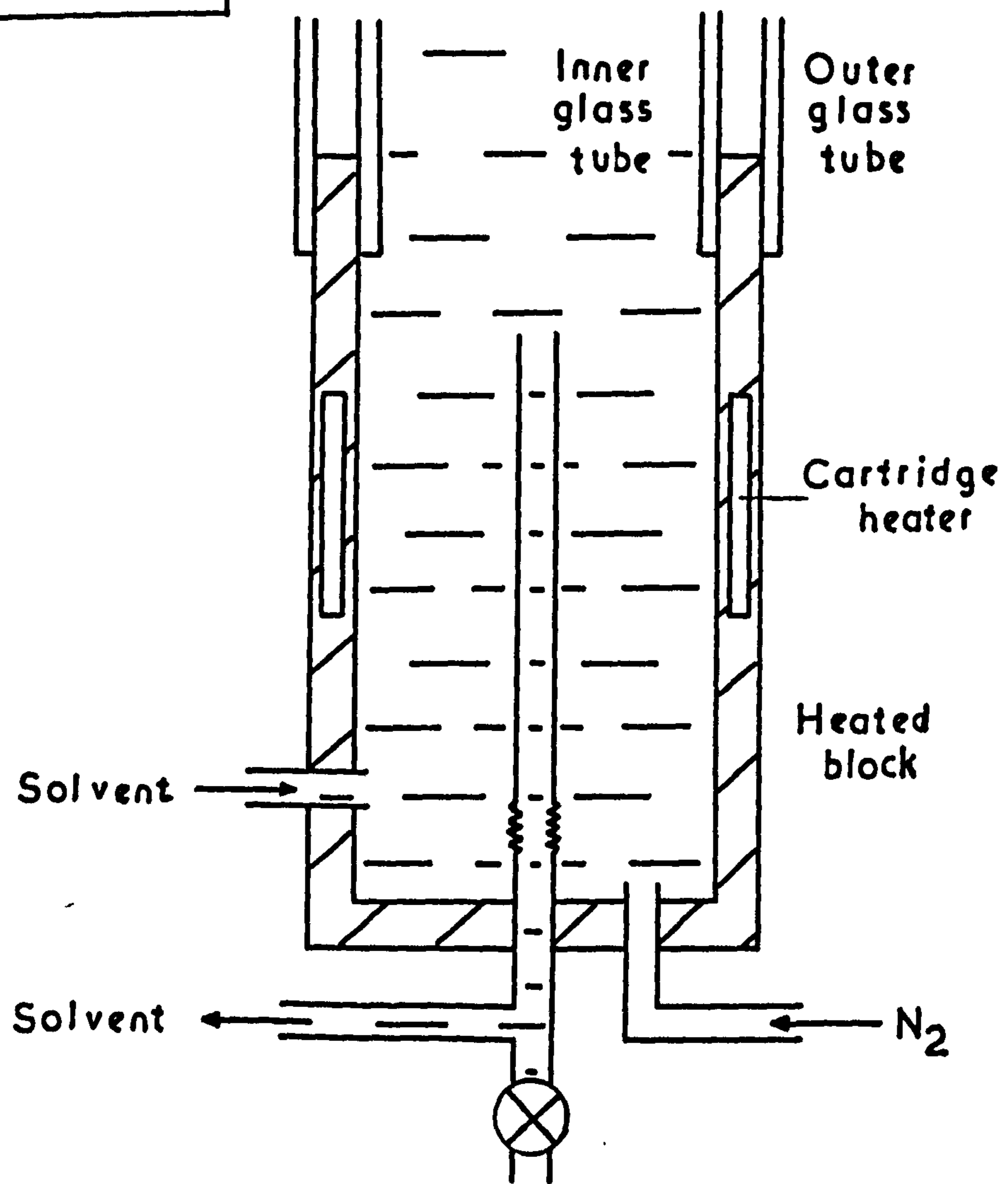


FIGURE 3.3

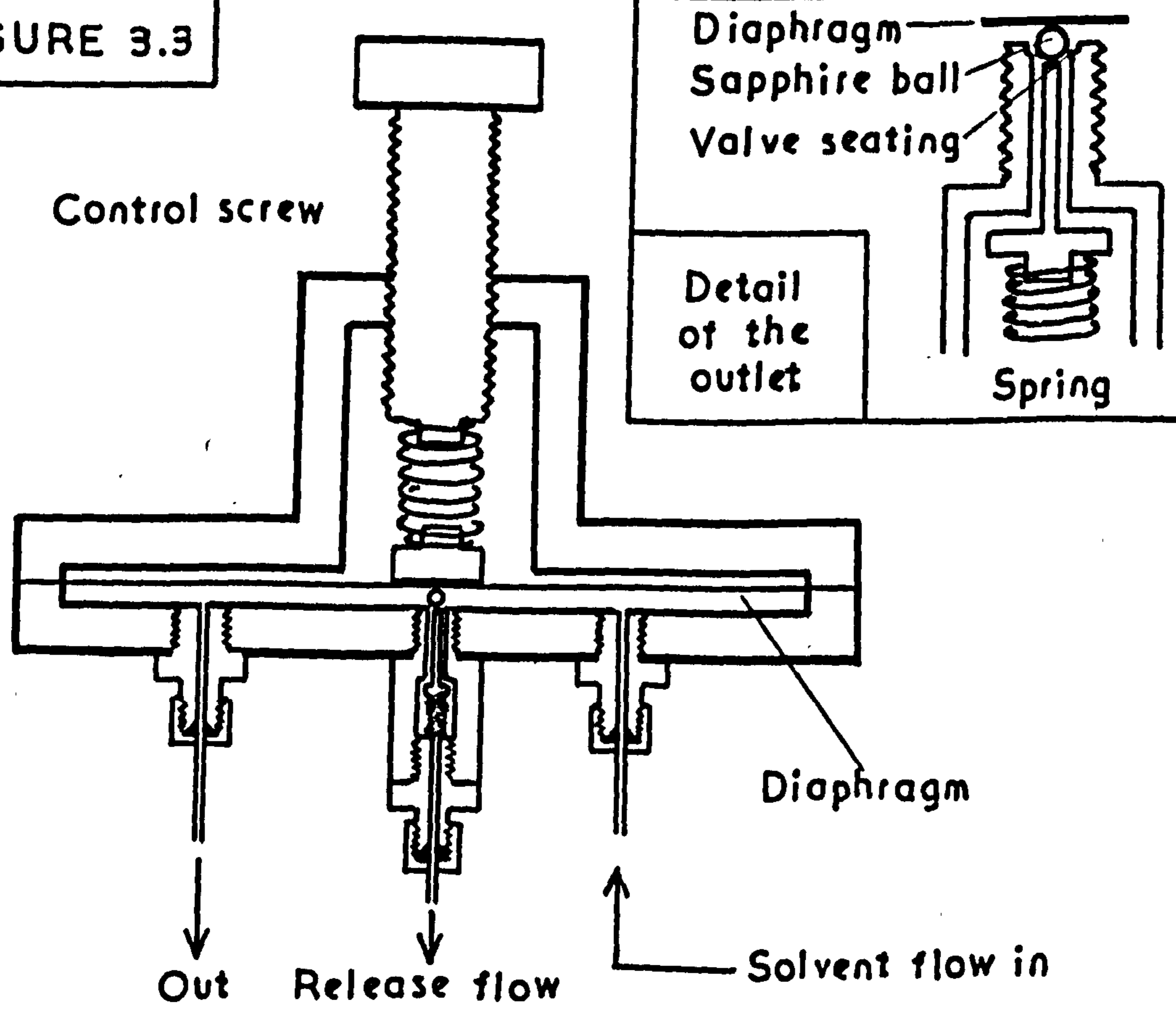
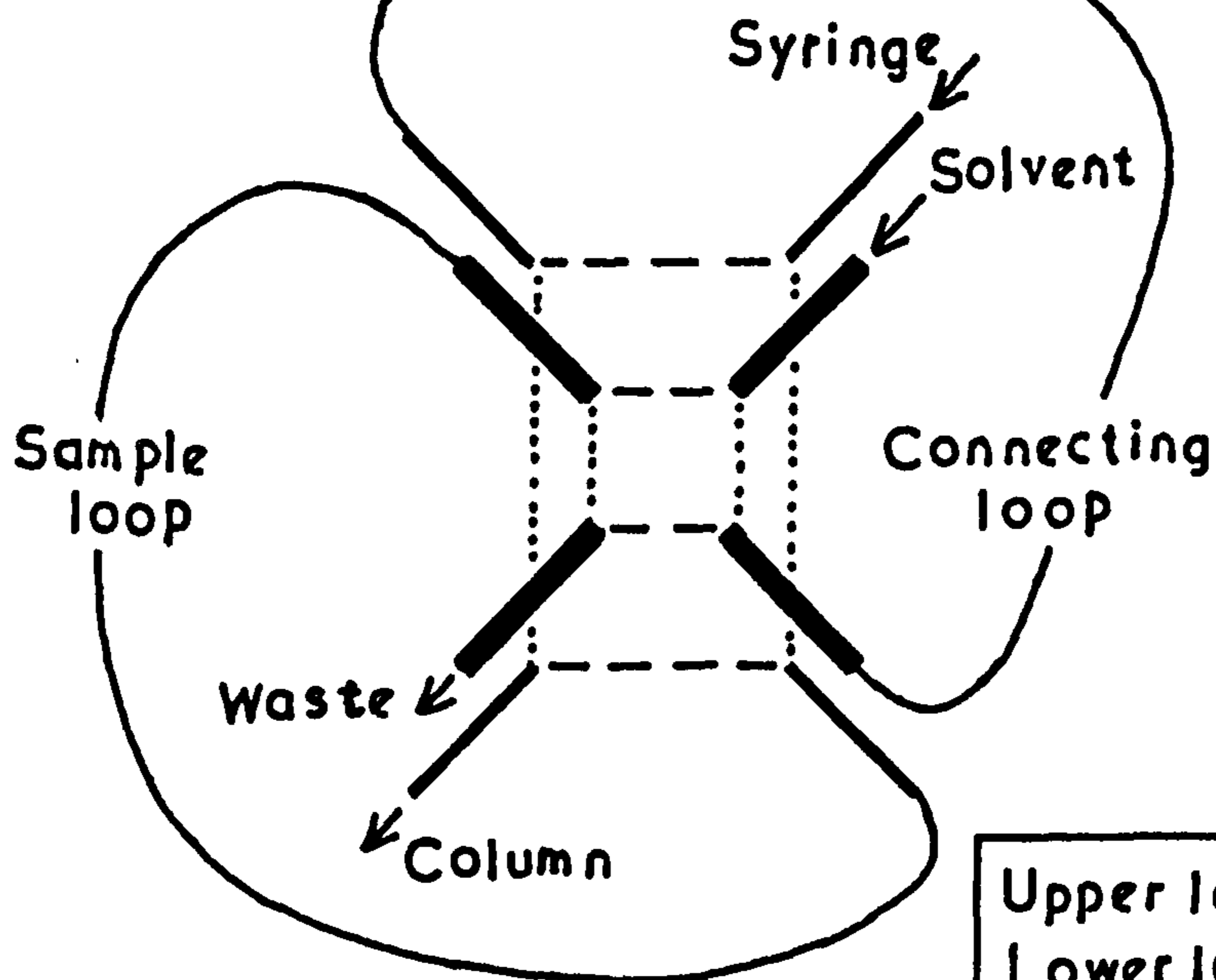
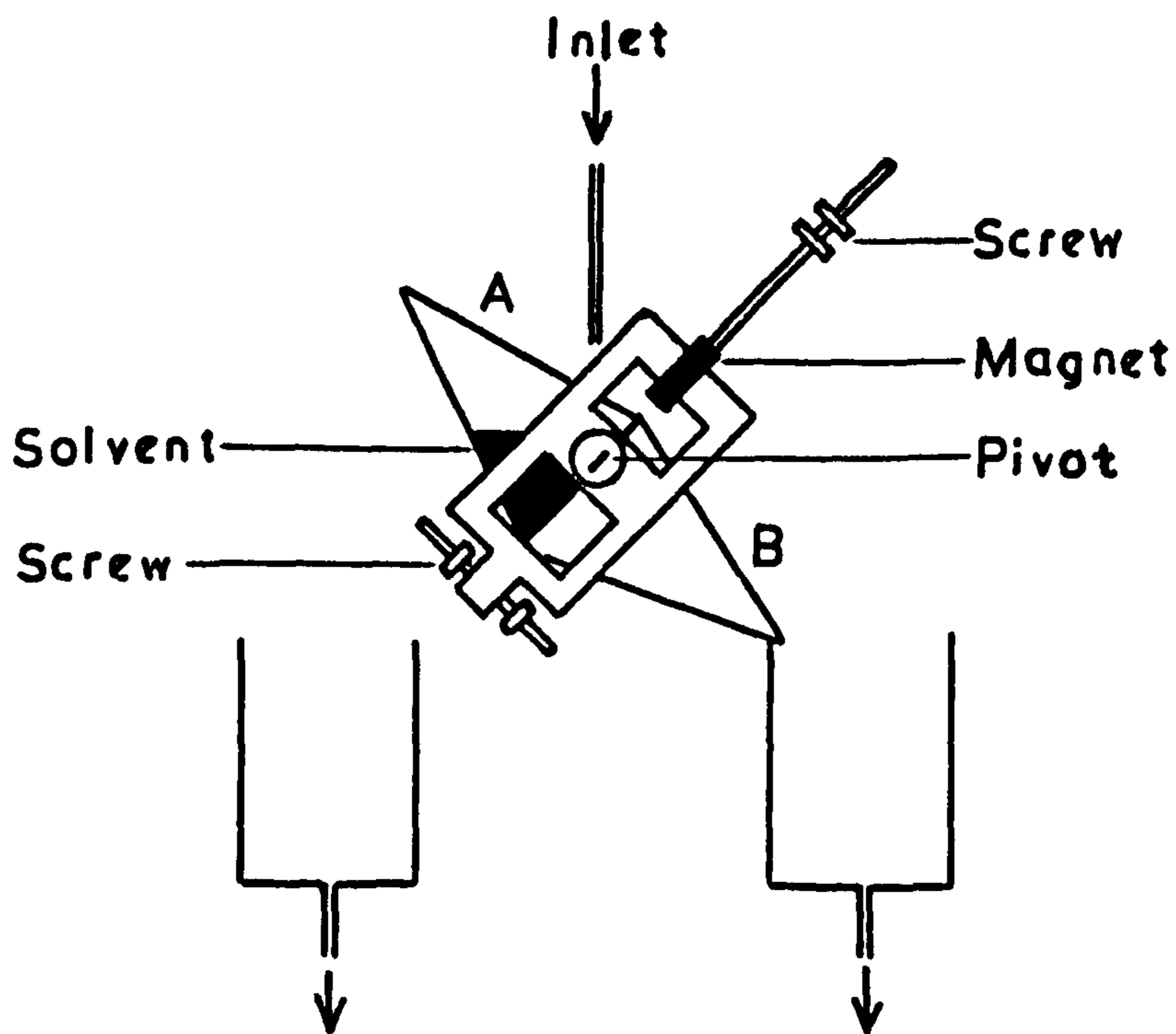


FIGURE 3.4



Upper level ports —
Lower level ports —
To fill loop
To inject - - -

FIGURE 3.5



movement of the magnet past the Reed Switch momentarily closed a circuit, which was arranged to short-circuit the recorder and so give a mark on the chart. The horizontally aligned screw permitted the rocker to be properly balanced. The vertically placed screw enabled the volume of solvent needed to overbalance the rocker to be varied: it was set to 2.5 ml. chloroform. The whole mechanism was enclosed in an insulated box, and there was provision for maintaining it at temperatures above ambient.

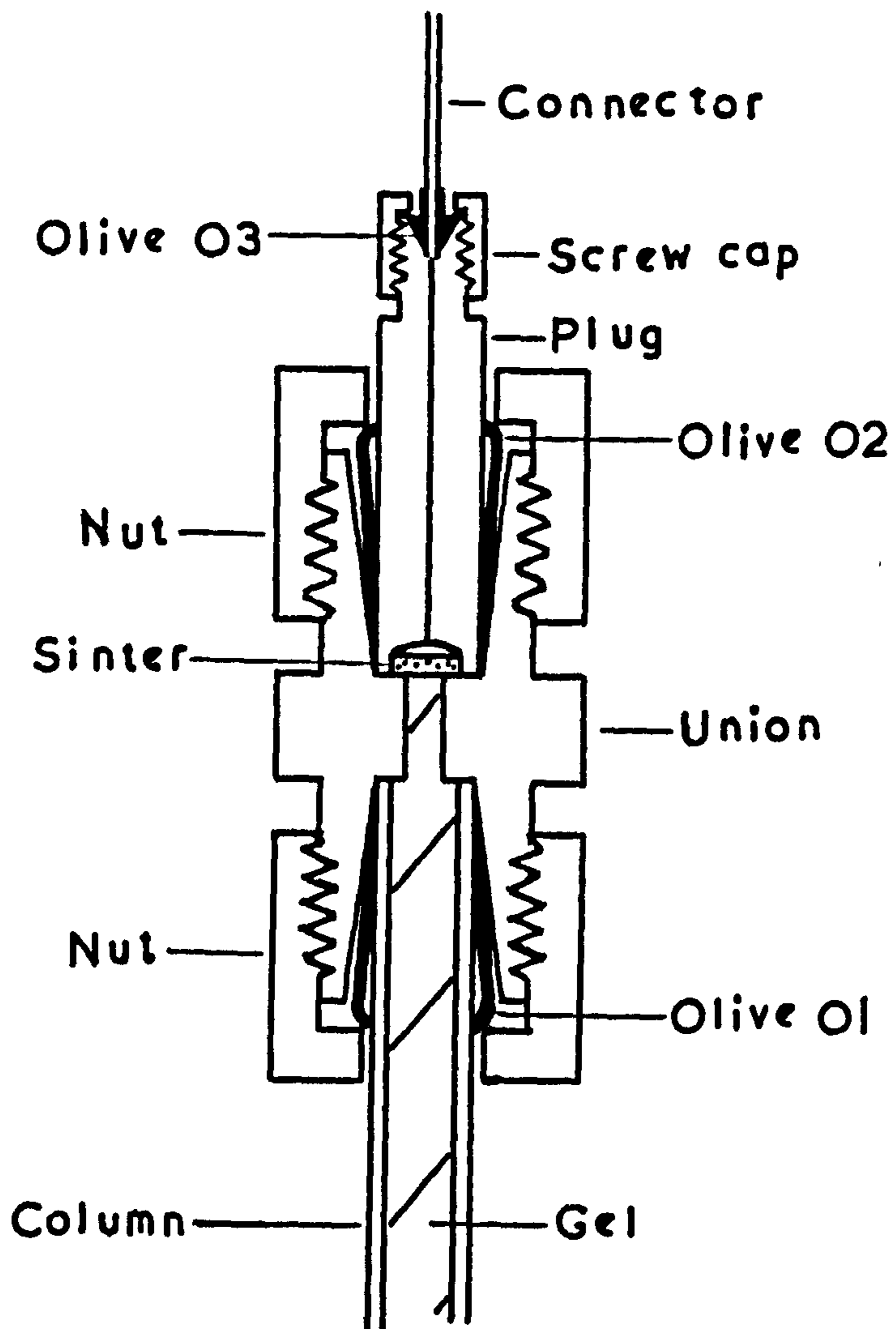
(t) Recorder. A Servoscribe RE 511 potentiometric record was used.

The diaphragm, the valve system, the damper and the over-pressure release valve were positioned upon a swivel-mounted plate, in order that they might be inverted for easy drainage during change of operating solvent. The valve at the base of the degasser also facilitated solvent change,

All components were connected by means of 1/16" O.D. stainless steel capillary piping except for non-permanent connections, which could be made with narrow-bore nylon tubing. Seals were effected at the points of entry and exit by compression fittings of the Simplifix type, but using olives turned out of Monel metal wire. (See, for instance, the description of the column end-fittings, below).

The columns, valves and filter, and the swivel-mounted plate with its attached parts, were enclosed in a shallow upright oven. Throughout these studies, the back of the oven consisted of slabs of expanded polystyrene, only, but there was arrangement for a proper door to be fitted, and provision for temperature control.

FIGURE 3.6



The columns themselves were made from 4' lengths of stainless steel tubing, $\frac{3}{8}$ " O.D., 20 S.W.G., and $\frac{3}{4}$ " O.D., 16 S.W.G.. The design of the end-fittings is represented in Figure 3.6. The end-fitting was sealed to the column by means of the steel olive O1; the plug, carrying a 5 micron steel sinter swaged into a depression in its lower end, was sealed to the union of the fitting by the olive O2. (The slight dishing in the plug above the sinter encouraged spread of the liquid over its entire area). The steel piping connector was sealed to the plug at the Monel metal olive O3, which was compressed by the screw cap.

3.3 OPERATION OF THE GEL PERMEATION CHROMATOGRAPH

The following summarizes the important points in the operation of the instrument.

(a) Solvent. The chloroform was laboratory solvent grade, distilled before use, with azeotropic drying; the used solvent was kept dry while awaiting re-distillation by anhydrous calcium chloride placed in the receiving bottle. Fresh solvent was siphoned into the tank via an opening at the top.

(b) Flow rates. From 0.2 - 1.0 ml./min. The tendency of the fine control valves to block, and alter their resistance, made it impossible to control flow rates by this means; therefore, these valves were left completely open, and the sample flow rate was adjusted by using the over-pressure release valve to vary the pump pressure. This meant that the sample and reference flows were not necessarily balanced. (See (f), below).

(c) Degasser. The block temperature was set at between 35° and 60°. Degassing close to the boiling point of the solvent seemed to result in a poor baseline. No nitrogen flow was used. (See (f) below).

(d) Column temperature. Ambient.

(e) Detector temperature. The thermostat on the circulating bath was set at 28°C. The bath was positioned close to the detector, and connection of the water flow was through short lengths of wide rubber tubing.

(f) Sensitivity settings, and baseline. The refractometer was used in the recording mode at X 32, the recorder at 20 mV. and 50 mV. The base-line at 20 mV. ranged from excellent (stable to 1 - 2% over 12 hours) to very poor. The impossibility of ensuring a balance between the sample and reference flows was undoubtedly partly responsible for the variability in the base-line stability. Excessively vigorous degassing lead to a deterioration, possibly because it caused variations in the residual water content of the solvent. At one stage, mechanical oscillation in an over-pressure release valve of another design permitted periodic collapses in pressure, bringing about the discharge of stale solvent from the dead spaces in the gauges; this too had an adverse effect on the base-line. Control of the detector temperature was apparently adequate.

If the base-line was poor at the 20 mV. recorder setting, the sensitivity was reduced, and more sample injected. In no tested case was this found to affect the resolution, or the relative peak areas in mixtures; showing both that the gel had not been saturated, and that the materials under study responded linearly at the concentrations employed.

(g) Sample injection. The weight of material required was 10-100 mgm., depending upon the number of columns in use, the heterogeneity of the sample, the sensitivity setting of the recorder, and the refractive index differences between the components and chloroform. This was dissolved in 5 ml. distilled chloroform, and passed through a fine sinter by air-pressure. The sample loop was flushed out with 20 - 30 ml. solvent by means of the syringe, and was then filled with the solution in the same way, taking care to exclude air-bubbles; washing solvent, and surplus solution, ran into a small vessel. Injection, by moving the lever of the injection valve over so that the sample loop entered the solvent line, was made to coincide with a volume count. After two more counts, the lever was returned to its original position, and the sample loop was flushed out with solvent.

Filtration of the solution to be injected was necessary to avoid blockage of the sinters in the column end-fittings. Even with this precaution, the sinters gradually blocked (probably with fragments worn from the interior parts of the injection valve) and needed periodic replacement if the working pressure was to be kept at a practicable level.

Injected samples always gave peaks other than those of the materials themselves, due to traces of impurity in the solvent; but the low molecular weight of these impurities ensured that their peaks did not normally interfere with those of the oligomers.

3.4 PACKING OF "STYRAGEL" COLUMNS

First attempts to resolve mixtures of the cyclic oligomers of

polyesters were with narrow ($\frac{3}{8}$ " O.D.) columns packed with "Styragel", rigidly cross-linked polystyrene beads supplied by Waters Associates. Procedures for packing such^{gel} have been published by Waters Associates⁴⁷, and have since been modified by Peaker and Tweedale⁴⁸, and by Shaw⁴⁹. The method described here largely corresponds with those reported.

The apparatus* is shown in Figure 3.7. The slurry reservoir, a 3' length of $\frac{3}{4}$ " O.D. steel tubing, was surmounted by an $\frac{1}{8}$ " aperture valve fitted with a glass funnel; below, it was joined by a machined adapter to a $\frac{3}{8}$ " O.D. pipe, bent into a semi-circle, diameter 12". The column to be packed was fitted on to form the other arm of the "U".

The packing pump was of the reciprocating type, with a $\frac{1}{4}$ " Stellite plunger passing through a gland packed with PTFE; its stroke was variable up to $1\frac{1}{4}$ ". It was powered by a 100 r.p.m. motor from Normand Electrical Co., and had a maximum capacity of 60 ml/min. The flow of solvent was controlled by four valves, each consisting of an $\frac{1}{8}$ " sapphire ball spring-loaded against a stainless steel seating. The solvent entered the reservoir at a point just below the $\frac{1}{8}$ " valve.

The gauge (Barnet Instruments, Ltd., Barnet) read up to 1600 p.s.i.. The release valve was an ordinary Holz needle type. Both these components were connected to the reservoir by leads, also emerging from just below the $\frac{1}{8}$ " valve.

* Thanks are extended to Mr. Sympton for constructing this packing apparatus, including the pump itself. The design was partly based on that of a rig used by Dr. G. Shaw at I.C.I. Fibres, Harrogate. Gratitude must also be expressed to Dr. Shaw, for making possible the use of his rig to pack columns required for certain other work in this laboratory, as well as for giving much valuable advice on the packing procedure.

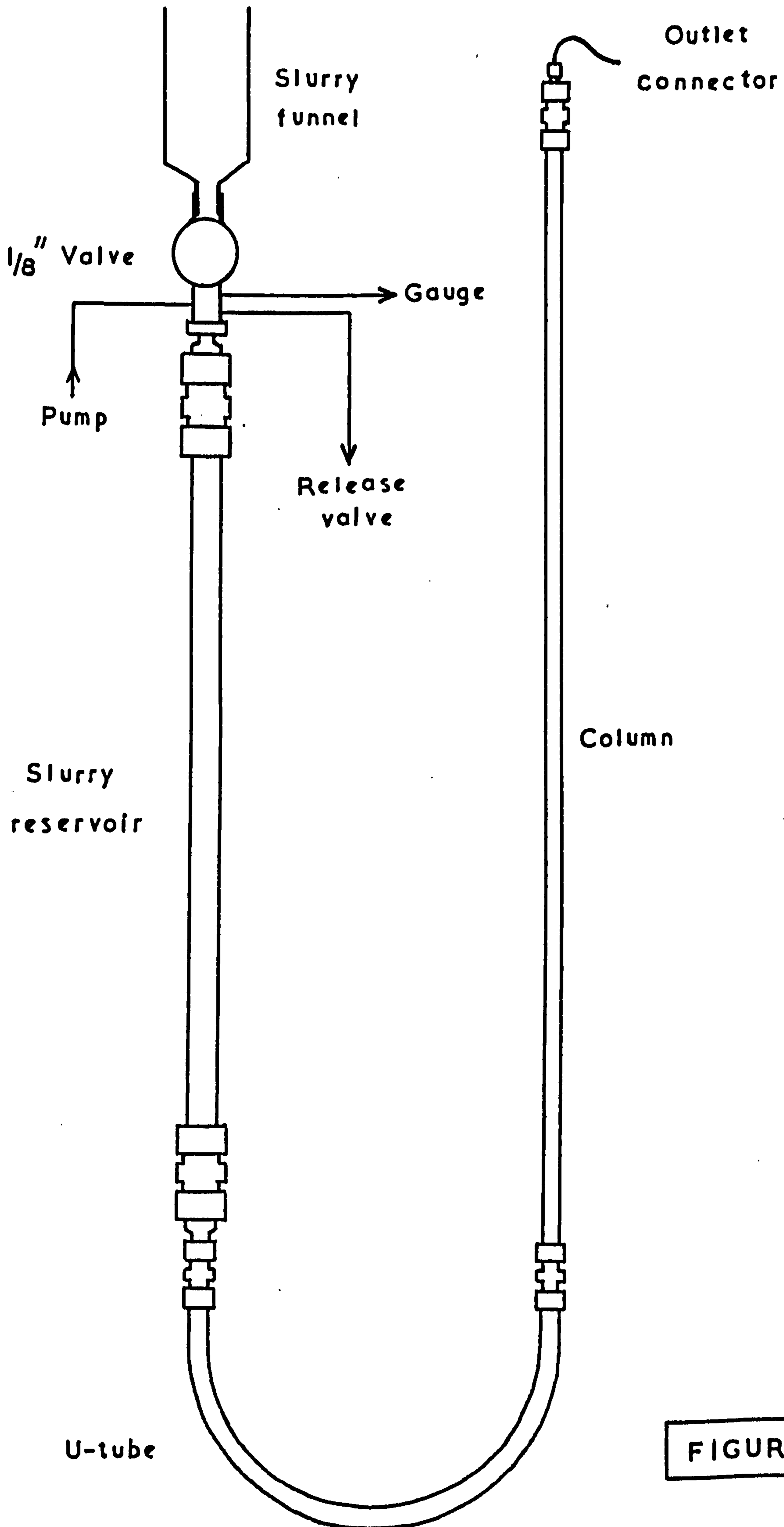


FIGURE 3.7

To pack the gel, it is made up as a slurry in a mixture of solvents of a density close to its own, so that it neither sinks nor rises during the packing. It is introduced into the reservoir and pumped round into the column with another solvent. In the previous methods, the gel was slurried in a 5:6 (by volume) mix of tetrachloroethylene and acetone, and pumped round with tetrahydrofuran. Here, chloroform was used in place of both the tetrachloroethylene and the tetrahydrofuran. Further, the mixture of solvents was used for the initial stages of the pumping.

To pack a single column, 80 ml. dry gel were thoroughly stirred with four or five 150 ml. portions of a mixture of 800 ml. chloroform and 960 ml. acetone; after each washing liquid was drawn off in a coarse sintered funnel until the gel was just damp. Finally the gel was slurried with exactly 150 ml. of the mixture, and degassed by refluxing for 30 mins. and cooling in a stoppered flask. Care was necessary to prevent violent bumping of the slurry during reflux.

After degassing, a sample of the slurry was centrifuged at high speed for several minutes. According to whether the gel sank or rose during centrifugation, chloroform or acetone was added from a burette and mixed well in, before another sample was centrifuged. This was repeated until the slurry remained homogeneous, or the gel divided, with part sinking and part rising; the final additions of solvent were of the order of 0.1 - 0.2 ml. The slurry was then degassed anew, and the balance checked. If necessary, a further addition of either of the solvents was made, the slurry was degassed again, and rechecked; and thus, until the freshly degassed slurry was correctly balanced.

Taking account of the original volume of the slurry, and the volumes of solvent titrated into it, the composition of the residual chloroform - acetone mix was now adjusted to closely match that of the slurry. A few hundred ml. were used to flush out the pump leads and wash out the tubing of the apparatus; the rest was degassed as described above. 500 ml. chloroform were also degassed.

The slurry was now introduced into the reservoir. To do this, it was poured down the side of a rod into the glass funnel. It was found that, if the valve were now opened, the gel would flow in only with the issue of air-bubbles and their passage through the slurry; this would not be desirable. (See below). So instead, the upper end of the column to be packed, as yet carrying only the olive O1 (in Figure 3.6) and its corresponding nut, was connected by rubber tubing to a filter pump, and the apparatus was evacuated; then the column was isolated from the pump by means of a screw clip, and the valve was opened carefully. The slurry was drawn smoothly into the reservoir.

Once the vacuum tube was removed, the column was provided with a full end-fitting. A short length of steel capillary piping emerging from this fitting was connected to several feet of narrow-bore nylon tubing with its end in a 20 ml. measuring cylinder. The pump was switched on, at high stroke, to rapidly fill the space in the reservoir above the slurry with the degassed solvent mixture, and then drive the air out of the interstices in the valve. When the liquid level rose up into the glass funnel, the pump was turned off and the valve shut. The pump was put back on, but with its stroke reduced to give a flow of approximately 1 ml./min. This flow rate was maintained until some 20 ml. had passed into the cylinder.

The cylinder was now replaced by a larger, and the pump stroke increased steadily. Provided the pump was in good order, the pressure now rose to above 800 p.s.i.; if it threatened to exceed the maximum reading of the gauge (1600 p.s.i.) it was released, by briefly opening the Hoke valve, and the stroke reduced. Pumping was continued at about 800 - 1500 p.s.i., 50 - 60 ml./min., until the supply of mixed solvents was exhausted (some 600 ml.). The pump was then turned off, and the solvent intake pipe of the pump transferred to the flask containing degassed chloroform; in doing this, care was taken to prevent entry of air bubbles into the intake line. Rapid pumping was resumed, and the 500 ml. chloroform passed through the column.

The pump was now switched off, and the pressure allowed to fall. A bowl having been positioned under the U-tube, the union between U-tube and reservoir was broken; the contents of the reservoir were discharged into a beaker by cautiously opening the valve at the top. Any liquid in the U-tube was emptied out, and the assembly of U-tube and packed column was inverted. The U-tube was removed, but leaving the actual union still on the column. If all had been properly carried out, the gel at the end of the column was tightly-packed. If necessary to avoid leaving any dead-space, a little of the surplus gel in the U-tube was put back into the union, and then the end-fitting plugs were put in place, and pressed down on the gel by tightening the upper nut. (Figure 3.6).

The column was inverted once again, so that the lowermost end was that which served as inlet during packing. A syringe containing chloroform was attached to the end of the nylon tubing, and raised, so that solvent percolated down through the column under gravity and ran

out of the lower end-fitting. When 1 - 2 ml. had passed out, and all air had been flushed from the fitting, the column was connected into the g.p.c., the direction of the solvent flow through it being the same as during packing. In making the connections, care was taken to exclude all air from the solvent lines leading into the column. The column was flushed out overnight at 1 ml./min. before testing, the efflux being rejected for re-distillation.

The gel in the U-tube was pumped out, and the reservoir washed out with solvent. About 30 ml. surplus gel could be recovered. This was filtered off and air-dried for future use.

If high resolution is to be achieved, the packing of the gel in the column must be uniform and tight⁴⁹. For uniformity, the gel slurry should be well-balanced; further, the more exactly its density is replicated by that of the mixed solvents used in pumping, the better. The slurry must also be properly degassed, and free from air-bubbles. For a tight packing, the pump must be able to give the high flow rates required, even at the high back-pressures generated. A number of the columns packed in the early stages gave poor resolution, because the pump was susceptible to back-flow through its valves at high working pressures; only when the valve balls had been spring-loaded could the necessary packing pressures be attained, and good packings achieved.

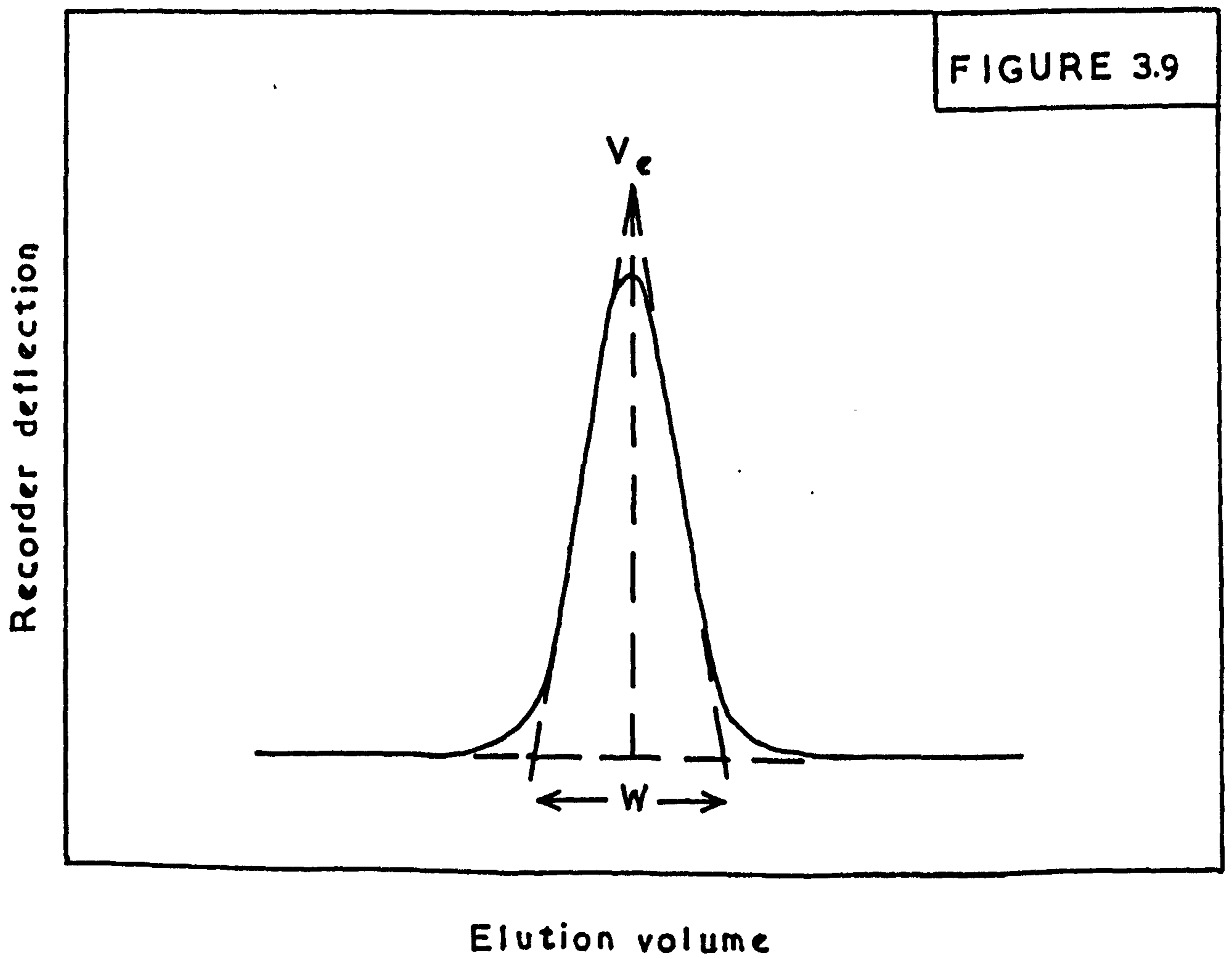
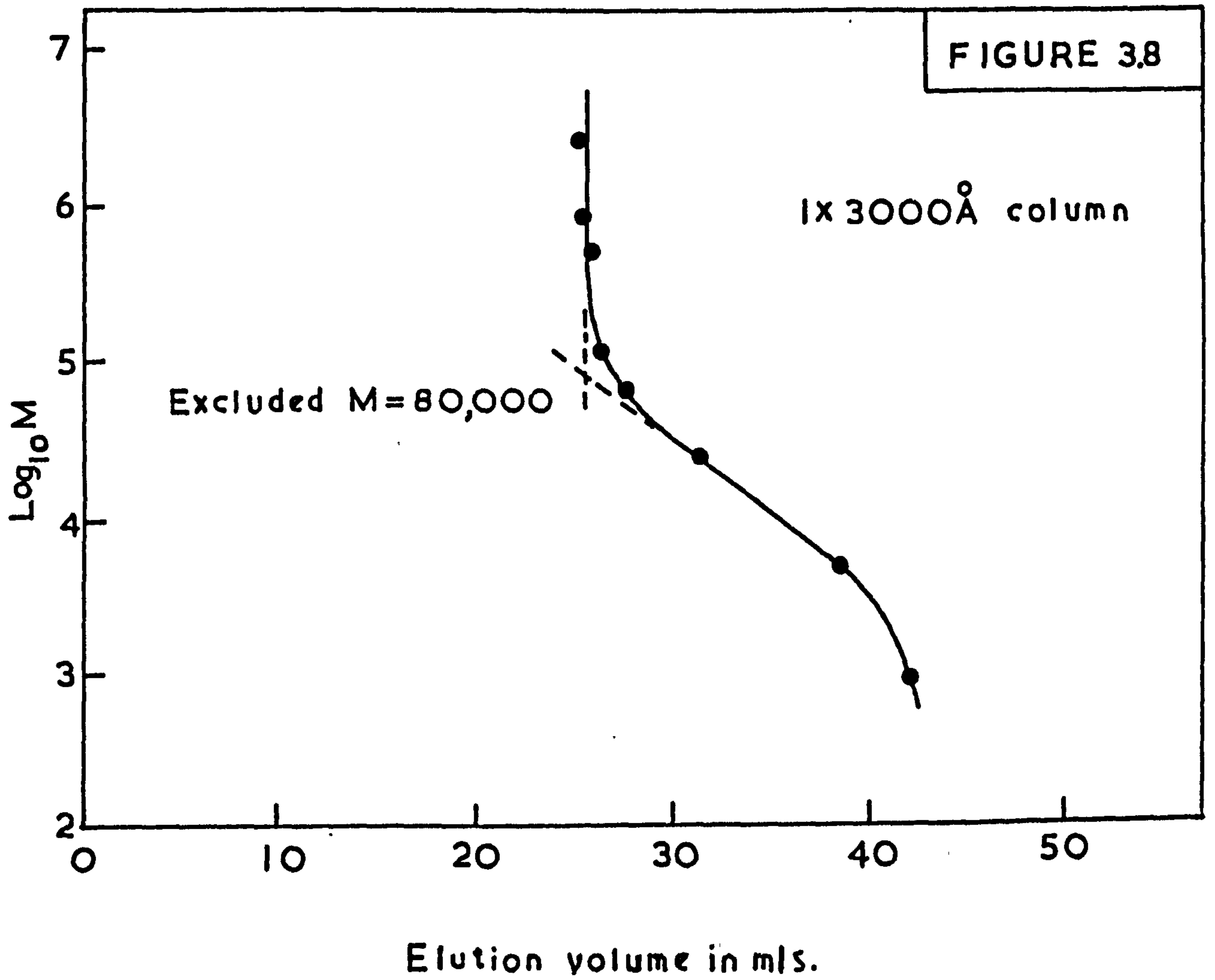
3.5 SEPARATIVE CAPABILITY OF "STYRAGEL" COLUMNS

The samples used in testing the columns were three mixtures of cyclic oligomers, those respectively of poly(ethylene terephthalate)

(henceforth PET), poly(decamethylene adipate) (FDA) and poly(ethylene succinate) (PES). To anticipate later findings, the first mixture contained trimer to decamer (in molecular weight, 576 to 1920), the second monomer to pentamer (284 to 1420), and the last dimer to heptamer (288 to 1008). The cyclic trimer of PET and the dimer of PES were available in pure form. FDA, of $M_w = 26500$, was used if it was necessary to have a material of molecular weight much above those of the oligomers. (The means by which these substances were obtained, and the properties they exhibited that lead to their characterisation, will be fully described in the appropriate Chapters.)

The separative capabilities of any column with respect to a particular mixture will be determined by its "calibration" (i.e. the dependence of the elution volume of a species upon its molecular weight, or, more precisely, molecular dimensions) and its "theoretical plate count", upon which depends the breadth of a peak eluting at a certain volume.

A typical calibration is shown in Figure 3.8; plotted as the logarithm of molecular weight against elution volume, the curve has a central linear part, but tails up at the upper end, and down at the lower. Extrapolation of the linear portion to the void volume, i.e. the volume of the solvent outside the beads in the column, gives the "excluded molecular weight", supposedly that of a species just too large to enter any of the pores⁴⁴. Often, this is re-expressed as a (nominal) "pore size", by converting the excluded molecular weight to a molecular dimension: if narrow polystyrene fractions have been used to set up the calibration, the molecular weight is divided by a factor close to 40 to find the pore size, in \AA units. It is important



to note, however, firstly, that the excluded molecular weight and the pore size are no more than nominal parameters, and secondly, that the actual working range of a gel lies very much below these limits⁵⁰.

The plate count of a column, or set of columns, may be found from a resolved peak by measuring its peak elution volume, V_e , finding the volume W equivalent to its "width" (Figure 3.9). and using the equation⁵¹:

$$N = 16 \left(\frac{V_e}{W} \right)^2$$

Commonly, the number of plates, N , is divided by the total length of the column(s) in feet, to give the "theoretical plates per foot", TPF. Broadly speaking, a higher TPF indicates a better-packed column: but care must be taken in the interpretation of the values obtained, since they depend upon many factors; notably, the molecular weight of the test substance, and the flow rate. Thus, at 1.0 ml./min., some of the columns packed gave counts of 900 TPF for the solvent impurity peaks; but none gave a value higher than about 300 for the cyclic trimer of PET. At lower flow rates (0.1 - 0.2 ml./min.) the trimer peak became narrower, and the TPF found rose towards 800; while the solvent impurity peaks underwent little change. Effects of this sort have been observed before; Heitz⁴¹ attributes them to the relatively slow diffusion of the higher molecular weight species in and out of the gel pores.

The first columns packed were with gels of pore sizes of 3000Å and over. For such gels, all the cyclic oligomers eluted close to (sometimes after) the major impurity peak (probably due to water). Later studies therefore concentrated on columns with pore sizes

60 Å - 1000 Å; and examples will now be given of separations achieved with various combinations of such columns. In the tracings, the peaks for the different cyclic components will be identified according to the number of repeat units per molecule.

(a) Figures 3.10 and 3.11 compare the peaks obtained when respectively the pure cyclic trimer, and the mixture of cyclics, from PET, were injected onto a single packed 150 - 350 Å column at a flow rate of 1 ml./min.; it was evident from this that higher species were indeed in the mixture.

(b) In Figure 3.12, the same mixture was injected onto a combination of the above 150 - 350 Å column with a 60 Å and a 100 Å, both supplied by Waters Associates. The trimer is now a distinct peak. In the following two Figures, the separations of the mixtures of aliphatic oligomers are shown. All three runs were at 1 ml./min..

(c) Replacement of the 60 Å column (which was noted to have most effect in separating the impurity peaks) by a packed 100 Å, and addition of a further packed 150 - 350 Å column, gave the tracing in Figure 3.15. The cyclic tetramer of PET is now apparent, as a slight bump between the trimer and the higher species.

(d) Figure 3.16 shows the PET oligomers injected onto the same set, save with the further addition of a packed 1000 Å column. The separation was unaffected; the elution volumes of the peaks were uniformly increased by the total solvent capacity of the new column. Separations of the aliphatic oligomers under same conditions are shown in Figures 3.17 and 3.18.

(e) Comparison should now be made between the tracings in Figures 3.12 and 3.15, and that in Figure 3.19. The first was obtained

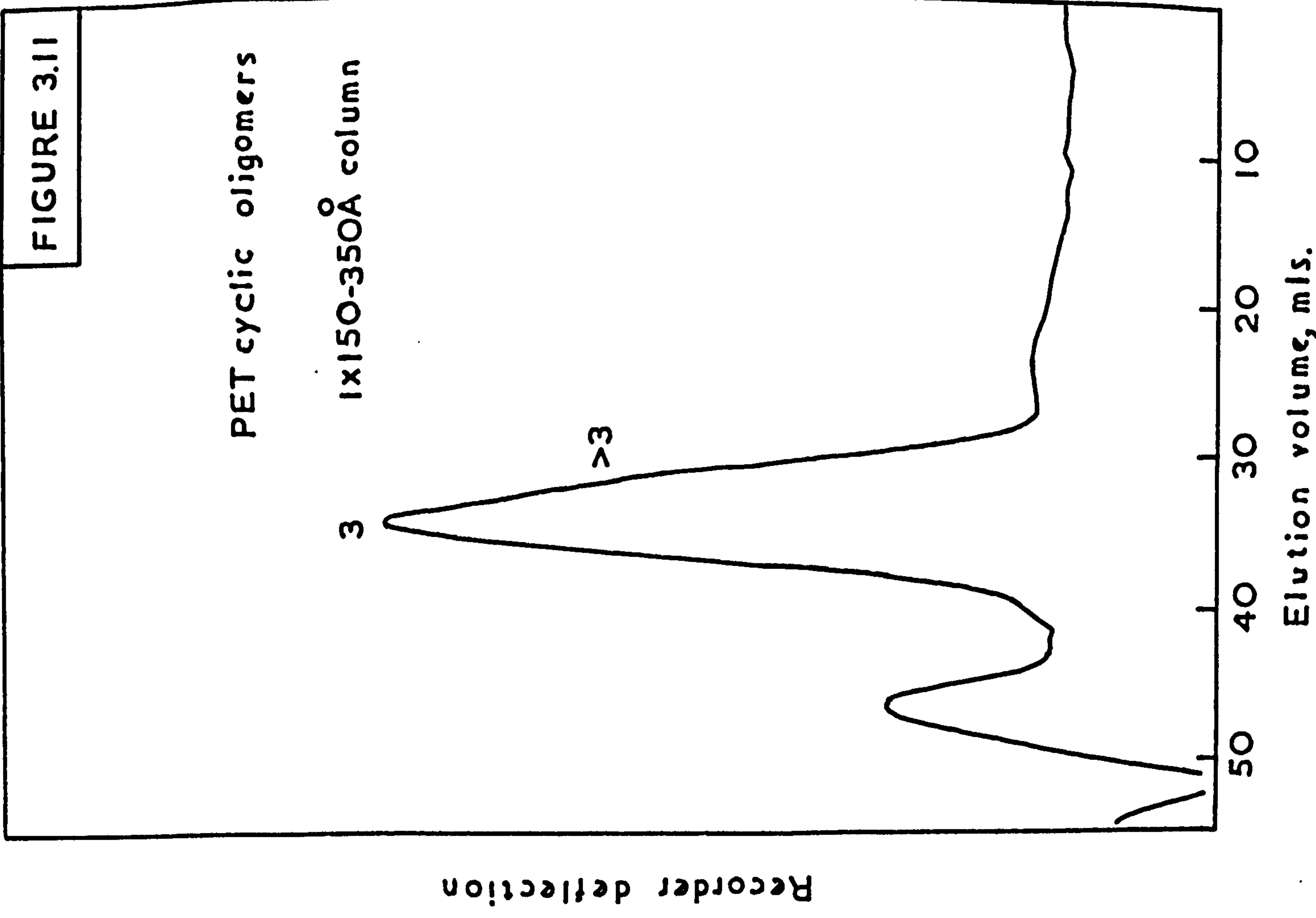
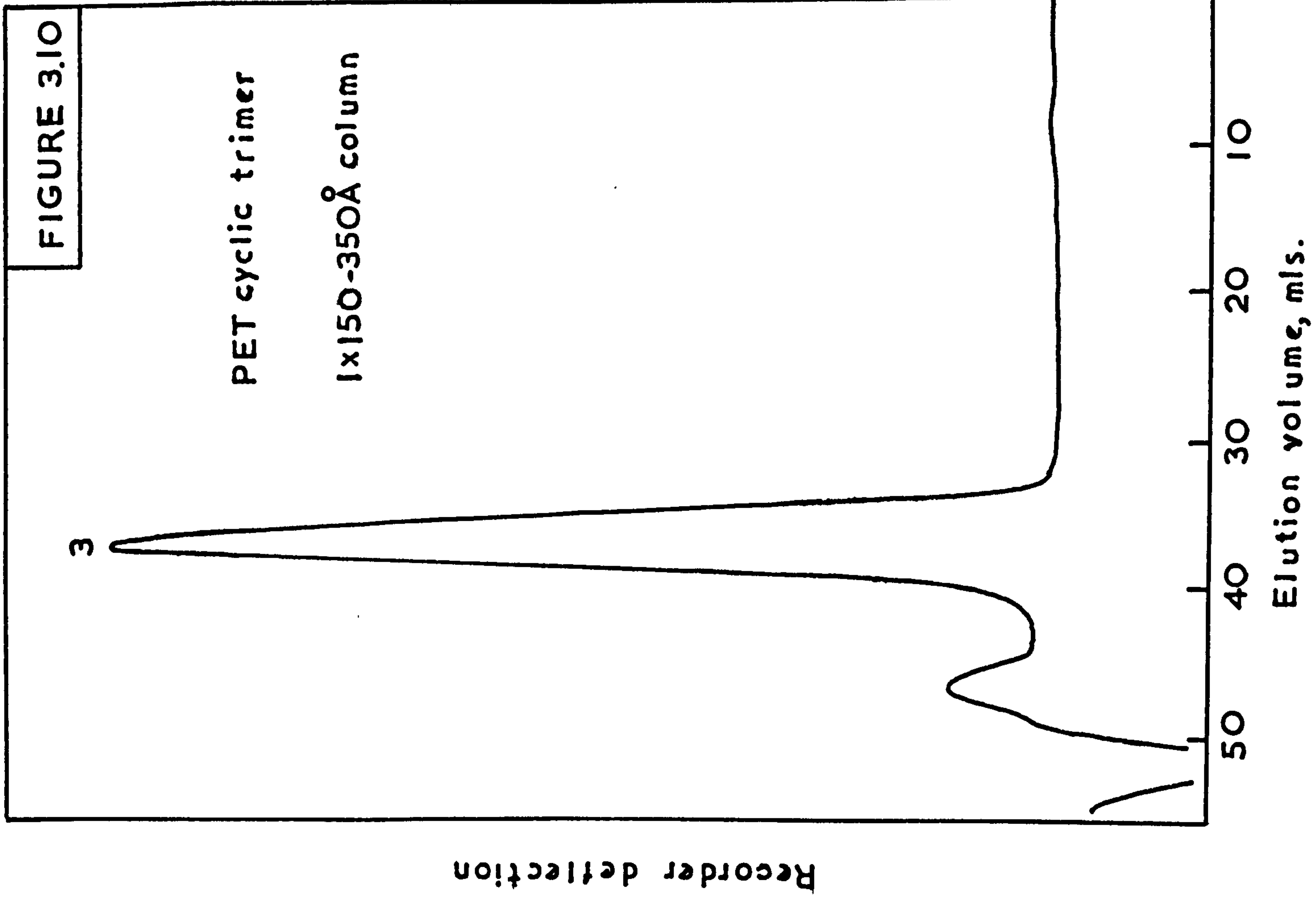
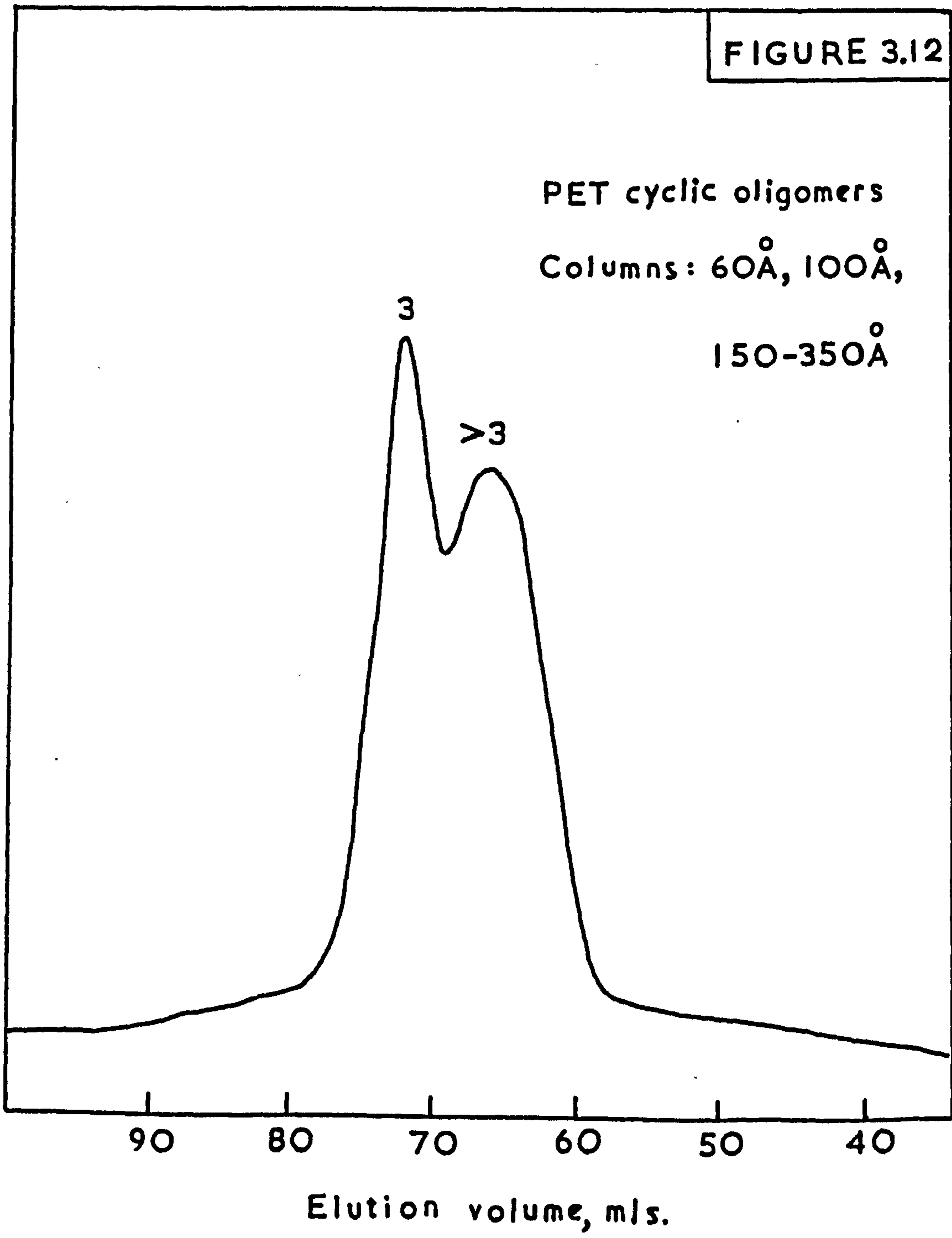
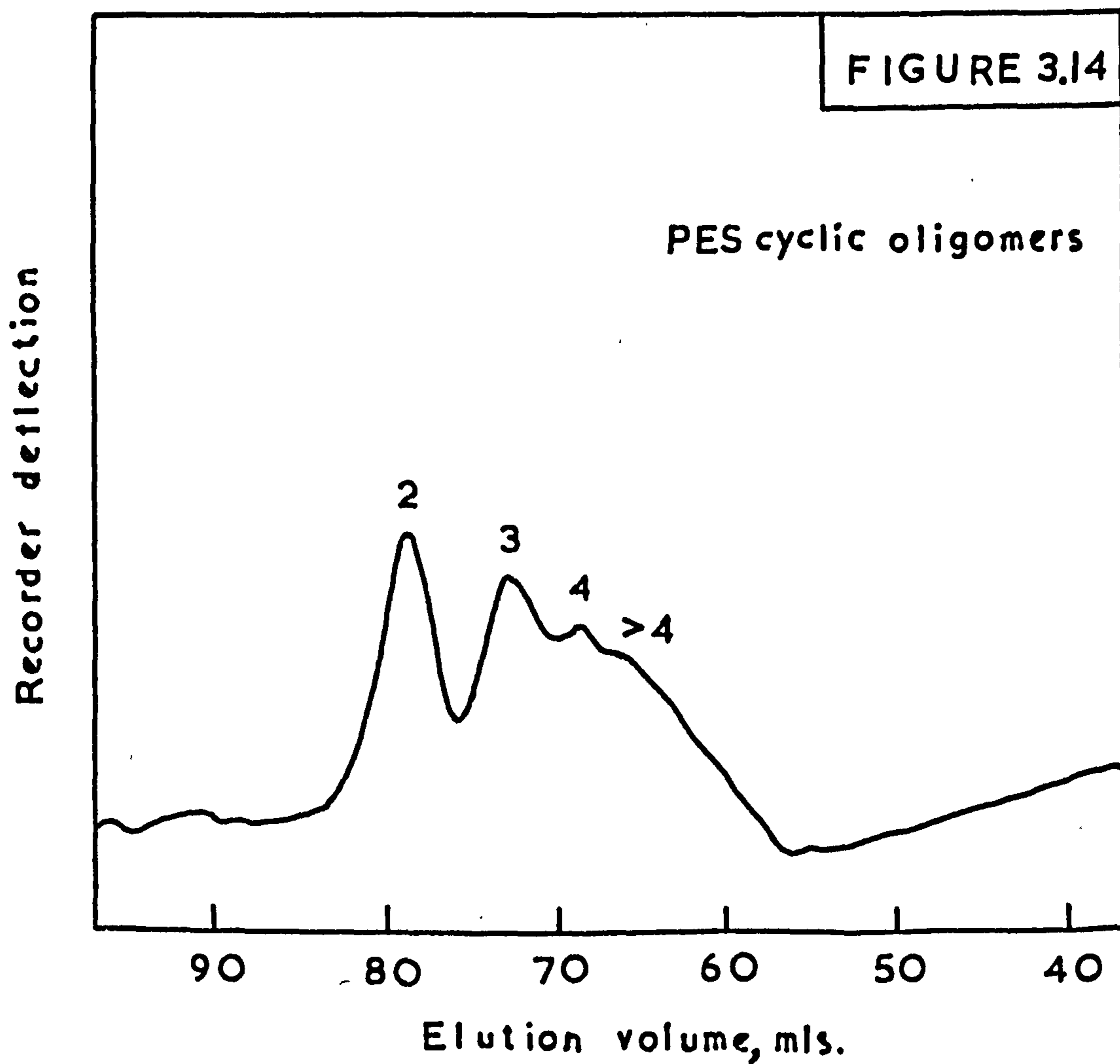
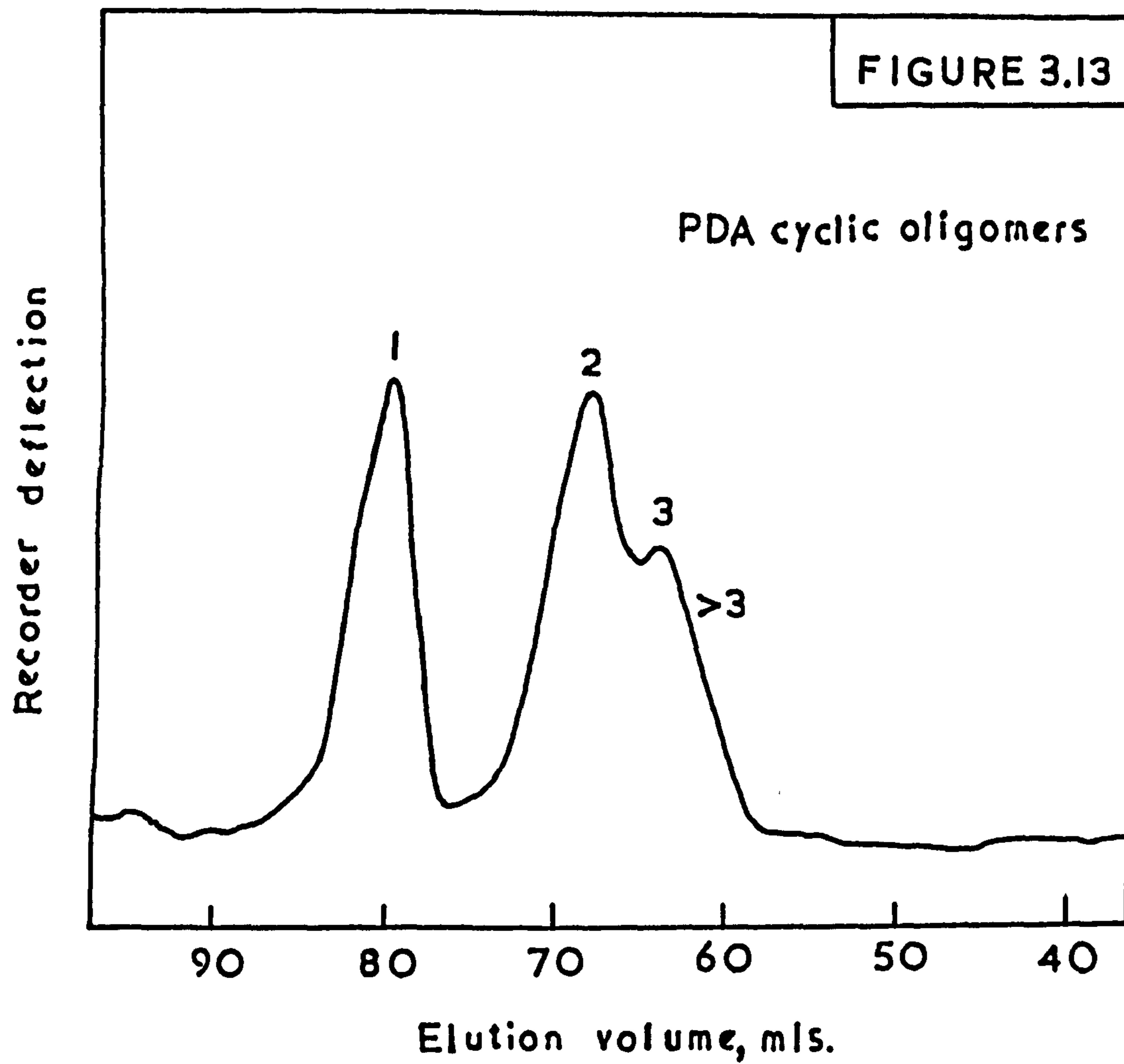


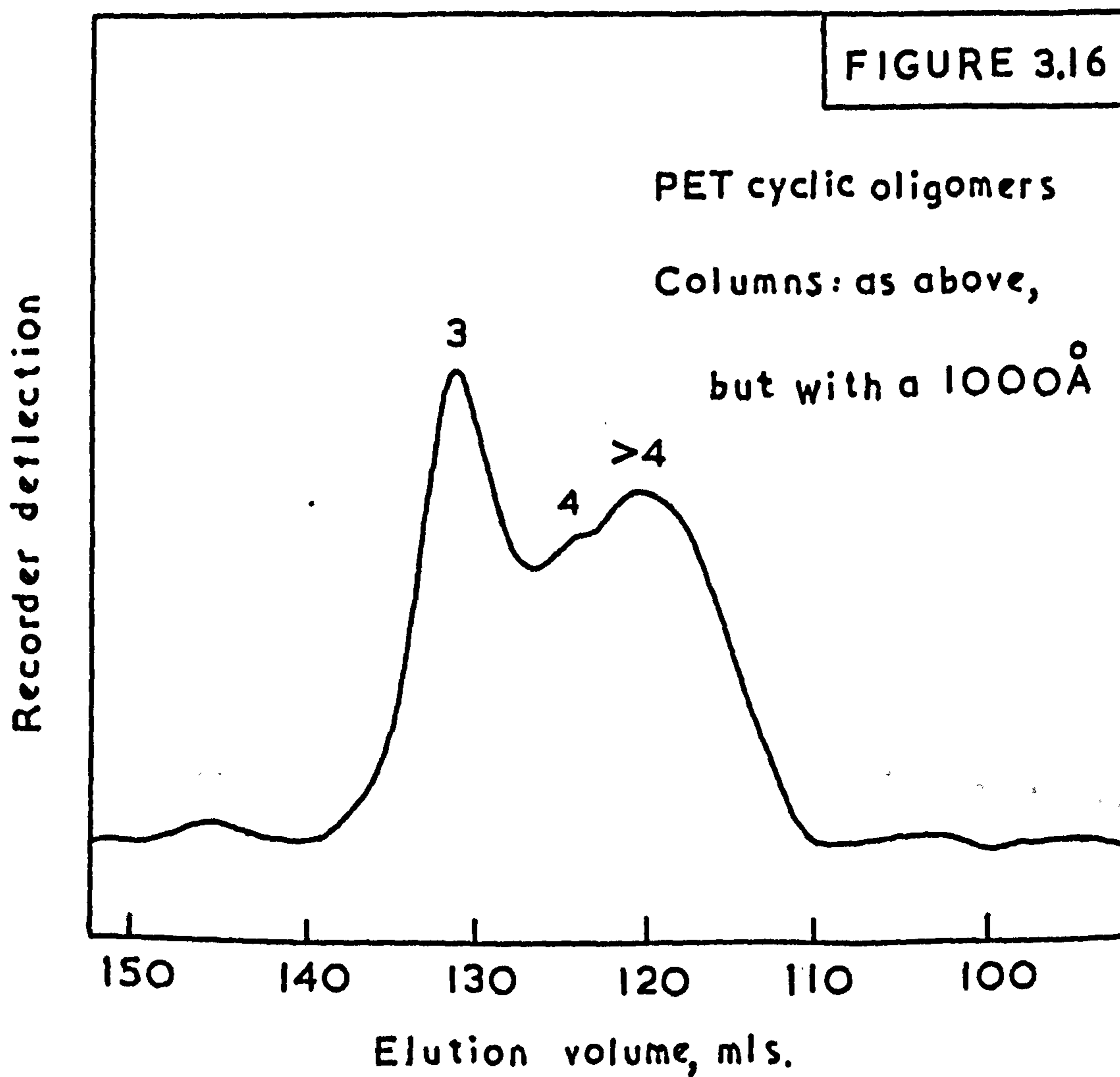
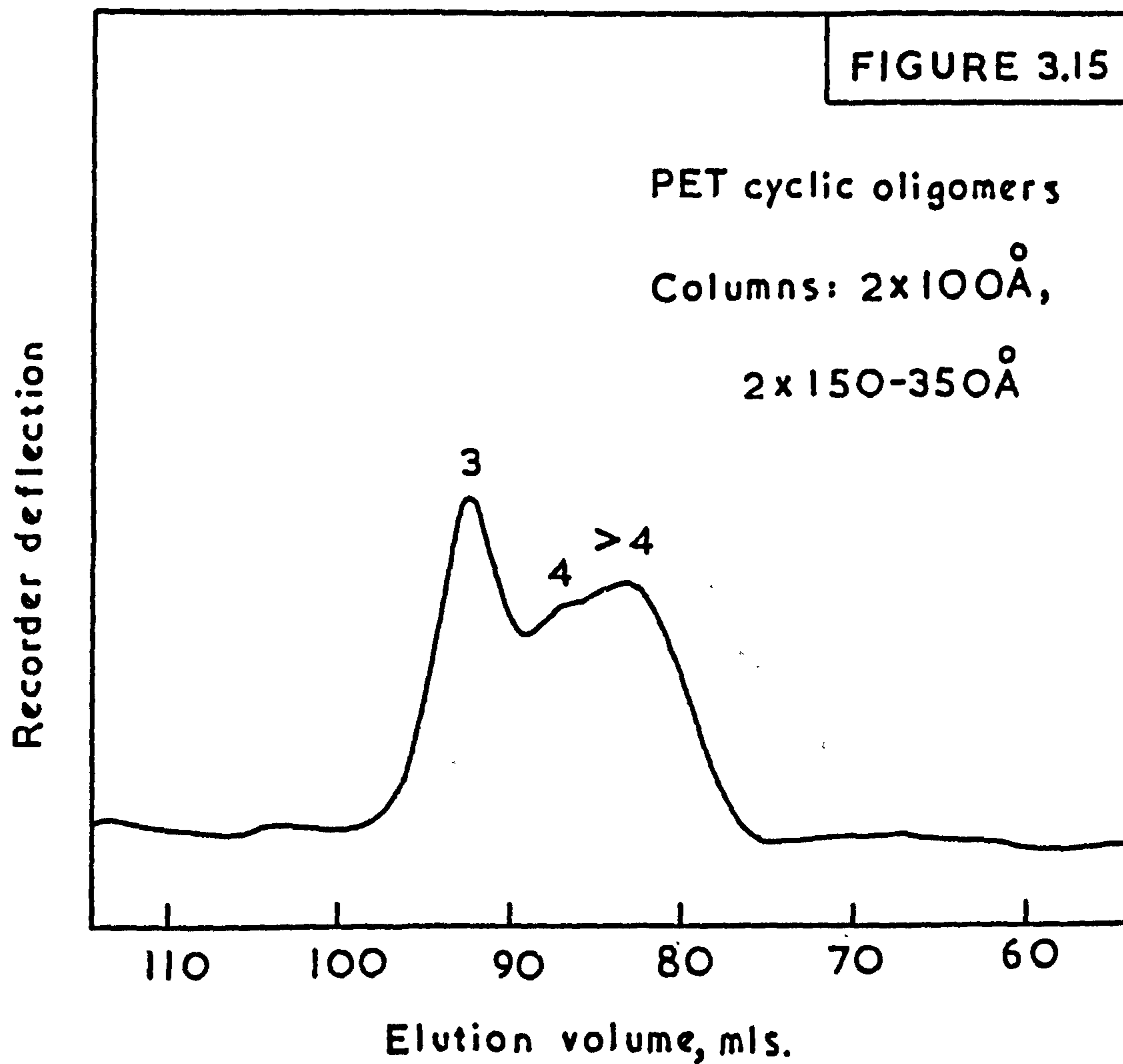
FIGURE 3.12

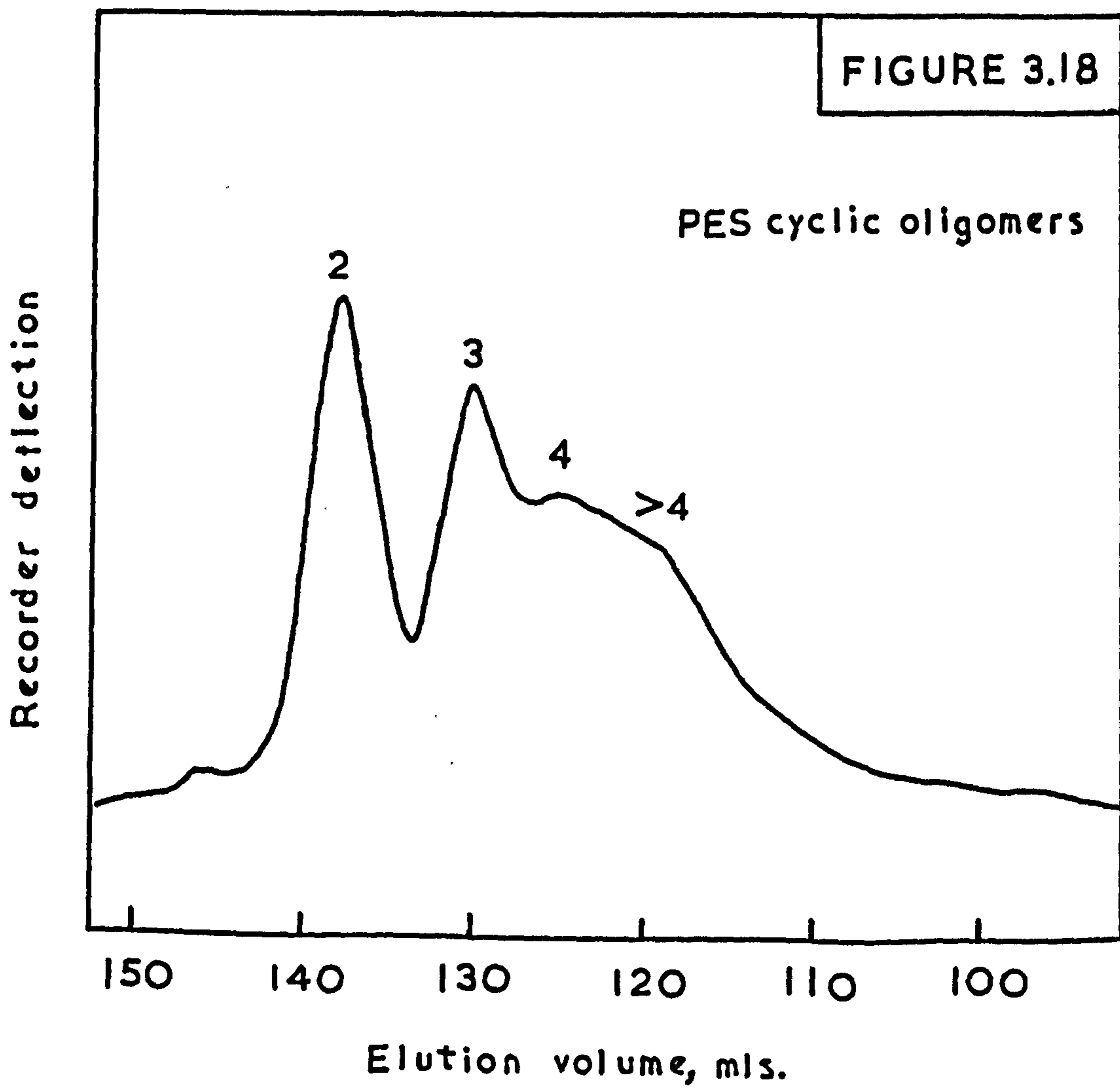
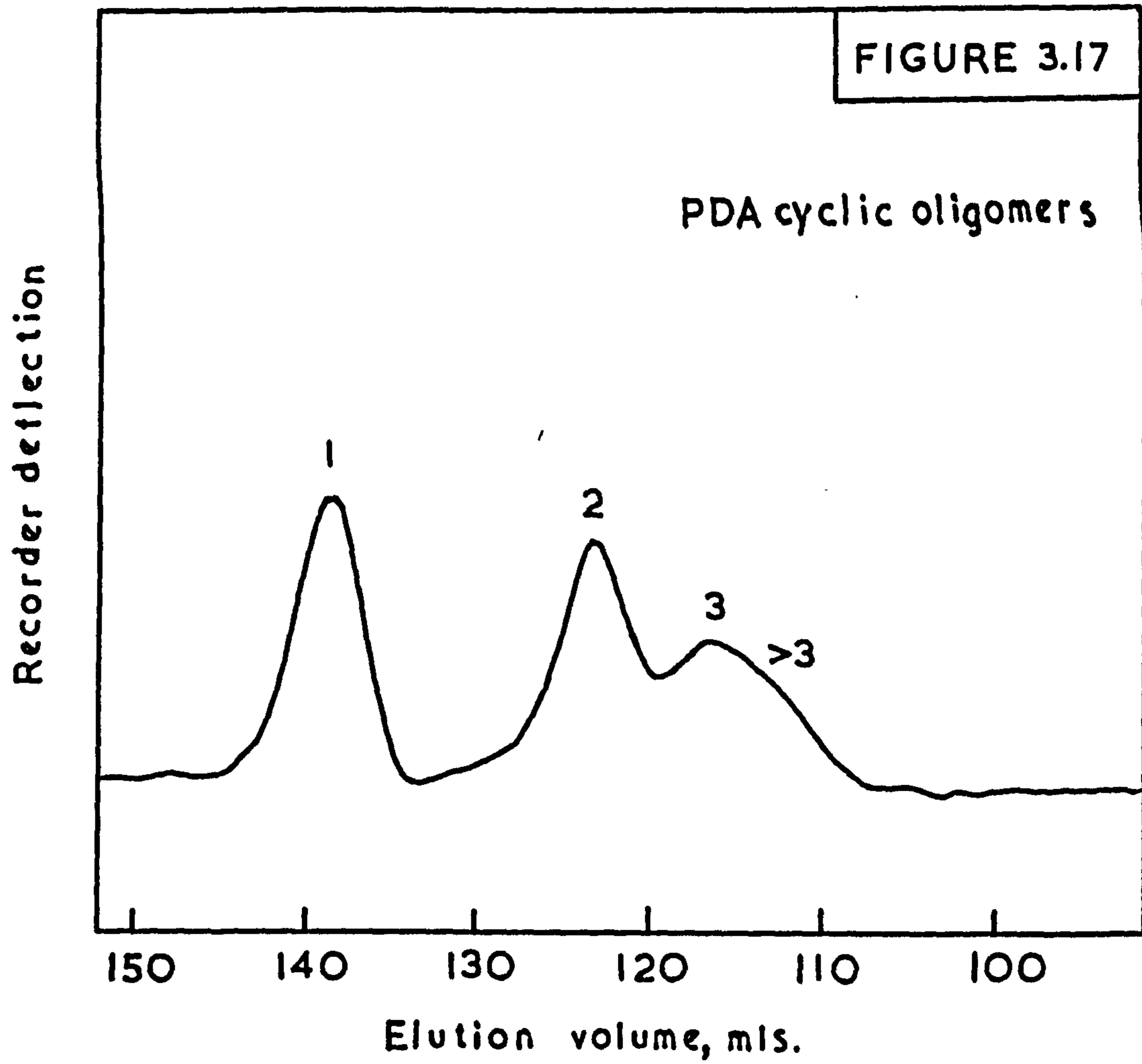
PET cyclic oligomers
Columns: 60Å, 100Å,
150-350Å

Recorder deflection









with three columns, the second with four, the third with three (2 x 150 - 350 Å, 1 x 100 Å); but for the last separation, the flow rate was reduced from 1.0, to 0.1 - 0.2, ml./min.. The separation is much enhanced; the cyclic trimer of PET is almost perfectly resolved, the tetramer is a distinct peak, and in the shoulder on the residual hump there is a clear indication of the pentamer. The separation of the oligomers of PDA was also improved (Figure 3.20).

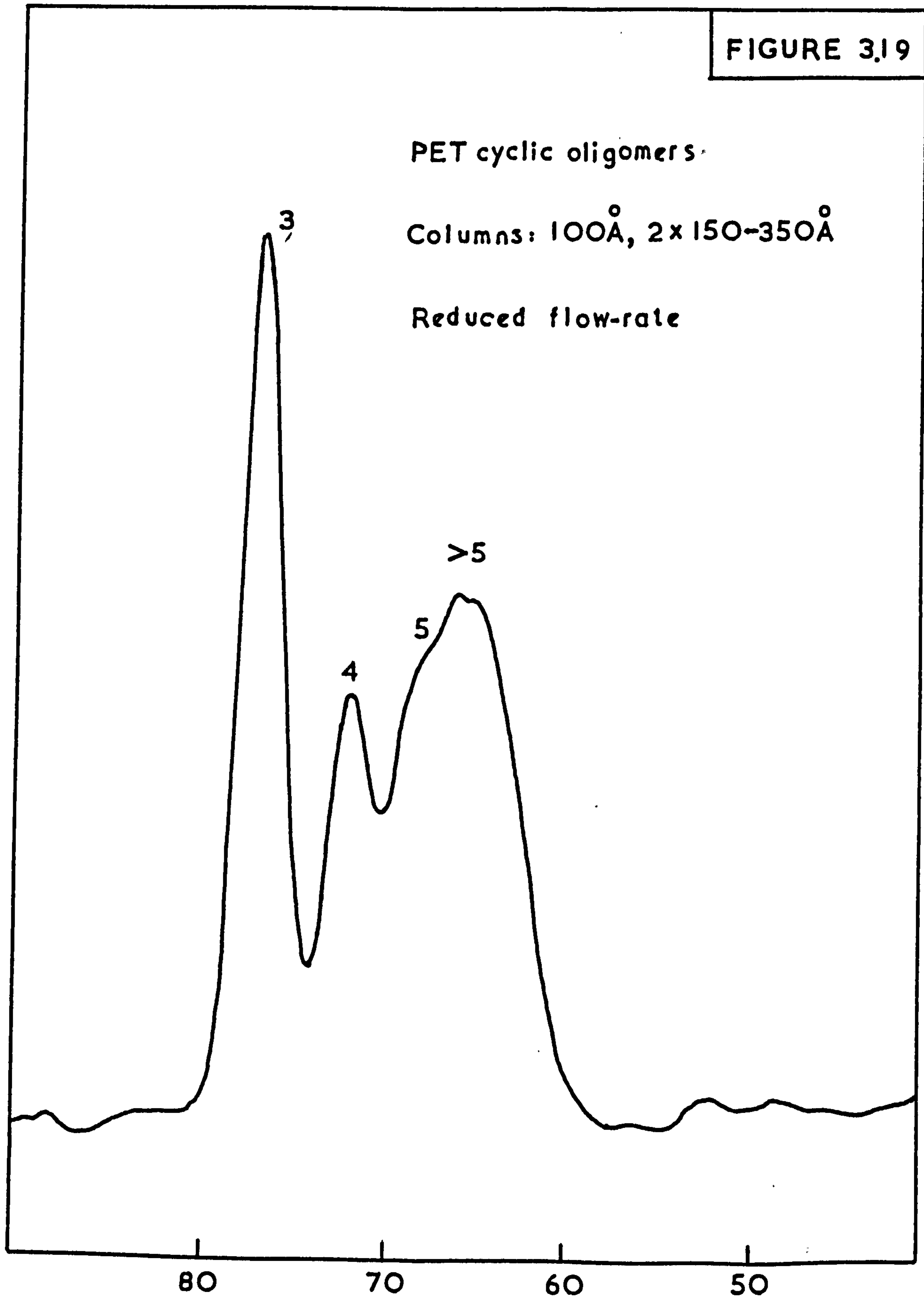
However, these were the best separations ever to be achieved with Styragel columns. For the cyclic trimer in the trace in Figure 3.19, the plate count is approaching 800 TPF, in comparison to the maximum of 1000 claimed for the commercially available columns; clearly there was little wrong with the packing. Yet, even with three columns, under conditions of low flow, the cyclics above tetramer remained subject to an intractable compression. Clearly the fault lay with the the separative characteristics intrinsic to the gels selected.

It was expected that properties intermediate to those of the 1000 Å gel (previously rejected as having too large a pore size), and the 100 Å and 150 - 350 Å gels in use, might be found in the gel marketed as having a pore size of 500 Å. But the results from this gel were disappointing; insofar as concerned the separation of the cyclic oligomers, it proved indistinguishable from the 100 Å and 150 - 350 Å gels. It would therefore appear that, despite the continuity in the range of nominal pore sizes in the gels available, there is a marked hiatus in their actual properties: for the Styragels up to 500 Å quoted pore size, the cyclic oligomers (of PET)

FIGURE 3.19

PET cyclic oligomers
Columns: 100Å, 2 x 150-350Å
Reduced flow-rate

Recorder deflection



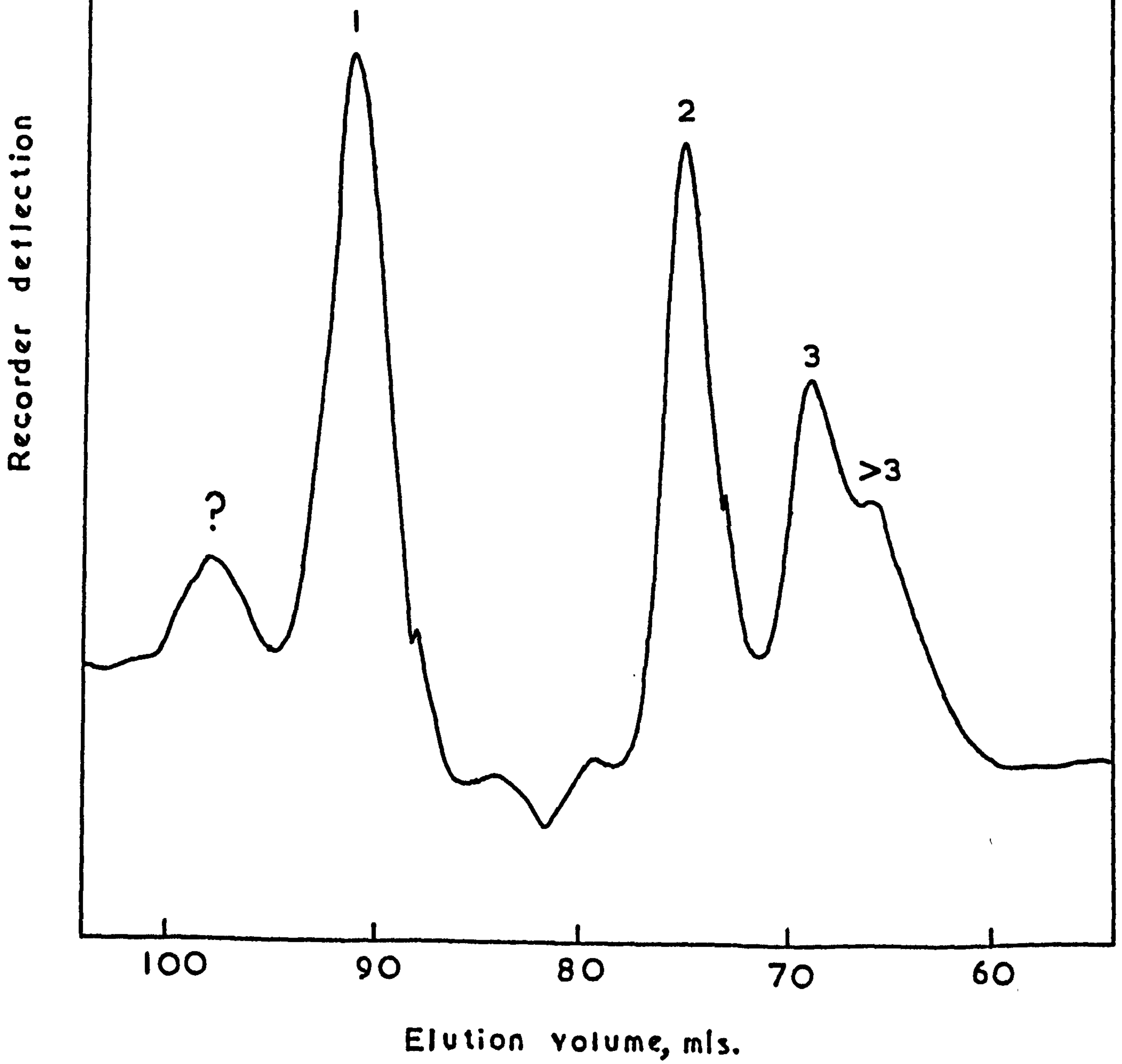
Elution volume, mls.

FIGURE 3.20

PDA cyclic oligomers

Columns: 100Å, 2x150-350Å

Reduced flow-rate



lie at the upper end of the useful separative range; for those above the 500 Å, they lie at the lower end. Conceivably, this break is connected with a change in the method of preparation of the gel (Section 3.1).

Since it was plain that the necessary separations could not be effected by means of Styragel, its use was discontinued.

3.6 PACKING AND PERFORMANCE OF "BIO-BEAD" COLUMNS

It being clear that use of Styragel was inappropriate for the analysis of the mixtures of cyclic oligomers under consideration, attention was directed towards other available media for gel permeation chromatography. That which was finally adopted, and which proved capable of separating the mixtures, was the polystyrene gel supplied as "Bio-Beads" (Bio-Rad Laboratories, St. Albans); and, in particular, the type specified as "SK-1".

Unlike Styragel, Bio-Beads are only lightly cross-linked, and are extensively swollen by many solvents. Therefore, the procedure for packing Bio-Bead columns must differ from that for Styragel: and that, on two counts. Firstly, the swollen beads are soft and rubbery, and cannot be packed under great pressure, for they deform; then, not only do they compress to a solid mass of high resistance to solvent flow, but, further, they become forced into the interstices of the end-fitting sinter, so that this is irremediably blocked. Secondly, they must be packed in the solvent used for the g.p.c.. Indeed, attempts were made to pack using gel slurried in a balanced mix of solvents, and then flush out these solvents before sealing the column: but the

resistance of these columns later rose to unworkable levels, undoubtedly because the gel was undergoing further swelling.

Several of the $\frac{3}{8}$ " O.D. columns* were packed using the rig described in Section 3.4. About 30 ml. dry gel were left for a day to swell with 200 ml. chloroform; then, as before, the slurry was degassed, introduced into the reservoir, and pumped round into the column. Because the density of the solvent had in no way been adjusted to match that of the gel, the swollen beads tended to rise upon standing; therefore, it was preferred to forego the initial period of slow pumping, normal when packing Styragel, and instead sweep the slurry into the column while it remained homogeneous. Finally, it was tamped in by 10 - 15 mins. pumping, at up to 600 - 800 p.s.i. Constant attention was essential at this stage, since the pressure could rise very suddenly and rapidly to well over 1600 p.s.i.

Even for the solvent impurity peaks, these columns did not exhibit high plate counts (only about 400 TPF), and so a packing procedure like that of Heitz and Coupek⁴³ was tried instead. In this, the column to be packed was extended by fitting another onto it, to serve as a slurry reservoir. The assembly was stood vertically; slurry was poured in through a funnel, and allowed to settle as the solvent dripped out of the lower end-fitting under gravity. When the level of the gel bed rose to the top of the upper column, this was equipped with an end-fitting, so that a slow flow of solvent could be pumped down

* Mulder and Buytenhuys⁵⁰ have recommended wider ($\frac{3}{4}$ " O.D.) columns. Here it was found, however, that with columns of this width every peak was preceded by a tail, spoiling the separation. It must have been, that part of the solvent was taking routes through the column that did not bring the sample into full contact with the gel; these preferred pathways may have lain along fissures in the gel bed itself, or perhaps between the bed and the column walls. No such effects were observed with the narrower columns.

through the bed. The flow rates tried were between 0.5 and 2.0 ml./min., sustained for periods of 12 - 48 hours; because the design of the pump on the packing apparatus did not permit it to produce such low flows over protracted periods, use was made instead of a Hughes metering pump, of the sort commonly used in g.p.c. systems. Once the pumping had been completed, the flow was stopped, the reservoir removed, and the column sealed with a second end-fitting; it was transferred to the g.p.c. for testing.

This method was not really suitable for such narrow columns, however. Firstly, it was difficult to introduce the gel slurry into the column-reservoir assembly without mixing in air-bubbles; and, secondly, it was not possible to stir the slurry above the actual gel bed, to ensure that it remained homogeneous, and settled down uniformly. In consequence, the columns that resulted were also of poor quality. Nevertheless, it was found possible to achieve the desired separations with such columns, as the following examples will show.

(a) Figures 3.21 and 3.22 show separations of the mixed oligomers of PET (Section 3.5) on a single column of typical resolving power. In the first trace, obtained at 1 ml./min., the plate count for the solvent impurity is about 300 TPF, for the cyclic trimer, only 200; in the second, obtained at 0.25 ml./min., the trimer gave a count increased to around 300. The trace in Figure 3.21 may be compared to that in Figure 3.11, for a single Styragel column at the same flow rate; and the trace in Figure 3.22, to that in Figure 3.19, for three Styragel columns at a slightly lower flow. The greater suitability of Plo-Beads for these analyses is at once apparent.

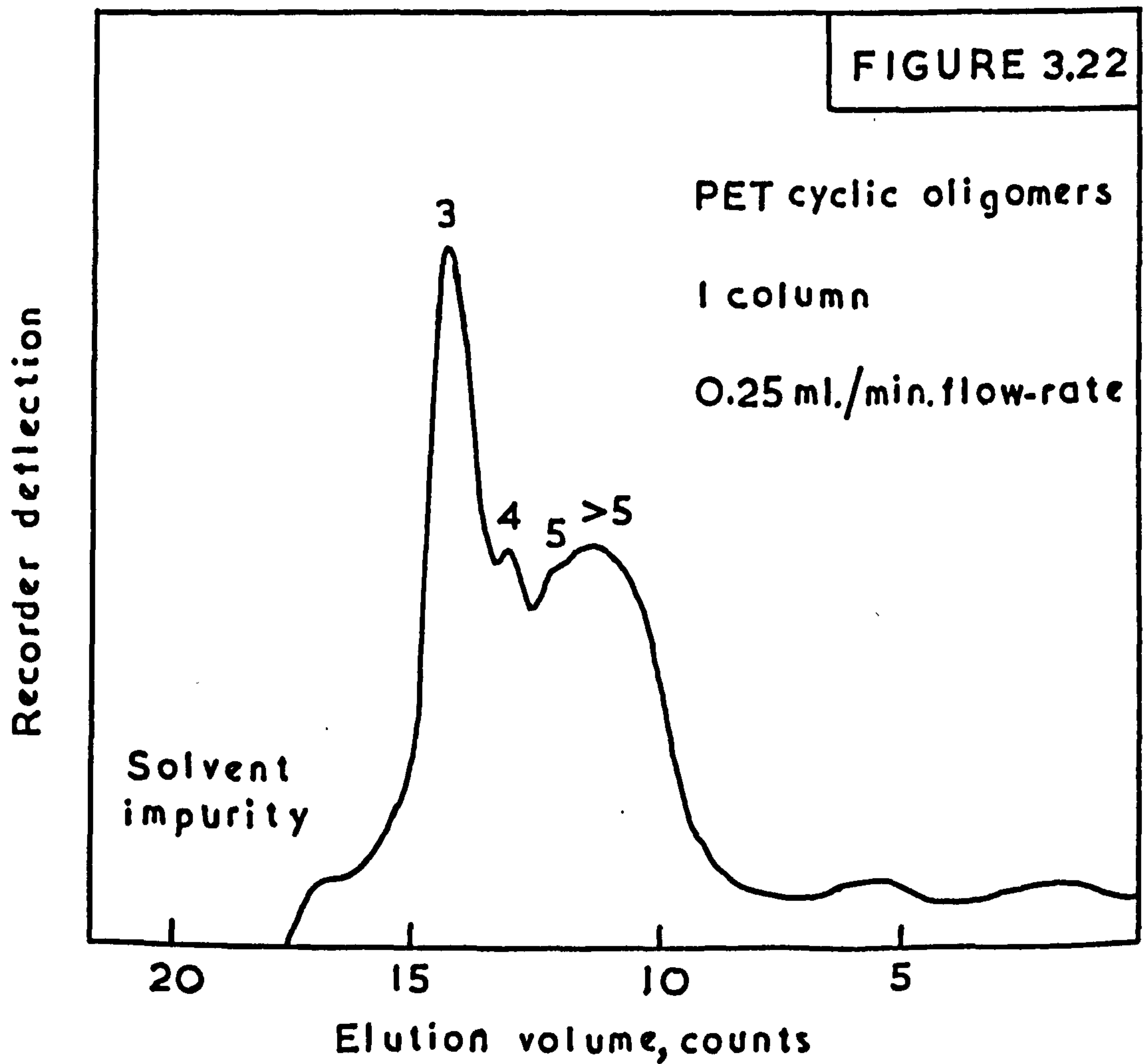
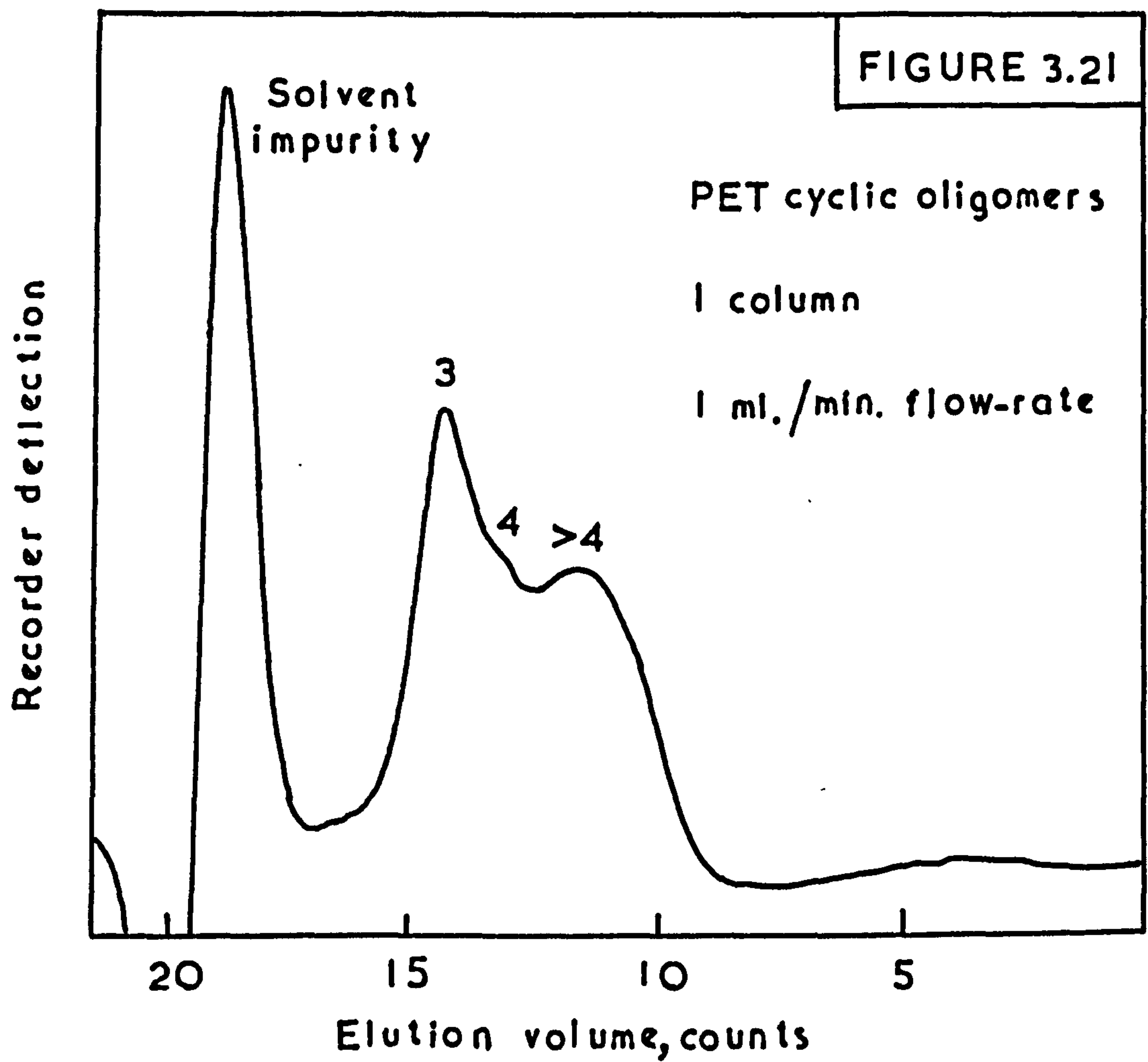


FIGURE 3.23

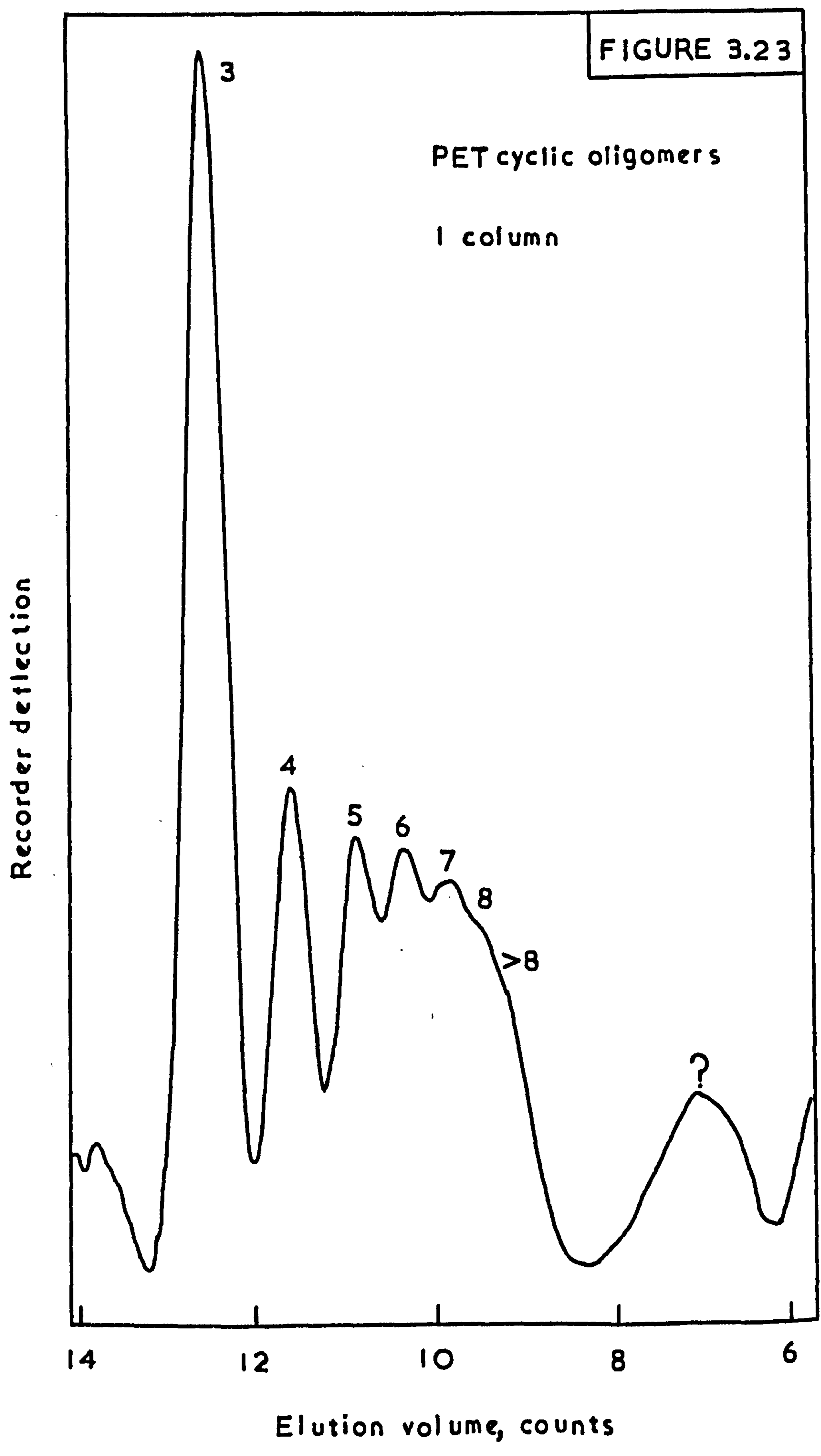


FIGURE 3.24

PET cyclic oligomers

2 columns

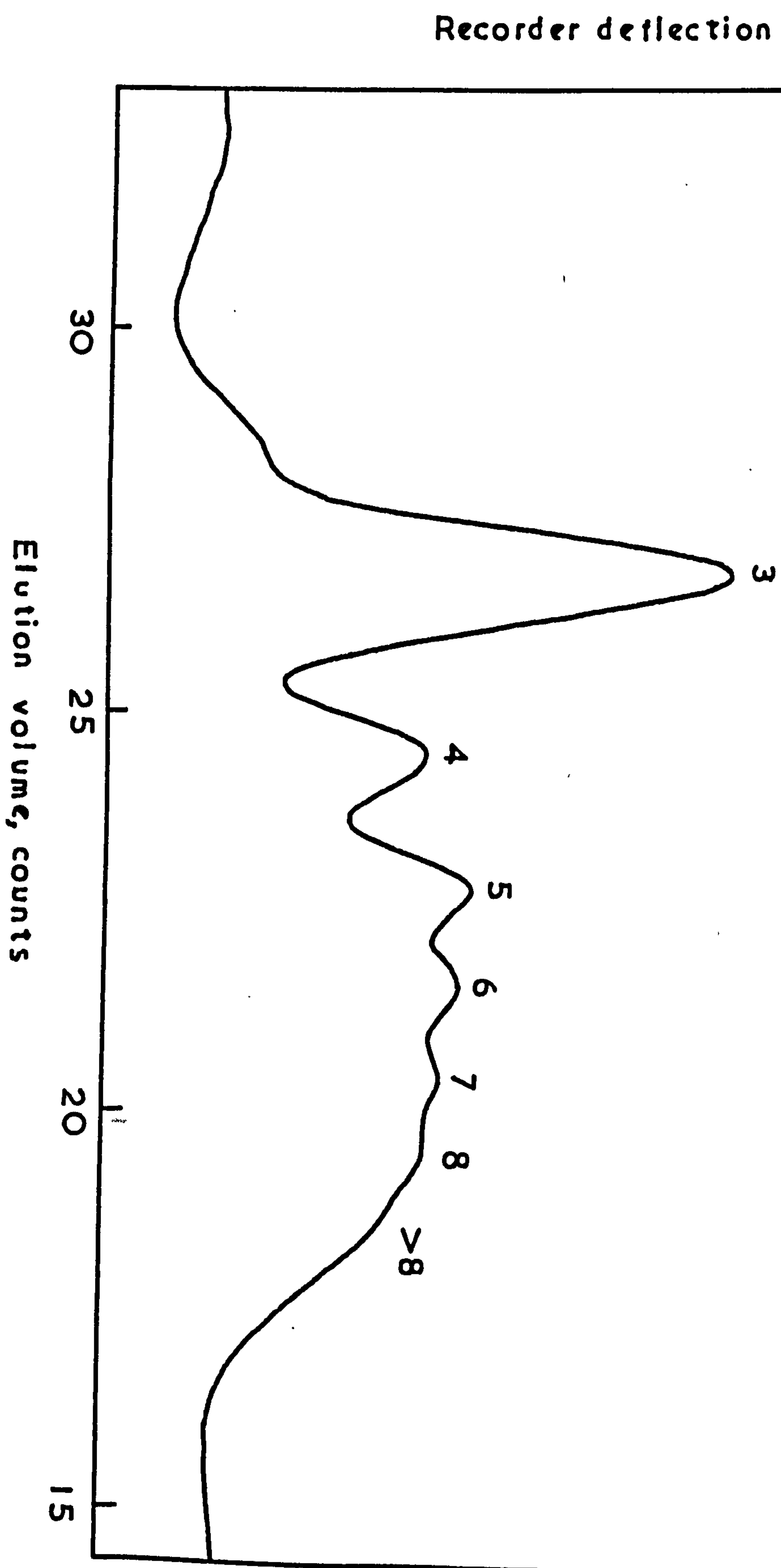


FIGURE 3.25

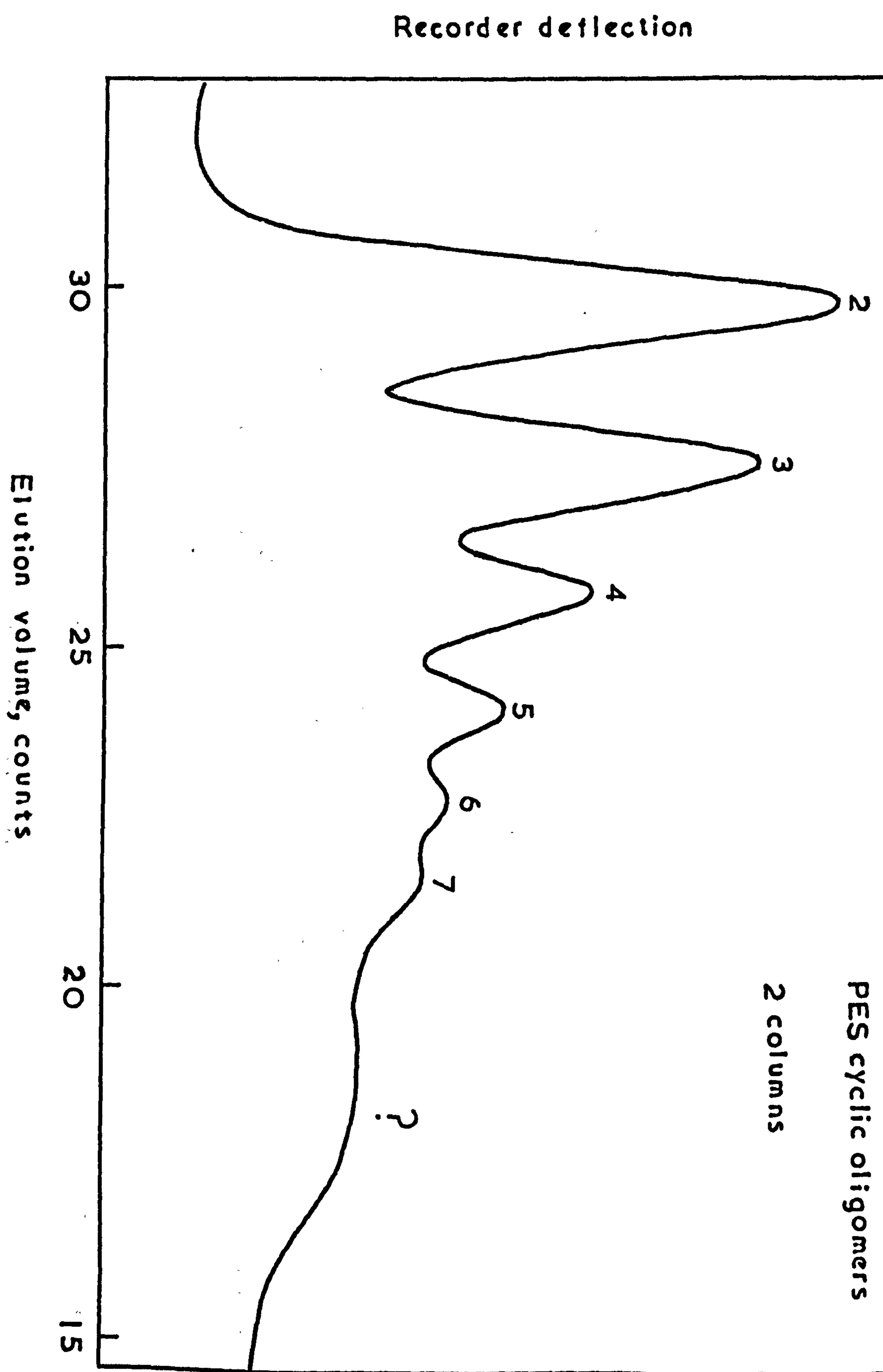
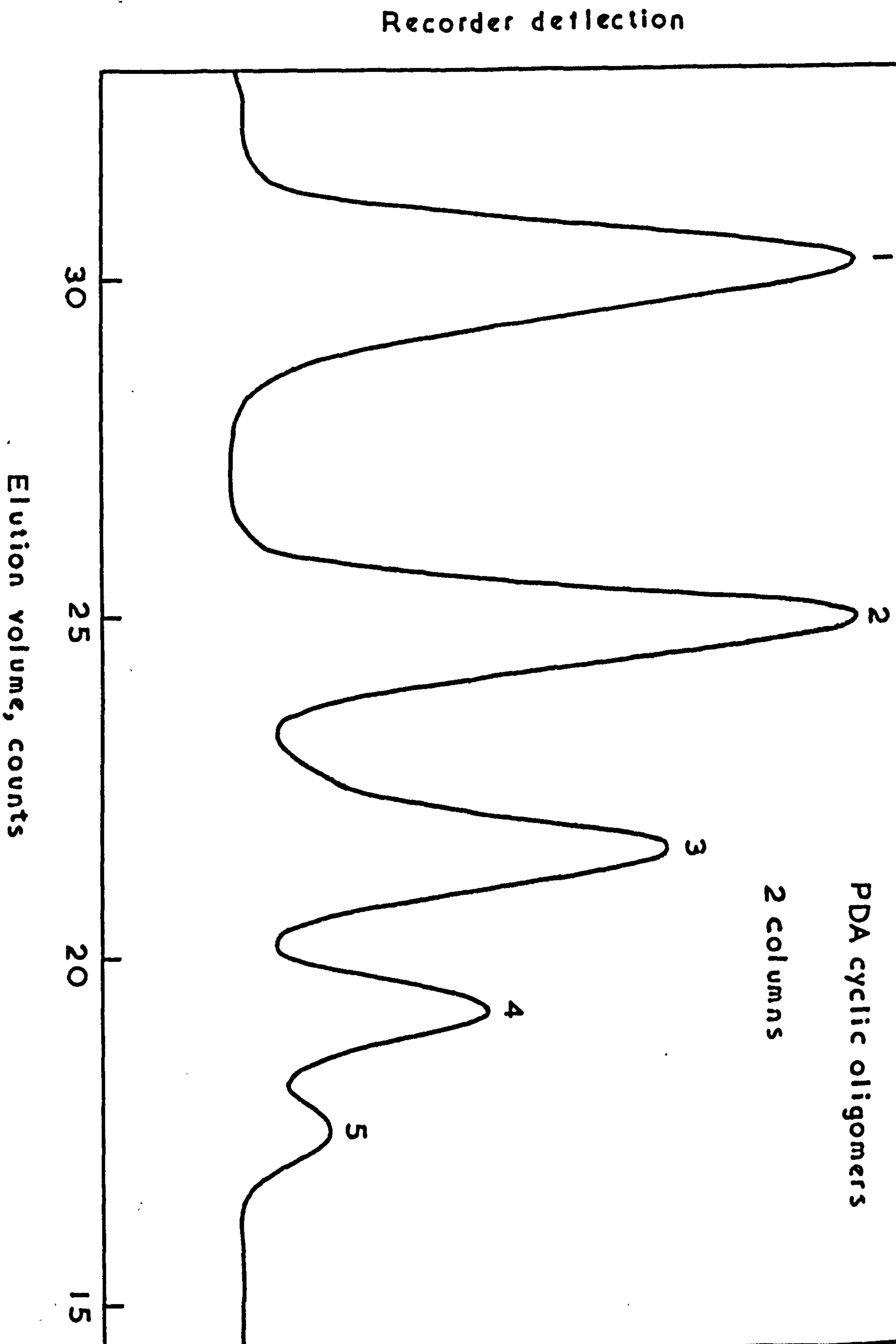


FIGURE 3.26



(b) The next Figure depicts the outcome of an injection of the same sample onto a single column that briefly showed an exceptional resolving power. Here it is possible to discern the cyclics up to octamer; and it would certainly be possible to estimate the proportions of trimer and tetramer from such a tracing. The plate count for the trimer is 1200 TPF. Regrettably, this column underwent a rapid deterioration, and afterwards gave no more than normal resolution.

(c) Figures 3.24, 3.25 and 3.26 show the oligomers of PET, PDA, and PES, respectively, analysed on a combination of two columns of typical plate counts, at flows of 0.2 ml./min.. The cyclics from PET are still imperfectly separated, but those from P.D.A. are almost completely resolved from monomer to pentamer. It would certainly be possible to estimate the proportions of all five of these rings.

(d) Finally, there are shown in Figures 3.27 to 3.29 the results of using four such columns in series. These runs were obtained at 0.15 - 0.30 ml./min.

In Figure 3.27, the tracing for the mixture of cyclic oligomers from PET is shown. In this, the species from trimer to nonamer are discernible as peaks; the decamer is visible as a distinct ripple in the curve. From this trace, it would be possible to directly determine the proportion of trimer in the mixture, to high precision; the tetramer, pentamer and higher rings could be estimated with diminishing accuracy. In conjunction with a computer analysis of the tracings, to be described in the next Chapter, it proved possible to determine the concentrations of the rings up to nonamer with adequate precision.

FIGURE 3.27

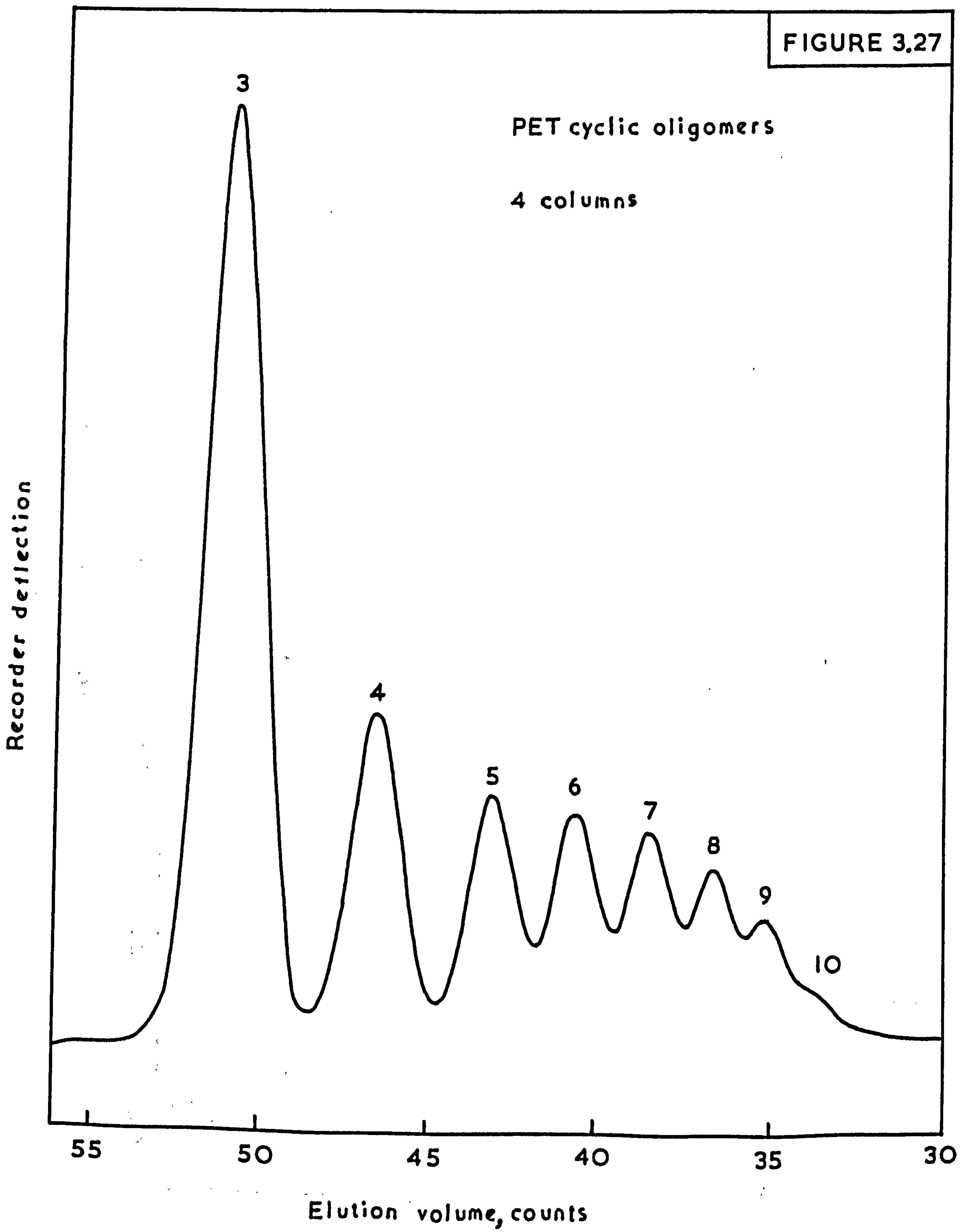
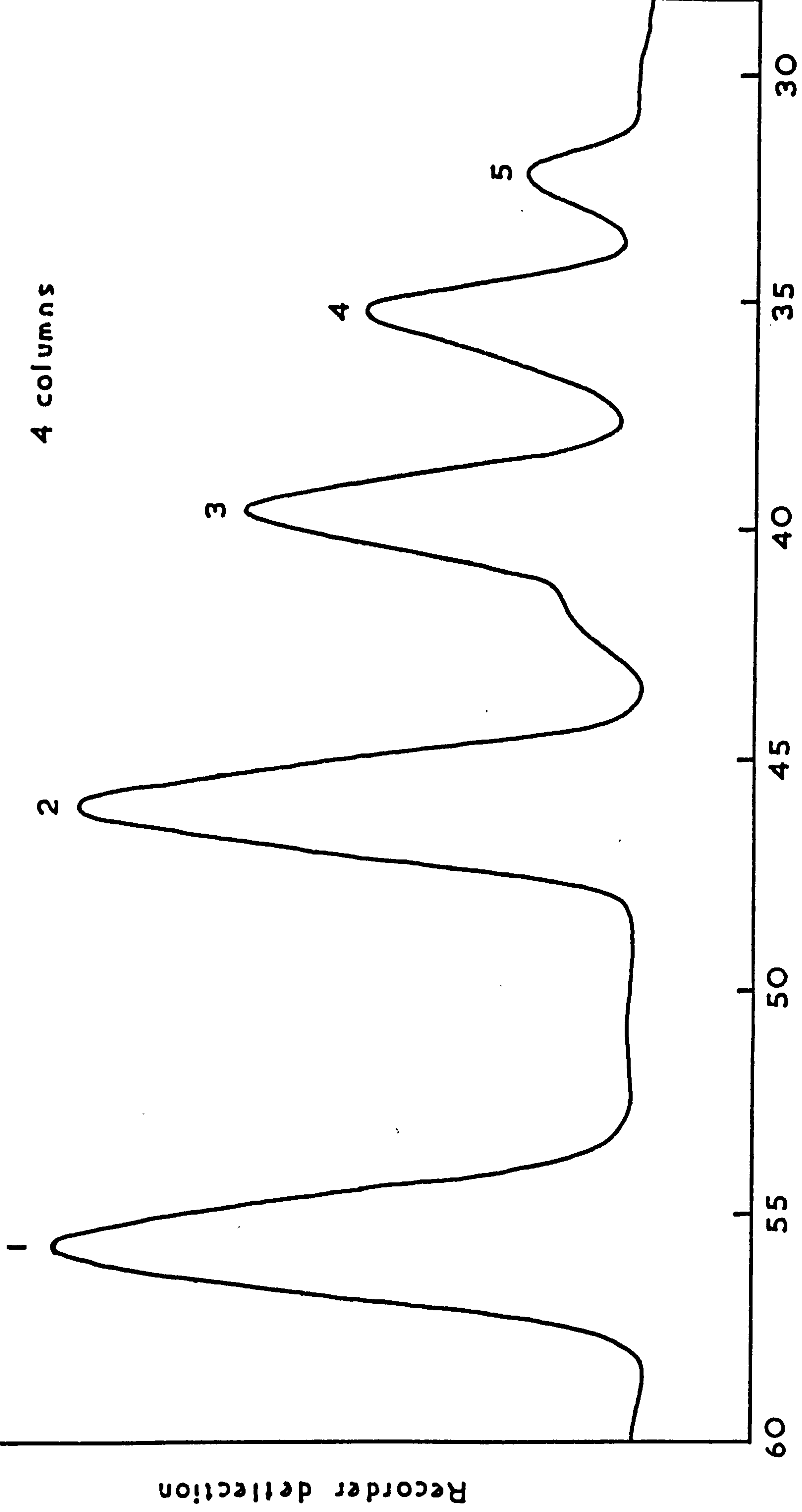


FIGURE 3.28

PDA cyclic oligomers

4 columns



Elution volume, counts

Recorder deflection

FIGURE 3.29

PES cyclic oligomers

4 columns

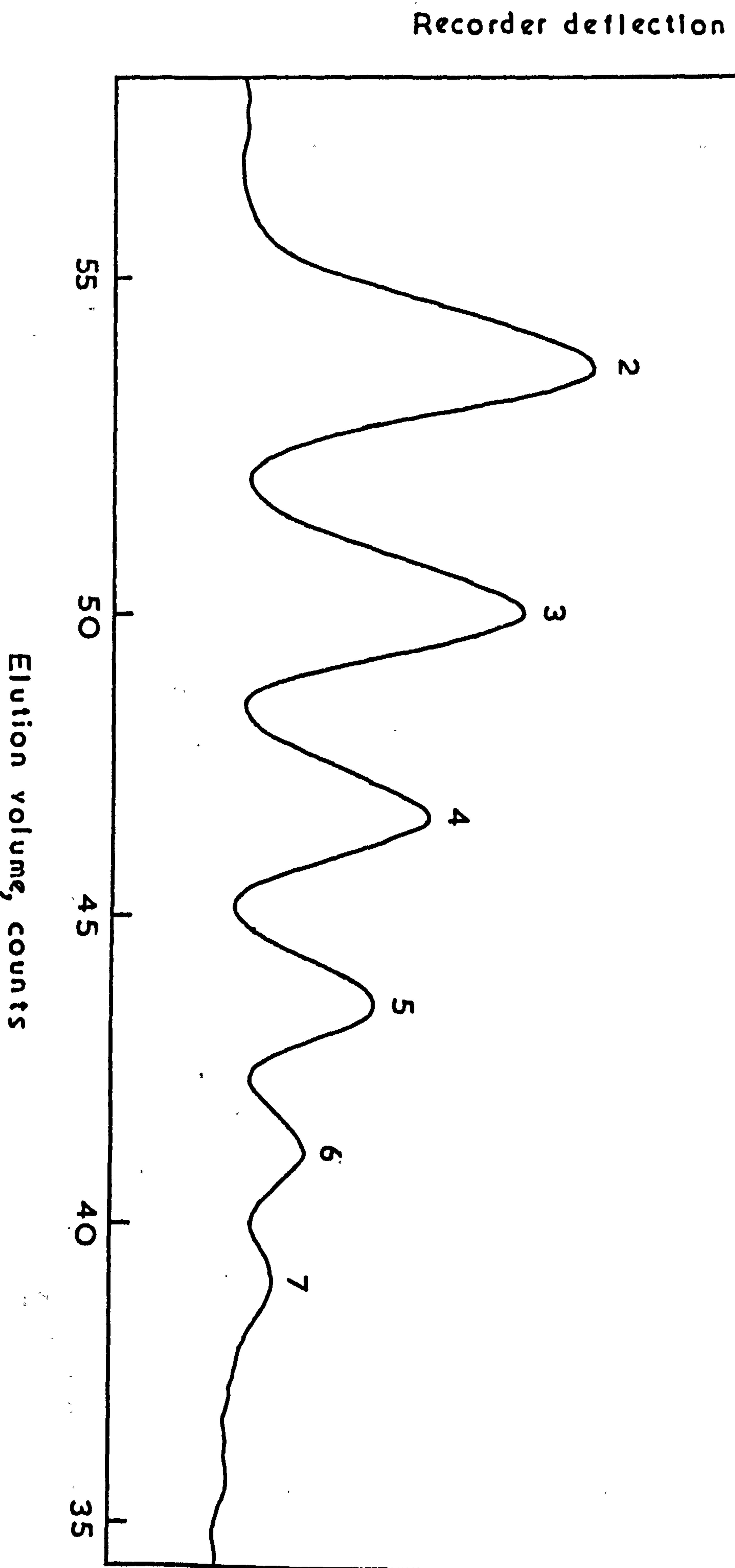


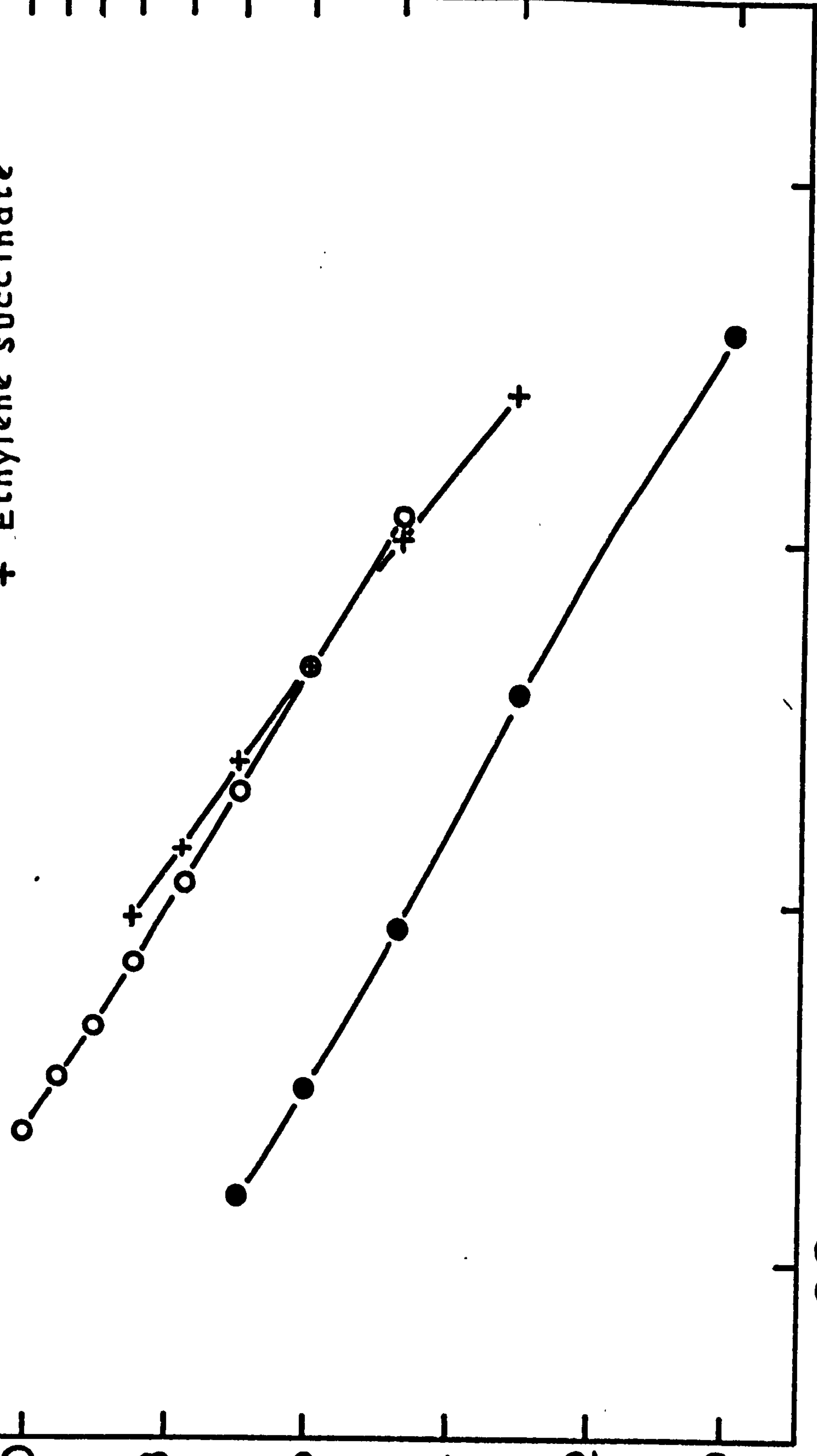
FIGURE 3.30

Cyclic oligomers of: ○ Ethylene terephthalate
 ● Decamethylene adipate
 + Ethylene succinate

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
 $\log x$

20
10
5
1
 x , no. of units

30 40 50 60
elution volume, counts



In Figure 3.28, the tracing for the mixture of oligomers from PDA is shown. The five species are now perfectly separated. Interestingly, it becomes clear from this tracing that part of the material eluting between the dimer and trimer in Figure 3.25 is in fact a minor impurity of some sort.

In Figure 3.29, the cyclics from PES are shown: the components (from dimer to heptamer) are almost perfectly resolved.

The final Figure (3.30) depicts a calibration* of these four columns for the three series of oligomers. The cyclics from different systems do not lie on the same line; nor would they be expected to do so, since they will not have the same molecular dimensions at the same number of repeat units. Indeed, even if the ordinate is converted to molecular weight, rather than degree of polymerisation, they do not share exactly the same line.

It is proper to recall that these results were obtained with columns giving only low plate counts. If the counts achieved for Styragel columns could have been reproduced with the Bio-Beads, then the aliphatic oligomers could have been analysed using no more than two columns at low flow rate, while with four good columns virtually all the PET cyclics present in the test mixture would have been resolved. It did not prove possible, however, to improve the plate counts; rather, it was noted that with the passage of time the resolving power of the columns actually in use tended to diminish. Nevertheless, the set of four Bio-Bead SX - 1 columns were found to be adequate for most of the intended purposes.

* In making comparisons between such calibrations, it was important to ensure that the same experimental conditions had been maintained. Changes in calibration would obviously arise if alterations were made to the lengths of connecting tubing, etc.; but, also, the susceptibility of the volume counting device to slight losses by evaporation made it necessary that the flow rates should be identical.

CHAPTER 4.

CYCLIC OLIGOMERS OF POLY(ETHYLENETEREPHTHALATE)

4.1 INTRODUCTION

In 1954, Ross, Coburn, Leach and Robinson¹⁹ reported that by prolonged solvent extraction of films of poly(ethyleneterephthalate) (hereinafter PET) they had isolated a small proportion of a material which they identified as the cyclic trimer of the polymer. (Cyclic tris(ethyleneterephthalate); $n = 2$ in Fig.4.1.) Giuffria²⁰ later confirmed these findings. Some years afterwards, Goodman and Nesbitt²¹ undertook a more comprehensive study. Having obtained low molecular weight extracts from PET fibre and chip, they separated the components by taking advantage of solubility differences; the extracts were found to contain not only the cyclic trimer, but also tetramer and pentamer. (Cyclic tetrakis- and pentakis- (ethyleneterephthalate); $n = 3,4$ in Fig.4.1). The later introduction by Zahn and Kusch²² of gel filtration as a means of resolving the extracts into individual cyclics lead to the additional isolation of the hexamer. ($n = 5$ in Fig.4.1). More recently, Peebles, Huffman and Ablett²³ have made similar use of adsorption chromatography to obtain small quantities of the cyclic trimer, tetramer and pentamer from such extracts.

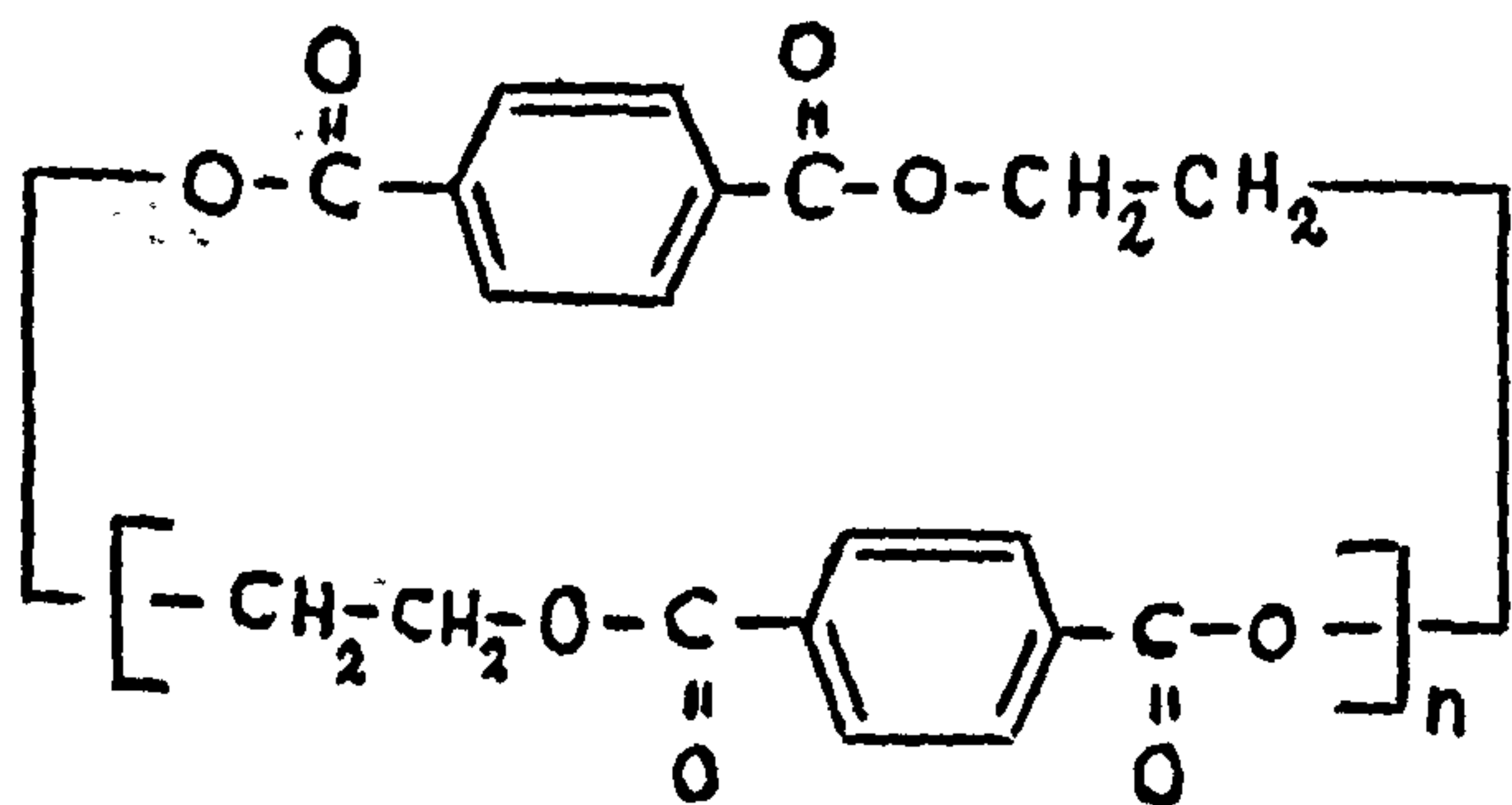


Figure 4.1

Methods have been developed whereby cyclic ethylene terephthalates may be obtained by direct synthesis rather than by extraction from samples of polymer. High dilution techniques for the preparation of the cyclic trimer have been described by Meraskentis and Zahn⁵² and also by Hamb and Trent⁵³. Huffman et al²³ showed that in the first method cyclic tetramer and cyclic dimer (cyclic bis(ethyleneterephthalate); $n = 1$ in Fig. 4.1) were formed as bi-products. The latter compound has not been isolated from normal polymer samples, but has been noted in the distillates taken from the polymerising melt²³, and can also be prepared at high dilution by a method due to Repin and Papanikolau⁵⁴. Another synthesis devised by Meraskentis and Zahn⁴⁶ yields cyclic tetramer as major product. Finally, Zahn and Repin⁵⁵ have evolved procedures for the preparation of the cyclic oligomers from trimer to heptamer.

Cyclic oligo(ethyleneterephthalate)s have figured in a number of physical studies. Seidel⁵⁶ made a comparison of the infra-red spectra of the cyclic trimer and of linear oligomers. Repin and Papanikolau⁵⁴, and Zahn and Repin⁵⁵, have discussed the assignment of bands in the infra-red spectra of the cyclic oligomers obtained by synthesis, with particular reference to the conformationally dependant absorptions found by Grime and Ward^{57,58} in the spectrum of PET. Trends in melting point⁵⁵ and in solubility^{23,55} have been described. X-ray diffraction studies of the cyclic trimer by Binns, Frost, Smith and Yeadon⁵⁹ and by Ito and Okajima^{60,61} have shown it to adopt several polymorphic forms. Hashimoto has noted the appearance of cyclic oligomers during the degradation of PET⁶² and has investigated the kinetic laws governing the formation of the cyclic trimer during degradation of the polymer by benzene⁶³.

The objective of the present studies of poly(ethyleneterephthalate) was to determine the amounts of the cyclic oligomers in a variety of samples of the polymer, and in particular those in which an equilibrium between the ring and chain molecules had been attained. The fundamental importance of confirming the cyclic nature of the species under study hardly requires emphasis. In seeking such confirmation use was made of a wide range of the methods of examination employed by the authors cited above.

4.2 EXAMINATION OF EXTRACTS FROM POLY(ETHYLENETEREPHTHALATE).

The method by which low molecular weight material was extracted from samples of poly(ethyleneterephthalate) will be described in Chapter 5. Here the discussion will concern the composition of the extracts and the validity with which they may be formulated simply as mixtures of cyclic oligomers. In the main, the results that will be cited were found for extracts obtained in initial experiments with commercial polymer samples; but they were largely typical of those for extracts encountered at later stages. Occasionally, extracts showed departures in behaviour; appropriate mention will be made of such deviations.

The relevant evidence may be summarised as follows:

(a) Simple physical properties: the extracts were soft, crumbly powders, except that, in some instances where the presence of linear species were suggested by other evidence, they tended to become gritty and tough. They ranged in colour from just off white to light brown.

(Part of this discolouration derived from decomposition of the solvent employed in extraction). Although the method of extraction involved their dissolution in chloroform, they showed variations in their solubility in this solvent. The most soluble dissolved to the extent of several per cent leaving only a faint haziness, probably due either to higher cyclic components (sufficiently soluble, however, to be extracted in the large volumes of solvent used) or to higher molecular weight chains resulting from slight polymerisation during evaporation and drying of the extracted material. Some extracts were mostly soluble, but tended to form aggregates that resisted dispersion. Often, in such cases, if the solid were first dissolved in a little of a more powerful solvent it would remain in solution upon dilution with chloroform; which suggests that kinetic, rather than thermodynamic, factors were involved. The presence of linear oligomers in samples often reduced their solubility in chloroform; some such mixtures were only partly soluble in sym-tetrachloroethane or dimethylformamide, which acted as good solvents for other extracts. Extracts showed only slight, and apparently selective, solubility in diethyl and petroleum ethers, acetone, methanol and ethanol. Trifluoroacetic acid was a powerful solvent for all extracts.

These findings are in partial disaccord with those of earlier workers. Goodman and Nesbitt²¹ have found the cyclic pentamer extremely insoluble in organic solvents, while Peebles, Huffman and Ablett²³ noted that their samples of tetramer were not soluble even in o-chlorophenol, a solvent for the polymer itself. It is possible that purely morphological considerations will explain the discrepancies between the results of the present studies and those previously published, as well as those between individual samples described here.

(b) Elemental analysis: the analytical results found for an extract are compared in the Table below with those expected for an empirical formula of $C_5H_4O_2$.

	Carbon	Hydrogen	Oxygen, by difference	
FOUND	63.69%	4.35%	31.96%	Table 4.1
CALCULATED	62.50%	4.19%	33.31%	

(c) Nuclear magnetic resonance spectroscopy: the n.m.r. spectra of deuteriochloroform solutions of the extract analysed above and of the pure cyclic trimer (obtained as described in Section 4.4) are shown in Figures 4.2 and 4.3. They are virtually identical, with only slight adsorption apart from the two major and equal peaks at $\tau = 1.9$ and at $\tau = 5.3$. (Ignoring the spurious adsorption at 2.7 due to protons in the solvent.) These findings are in complete agreement with those of Ito and Okajima⁶¹ for the trimer. These workers assigned the peak at lower magnetic field to the protons of the aromatic ring and that at higher to those of the ethylene glycol residue. Over the range scanned there were no peaks attributable to carboxyl or hydroxyl end-groups; but these can often lie at still lower magnetic fields, and in any case the extracts were often insufficiently soluble in deuteriochloroform for easy detection of such protons, which would be expected to be present at low levels only. Trifluoroacetic acid was a preferred solvent, since it was then possible to examine solutions concentrated enough to reveal even small proportions of impurity. In general the two main peaks (shifted in this solvent to τ -values of 1.8 and 5.1) comprised at the least 95% of the total absorption.

FIGURE 4.2 : PET Extract

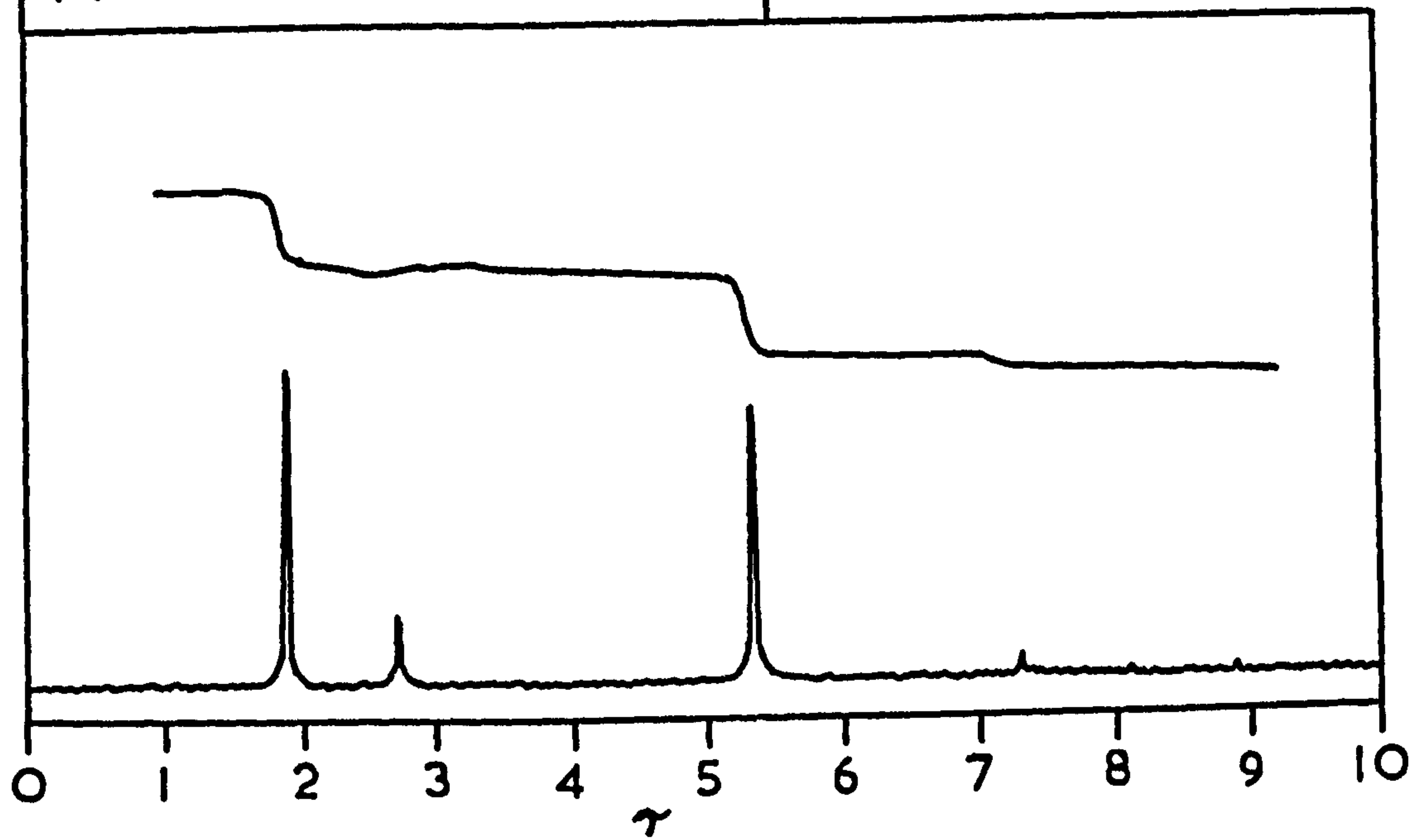


FIGURE 4.3 : PET Trimer

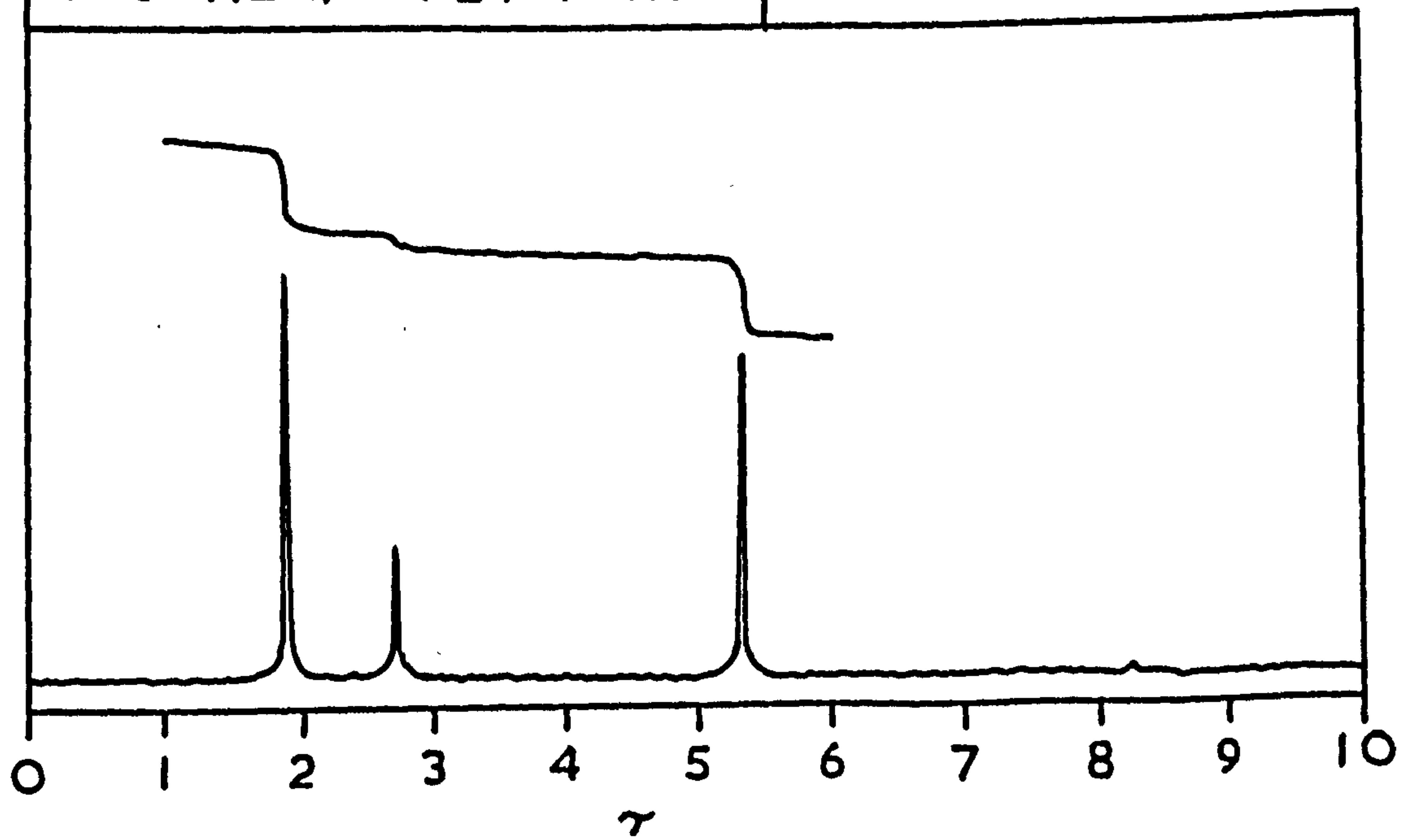


FIGURE 4.4: PET Extract

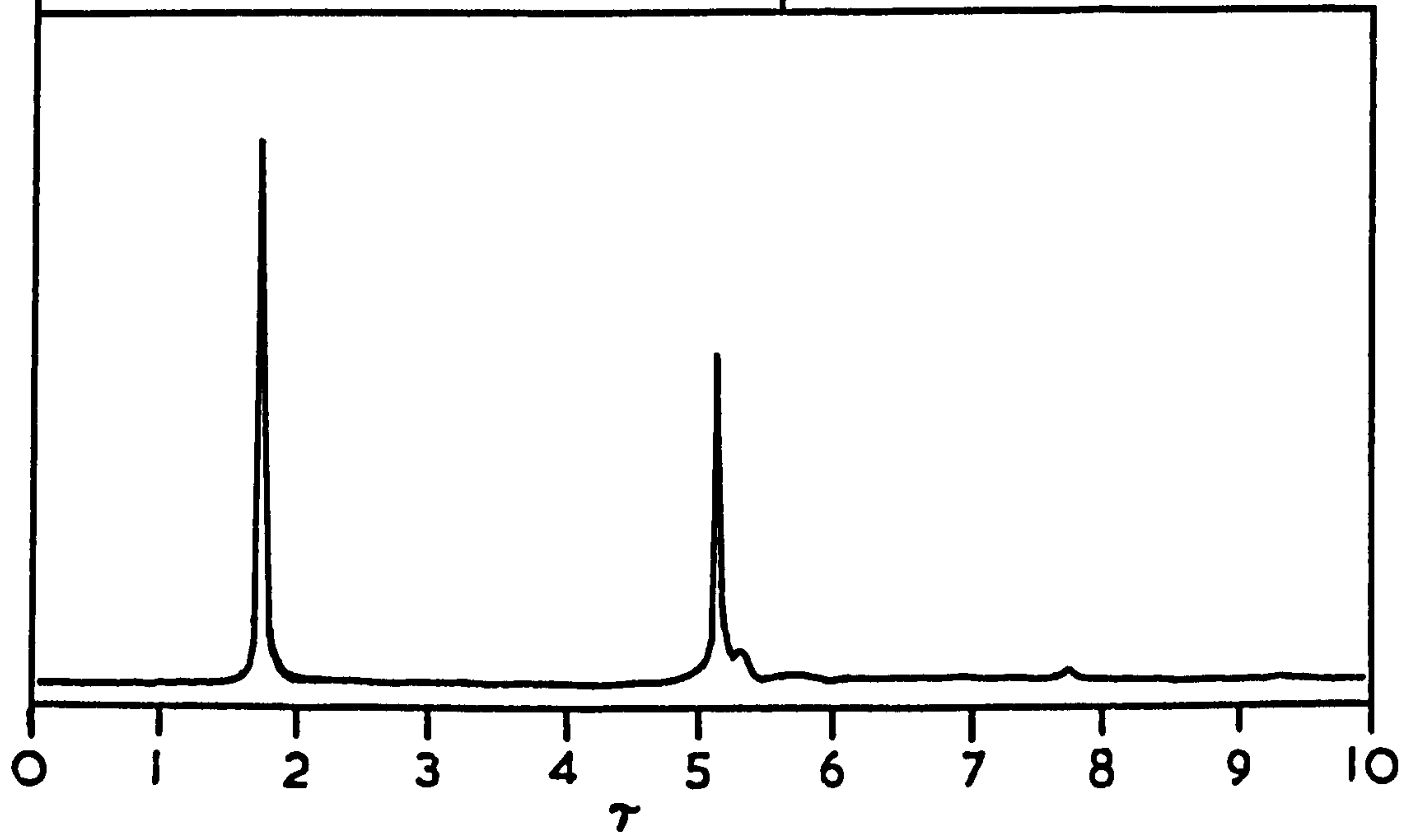
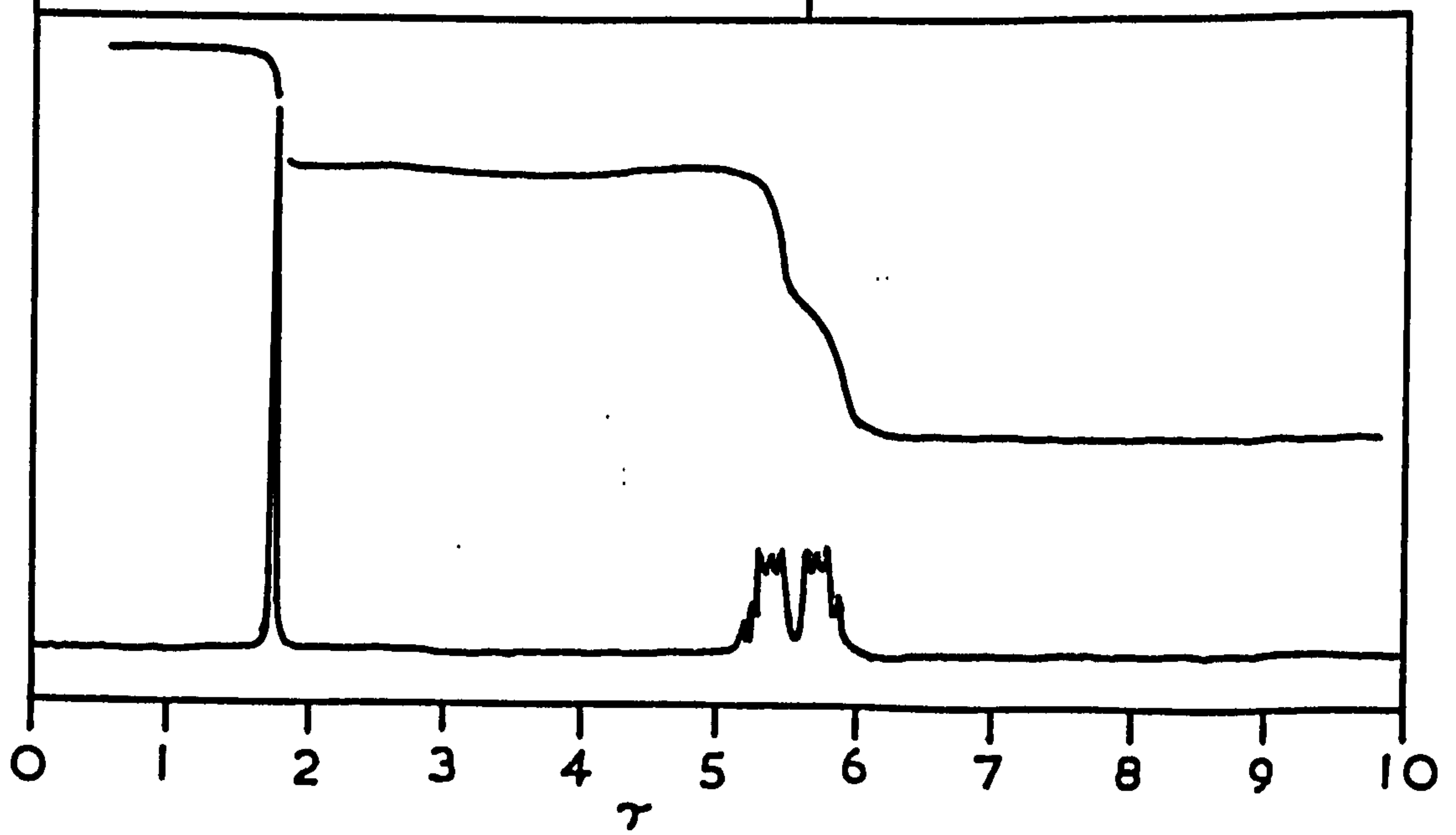


FIGURE 4.5: BHET



Some extracts showed broad and weak absorptions in the regions of $\gamma = 5.3$ and 5.7 . By comparison with the spectrum of the glycol-terminated linear monomer (bis(hydroxyethyl) terephthalate, $\text{HOCH}_2\text{CH}_2\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot\text{CH}_2\text{CH}_2\text{OH}$) these bands might be attributed to the protons of ethylene glycol end-groups. (Figures 4.4 and 4.5).

The simplicity of the n.m.r. spectrum of the ethylene terephthalate unit permitted the use of this tool to be extended to making quantitative estimates of the level of impurities in certain samples. This found specific application to a number of extracts contaminated with additives to commercial polymer fibres. Evidently, information must be available, concerning the proton densities of the contaminants, for this to be possible.

(d) Infra-red absorption spectroscopy: the infra-red spectra between 2000 and 15000 nm. wave length of a typical extract, of pure cyclic trimer and of high molecular weight PET are shown in Figures 4.6, 4.7 and 4.8. (These spectra were obtained from potassium bromide discs.) The three spectra are very similar and also match well with those published by Zahn and Repin⁵⁵ for the pure cyclic oligomers.

Assignments can be made at once for several of the prominent bands: that at 5870 nm. to carbonyl stretching, that at 7900 nm. to $=\text{C}-\text{O}$ stretching, that at 7120 nm. to the $\text{C}-\text{C}$ terephthaloyl stretching^{21,54}; the origin of the band at 9090 nm. has been the subject of discussion^{57,64}. Bands apparently specific to the trans- or gauche- conformation of the $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$ glycol residue are appropriately indicated; parenthesis of an identification is meant to convey that the band is not recognised

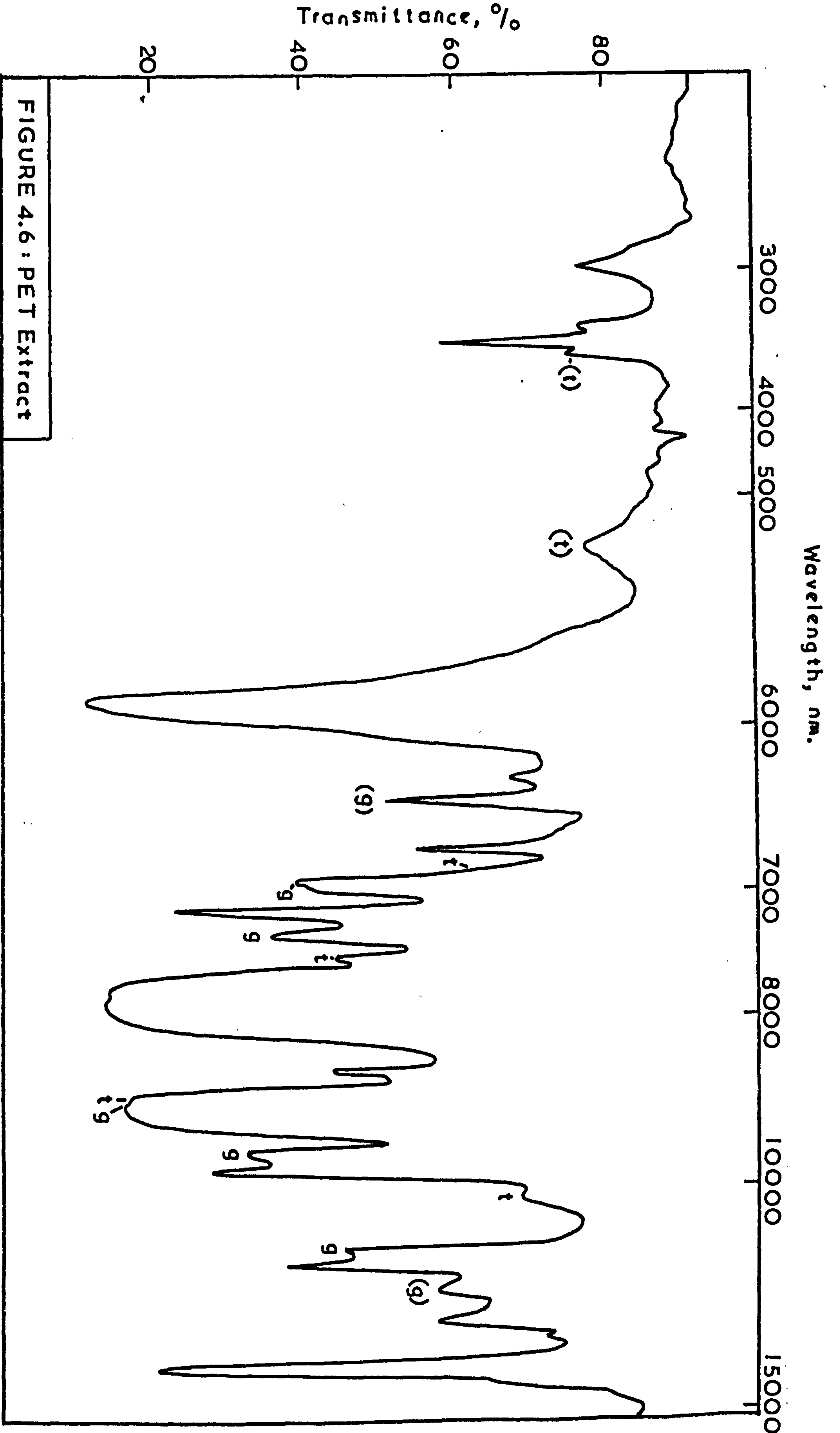


FIGURE 4.6: PET Extract

Wavelength, nm.

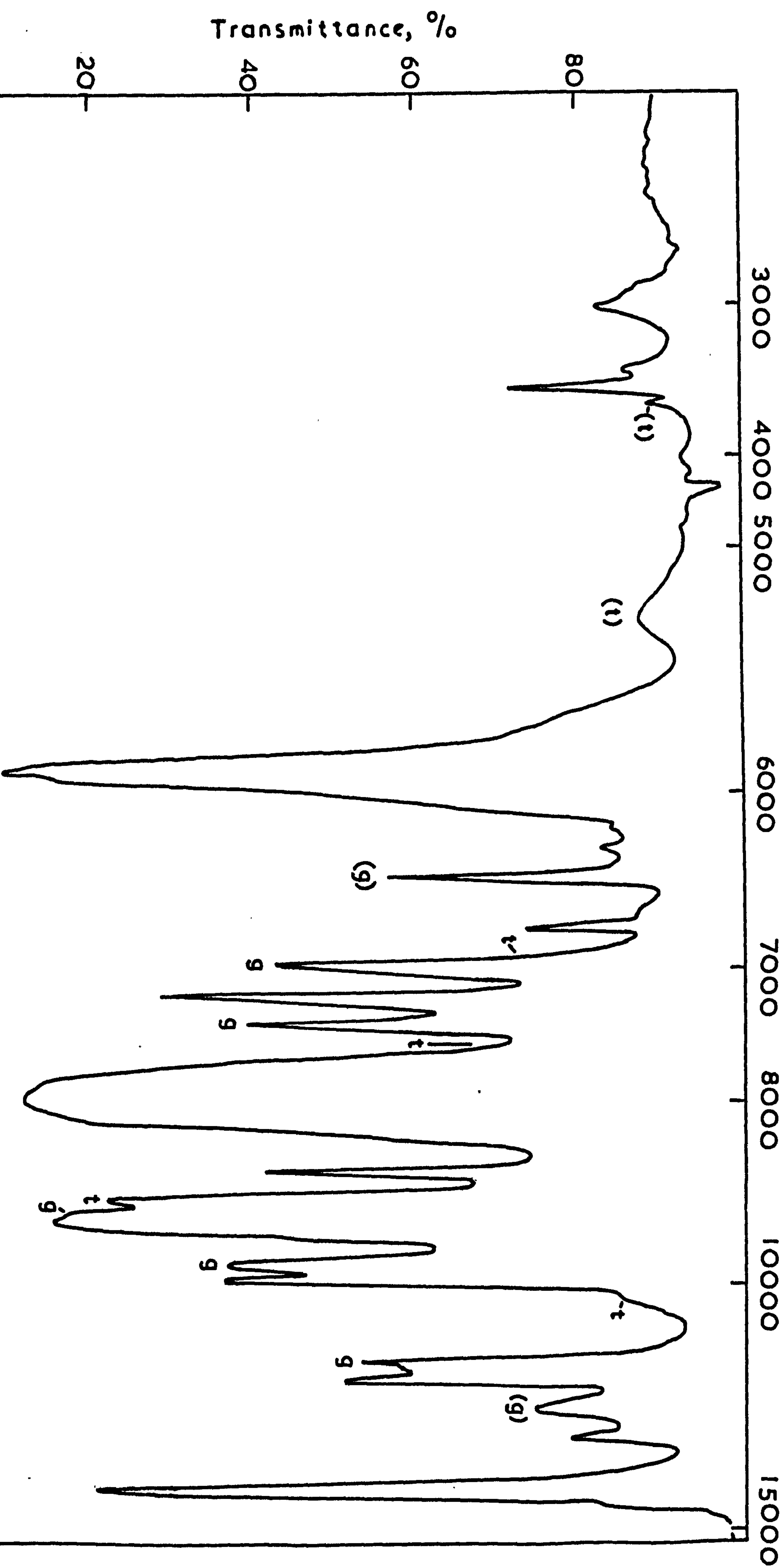


FIGURE 4.7: PET Trimer

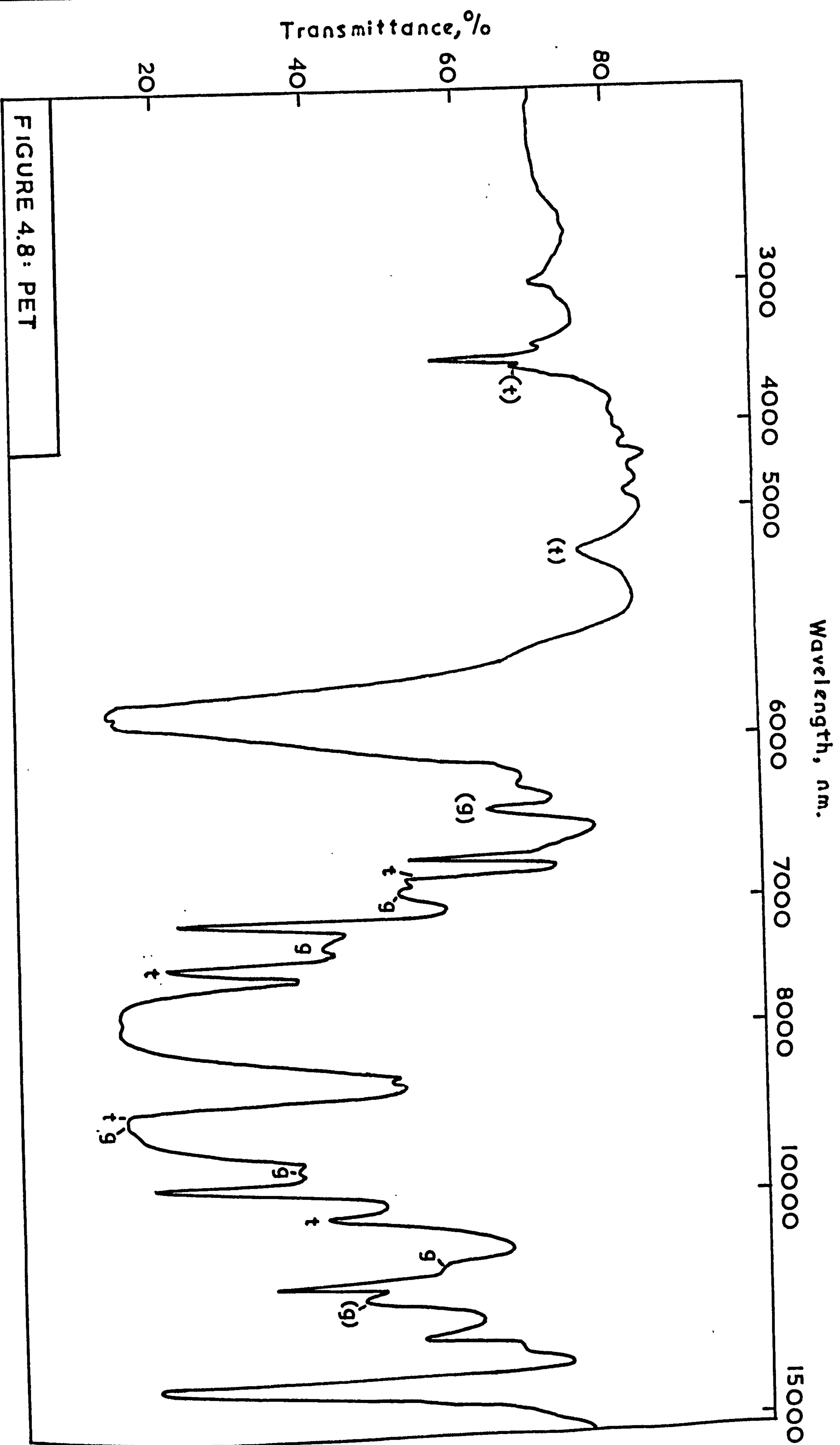


FIGURE 4.8: PET

in the literature as conformationally dependant. As regards these bands, the extract resembles the pure higher oligomers in lying intermediate to the cyclic trimer and the polymer.

The primary usefulness of the technique, however, lay not in confirming in this way that the components of the extracts were basically made up of ethylene terephthalate units (since the evidence from n.m.r. was quite conclusive in this respect) but in attempting to distinguish between linear and non-linear species by the detection of hydroxyl or carboxyl end-groups*. These groups absorb strongly in the regions of 2850 - 3100 nm. and 2700 - (about) 4100 nm., respectively⁶⁵. The carboxyl absorption is absent from all three of the spectra given above, while that for the hydroxyl is weak, and, furthermore, undoubtedly derives part of the strength it actually shows, to moisture, picked up during preparation of the potassium bromide discs. (See Chapter 2).

On the other hand, among the wide range of extracts examined, there were some giving less unequivocal results. It becomes necessary in such cases to have available the spectra of suitable standard compounds, with which to make a comparison. Terephthalic acid served as such a standard; its spectrum between 2500 nm. and 6000 nm. is shown in Figure 4.9. Other useful materials were bis(hydroxyethyl) terephthalate (Figure 4.10) and a mixture of glycol-terminated linear oligomers approximating to a dimer composition (Figure 4.11); the means by which these were obtained will be described in Section 5 of this Chapter. PET Samples known to be of quite high molecular weight were

* While it is true that (especially in degraded or pyrolysed samples) PET chains can carry olefinic end-groups: $-COOCH:CH_2$ which would escape detection by these means, their appearance is invariably accompanied by that of carboxyl groups⁶⁶⁻⁶⁹.

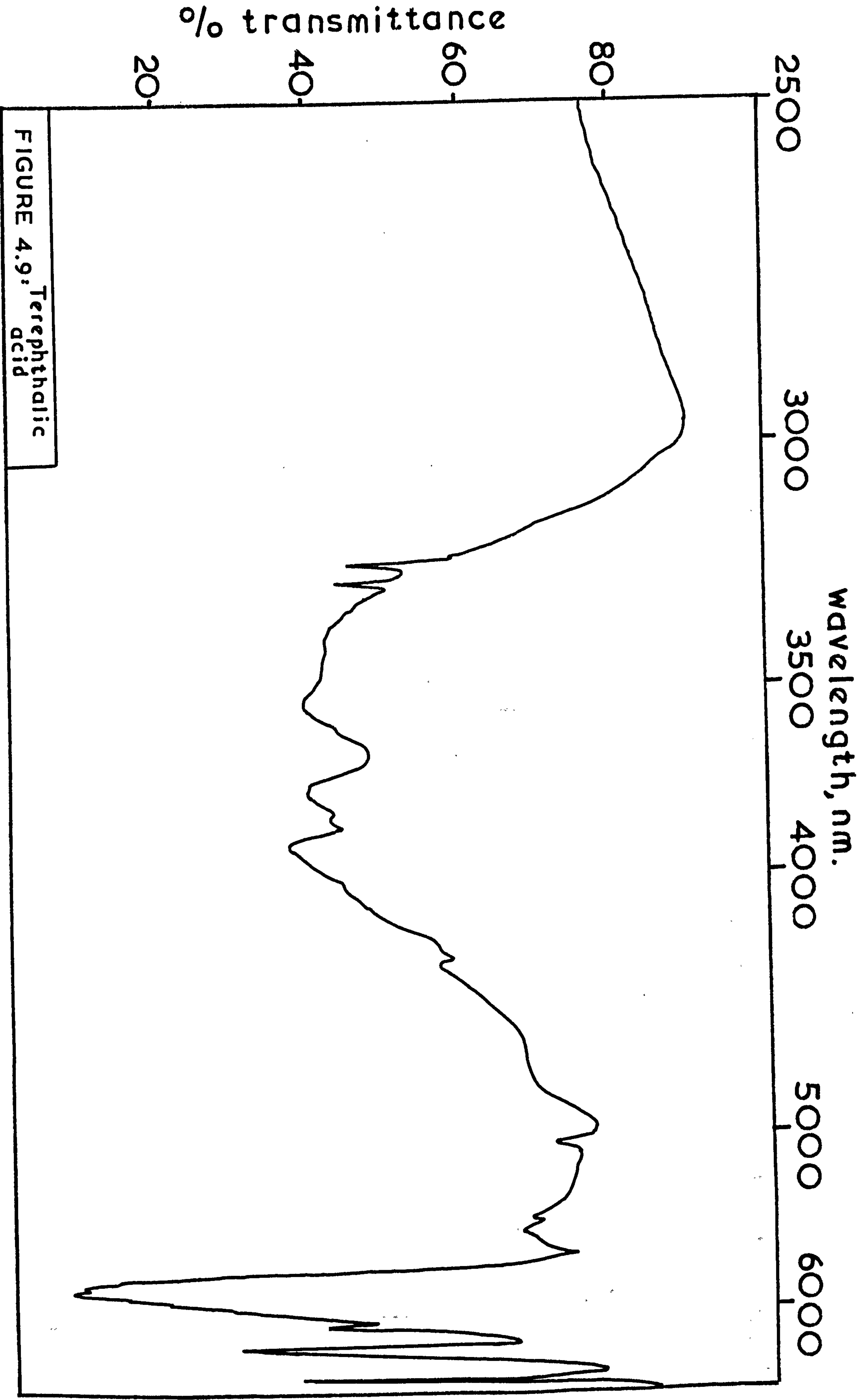


FIGURE 4.9: Terephthalic acid

% transmittance

2500

3000

3500

4000

5000

6000

wavelength, μm .



FIGURE 4.10: BHET

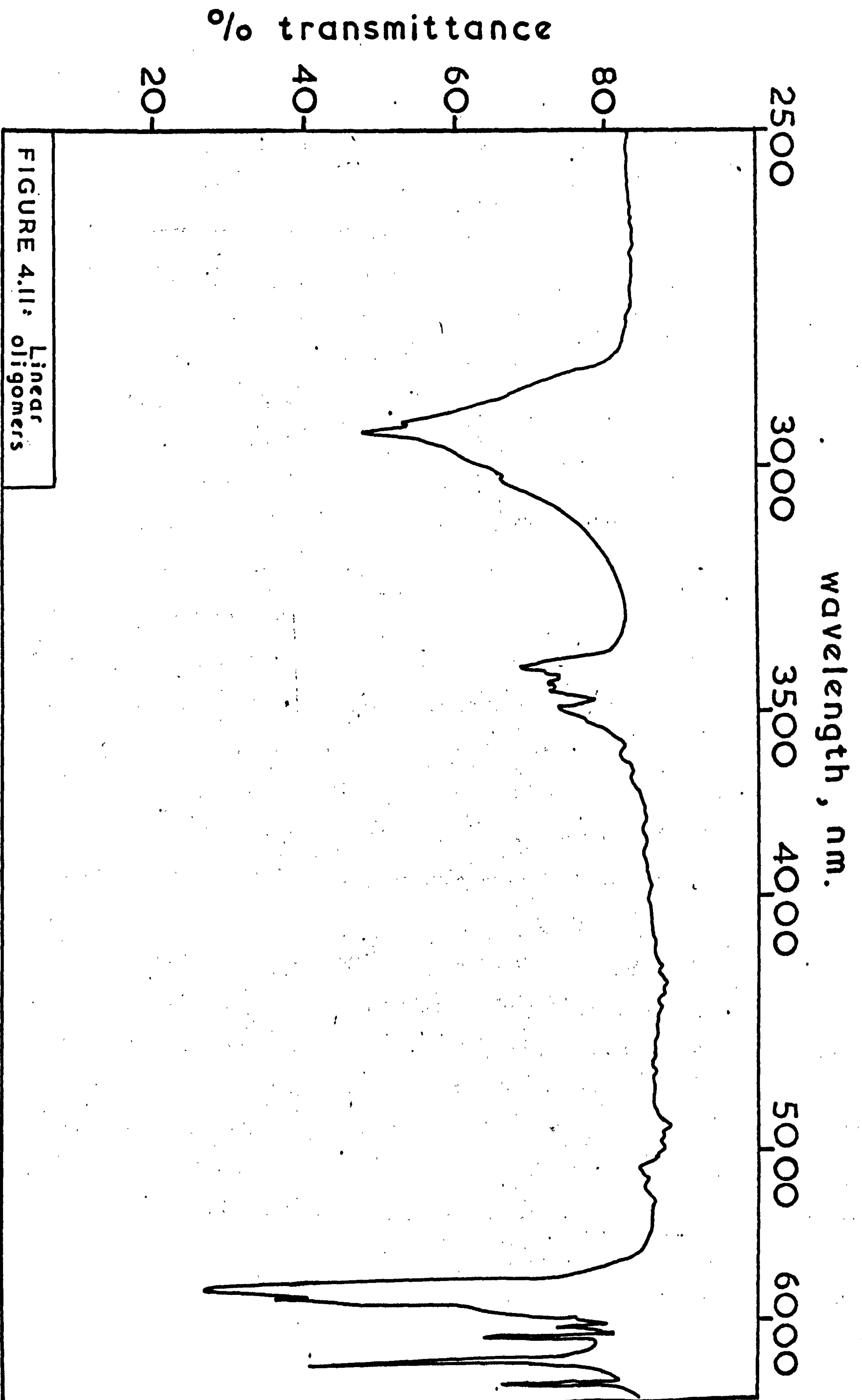


FIGURE 4.11: Linear oligomers

were also examined. (All spectra being taken as mulls in hexachloro-butadiene).

The spectra of these standard compounds may now be compared with those of a variety of extracts:

Figure 4.12 shows that for another extract from a commercial polymer. Again, there is no carboxyl absorption, and the hydroxyl band is of such low intensity that it is clear that end-groups are almost completely absent.

Figure 4.13 shows that for an extract (denoted (XV)-A) derived from an equilibrated sample. Hydroxyl absorption is low, but there is slight absorption due to carboxyl groups^{*}, including the two bands at 3700 and 3900 nm. due to the dimer of the carboxylic acid. This absorption is many times less intense than that for terephthalic acid; but, on the other hand, it must be recognised that many of the components of the mixture may have molecular weights sufficiently high for the level of end-groups within them to in any case be low. Hence, for such samples, it could not be ascertained by this method alone that linear species were not present in significant amounts.

Figure 4.14 shows that for another extract ((XVI)-2A) from an equilibrated sample. Here the intensity of the carboxyl absorption is so great that there could be little doubt that linear species were present in substantial proportion. This was to a large extent confirmed by other results. (See (f) below).

* It is not entirely clear why the absorption for such samples extends towards 2700 nm. while that for the pure acid stops at 3000nm. Aliphatic diacids and low molecular weight polymers show the broader band found for these extracts. (Chapter 8).

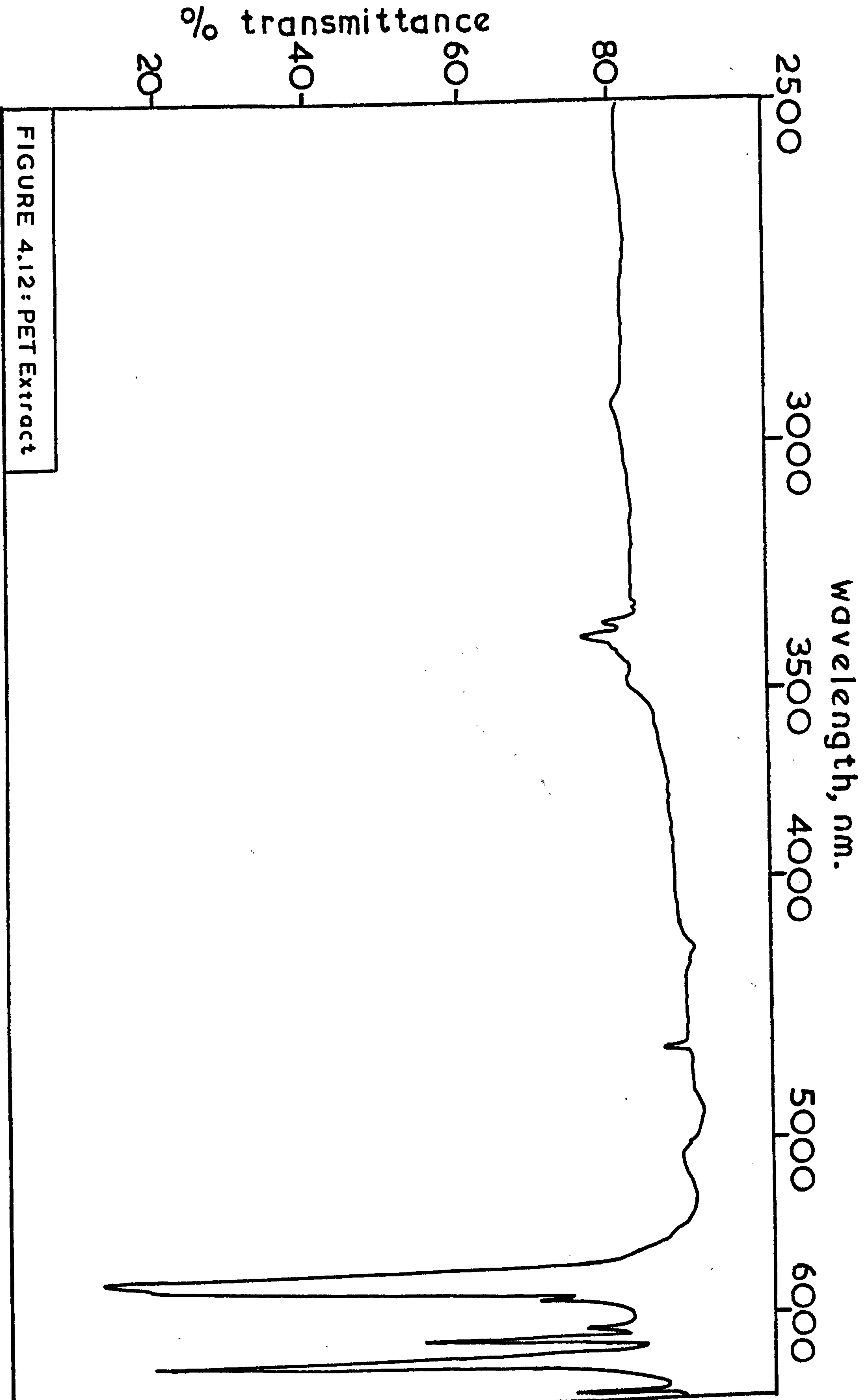


FIGURE 4.12: PET Extract

% transmittance

20

40

60

80

2500

3000

3500

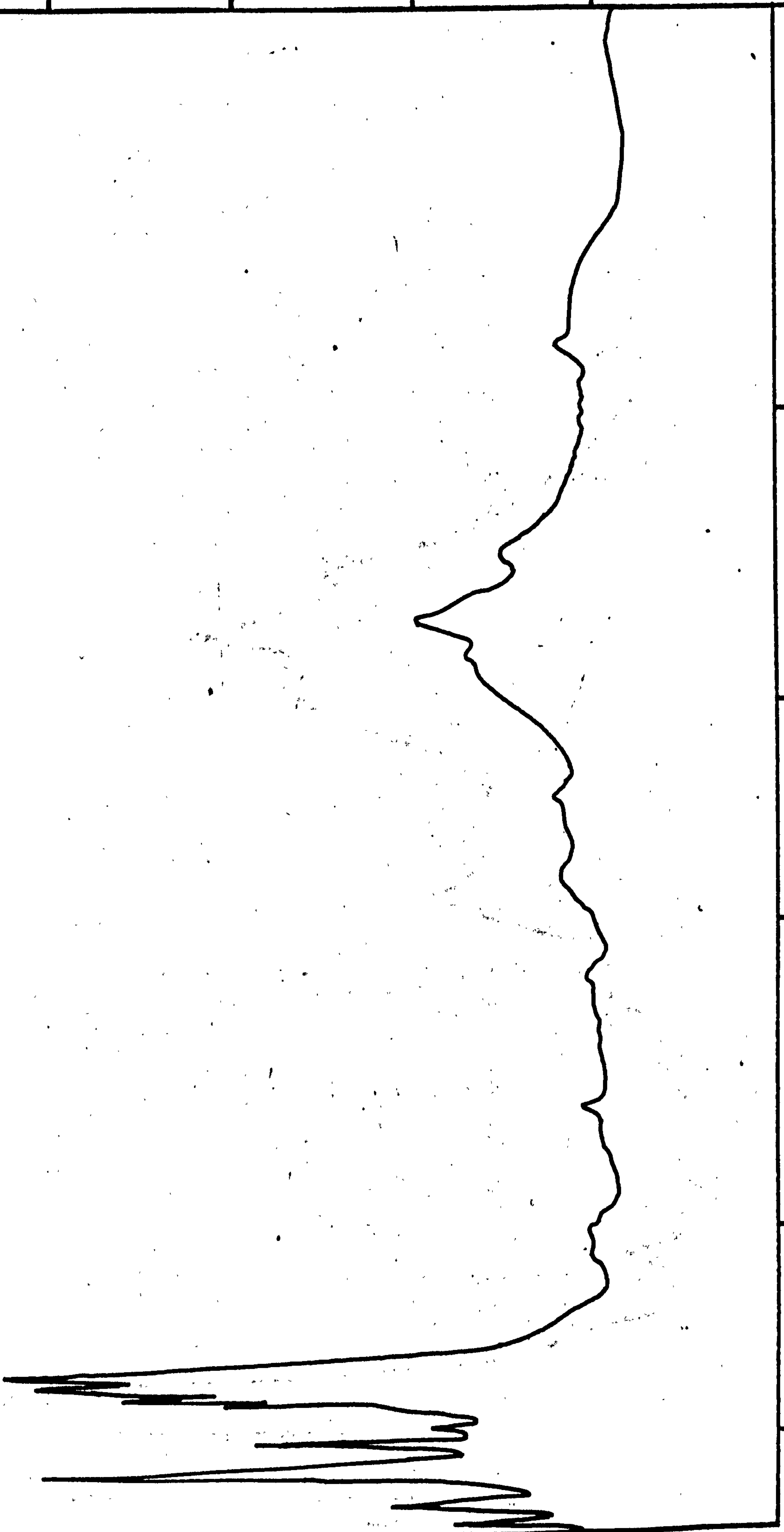
4000

5000

6000

wavelength, nm.

FIGURE 4.13: Extract (XV)A



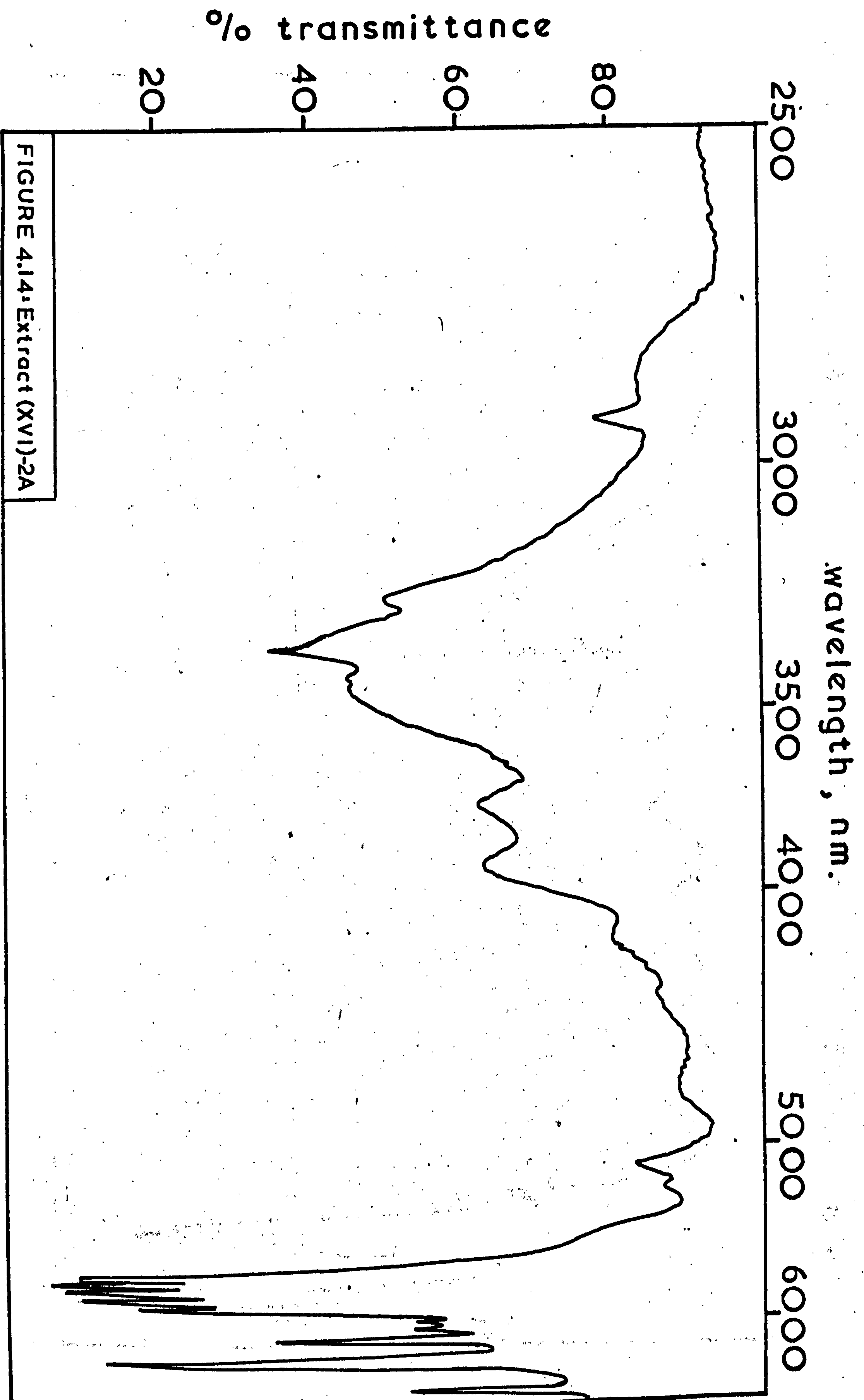


FIGURE 4.14: Extract (XVI)-2A

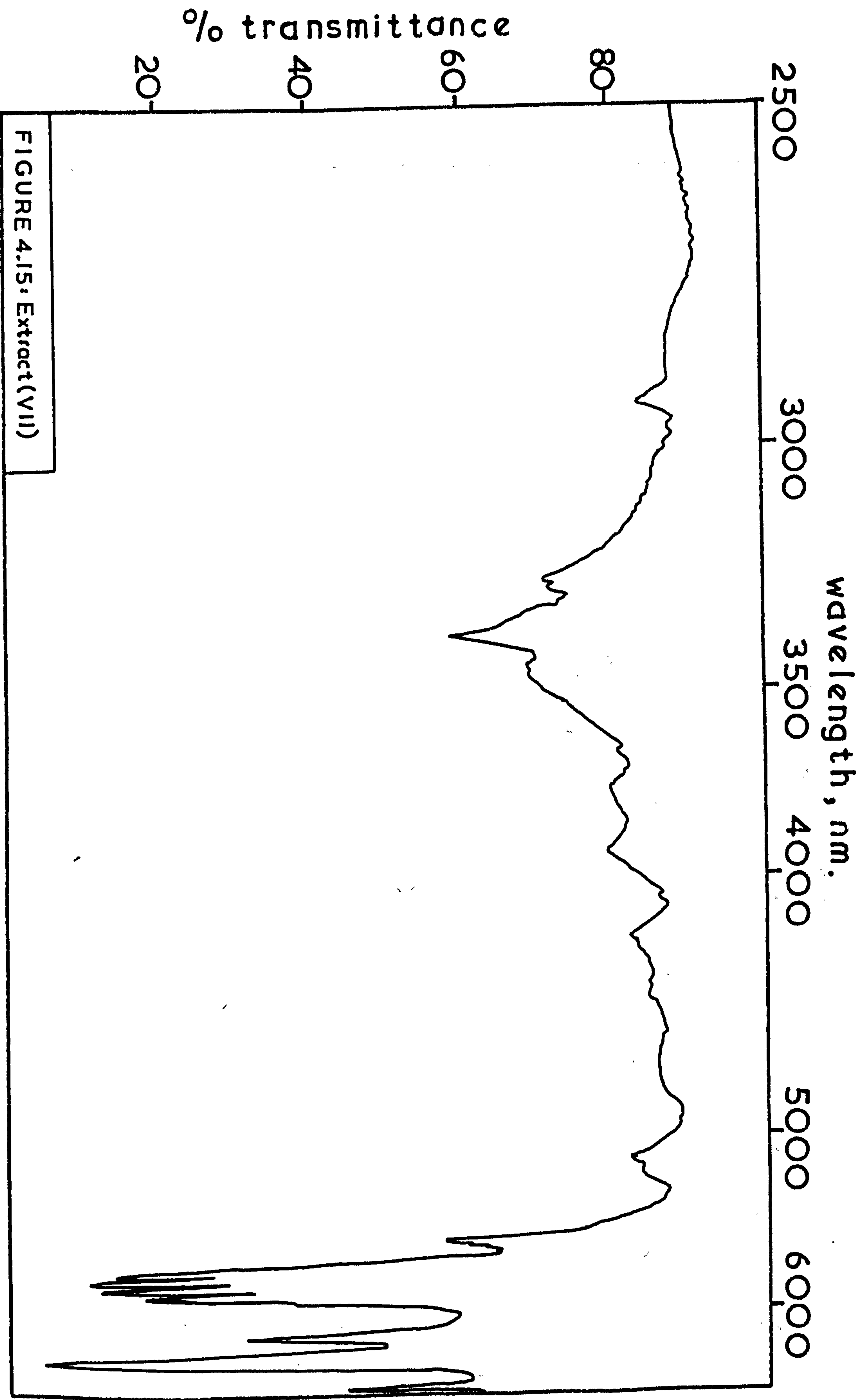


FIGURE 4.15: Extract (VII)

% transmittance

20-

40-

60-

80-

2500

3000

3500

4000

5000

6000

wavelength, nm.

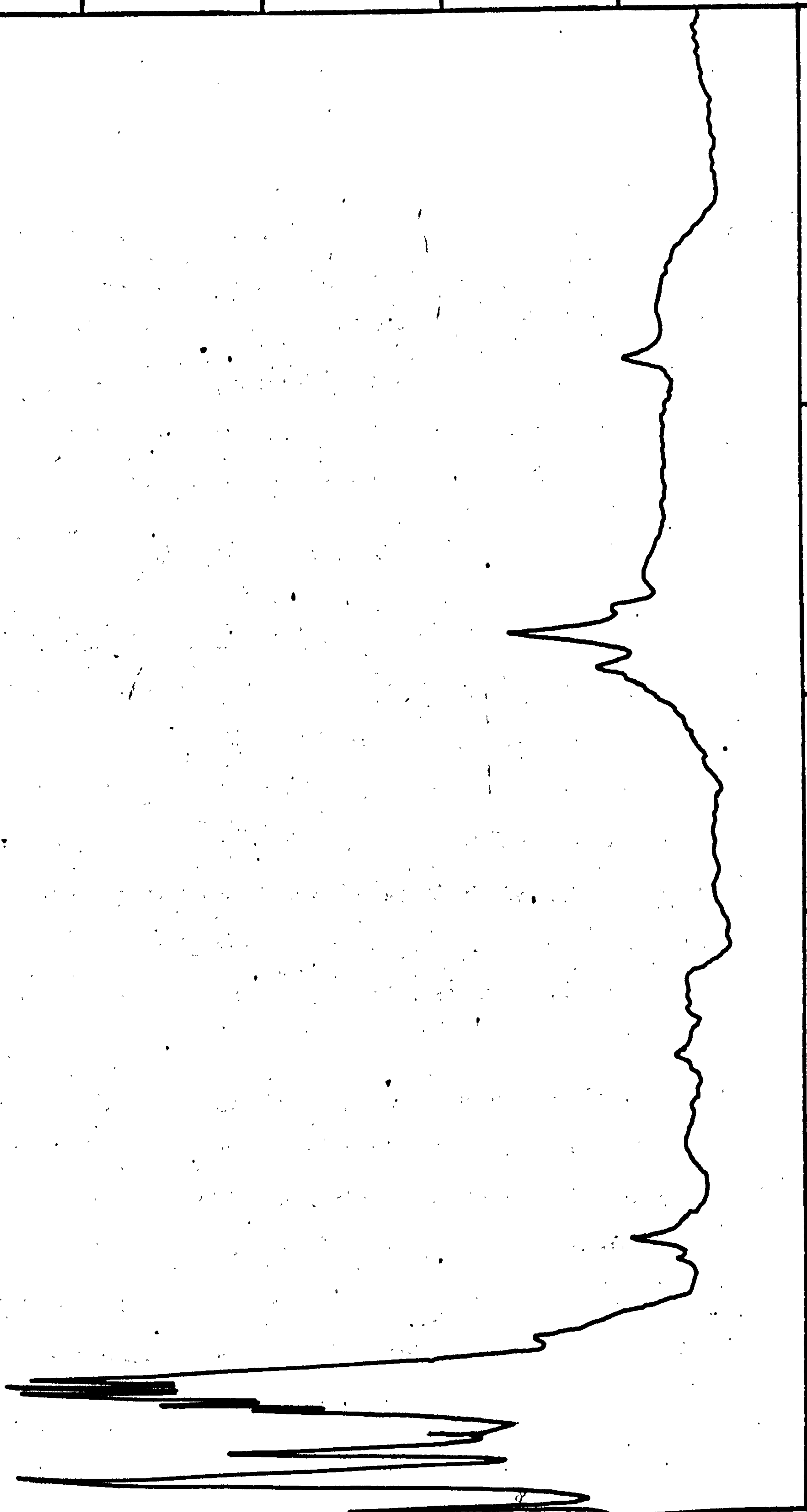


FIGURE 4.16: PET from (VII)

Figures 4.15 and 4.16 show the spectra of yet another such extract (VII)-1A), and of the PET residual from extraction, respectively. The latter was found by other means to have a number-average degree of polymerisation approaching twenty, and yet it shows carboxyl absorption almost as intense as that for extract (XV) - 1A in Figure 4.13, although less intense than that for its own extract.

In summary, it was found that infra-red spectroscopy could in favourable cases offer very strong evidence for the cyclic nature of extracts, but in some other cases it left an element of doubt as to the precise extent to which the cyclic oligomers were contaminated with linear species.

(e) Gas - liquid chromatography: the low volatility of the cyclic oligomers of PET severely limits the applicability of this technique to their study. However, it has been noted in the past that the trimer may be detected by this method⁶¹. Here, it was found that, for a 4' column packed with silanized Embacel coated with 8% by weight Pye's E.30 silicone gum and a nitrogen flow-rate of 50 ml./min., a major component of the extracts eluted after $4\frac{1}{2}$ min. at 380°C. Pure trimer gave a single peak at the same point. At 325°C. elution was after 25 min..

(f) Gel permeation chromatography: in the previous Chapter, examples were given of the tracings that were obtained at various stages of the development of the g.p.c. system, when extracts from PET were injected; and finally calibrations for the supposed cyclic oligomers of poly(ethylene terephthalate), poly(ethylene succinate), and poly(decamethylene adipate) were compared. For convenience, the calibration plots are reproduced in Figure 4.17.

FIGURE 4.17

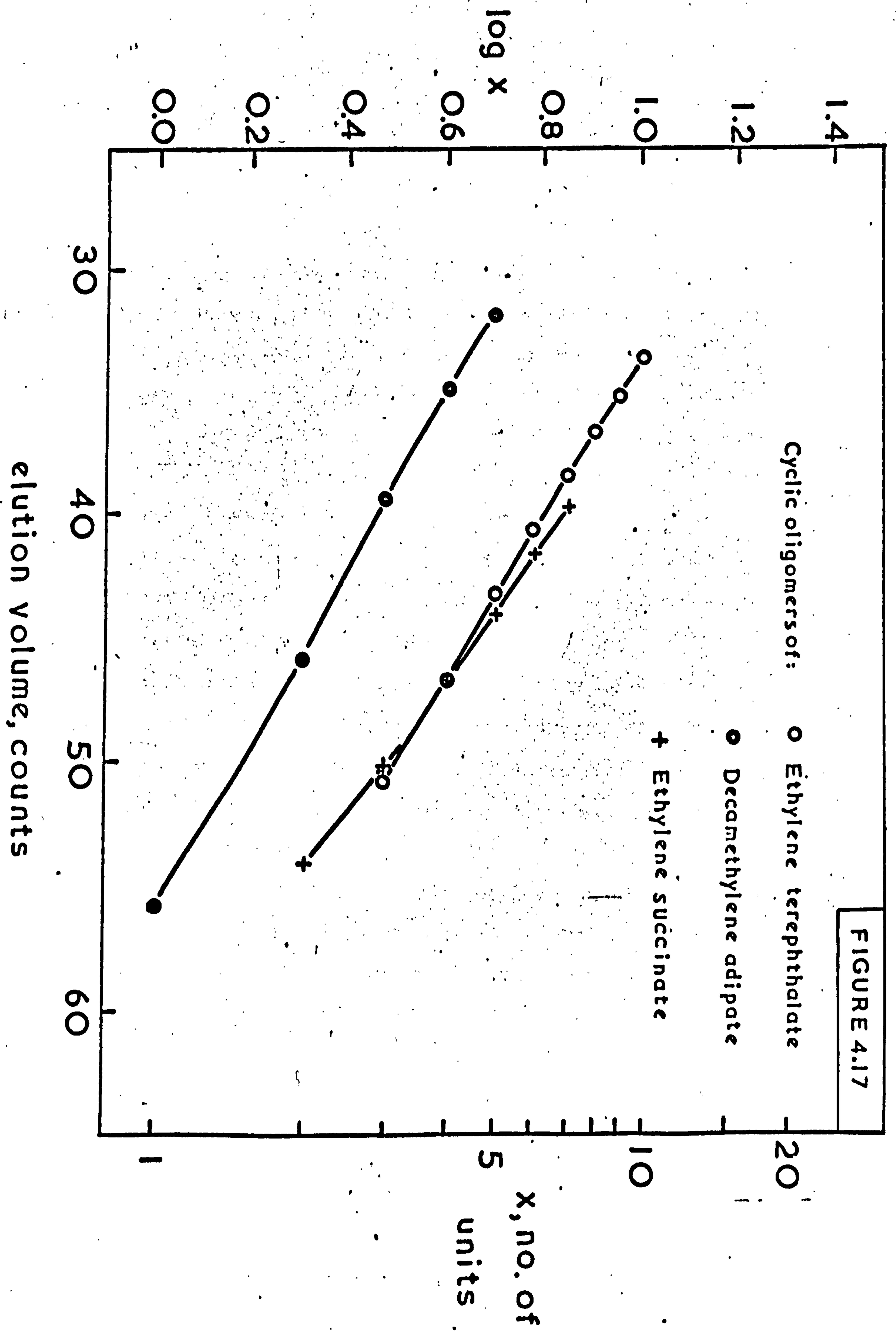
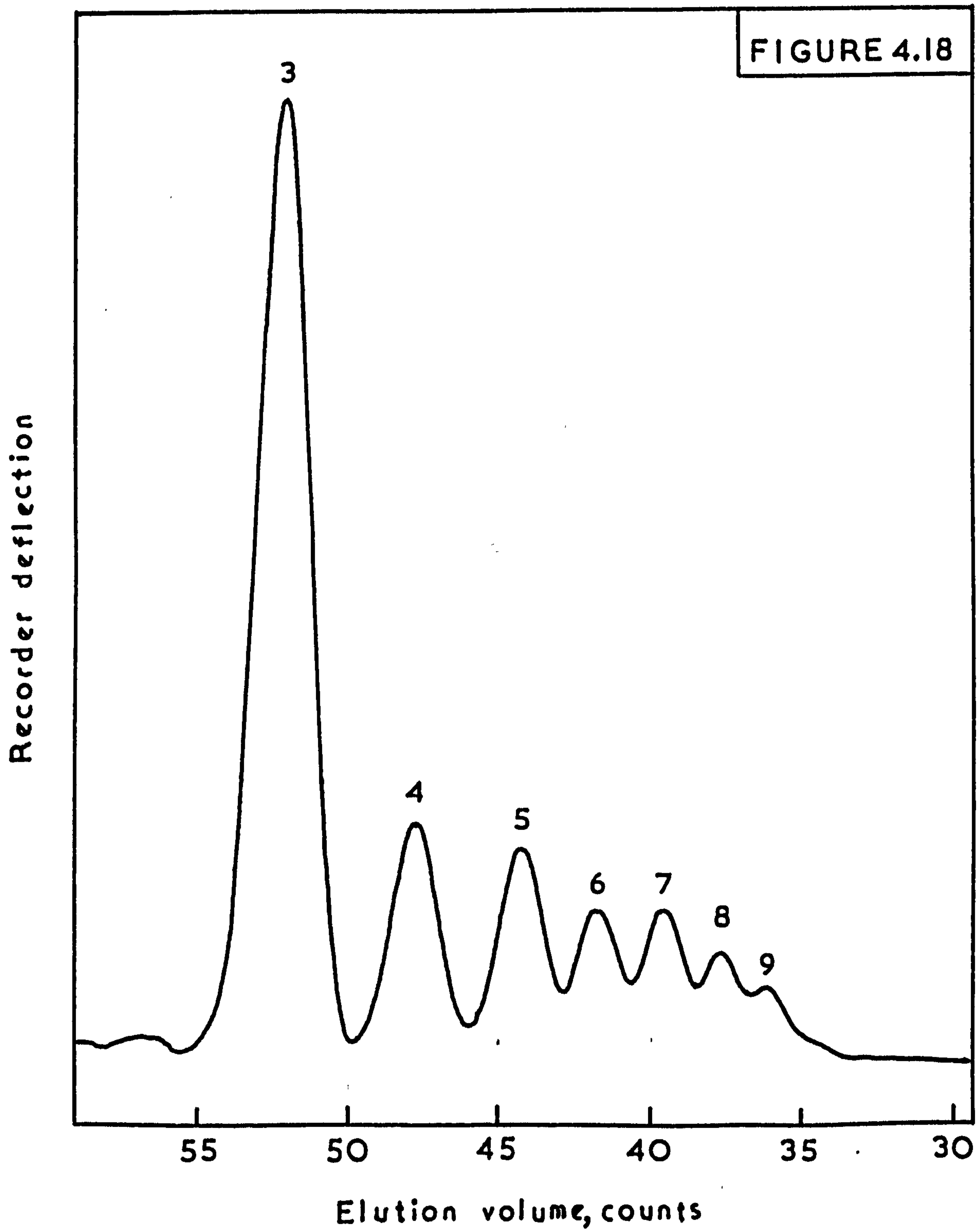


Figure 4.18 shows another typical separation of an extract from PET. If injection of such a sample were followed by that of a sample of pure cyclic trimer, taking care to maintain the same conditions, it gave a peak at the same elution volume, and in the same sense, as the greatest peak for the extract. Furthermore, extracts obtained by conventional means, which earlier workers found to contain cyclics from trimer to pentamer²¹ or hexamer²², also showed (at least) the peaks denoted 3, 4, 5 in Figure 4.18. (The components in subsequent similar tracings will also be identified in this way, i.e., according to the number of structural units they possess.) Clearly, these peaks must represent the first members of the series of cyclic homologues. That the other components extend this series is suggested by the overall linearity of the logarithmic calibration plot. The slight upwards curve at low elution volume (amounting, in any case, to a discrepancy in molecular weight of only 5%, for the decamer) is quite in conformity with the pattern for the supposed cyclic oligomers of the aliphatic polyesters; in this respect, the assignments for the aliphatic and the aromatic cyclic oligomers are mutually supporting.

Further evidence for the cyclic nature of the principal components of the extracts comes from a knowledge of the behaviour of certain linear species. In Figure 4.19 the calibration curve for glycol-terminated chains is compared with that for the extract components. From this, it may be seen that, although initially peak elution volumes roughly coincide (linear dimer with cyclic trimer, linear trimer with cyclic tetramer) they afterwards separate and therefore fall out of step.



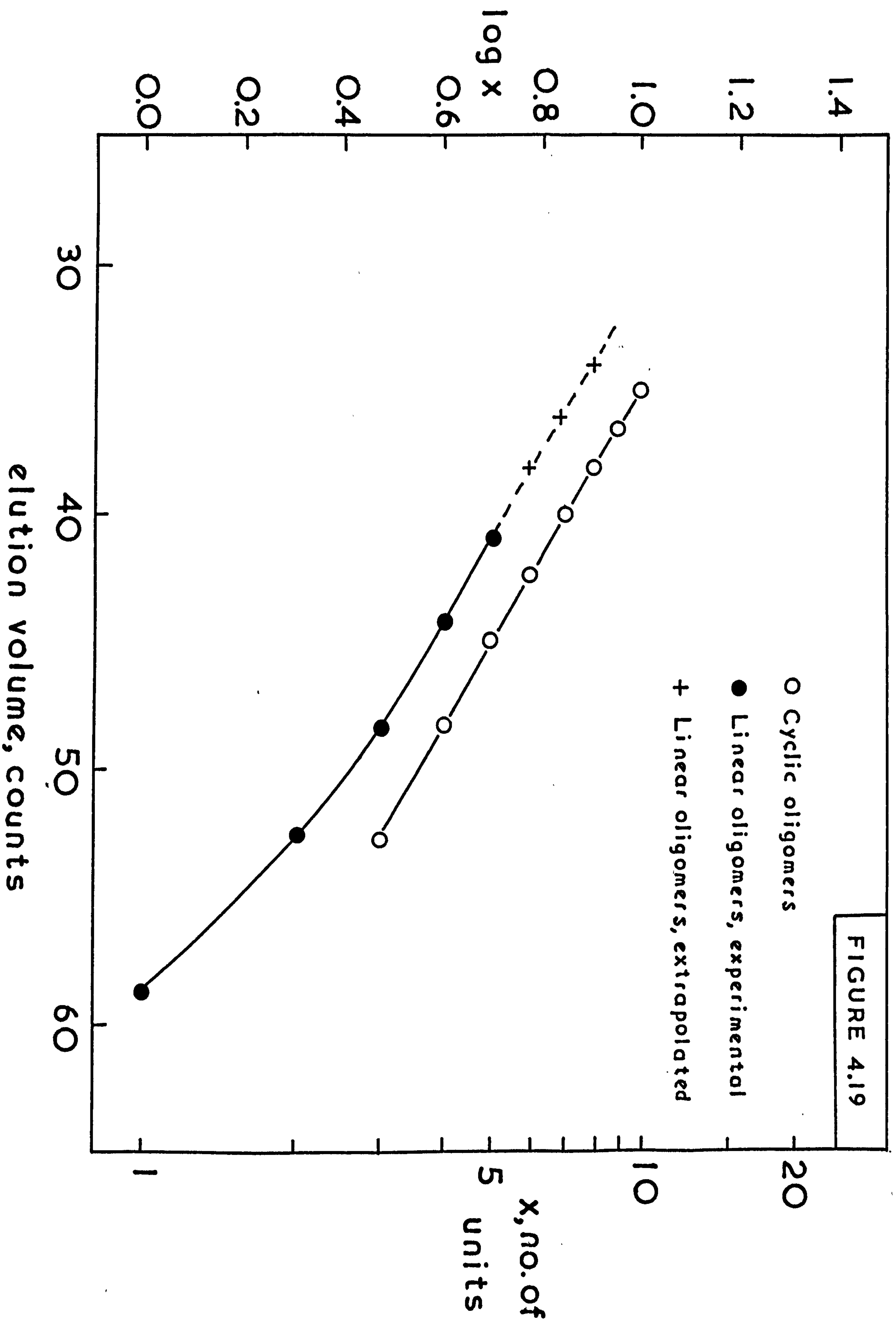


FIGURE 4.19

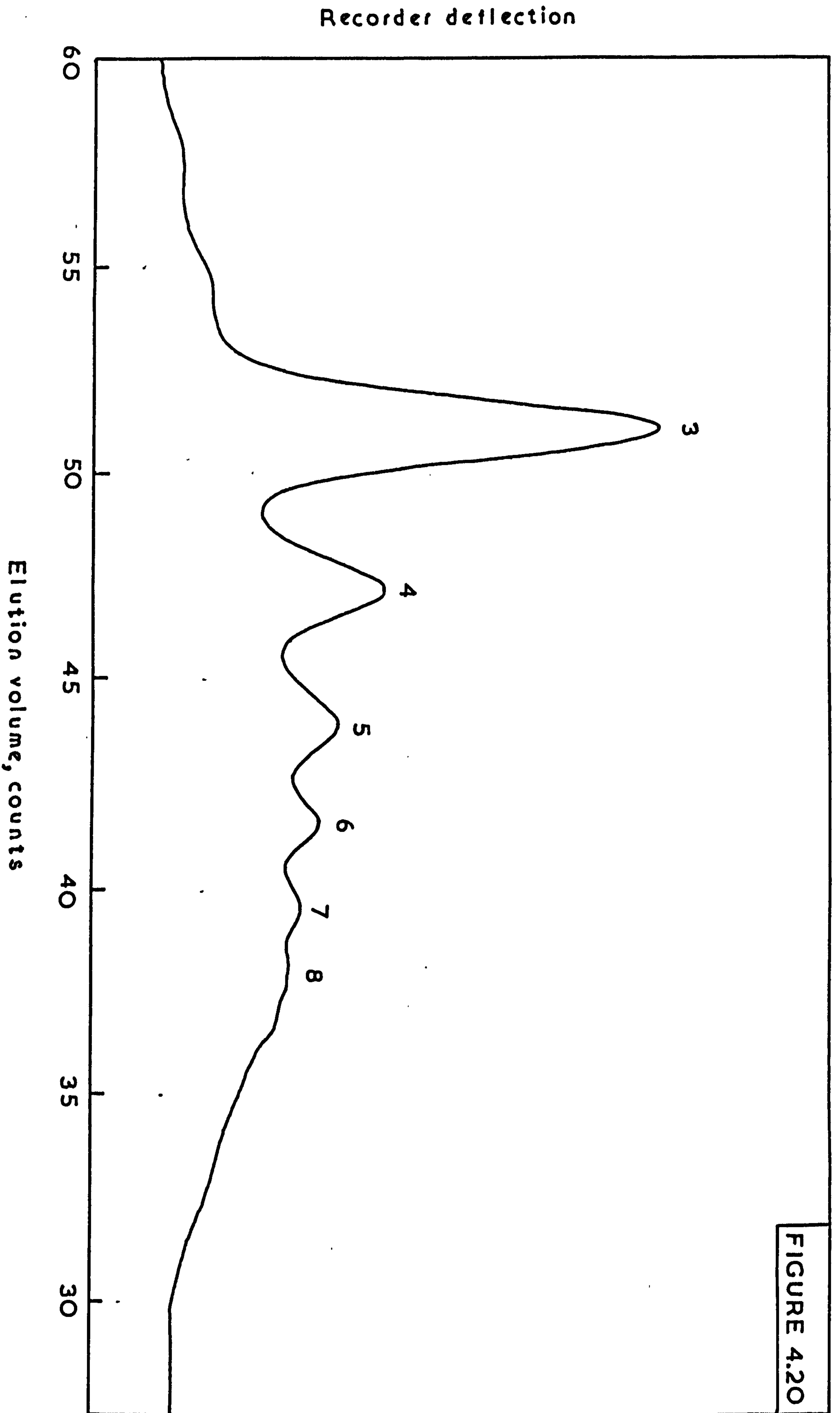


FIGURE 4.20

There is an important consequence of the marked differences in the elution volumes of cyclic and linear species: contamination of a cyclic extract with chain oligomers reduces the definition of the peaks obtained in g.p.c. The variety of possible chain species, each eluting at a different point, will accentuate this effect. An example is the tracing in Figure 4.20, for the extract (XVI) - 2A of which the infra-red spectrum has been discussed in (d) above. This tracing shows, too, another feature indicative of the presence of large proportions of linear species: material eluting in substantial quantity after the cyclic trimer.

As will be described in Section 3. of this Chapter, for many extracts, the overall g.p.c. tracings could be quantitatively accounted for as composites of the peaks of the cyclic components. The exactitude of the fits obtained in this way is strong evidence for the absence from these extracts of more than very small amounts of other compounds.

G.p.c., therefore, served not only to confirm the cyclic nature of the main constituents of the extracted material, but also provided further information upon their freedom from contamination with linear species.

(g) Analysis of diethylene glycol content: although Goodman and Nesbitt²¹ found in their extracts from PET no cyclic dimer of ethylene terephthalate, they did note another dimer, in every molecule of which one ethylene glycol linkage had been replaced by a diethylene glycol

residue (cyclic (ethylene 3-oxapentamethylene diterephthalate)):

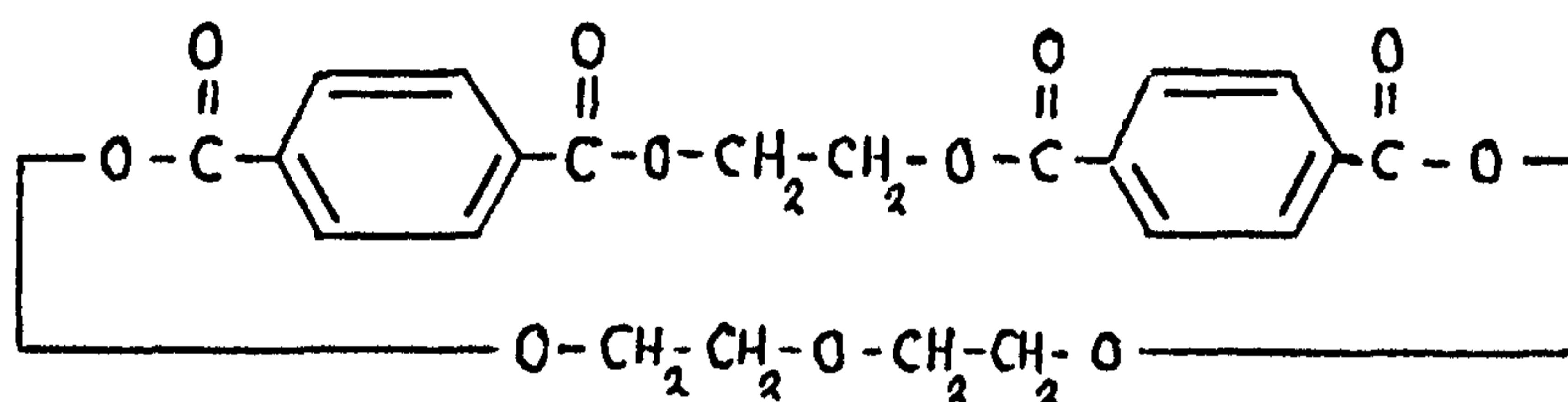
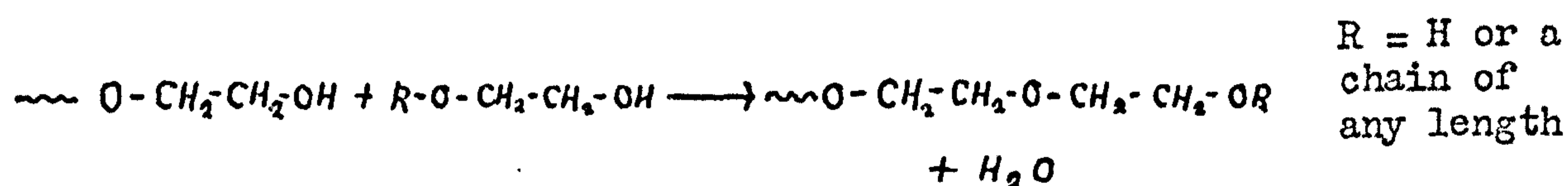


Figure 4.21

They suggested that this substance owed its appearance to the presence in commercial PET of a certain fraction of diethylene glycol linkages, incorporated during melt polymerisation by polycondensation with loss of water, rather than the expected ethylene glycol⁷⁰:



or by dehydration of the glycol prior to reaction⁷⁰:



or possibly by other mechanisms⁷¹.

More recently, Peebles, Huffman and Ablett²³ isolated from their extracts a cyclic pentamer containing one diethylene glycol linkage to every molecule, and furthermore detected such linkages in still higher species; while Goodman and Nesbitt's dimer is now available synthetically⁴⁶.

In the light of these previous findings, it was necessary to give consideration to the diethylene glycol content of the PET extracts under study. Readily available evidence was that the n.m.r. gave no sign of such linkages; but to gain more precise information, use was made of a method based upon that of Gaskill, Chasar and Lucchesi⁷², and consisting of gas chromatographic estimation of the diethylene glycol

released by partial saponification of PET with methanolic sodium hydroxide*. The results of these quantitative analyses were surprising. It was found that while, indeed, the diethylene glycol contents of the commercial samples of PET used in these studies fell within the normal range, those of the extracts were very low. For instance, the extracts from two polymers with contents of 0.90 and 2.30 mole %, respectively, both had levels of diethylene glycol below the limit of detection under the conditions used (< 0.2 mole %).

The rationalisation of these findings is not easy. It might indeed be expected that the content of the extract would be lower than that of the parent polymer, since several of the major cyclic components, most notably the trimer, probably adopt special favourable conformations, not open to the equivalent species containing a diethylene glycol residue; but the magnitude of the departure is surprising. This may be evidence that the conformational properties of many of the observed cyclic oligomers of PET are in fact radically affected by the introduction of just one such foreign residue.

To summarise the evidence presented in this Section, it is almost beyond doubt that the major components of the extracts were indeed the cyclic oligomers of poly(ethylene terephthalate). For many extracts, the evidence was also strong, that these were effectively the only substances present; for some others, the evidence pointed to the presence of substantial amounts of linear species; for others, again, it was not possible to say on this evidence alone exactly to what extent the extracted cyclic oligomers were contaminated with linear oligomers.

* Thanks are extended to Mr. A.J. Thompson, of the Research Department, I.C.I. Fibres, Harrogate, for performing these analyses.

4.3 QUANTITATIVE G.P.C. ANALYSIS OF EXTRACTS

From obtaining the g.p.c. tracing for an extracted mixture of cyclic oligomers, such as that shown in figure 4.18, there are only two steps to the quantification of the analysis. Firstly, it is necessary to correctly apportion the area of the total tracing between the different cyclic species; secondly, to establish relationships between the area fractions of species and their weight fractions in the sample; that is, determine the relative responses.

(a) Division of the tracing: only for the trimer, is the peak sufficiently well resolved to permit its area to be found immediately with adequate precision. To subdivide the rest of the chromatogram between the various components, the tracing was cut along lines dropped vertically down from the minima. In effect, this attributed to each of the components a sector, of width increasing roughly logarithmically with peak elution volume, within which that substance alone was assumed to elute. At first sight, this may seem a crude approximation; but closer examination suggests that it will be reasonably accurate. For this part of the chromatogram consists of a series of overlapping peaks, approximately equally spaced, and of areas decreasing in an approximately linear fashion from left to right; and so although the total area in the sector assigned to a particular component is increased, to the extent that the contribution to it from left-hand neighbouring components exceeds the loss from it into the left-hand sectors, an almost exactly compensating decrease will result from the corresponding exchange with its right-hand neighbours.

This qualitative expectation was fully confirmed by a quantitative analysis. Use may be made of the method of least squares to obtain the "best" fit of the true peak heights of the species to the overall experimental tracing. The mathematical analysis, and the computer programme written to handle the calculations, are fully described in Appendix A: here it is necessary only to show that the results agree closely with those of the simpler procedure.

To give examples: Figures 4.22 - 4.24 show the fits obtained for three typical tracings, of which two have been presented earlier, while in Table 4.2 comparisons are made between the area fractions found from these fits, and those found by simply dropping perpendiculars. (In the Figures, the small circles represent the fitted points).

	Area fraction of x-mer found by fitting			Area fraction of x-mer found directly		
x	A	B	C	A	B	C
3	0.459	0.550	0.343	0.449	0.534	0.343
4	0.148	0.121	0.155	0.145	0.119	0.161
5	0.104	0.105	0.130	0.102	0.108	0.127
6	0.094	0.073	0.120	0.092	0.074	0.119
7	0.080	0.068	0.094	0.077	0.074	0.089
8	0.057	0.046	0.074	0.061	0.051	0.076
9	0.040	0.029	0.050	0.045	0.030	0.047
>9	0.017	0.008	0.035	0.024	0.010	0.038

Table 4.2

FIGURE 4.22:
TRACING A

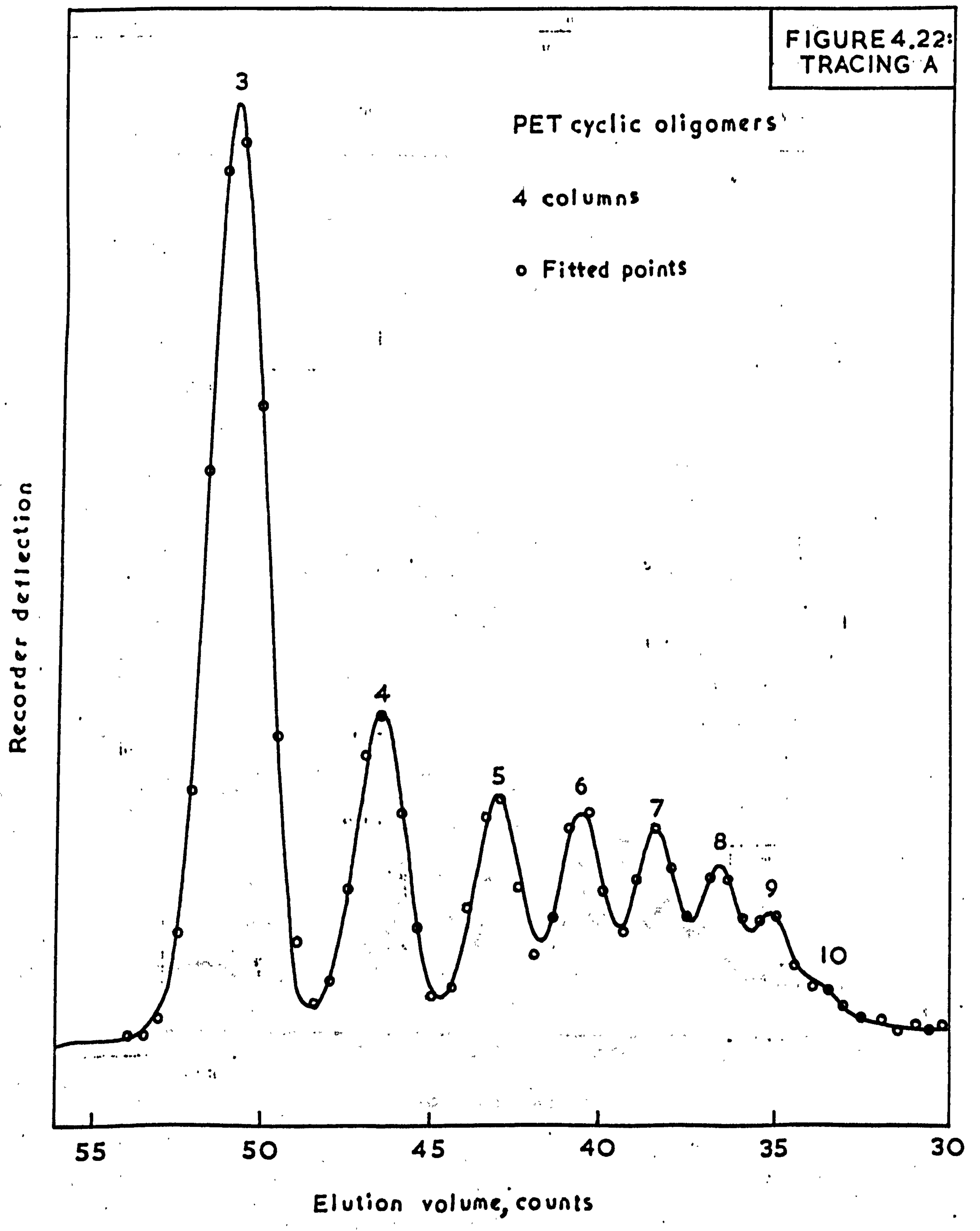


FIGURE 4.23 : TRACING B

Recorder deflection

o Fitted points

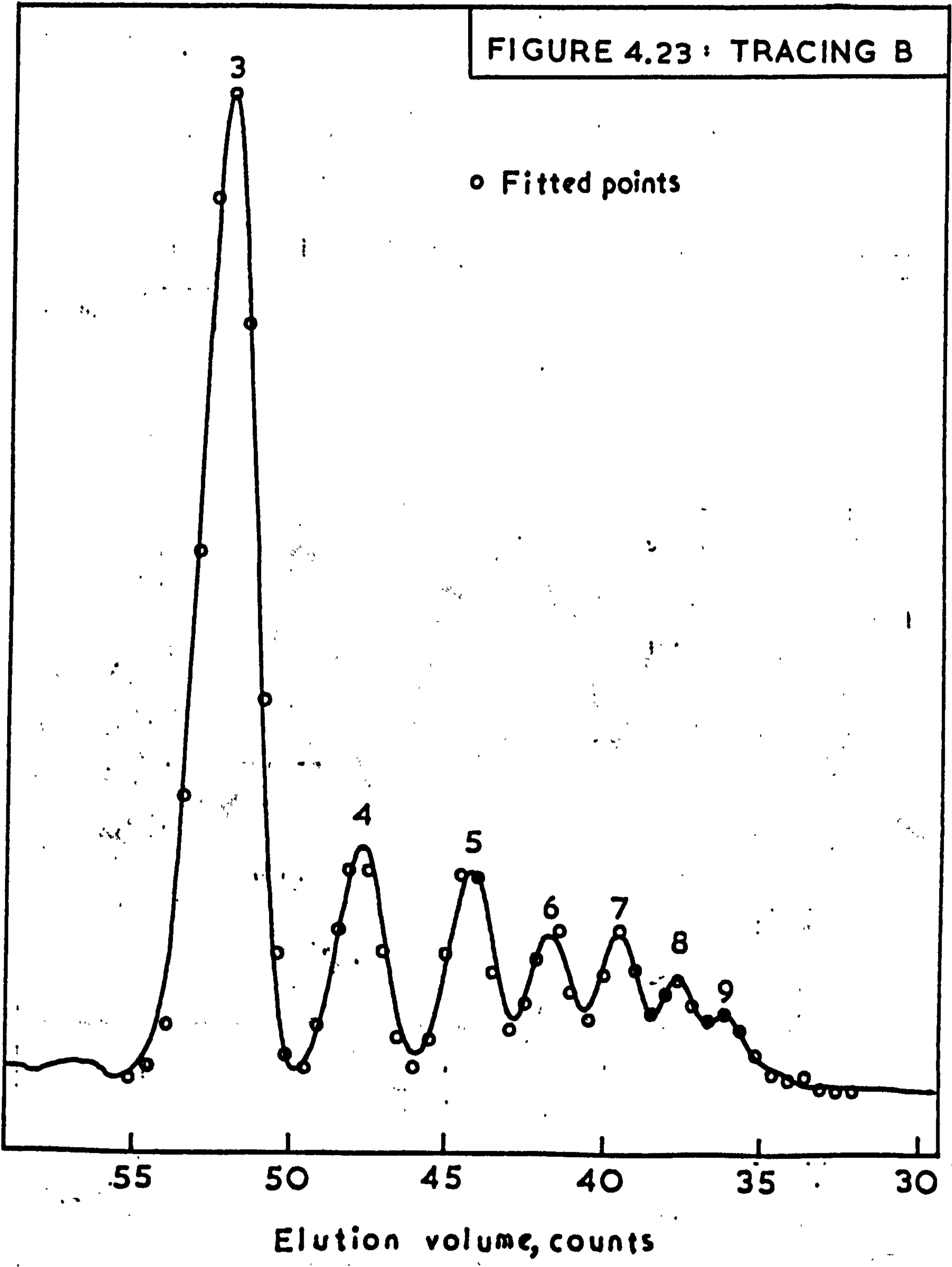
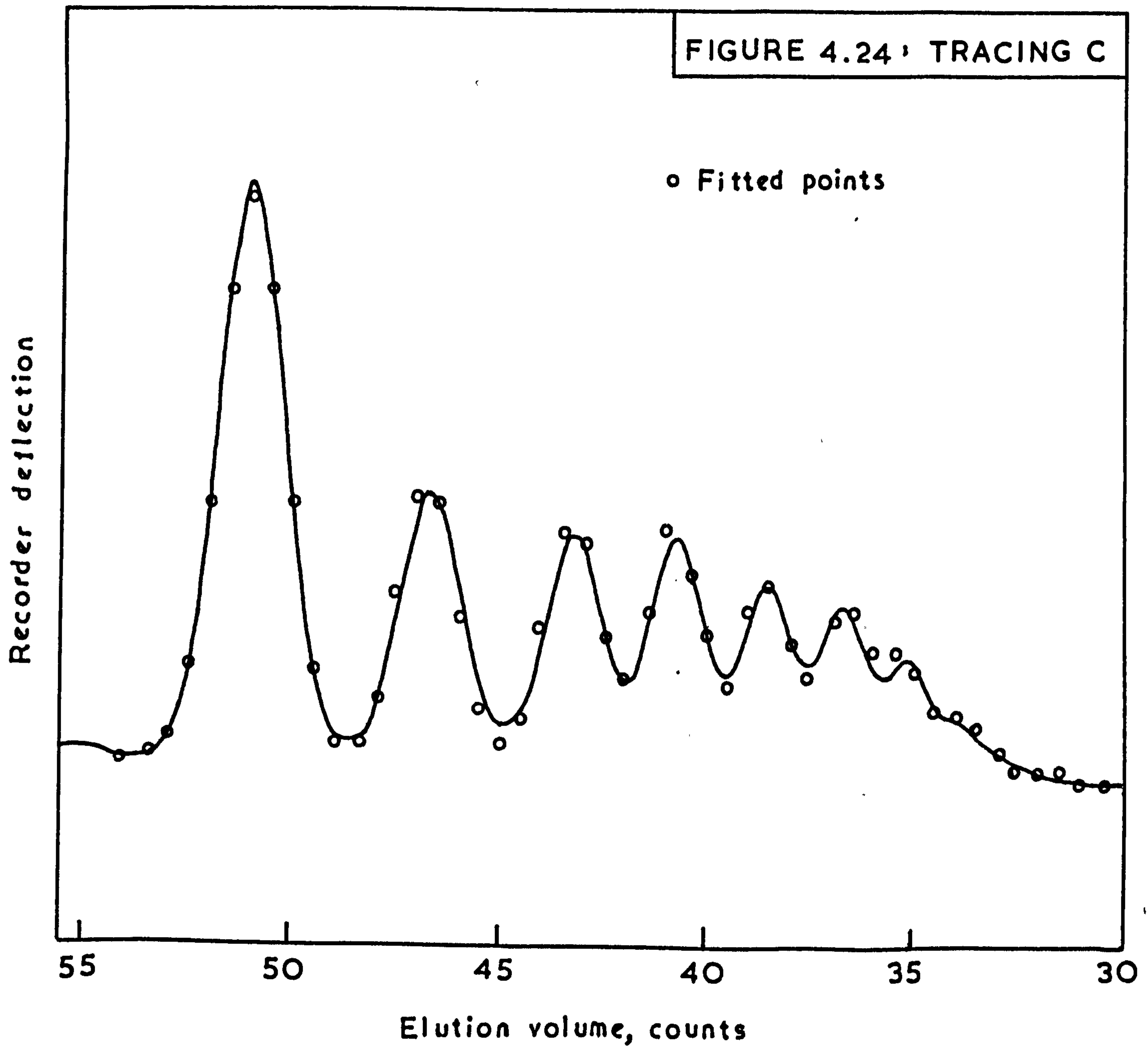


FIGURE 4.24, TRACING C



The agreement is so good that regular use of the more complicated method was hardly justified, and accordingly the method normally applied was to trace out the chromatogram onto thicker paper, cut out the sectors, and weigh them. Under conditions of good baseline, this could be done with a reproducibility of 5% for the trimer, diminishing to about 10% for the nonamer. (Table 4.3). Again, provided the base-line was good, duplicated injections of samples gave identical results within roughly these limits. (Table 4.4). Not infrequently, however, the base-line was not this stable; then it would be necessary to repeat the run to obtain reliable mean values.

Table 4.3

x	Area fraction of x-mer	
	1st. estn.	2nd. estn.
3	0.480	0.497
4	0.154	0.150
5	0.080	0.087
6	0.069	0.072
7	0.051	0.049
8	0.051	0.046
9	0.029	0.026
>9	0.029	0.017

Table 4.4

x	Area fraction of x-mer	
	1st. run	2nd. run
3	0.524	0.546
4	0.163	0.176
5	0.088	0.083
6	0.075	0.068
7	0.061	0.054
8	0.044	0.040
9	0.027	0.020
>9	0.014	0.007

(b) Relative response factors* : it was possible, in this regard, to do no more than compare the response of the one cyclic available in pure form, the trimer, with that of the other cyclics as a whole, and

* The linearity of the responses has already been established (Section 3.3), and will not be discussed further here.

assume that all the higher species responded equally; in view of the final conclusion, that the response of the trimer was only a little different from that of the higher oligomers, it is unlikely that the higher oligomers differed sensibly amongst themselves. Even for this limited purpose, however, it proved rather difficult to obtain consistent information.

Preliminary to the study, a "working unit of response" was defined, to take into account the effect upon the areas of the peaks obtained of the differences, from run to run, in the amount of sample injected, the flow rate, the chart speed and the sensitivity settings. All the response factors hereinafter discussed will be expressed in these units.

The average response for ten different samples containing cyclic oligomers in the normal sort of distribution (i.e., similar to those shown in Figures 4.22 - 4.24) was found to be 0.34, with a mean deviation of 0.02; while the response for pure cyclic trimer was determined as 0.43. (0.436, 0.429 on two runs with different solutions.) By using the trimer factor to estimate the weight of trimer injected, for each of the ten samples with complete distributions, and finding the weight of the other cyclics by difference, it was possible to obtain a value of 0.26, mean deviation 0.03, for their factor. This would imply that the trimer is 65% more responsive than the higher rings.

The ten samples had shown a range of solubility behaviour; not all dissolving completely. Provided that only a small fraction remained undissolved, and that its composition did not depart greatly from that of the sample as a whole, this would not much affect the relative areas for the components, in the chromatogram; but it would lead to a

significant diminution in the overall response, which, by the procedure described, would carry through to give spuriously low response factors for the higher cyclics. Furthermore, the reliance of the calculation upon finding the weight of the oligomers above trimer by difference implies that the relative error in the response factor finally to emerge will be roughly double that in the total amount injected.

These considerations suggested that the more correct values for the response of the higher cyclics would be those found for the more soluble samples of the ten, i.e. values at the upper end of the range; and an interim value of 0.30 was adopted. Certain of the later results, however, argued against so low a figure. Specifically, the percentages by weight of cyclic trimer in commercial melt polymers were somewhat low compared to seemingly reliable literature values; for example, 1.05% and 1.16%, as against 1.3%²⁰ and 1.15% - 1.50%²¹. (See Chapter 5.) Also, the trimer concentrations for melt-equilibrated samples were lower than these literature values, for non-equilibrated samples; e.g. 1.25%. (Chapter 6.) To render the new results compatible with the old required a response factor of at least 0.35 for the cyclics other than trimer.

Furthermore, there became available a sample which contained only these higher oligomers. (See Chapter 5.) By direct determination, due allowance being made for a small amount of contamination in the extract, their response factor was found to be 0.38, with an estimated error of ± 0.04 .

The value finally adopted, therefore, was 0.35. Lying between the highest values found indirectly, and that found directly, it is

sufficiently high to reconcile the new results for the trimer with those in the literature. It corresponds to a response for the trimer enhanced by just 20% over that for the other cyclics. The error attached to this factor is about ± 0.06 , or 15%; but it may be pointed out that, just as in finding relative response factors by the indirect method, errors are subject to magnification, so in using them, errors are diminished. This is made clear in Table 4.5 where comparison is made between the weight fractions of species, calculated from a single set of area fractions assuming the responses of higher cyclics and trimer to be in the different ratios 1:1.0, 1:1.2, and 1:1.4.

x	Weight fraction of x-mer, for ratios in response of:		
	1.0 :1.0	1.0 :1.2	1.0 :1.4
3	0.535	0.489	0.451
4	0.170	0.186	0.201
5	0.086	0.094	0.102
6	0.072	0.080	0.085
7	0.058	0.064	0.068
8	0.042	0.046	0.050
9	0.024	0.026	0.028
>9	0.010	0.011	0.012

Table 4.5

4.4 PREPARATION OF CYCLIC TRIS(ETHYLENE TEREPHTHALATE).

The method whereby the cyclic trimer of PET was obtained was analogous to that of Carothers^{2,3} for the preparation of macrocyclic esters of aliphatic diacids.

The basic apparatus consisted of a water-cooled probe of 17 mm. diameter, passing centrally down an outer jacket equipped with a B24 male joint. The jacket was fitted to a 100 ml. flask, into which the probe protruded for some 7 cm. A take-off from the far end of the jacket was connected to a vacuum pump.

In use, about 10 gm. of high molecular weight PET, mixed with catalyst, were put into the flask, and the apparatus was set up horizontally with the flask placed in the centre of an electrical heating mantle, controlled by a Variac and fitted with a thermometer. To reduce heat losses, asbestos rope was wound around the jacket where it emerged from the mantle, and the mantle itself was covered over with aluminium foil. (Figure 4.25).

After evacuation to about 0.05 mm., heat was applied steadily, and the temperature taken to 300° - 310°C. over some hours. From about the melting point (260° - 270°C) care was necessary that the heating rate was not so great that the polymer bubbled up over the probe. These conditions were maintained for 36 - 48 hours, and the heating was then turned off. When the apparatus had cooled sufficiently, the mantle was removed, and the flask wrapped in a cloth. These was a necessary precaution because, on solidifying, PET melts grip the glass of any container, and the differential contraction accompanying further cooling will often cause the vessel to shatter violently⁷³.

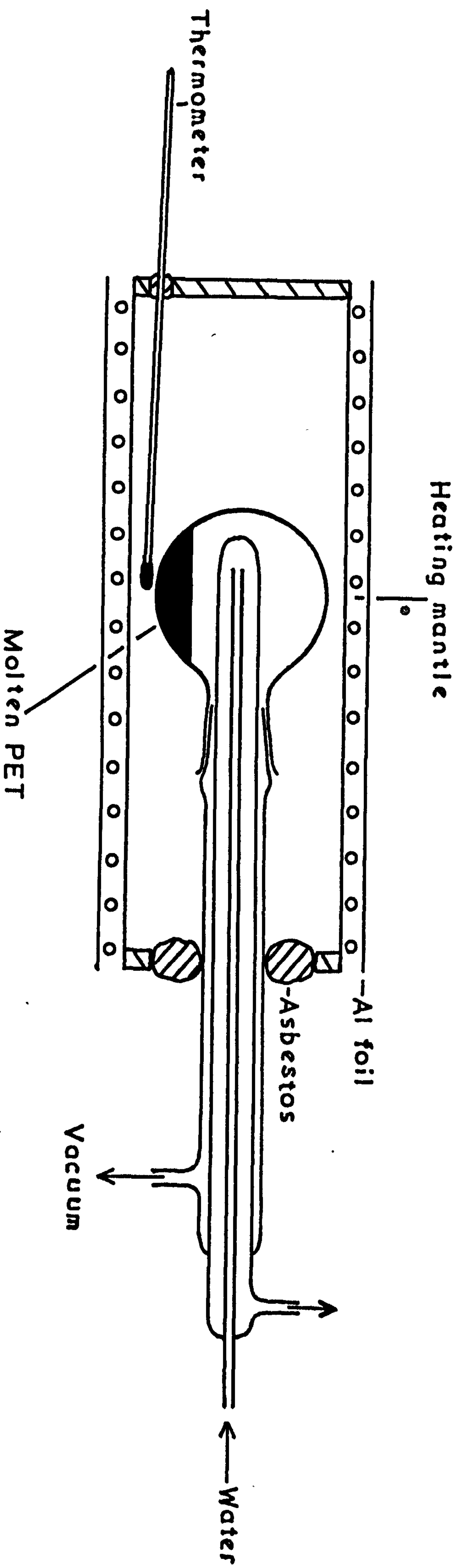


FIGURE 4.25

The apparatus was allowed to cool to $30^{\circ} - 40^{\circ}\text{C.}$, under vacuum, when air was admitted and the probe carefully withdrawn from the flask. Whatever care had been taken, the probe was invariably found to be contaminated with charred polymer; but this could easily be picked off. The yellowish sublimate was removed from the probe by scraping, and washing with chloroform.

In infra-red spectroscopy, the sublimes gave more or less intense carboxyl bands. (Figure 4.26.) Extraction with chloroform left insoluble residues also showing intense carboxyl absorptions, and melting with much sublimation above 345°C. ; these are properties characteristic of terephthalic acid. The extracts were concentrated to 5 - 10% solutions, and refiltered if necessary; then about double the volume of diethyl ether was added, and the mixtures cooled in ice. Fine white crystals appeared over several minutes. After some hours at 6°C. , the solids would be filtered off, washed with a little ice-cold ether, and air-dried. They gave no carboxyl, and only very slight hydroxyl, absorption. (Figure 4.27). They melted over three to four degree ranges in the region $308^{\circ} - 316^{\circ}\text{C.}$

The best catalyst used was antimony trioxide (ca. 1%) giving over 36 hours 1 gm. of sublimate, containing only a little terephthalic acid. Over 48 hours, lead monoxide (2 - 5%) gave only 0.75 gm., markedly more heavily contaminated with acid. Magnesium chloride hexahydrate, a good catalyst for the preparation of aliphatic macrocyclic esters, was much less effective and gave a product consisting mainly of the acid.

The crude trimer products from different experiments were combined (about 1 gm. in total) and reprecipitated from 10 ml. warm chloroform

% transmittance

wavelength, nm.

2500

3000

3500

4000

5000

6000

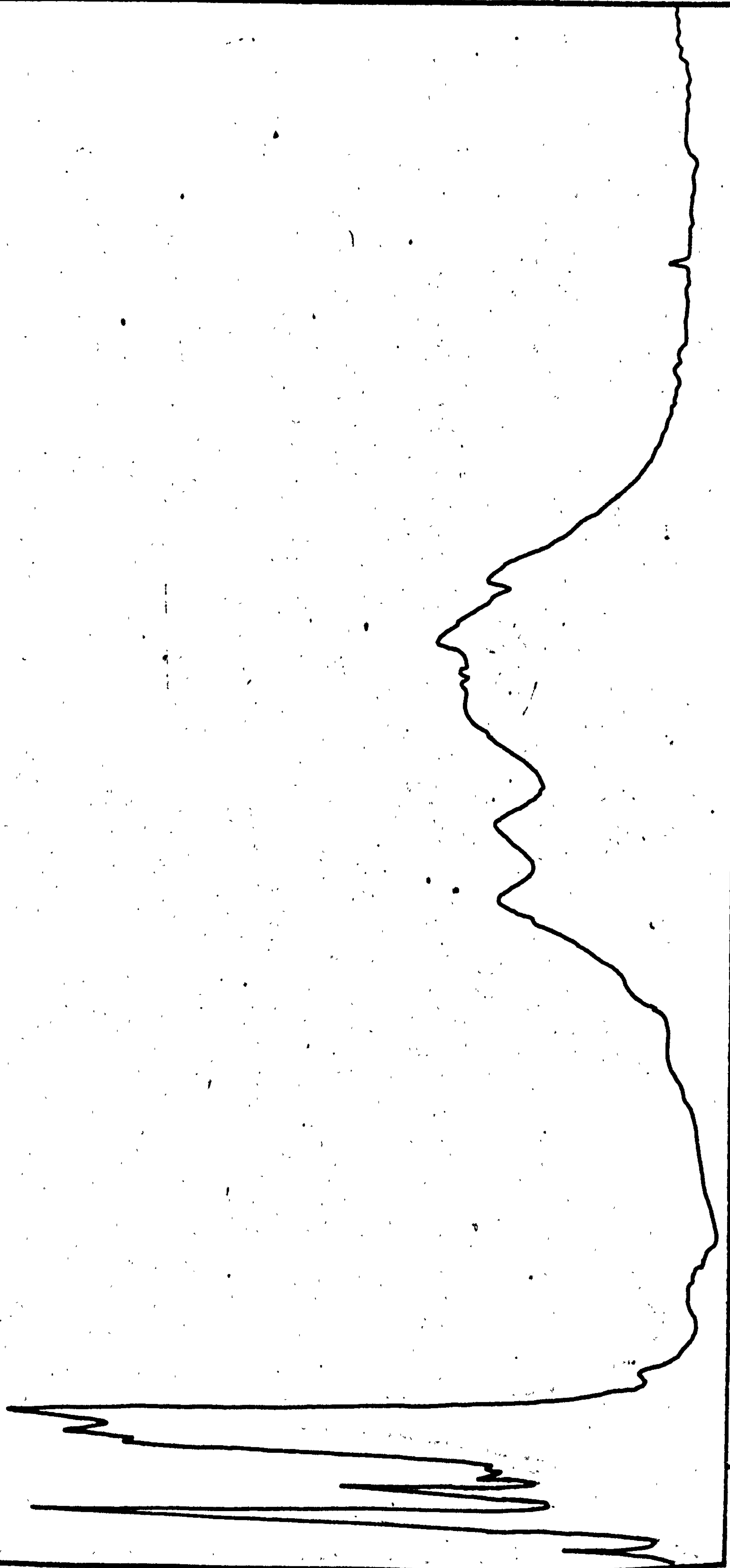
20

40

60

80

FIGURE 4.26



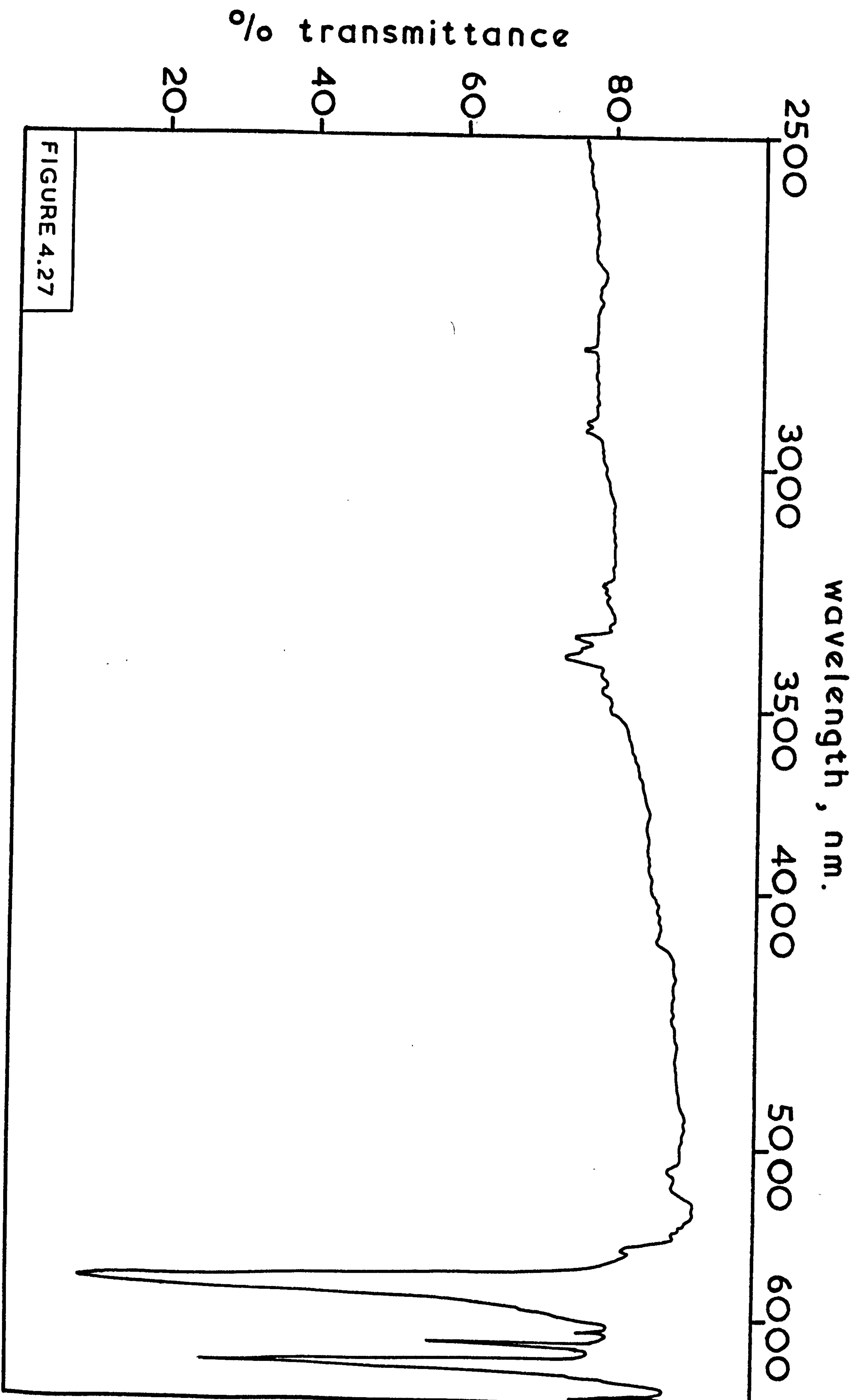


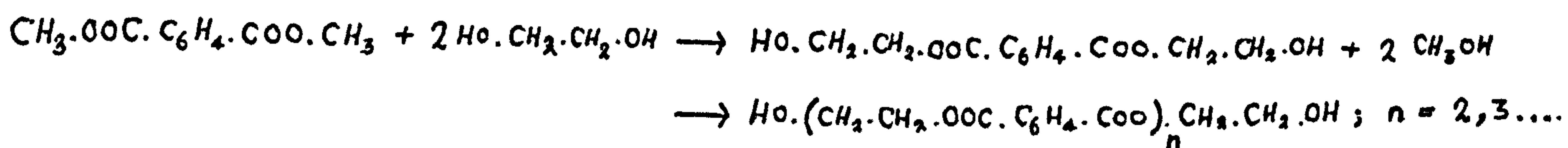
FIGURE 4.27

with 20 ml. diethyl ether, with cooling on ice. The solid (0.5 gm.), filtered, washed and air-dried, melted at 314° - 316°C., with preheating of the block to 311°C. (Literature: 314° - 316°²¹, 318°²², 319°²³, 315° - 316°⁵²). Without pre-heating, the crystals discoloured slightly during the earlier stages of heating, and melted somewhat lower. It gave the n.m.r. and infra-red spectra mentioned earlier. Elemental analysis: carbon, 62.14%, hydrogen, 4.16%. (Calculated, 62.50%, 4.19%.) Molecular weight found by vapour pressure osmometry in chloroform was 517. (Calculated, 576). In g.p.c. at I.C.I. Fibres, using m-cresol at 105°C. as solvent, it gave a peak identical to that found for trimer obtained by extraction from polymer.

In terms of simplicity, speed and absolute yield, this new method of preparation has quite distinct advantages over that of Meraskentis and Zahn⁵². It also compares favourably with the later procedures of Zahn and Repin⁵⁵, and Hamb and Trent⁵³. Undoubtedly, it is capable of refinement, and could be operated on a larger scale without difficulty.

4.5 PREPARATION OF GLYCOL-TERMINATED LINEAR OLIGOMERS

These were obtained during an attempt to prepare bis(hydroxyethyl) terephthalate by the transesterification of dimethyl terephthalate with ethylene glycol⁷³:



151 gm. (0.75 mole) dimethyl terephthalate (recrystallised from methanol, m. $137.0^{\circ} - 137.5^{\circ}$), 112 gm. (1.71 mole) ethylene glycol (distilled off sodium under nitrogen⁷³, b. 194°) and 0.25 gm. calcium acetate catalyst, were put into a 500 ml. flask, fitted with a nitrogen bleed and equipped with a still-head and condenser for take-off. Heating was applied, by means of the vapours of boiling glycol; the mixture completely liquified over thirty minutes, and evolution of the methanol commenced. The reaction was complete within 3 hours, by which time some 60 ml. of methanol had collected in the receiving vessel. While still molten, the contents of the flask were turned out into a Pyrex evaporating dish, to facilitate later handling.

The melt solidified to a sticky, white lump, weight 212 gm., melting over the broad range of $75^{\circ} - 130^{\circ}$. G.p.c. analysis gave the tracing shown in Figure 4.28; the very large and broad peak, upon which the chain peaks sit, was due to ethylene glycol. The lump was broken up and extracted with 600 ml. hot water; on cooling the solution, about 18 gm. of crystalline solid were obtained. This was recrystallised from acetone to give bis(hydroxyethyl) terephthalate. (11 gm. of white platelets; identified by solubility behaviour and by melting point: 108° , compared to literature values of 109° ^{74,75}). It gave a single peak in g.p.c. (Figure 4.29). The insoluble residue formed the mixture of glycol-terminated short chains referred to in an earlier Section. It was shown by g.p.c. to consist mainly of dimer. (Figure 4.30).

Bis(hydroxyethyl) terephthalate was obtained in much higher yield if a five-fold excess of ethylene glycol were used in the preparation.

FIGURE 4.28: Crude product

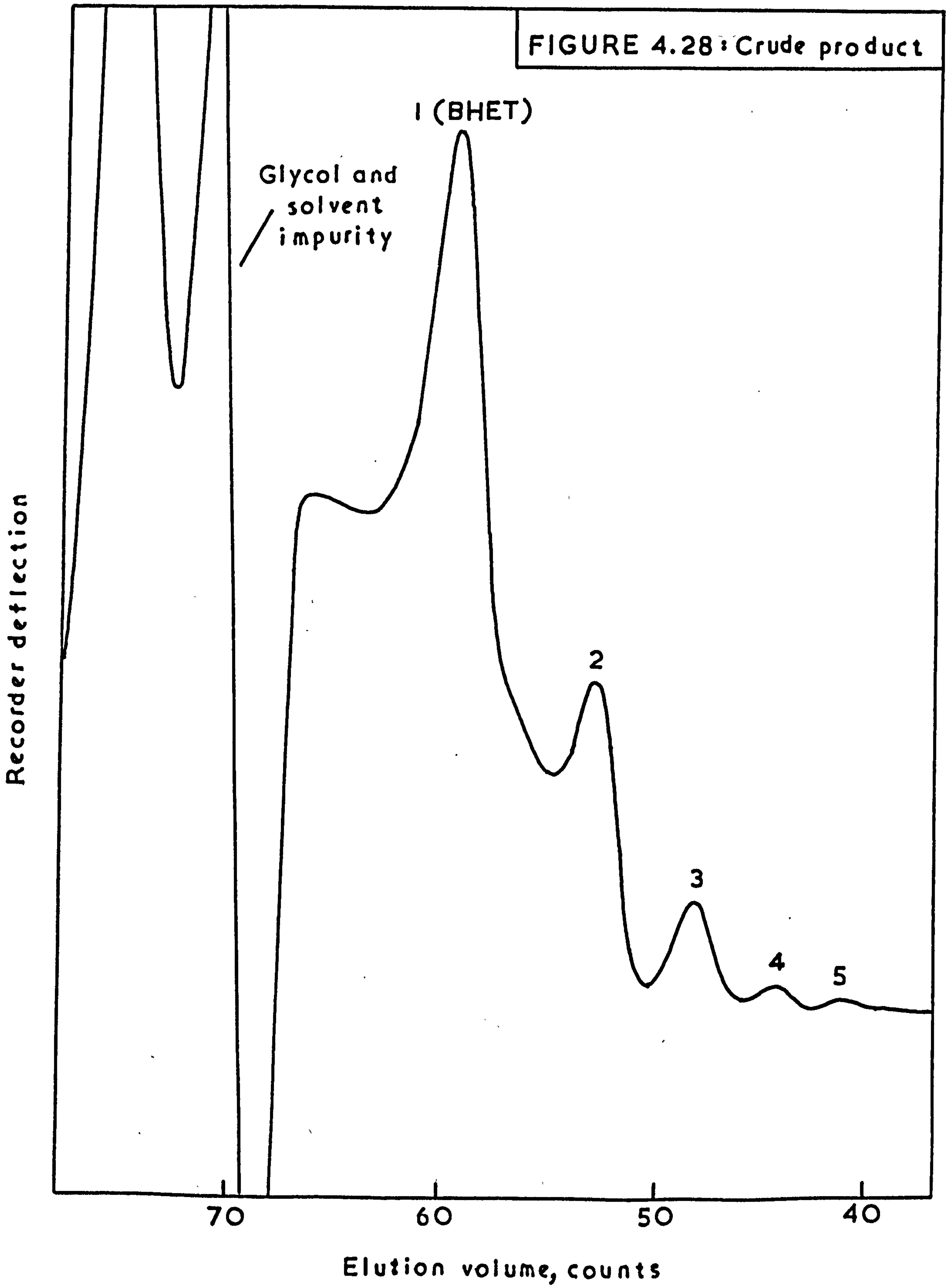


FIGURE 4.29: BHET

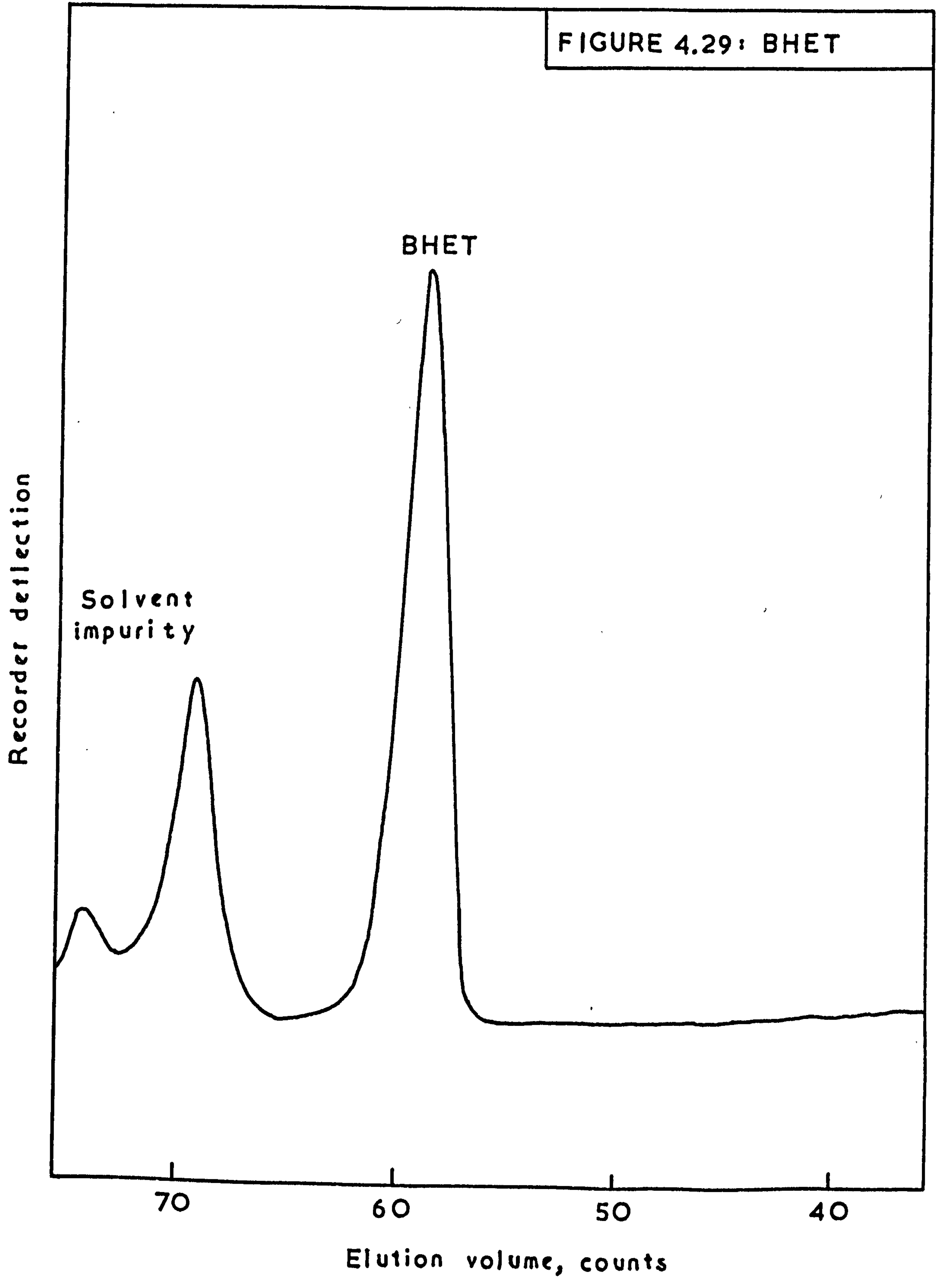
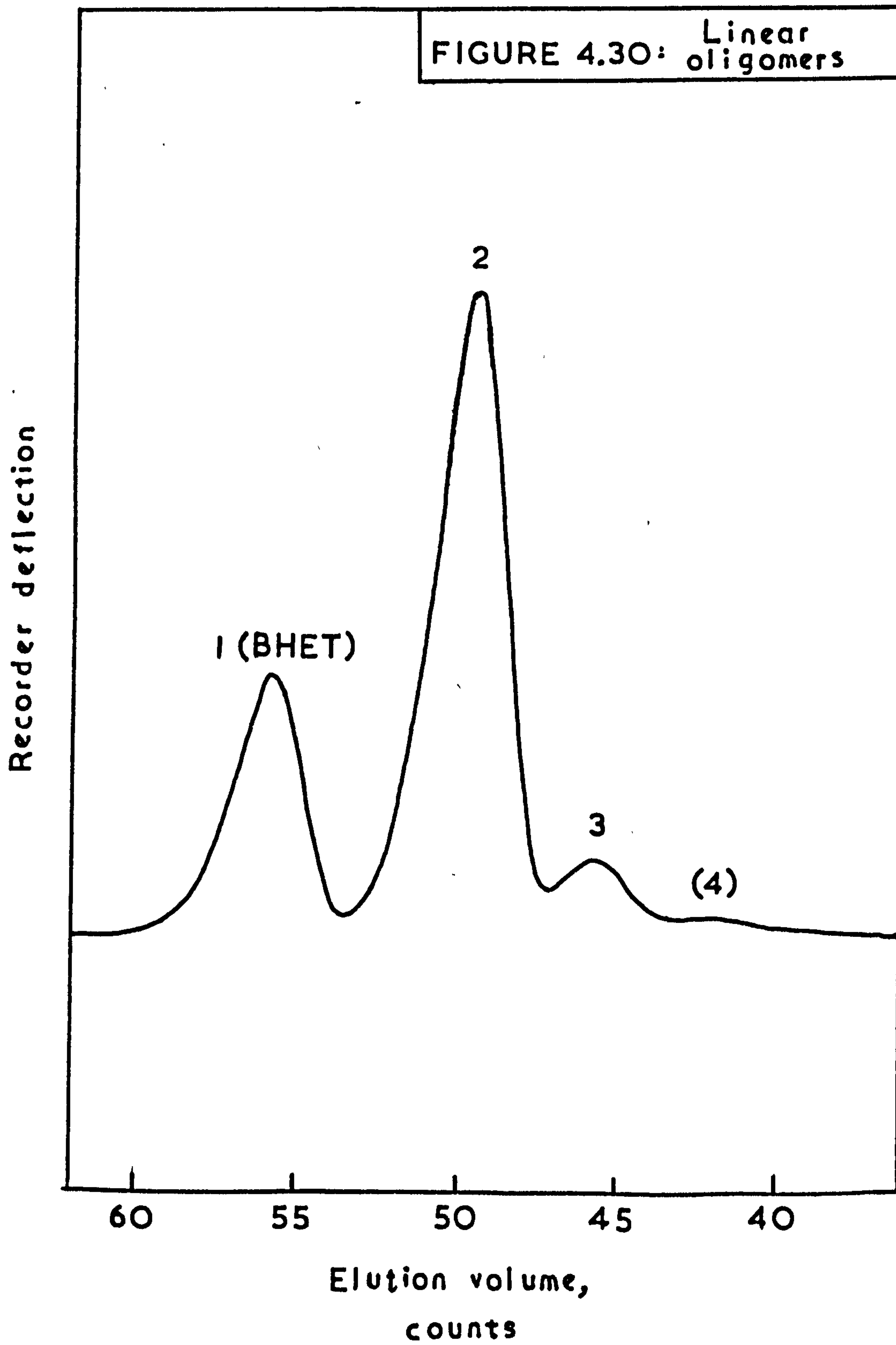


FIGURE 4.30: Linear oligomers



CHAPTER 5.

EXTRACTION OF CYCLIC OLIGOMERS FROM
POLY(ETHYLENE TEREPHTHALATE).

5.1 INTRODUCTION

With few exceptions, the previous studies of the low molecular weight fraction of poly(ethylene terephthalate) put reliance upon the extraction of the polymer, as normally handled, by fairly volatile solvents.

The method of Ross, Coburn, Leach and Robinson¹⁹ was to extract film with trichloroethylene; Giuffria²⁰ modified this only in the additional use of chloroform and xylene as solvents. In both cases, trimer (by weight, ca. 1%, and 1.3%, of the film) was the only cyclic oligomer found in the extracts.

Goodman and Nesbitt²¹ extracted fibre and chip with xylene and with 1,4-dioxane to obtain extracts comprising 1.3 - 1.7% of the polymer, and containing cyclic tetramer and pentamer as well as trimer. They found as typical these weight percentages of individual rings:

Trimer	Tetramer	Pentamer
1.4%	0.11%	0.03%

Extraction with dioxane was also the method selected by Zahn and Kusch²²; they were able to isolate from their extracts cyclics from trimer to hexamer.

Peebles, Huffman and Ablett²³ again used xylene and dioxane, but by designing their extraction apparatus so that nearly boiling solvent came in contact with the fibre or finely-powdered chip they could obtain extracts in the range 2.0 - 3.8%, containing substantial amounts of the higher oligomers.

The trend to emerge from these successive studies is that the yields of cyclic oligomers, especially those above trimer, increase with the severity of the extraction conditions. Incomplete extraction would offer an immediate explanation of the rapidity with which the concentrations found for these species decline with increasing ring size, in comparison with both theoretical prediction (see Chapter 7.) and the experimental results from other systems. It was therefore proper to pay special attention to the method of extraction to be used.

Fuchs⁷⁶ has examined the efficiency with which crystalline polymers are extracted by volatile solvents. He argued that occlusion in the crystalline regions would render part of the soluble material inaccessible to solvents of low, or only moderate, power. In the instances of polypropylene and polyethylene, he showed that, in order to remove all the material, it was necessary to entirely dissolve the polymer in hot solvent and then reprecipitate the high-molecular weight part by cooling. Part of the soluble fraction would remain in the supernatant liquid; the rest could be extracted from the precipitated polymer with cold solvent. The method he adopted in extending these studies to PET may well have lead to degradation, or re-equilibration, of the polymer, and so given him spuriously high levels of extractable material; but his results nevertheless strongly suggested ~~that complete~~

that complete extraction of the cyclic oligomers from PET could only be ensured by dissolving the whole sample, rather than by just extracting the fibre or chip with volatile solvent.

The principal obstacle to the development of such a technique lay in the experimentally inconvenient characteristics of the common solvents for PET, which are mostly involatile, and often dissolve the polymer only at elevated temperatures; several are too noxious to be suitable for regular use. The complex morphology of the polymer exacerbates this difficulty, since an effective solvent for one sample may well fail to dissolve another. Thus, PET fibres will often dissolve in warm dimethylformamide, and cooling, or addition to diethyl ether, will lead to precipitation of the high molecular weight chains and their separation from the oligomeric fraction; but many other samples will not dissolve in hot DMF. M-cresol at 150° - 200° proved a generally effective solvent, and the polymer could be precipitated as a fibrous mass by addition of ether to the warm solution; but removal of the cresol from the filtered solution needed excessively high temperatures, under vacuum. Trifluoroacetic acid is a powerful solvent, and volatile; but noxious, and also costly.

The usefulness of 1-methylnaphthalene in the removal of low molecular weight material from PET has been pointed out by Siggel and Kleine⁷⁷. For this purpose, it is far from ideal, for several reasons: firstly, it becomes effective as a solvent for PET only at about 200°C; secondly, it is high-boiling (243°C); thirdly, it is slightly unstable, chemically, and tends to darken upon exposure to light or heat, especially in the presence of air. However, it proved possible to devise procedures whereby quite satisfactory results could be obtained by its use; and

so, in the absence of a better alternative, this was the solvent employed in these studies.

5.2 EXTRACTION PROCEDURE

Extraction of the cyclic oligomers from PET was achieved in this way: 15 - 20 gm. PET (as chips, or fibre cut into short lengths) were put into a 250 ml. 3-necked flask with about 100 ml. 1-methylnaphthalene (distilled under vacuum through a 15" Vigreux column, with rejection of a large first fraction). The flask was provided with a centrally placed Teflon stirrer, reaching right to the bottom: on one side-arm, there was an inlet for nitrogen; on the other, a condenser, through which a thermometer passed to enter the body of the flask. The nitrogen lead was constructed of wide-bore tubing, bent so that when the stirrer was running it still dipped into the moving liquid, and yet was avoided by the rotating blades. The position of the thermometer along the condenser was determined by the same considerations. A plug of tissue at the top of the condenser reduced the emission of solvent fumes into the air. (Figure 5.1)

The mixture was stirred steadily over a few minutes, while a vigorous stream of nitrogen swept out all air. The stirring rate was then very much increased, and strong heating was applied by means of an electrical mantle. Notes were made of the temperature at timed intervals so that the procedure could be closely reproduced later. Typically, the temperature would be taken to 200° - 210° over 8 - 10 minutes, by when the mixture would have turned cloudy and the polymer would be sufficiently softened to begin to disperse. After a further

FIGURE 5.1

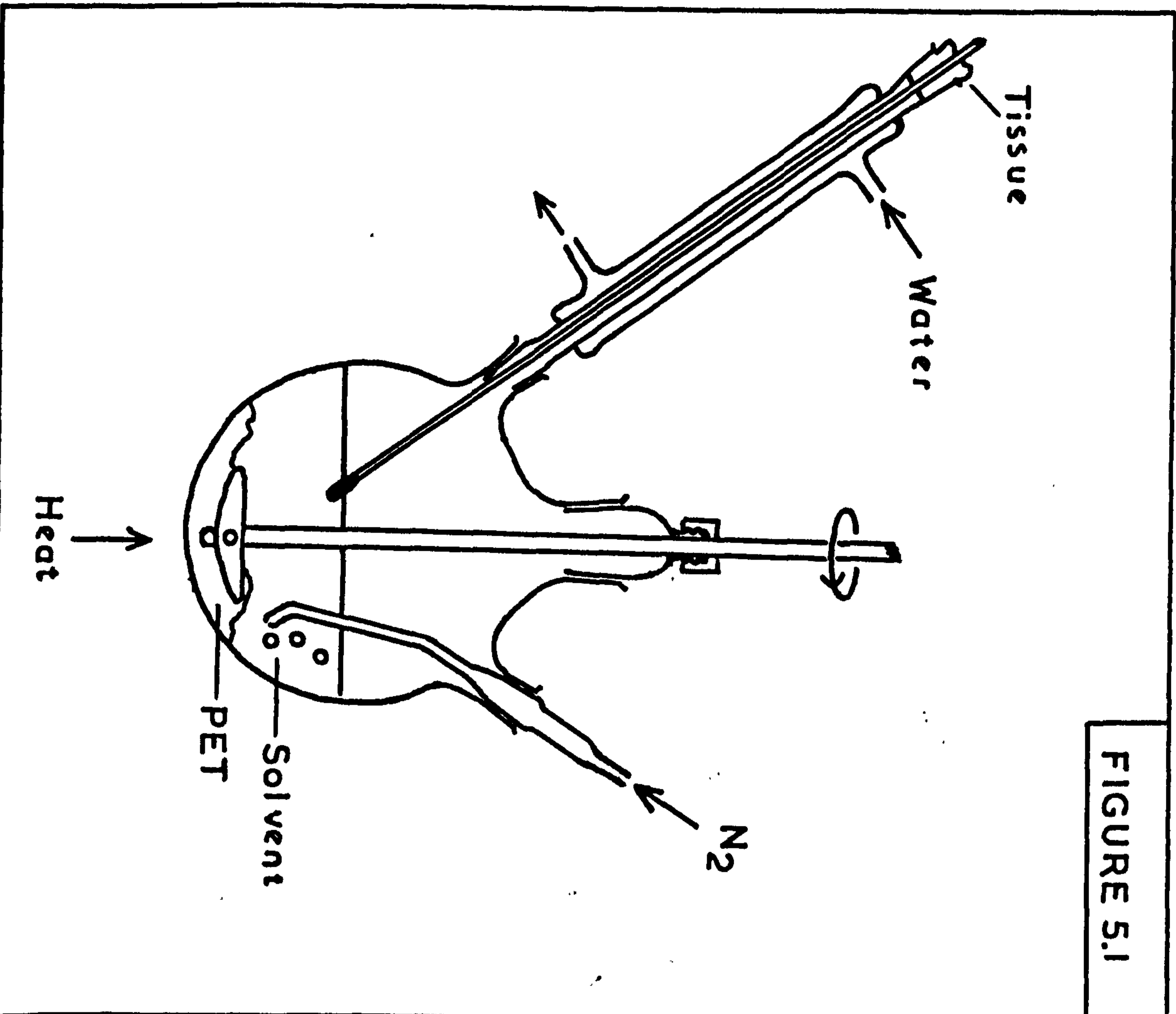
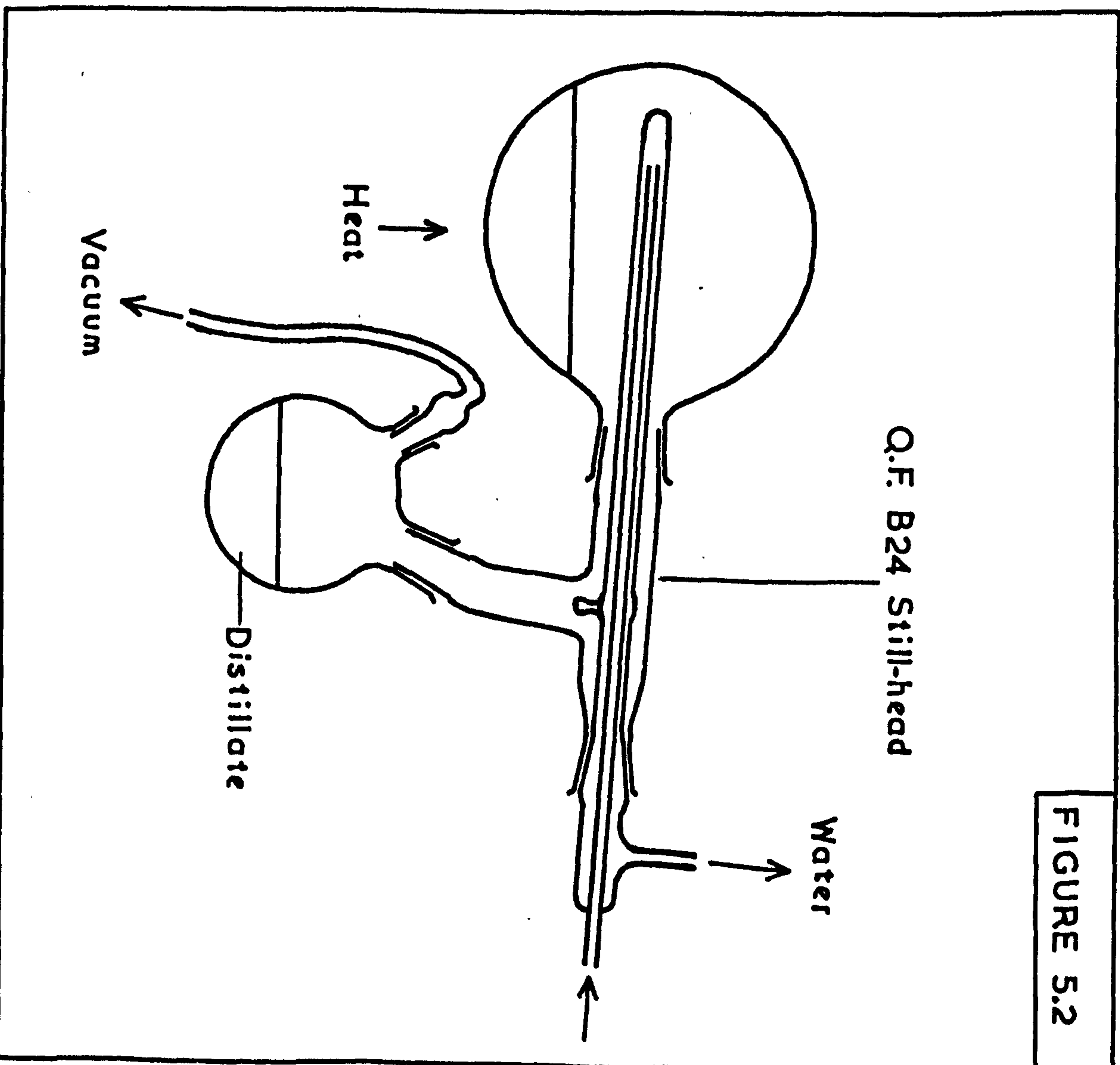


FIGURE 5.2



5 - 10 minutes, the PET would have disappeared, to leave a turbid, viscous liquid, in which the greater part of the polymer was dissolved, while the residue was completely dispersed as swollen droplets. The mixture would be white, unless the initial sample itself was discoloured.

The stirring would be stopped, and the heating replaced by cooling by means of an air-blower; within 5 minutes, the temperature would have dropped to 170° , and the PET would reappear throughout the entire volume of the solution. The nitrogen flow was turned off, and the apparatus left for some hours to cool properly.

The details of the temperature cycle naturally varied somewhat from sample to sample. Fibre disappeared after a few minutes at 195° ; but some high molecular weight chips needed up to 15 minutes at 215° for complete dispersion. The stirring rate, also, was important; generally it was preferred to maintain it as high as possible, to discourage the chips from forming clumps, or adhering to the sides of the flask.

When thoroughly cooled, the contents of the flask were turned out into a weighed beaker. The texture of the reprecipitated polymer at this stage depended markedly on its molecular weight. Normal samples (say, \bar{M}_n about 15000) were spongy, and easily worked to a cream with chloroform. At higher molecular weights, the gel became tough, and exhibited rubber-like properties; one sample had to be pulped in a mortar and pestle before it could be processed further. At molecular weights below normal, the polymer became rather sticky, and difficult to handle and to filter; while for extensively degraded samples (\bar{M}_n perhaps 5000) the product was a fine powder.

Whatever the character of the polymer, the mixture was now stirred with chloroform (300 ml.), stood for at least an hour, and then filtered. The polymer was then returned to the beaker, and re-extracted with more chloroform; this was repeated at least until it was free from 1-methylnaphthalene (5 - 6 times) and often beyond this, until not traces of solid was left upon evaporation of the chloroform. The combined extracts were transferred to a weighed flask and rotary evaporated at 30 - 50°C to remove the chloroform as thoroughly as possible; then the 1-methylnaphthalene was evaporated at less than 5 mm., using the short-path distillation apparatus shown in Figure 5.2. During the initial stages, the removal of residual chloroform could lead to bumping, and so the heating was gentle, and the still was set up for reflux of the condensate on the probe; afterwards it was carefully rotated into the position in which it is shown. The evaporation could be taken to perfect dryness, without at any time exceeding a temperature of 50°C. Using a conventional vacuum distillation set-up, this proved quite impossible.*

The flask containing the dried extract was now reweighed, and the solid was then completely transferred to an evaporating dish, using chloroform to wash out the flask. When this solvent had evaporated, the extract, rather light and fluffy, and only just off white for a polymer not initially discoloured, was mixed to a uniform powder. The high molecular weight part was air-dried, and then put under vacuum until quite dry; then it was weighed, as a check. If it had been frequently broken up during the drying process it would be a very fine powder.

* In part, the efficiency of the evaporation depended upon the poor quality of 1-methylnaphthalene as a solvent for the cyclic oligomers of PET. M-cresol, a good solvent, could not be removed with comparable ease.

5.3 EXTRACTS FROM COMMERCIAL SAMPLES

Initial extractions of cyclic oligomers were carried out on commercial polymer samples*. The results of the g.p.c. analyses of five extracts obtained by the procedure described above are given in Table 5.1 below.

Weight % x-mer for these polymers:

x	H1	H2	H3(1)	H3(2)	H4
3	1.15	0.32	1.27	1.25	0.33
4	0.29	0.10	0.12	0.19	0.12
5	0.24	0.06	0.29	0.27	0.07
6	0.19	0.05	0.14	0.18	0.06
7	0.14	0.04	0.18	0.16	0.04
8	0.10	0.04	0.13	0.11	0.04
9	0.06	0.02	0.06	0.07	0.02
>9	0.06	0.02	0.03	0.03	0.01
TOTAL	2.24	0.66	2.22	2.27	0.73

Table 5.1

Polymers H1 and H3 had been prepared in the melt and had \bar{M}_n 15000. Although the total weight % of extractables was similar in both cases, g.p.c. analysis revealed that the extracts had rather different

* Thanks are extended to I.C.I. Fibres, Harrogate, for the provision of these samples.

distributions. That for H1 conformed more closely to expectation, with a monotonic decrease in the amounts of the rings as they grew bigger. The extracts from H3 showed anomalous distributions, with markedly less tetramer than pentamer. (Figure 5.3). For the extract (1), also, there is apparently a little less hexamer than heptamer. (Figure 5.4). Probably this is an aspect of the non-equilibrium nature of these samples, for which the relative proportions of cyclic oligomers will be determined by a variety of poorly-understood kinetic factors. The agreement between the two independent extracts is excellent, except for the tetramer, and, to a lesser extent, the hexamer; and modification of these values for first extracts ("Extracts A") by introduction of the results for the second extracts ("Extracts B"), as described in the succeeding Section, could well improve the correspondence further.

The polymers H2 and H4 had also been prepared in the melt, but had then been held for some hours at a temperature somewhat below the melting-point. There is no reason to doubt that the initial melt polymers had cyclic populations much like those for H1 and H3; yet the concentrations in the final products are dramatically lower. Interestingly, apart from the trimer and tetramer, the actual distributions resemble that at bulk equilibrium (see Chapter 6, Section 2), but with absolute amounts lower by a factor of about seven; the factors are lower for the two smaller rings. (See Figure 6.5). Remembering that PET is a highly crystalline polymer, and that the degree of crystallisation is advanced by annealing at higher temperatures, it may be supposed that the effect of tempering was the elimination of cyclics from crystalline regions, where the polymer chains are

FIGURE 5.3

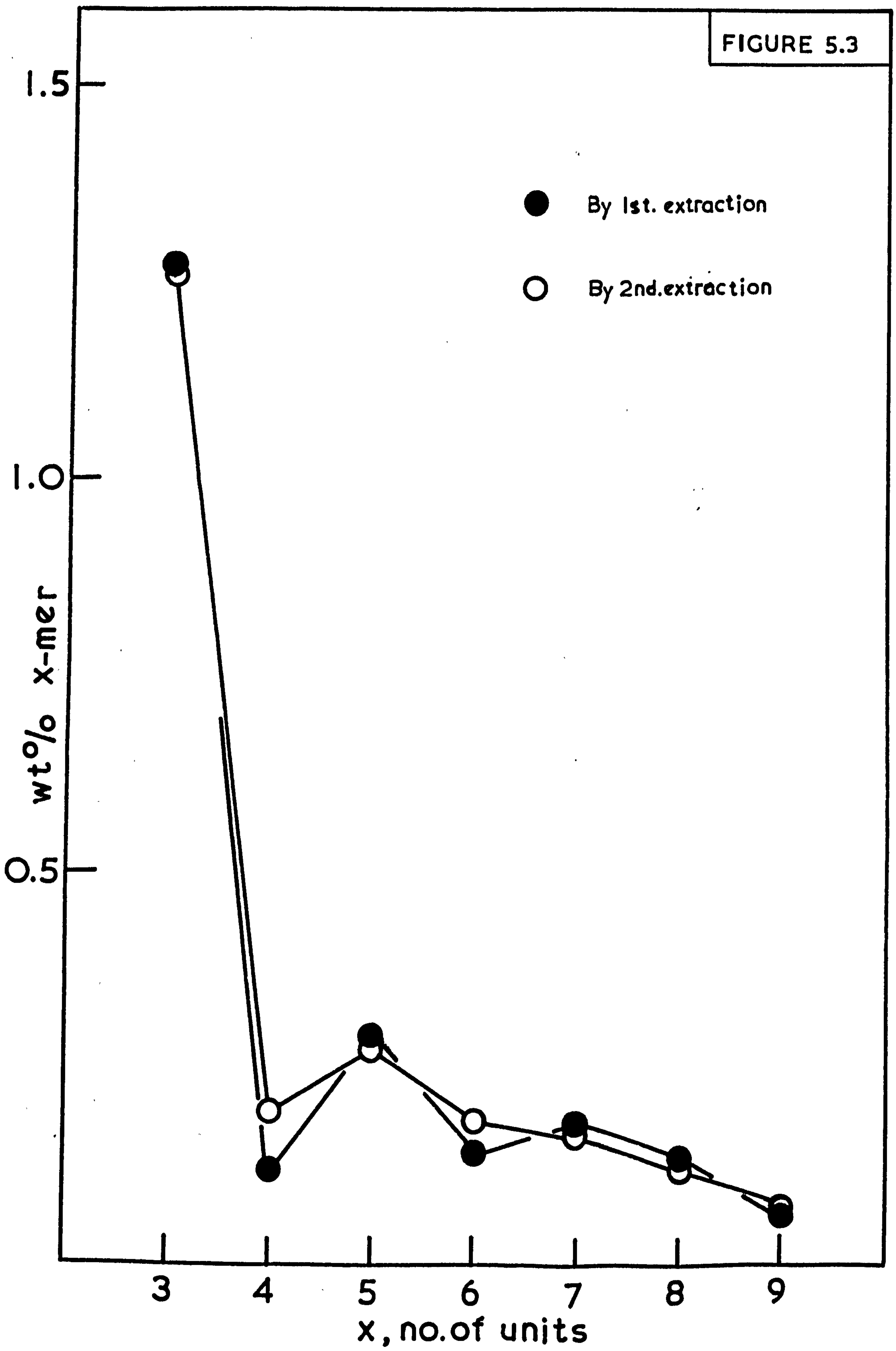
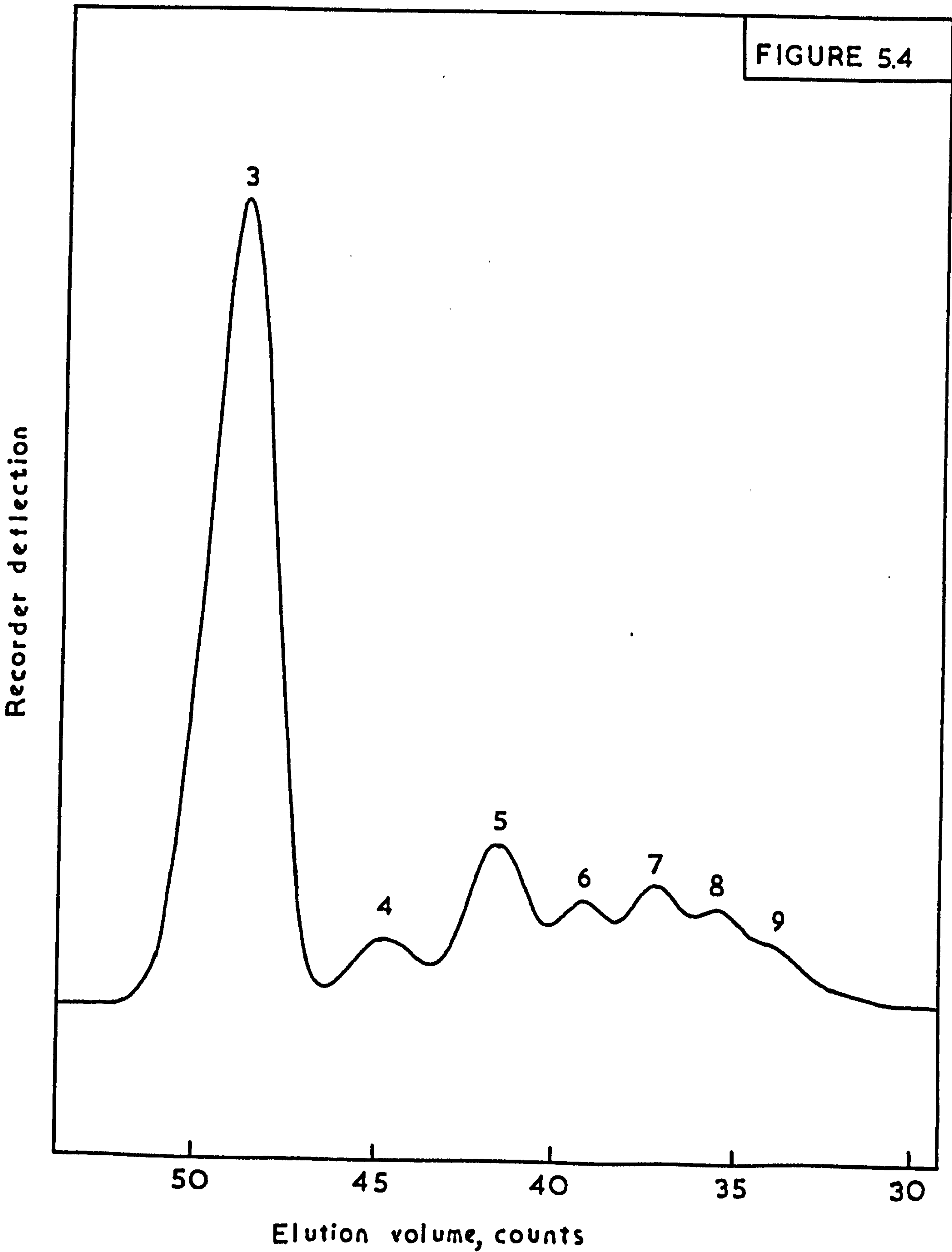


FIGURE 5.4



highly extended, and the partial attainment of a ring-chain equilibrium in the residual amorphous regions*. This could account for the observation of Goodman and Nesbitt, that extracted PET could be heated for many hours in the solid state without regeneration of cyclic species, as well as that of Peebles, Huffman and Ablett, that the cyclic content of drawn fibre was significantly lower than that of undrawn.

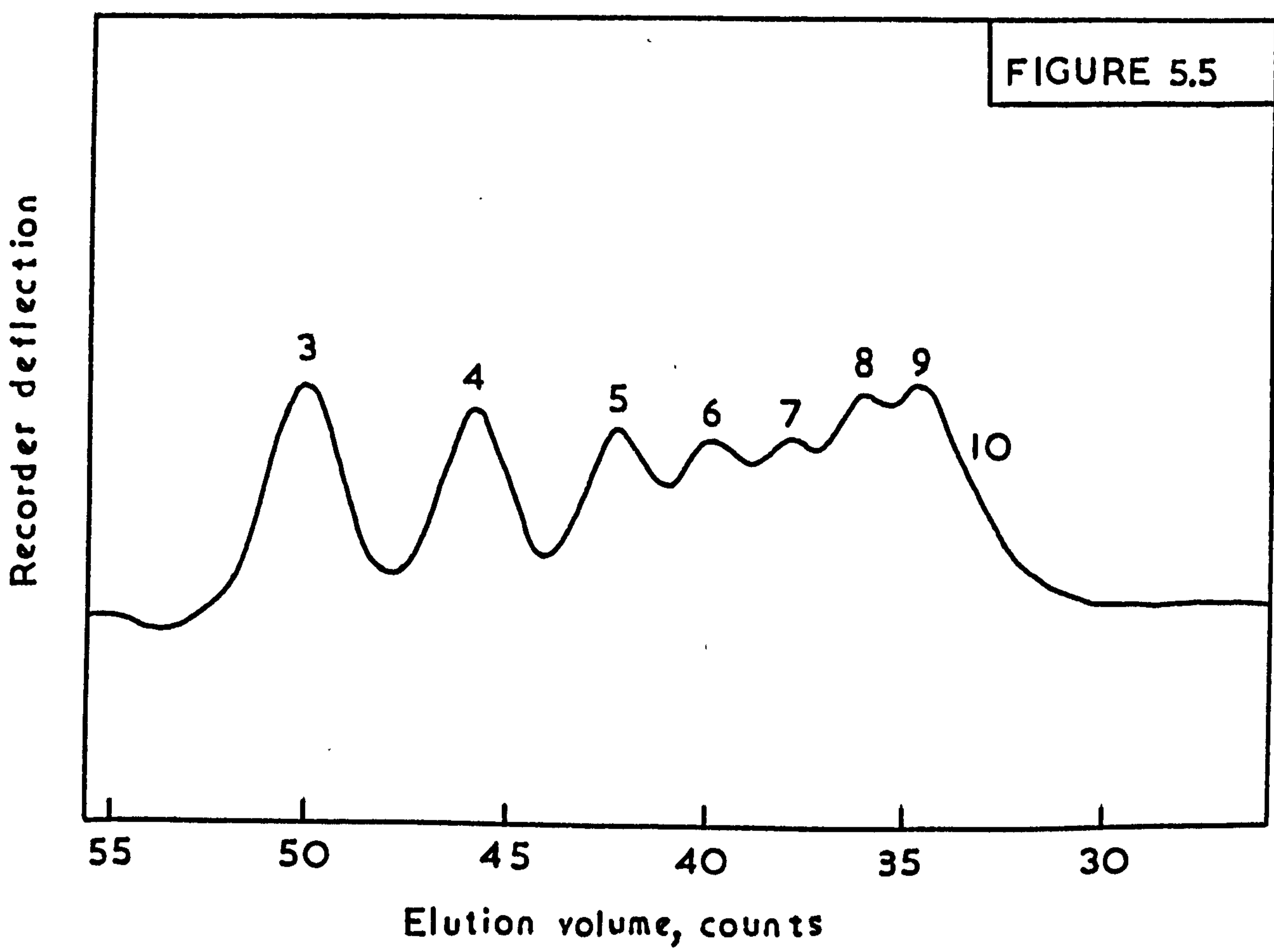
5.4 RE-EXAMINATION OF THE EXTRACTION PROCEDURE

It was essential to establish the reliability of the extraction procedure, and particularly in two important respects: firstly, how completely the cyclic oligomers were removed, and secondly, to what extent the dissolution at high temperatures had led to generation of extra cyclics by shift of the ring-chain equilibrium with dilution. In these respects, crucial information derived from subjection of extracted polymer samples to a repetition of the extraction process.

When the sample of commercial polymer H3 from the extraction (1) in the preceding Section was re-extracted, taking care to reproduce the original conditions, especially of temperature, the "Extract B" obtained comprised only 0.35% of the polymer, in comparison to 2.22% for the "Extract A". B was rather discoloured; but n.m.r. examination immediately showed the impurities to be at insignificant levels. Analysis by g.p.c. of this extract gave the tracing shown in Figure 5.5. Compared to Extract A (Figure 5.4), the distribution has shifted dramatically towards the higher rings. Qualitative examination alone

* Very similar observations have recently been made by J.M. Andrews¹⁴, in the case of polyamide - 6.

FIGURE 5.5



suggests that re-equilibration during extraction cannot have been extensive, and also that for the lower cyclics, at least, extraction had been efficient; but it is possible to proceed to put these observations upon a semi-quantitative basis, by anticipating information from the equilibrium studies described in the next Chapter.

In a situation such as that hypothesised for the extraction mixture, where rings are being generated from chains without significant back-reaction, it may be initially supposed that the distribution of species would resemble that at equilibrium, except insofar as the relative amount of each ring would be increased in proportion to its symmetry number. (Chapter 1). The assumption in this scheme is that the intrinsic susceptibility of each repeat unit to reaction back from ring to chain does not vary with ring size. In the limit of large rings, this assumption holds, and, Gaussian chain statistics being applicable, there would be approach to the prediction of Kuhn³⁰, that the mole fraction of any x-meric ring will decrease according to $x^{-\frac{3}{2}}$. The weight fraction of each cyclic in this "kinetic" distribution may be found by multiplying the corresponding equilibrium fraction by x and then normalising the new distribution.

This being done, the equilibrium values in the second column of Table 5.2 are replaced by the non-equilibrium values in the sixth. It will be noticed that the proportions of higher cyclics have been increased at the expense of the lower, the "fulcrum" of this movement lying between the tetramer and pentamer. The data displayed in the intervening columns are for experimental samples whose distributions cover the range between the two theoretical extremes. The column headed I is for an extract from the polymer H3, taken at an early

stage, when less regard was paid to the possibility of re-equilibration. That marked II is for the melt PET(XII), that will figure in the next Chapter as a partially equilibrated sample. The column III is for PET(X), an intermediate in the process of equilibration in dilute solution. Broadly, these experimental data support the reasoning underlying the predicted kinetic distribution. This latter is expressed as amounts relative to trimer in the last column of Table 5.2.

Weight fraction of x-meric cyclics?						
x	Equil ^m .	I	II	III	Kinetic	Kinetic
3	0.416	0.404	0.371	0.322	0.290	1
4	0.174	0.157	0.150	0.144	0.162	0.56
5	0.102	0.110	0.126	0.149	0.118	0.41
6	0.089	0.099	0.121	0.124	0.124	0.43
7	0.073	0.083	0.087	0.105	0.119	0.41
8	0.056	0.066	0.077	0.074	0.104	0.36
9	0.040	0.075	0.048	0.044	0.084	0.29

Table 5.2

The maximum extent of re-equilibration during extraction can now be calculated by assuming that all the trimer in the second extract has been generated, and using these factors to find the amounts of the higher cyclics that would be produced concomitantly. The results for the extract B from polymer H3, discussed above, are shown in Table 5.3. Subtraction of the maximum amount generated leaves for each ring the minimum amount genuinely extracted in B, which must be at once added to that found in A.

x	Wt. % in. A	Wt. % in. B	Max. % ngen'd	Min. % extr'd	Total %	Error, %
3	1.27	0.057	0.057	-	1.27	0.06
4	0.12	0.063	0.032	0.031	0.15	0.03
5	0.29	0.049	0.023	0.026	0.32	0.02
6	0.14	0.040	0.024	0.016	0.16	0.02
7	0.18	0.036	0.023	0.013	0.19	0.02
8	0.13	0.040	0.021	0.019	0.15	0.02
9	0.06	0.023	0.017	0.004	0.07	0.02

Table 5.3

It will be apparent that the maximum amount generated in the second extraction represents part of the uncertainty in the total weight percentage of each ring. At one extreme, the full calculated quantity was indeed generated; in which case it was also generated in the first extraction, and should be subtracted from the total. At the other extreme, no rings at all were generated, in either extraction: the calculated amount should be added to the total. Accordingly, in the last column of Table 5.3, the weight percentages predicted as the maximum possibly generated are treated as errors in the total percentages.

The errors are not great, even for the largest rings, although this was a typical, rather than unusually favourable, case: in another instance, the Extract B was so small, and weighted so heavily in favour of the higher cyclics, that it made negligible contributions to the concentrations, below that of octamer.

The quantitative treatment, of course, is fairly crude. Probably it will over-estimate the degree of re-equilibration, since the powdered polymer from the first extraction dissolves more rapidly during the second, and so spends longer actually in solution. Again, the principles upon which the "kinetic" distribution has been derived undoubtedly present an over-simplified picture. Use of the equilibrium distribution instead gives much the same results; but regard has been paid to the absence of a back-reaction for the sake of rigour in the argument.

It is appropriate to now attempt to assess the magnitude of the errors accumulated during extraction and analysis. The random errors associated with extraction, and with division of the area of the g.p.c. tracing, combine to an uncertainty of rather less than 10% for the trimer, rising to about double that for the nonamer. (Provided the latter has been fully extracted). The further, systematic, unreliability of the response factors means that the greatest precision with which concentrations could ever be determined would be perhaps 15% for trimer, 25% for nonamer. But, further, it might be necessary in some cases to take into account possible contamination of the extract with extraneous material, especially linear oligomers. The error from this source falls most heavily upon the higher cyclics, poorly resolved and themselves representing only a small part of the extract. The relative uncertainty for a ring such as octamer could well exceed 50% in these circumstances.

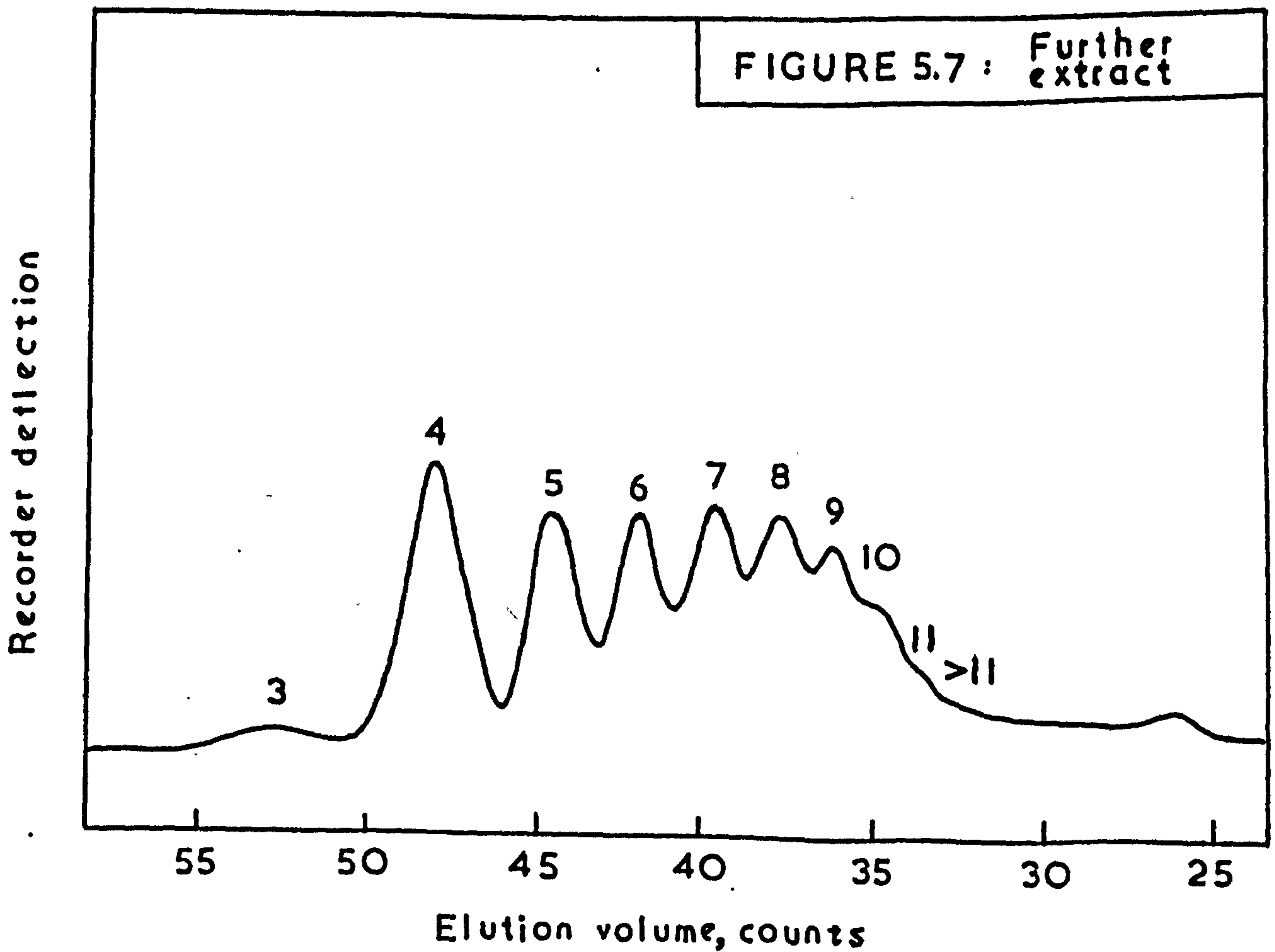
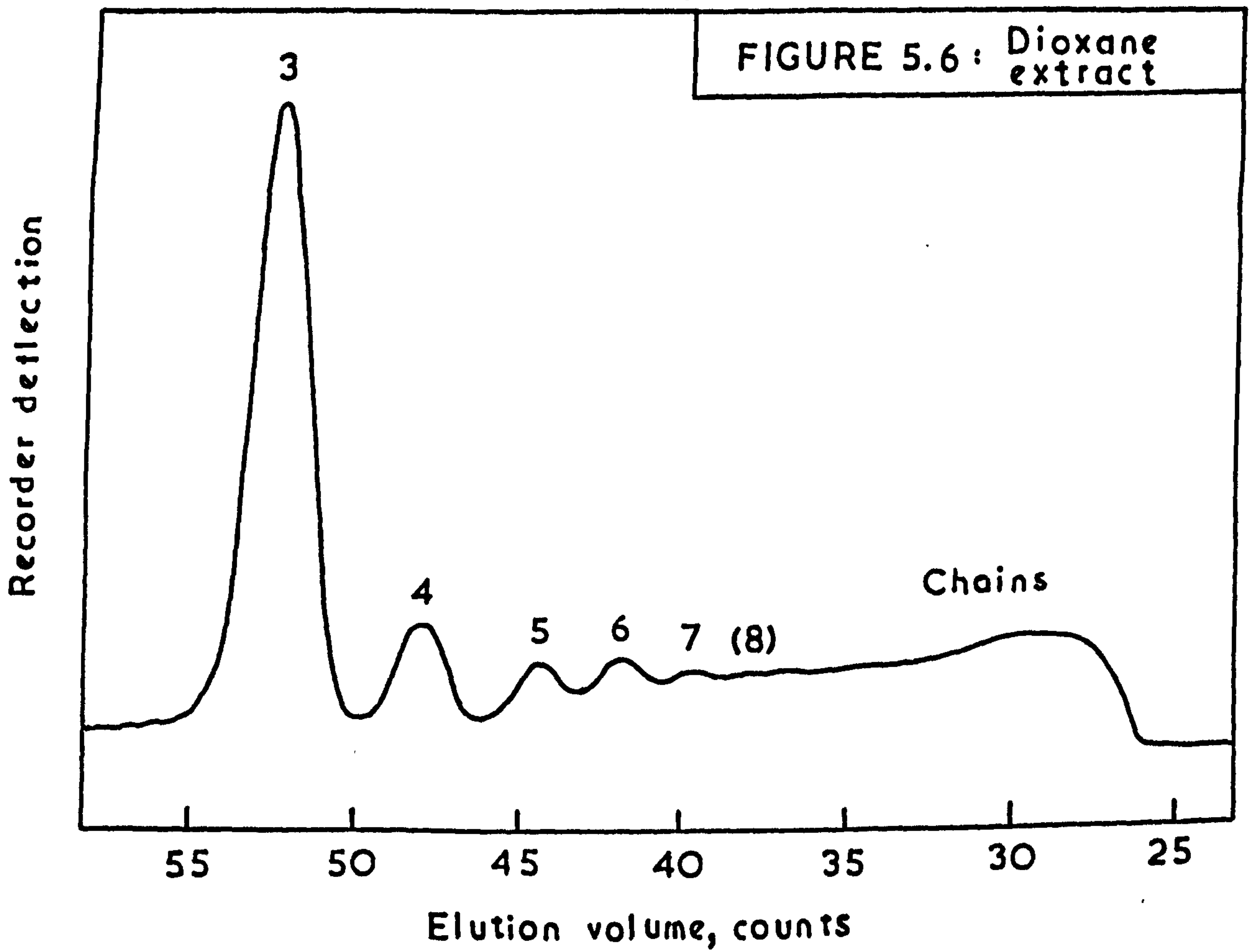
5.5 COMPARISON OF EXTRACTION METHODS

The concentrations found for the cyclics above tetramer in the melt polymerised samples H1 and H3 are much higher than the typical values cited by Goodman and Nesbitt (Section 5.1). For the polymer H1, the proportion of tetramer, also, is about three times the literature value. Without doubt, in part these discrepancies arose from limitations in the methods available to the earlier workers for the analysis of the extracts; however, it was also possible to demonstrate by direct comparison that the dioxane extraction method is not efficient for the higher cyclics.

In a qualitative demonstration, fibre which had previously been exhaustively extracted with dioxane*, to give rather less than 2% soluble material, was re-extracted by the new method. It was possible to obtain a further 0.61 (± 0.15)%. The dioxane extract was imperfectly soluble, even in hot sym-tetrachloroethane. The part that dissolved in a little of this solvent, warm, and was not re-precipitated by dilution with chloroform, gave the g.p.c. tracing in Figure 5.6; by which it was shown to be about half cyclic trimer, less than a quarter higher rings, and for the rest, material of higher molecular weight. (Chains, of molecular weight up to several thousand). The further extract, which was more soluble, gave the tracing in Figure 5.7. It contained very little trimer, but the usual range of higher rings; there was only a trace of high molecular weight chain.

Not only can it be concluded from these results that the dioxane extraction was incomplete, but also that during it, the extract had been

* Thanks are due to Dr.K. Robinson, of the Research Department, I.C.I. Fibres, Harrogate, for carrying out the dioxane extractions.



spoiled. Clearly, the chain part had not truly been extracted from the fibre, since species of much lower molecular weight had been imperfectly removed; it could only have derived from polymerisation of cyclics in the reflux vessel of the extraction apparatus. It is also noteworthy, in this context, that the extracts of Huffman, Peebles and Ablett²³, obtained using rather more severe conditions, contained up to 50% of components that were insoluble, and remained at the origin in thin layer chromatography.

In making a quantitative comparison, the following course was taken: part of a batch of PET fibre was first extracted with dioxane, and then re-extracted, as above, while another part was extracted directly according to the new procedure. Ideally, the last extract should represent the sum of the first two. How close a correspondence was found may be seen from Table 5.4. (In which the amounts of rings are given as weight percentages of the fibre).

x	Dioxane extract	Further extract	SUM	Direct extract
3	1.29	0.05	1.34	1.11
4	0.07	0.26	0.33	0.36
5	0.05	0.12	0.17	0.20
6	0.02	0.11	0.13	0.16
7	-	0.11	0.11	0.14
8	-	0.10	0.10	0.10
9	-	0.08	0.08	0.09
>9	-	0.15	0.15	0.14
TOTAL	1.46	1.00	2.46	2.33

Table 5.4

The agreement is good; even for the trimer values the discrepancy is hardly greater than the error estimated in Section 5.4. In fact, the uncertainty associated with the sum for the trimer is somewhat larger than this since it was necessary to apply a correction for heavy contamination of the dioxane extract with additives to the fibre*. In this instance, the dioxane extract was soluble, and did not contain detectable levels of chain species, perhaps because the duration of the extraction was rather shorter than before. (About ten hours).

In summary, the evidence presented in this Section fully supports that in the last, that the newly devised method of extraction is efficient and accurate. It also makes clear the inapplicability of the standard techniques of extraction with volatile solvent to the determination of the concentrations of the higher cyclics, adequate though such methods may be for study of the trimer content.

* The cyclic oligomers were purified by precipitation from chloroform with diethyl ether; the precipitate represented 44% of the extract. N.m.r. estimation of the small amounts of cyclics left in solution with the additives enabled this to be corrected to 47(\pm 5)% of the extract; that is, 1.46(\pm 0.25)% of the fibre. N.m.r. estimation for the original extract gave 50 (\pm 10)%.

CHAPTER 6.

EQUILIBRIUM CYCLIC CONCENTRATIONS IN
POLY(ETHYLENE TEREPHTHALATE).

6.1 INTRODUCTION

An important aspect of the studies of Goodman and Nesbitt²¹ was their demonstration of the interconvertibility of the cyclic ethylene terephthalates and the polymer. Heating the cyclic trimer, tetramer or pentamer to 275° - 310°C with catalysts brought about their conversion to poly(ethylene terephthalate); the trimer also partially reverted to polymer when boiled with a catalyst in 2-methylnaphthalene. Equally, melting exhaustively extracted PET lead to regeneration of the cyclics. Heating in the solid state, however, did not have this effect.

Peebles, Huffman and Ablett²³ carried out some similar experiments, designed to establish the precise mechanism whereby the rings are regenerated. The rate of their reappearance upon brief melting of extracted chip seemed to decrease with increase in the molecular weight of the polymer, suggesting that they formed by attack of active end-groups upon units further down the chain, rather than by the elimination of central units following on ester interchange reactions within, or between, chains.

From these observations it is clear that the origin of the cyclic oligomers in PET lies in a reversible interchange with the polymer, and that, under the correct conditions, it should be possible to establish ring-chain equilibria within PET systems. Experimental difficulties

were encountered, however, in actually doing so. In essence, the rate of cyclic generation was not high enough in comparison to the rate of degradation at the temperatures involved. The instability of the most efficient catalyst to prolonged heating further slowed the approach to equilibrium. On the other hand, equilibration was simplified by the ready availability in the polymer H2, described in Section 5.3, of a starting material of both high molecular weight, and low initial cyclic content.

6.2 EQUILIBRATION IN THE MELT AT 270°C.

To prepare equilibrates, PET H2, mixed with about 0.5% by weight antimony trioxide, was sealed in ampoules under less than 5 mm., and heated for periods of 1, 12, 24 and 36 hours at temperatures in the range 270° - 275°C. At the lower end of the temperature range, the chips were soft and glistening, but were rather slow to coalesce; at the upper end, coalescence was quite rapid. The samples steadily became discoloured; for the three heated longest, a dark stain (antimony) developed at the bottom of the ampoule.

After the prescribed periods, the ampoules were removed from the heater, wrapped in cloths, and left to cool. They were then first opened at the top, to admit air, and afterwards broken altogether, to release the mass of PET. The polymer was off white, or brownish, in colour, depending upon the duration of heating; for the darker samples there was a slight acrid smell. Other than for the 1 hour run, the polymer was rather brittle, and the mass could be broken up in a mortar and pestle, and then parts taken and crushed further.

A portion of each equilibrate was extracted, according to the procedure detailed in the last Chapter, and the extracts analysed by g.p.c., as described in Section 4.3. For the 1, 12 and 36 hour runs (designated respectively PET(XII), PET(XIV) and PET(XV)) both extracts A and extracts B were taken, to give the results tabulated below, and also plotted in Figure 6.1. For completeness, the data for the starting material H2 are also given.

Weight percentages of x-meric cyclic:

x	H2, starting material	PET(XII) (Heated 1 hr.)	PET(XIV) (Heated 12 hrs)	PET(XV) (Heated 36 hrs)
3	0.32	0.74	1.39	1.32
4	0.10	0.31	0.57	0.56
5	0.06	0.26	0.34	0.38
6	0.05	0.25	0.29	0.32
7	0.04	0.18	0.22	0.26
8	0.04	0.17	0.19	0.22
9	0.02	0.12	0.11	0.16

Table 6.1

Figure 6.2 illustrates the effect of the contributions from extract B, for the case of PET(XV).

For the 24 hour run (designated PET(XVII)) and extract A, only, was taken. Analysis gave results lying intermediate to those for the extracts A from PET(XIV) and PET (XV):

FIGURE 6.1

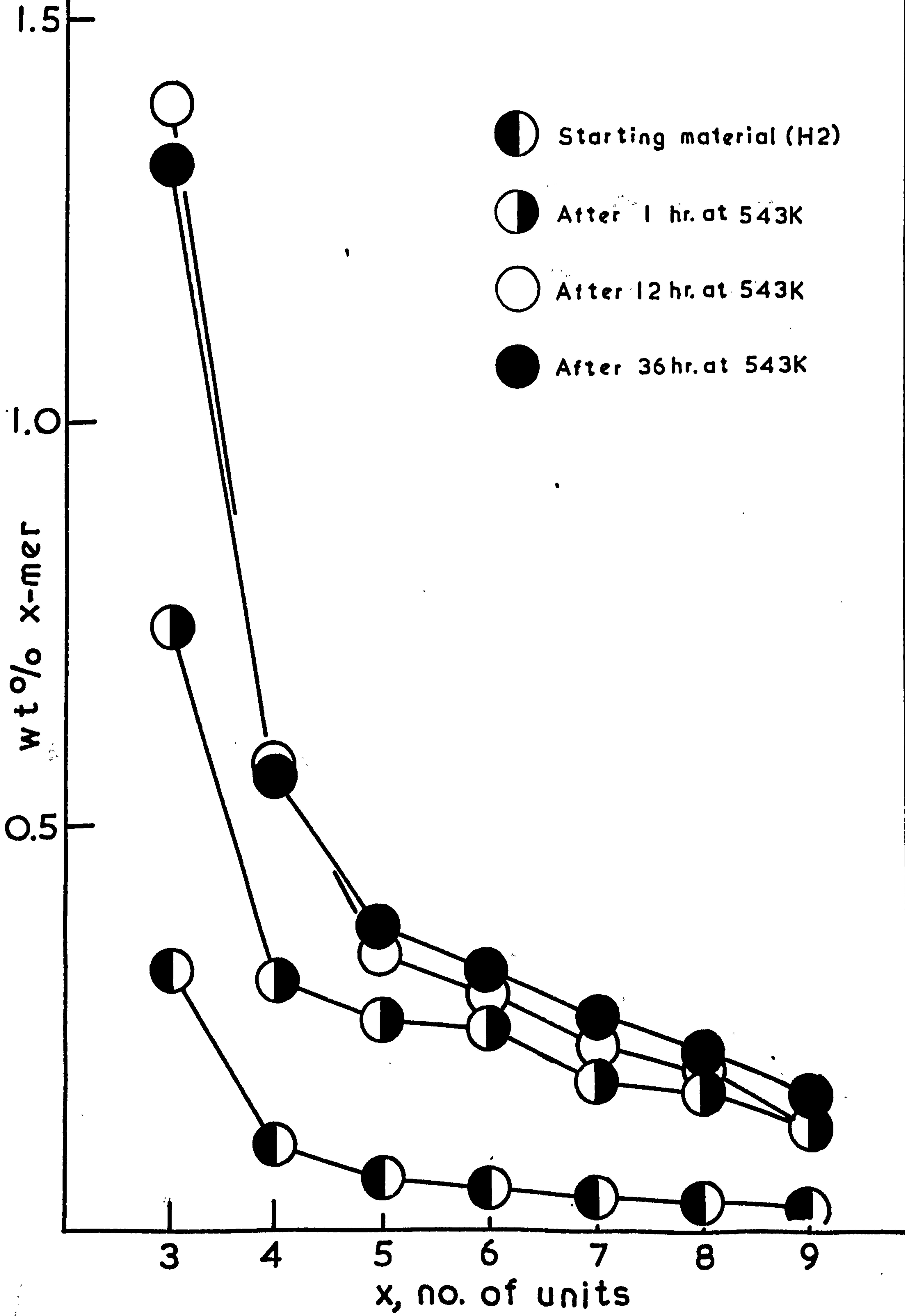
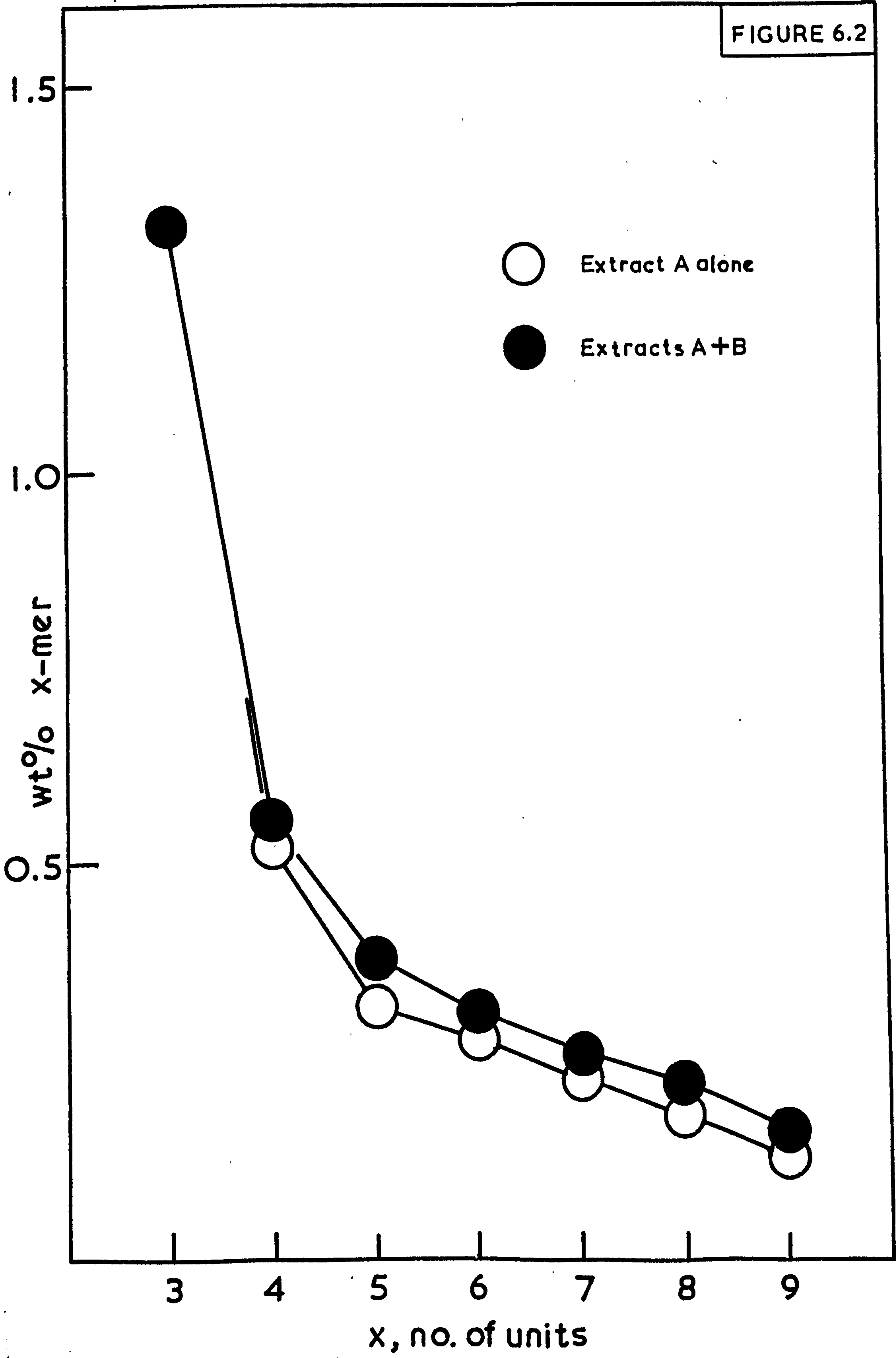


FIGURE 6.2



Weight %'s of x-mer, from A.

x	PET(XIV) (Heated 12 hrs)	PET(XVII) (Heated 24 hrs)	PET(XV) (Heated 36 hrs)
3	1.39	1.33	1.32
4	0.53	0.51	0.52
5	0.27	0.29	0.32
6	0.23	0.24	0.28
7	0.18	0.20	0.23
8	0.13	0.15	0.18
9	0.07	0.11	0.13

Table 6.2

The differences between the values for the three runs do not exceed the minimum experimental errors cited in the previous Chapter (Section 5.4), even taking into account that the unreliability of the response factors has no relevance to the comparison. However, the uncertainties in some of the ring concentrations may be regarded as greater than would be optimal, since the evidence of infra-red spectroscopy suggested that there could be significant amounts of linear species in the extracts. (The spectrum of the extract A from PET(XV) has been discussed in Section 4.2). The small discrepancies between the runs are less consistent with continued equilibration than with the appearance of small quantities of chain in the extracts; for they occur not with the lower, but with the higher, cyclics, which should come to equilibrium more rapidly (see Section 5.4), and which are more susceptible to the analytical errors arising from contamination

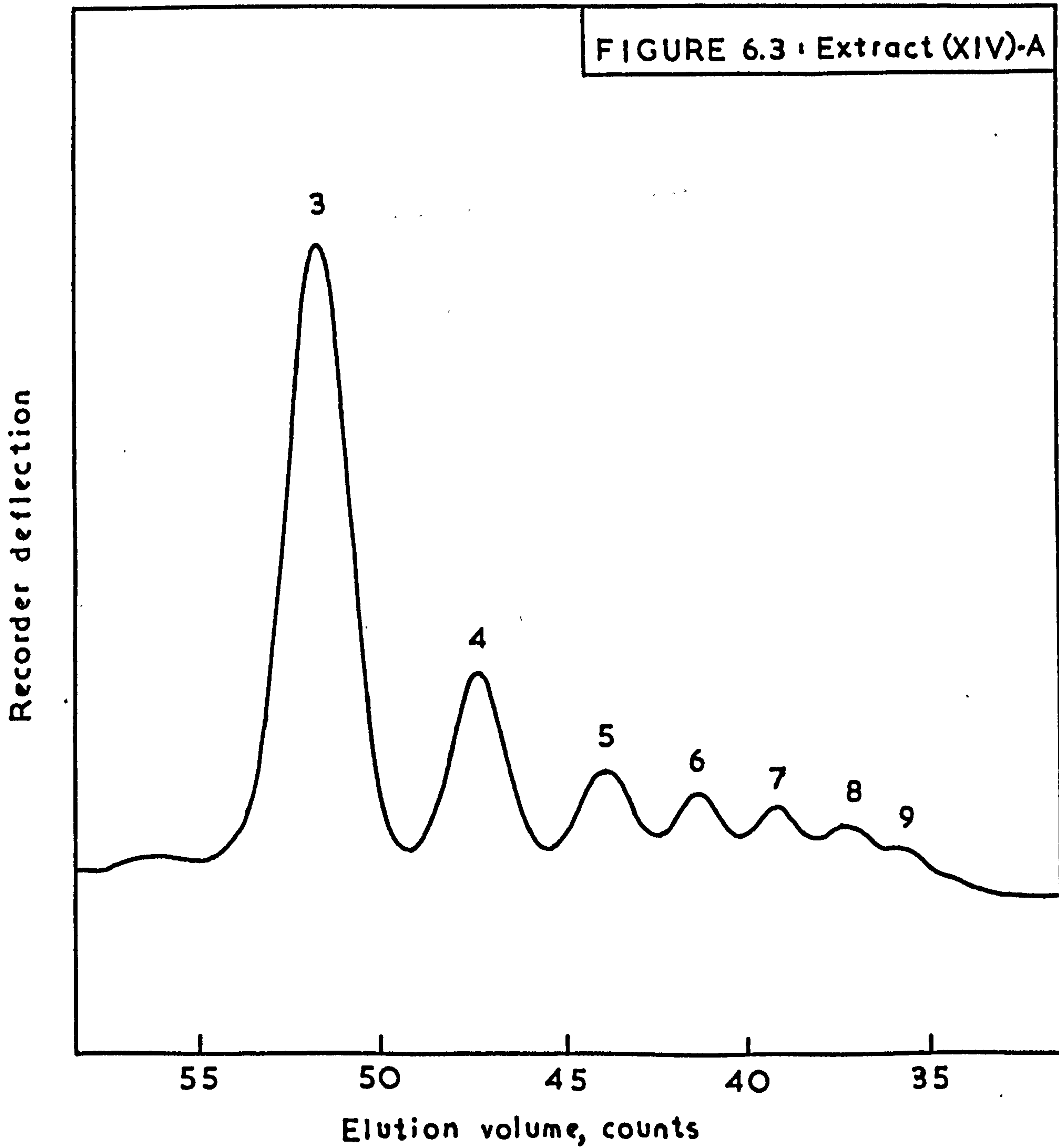
with linear species. In the g.p.c. the resolution was about normal for the extract from (XIV), (Figure 6.3) perhaps a little poorer for that from (XV) (Figure 6.4): although the least squares fit (Chapter 4) to the latter tracing is quite adequate, which would not be the case for an extract containing substantial amounts of chains. But even if the differences between the runs were entirely due to increase in the levels of chains, it would not imply that the extract from PET(XIV) was significantly contaminated: rather, the reverse. For these small increases resulted from heating for a further 24 hours polymer, that was already partially degraded; whereas in the preparation of PET(XIV), the heating was for only 12 hours, and the polymer was initially of high molecular weight.

Hence, while these findings, taken altogether, are, of course, in full accord with the expectation of a progressive rise in the cyclic concentrations from the very low initial levels to those of ring-chain equilibrium, it may not be wise to give preference to any particular one of the last three runs.

These results must now be expressed as moles/dm³, making use of a value for the melt density of 1.22 kg./dm³, and the factors p^x introduced to convert molarities to molar cyclisation equilibrium constants, K_x . (Chapter 1.)

For the starting material, H₂, and the intermediate sample PET(XII), Flory's fractional extent of reaction, p , was taken as unity. For the other equilibrates it was calculated from the equation : $p = (1 - \frac{1}{\bar{x}_n})$, where \bar{x}_n was the (number) average number of ethylene terephthalate units for the chains in the equilibrate. This definition of \bar{x}_n , and so of p , represents a departure from the more

FIGURE 6.3 · Extract (XIV)-A



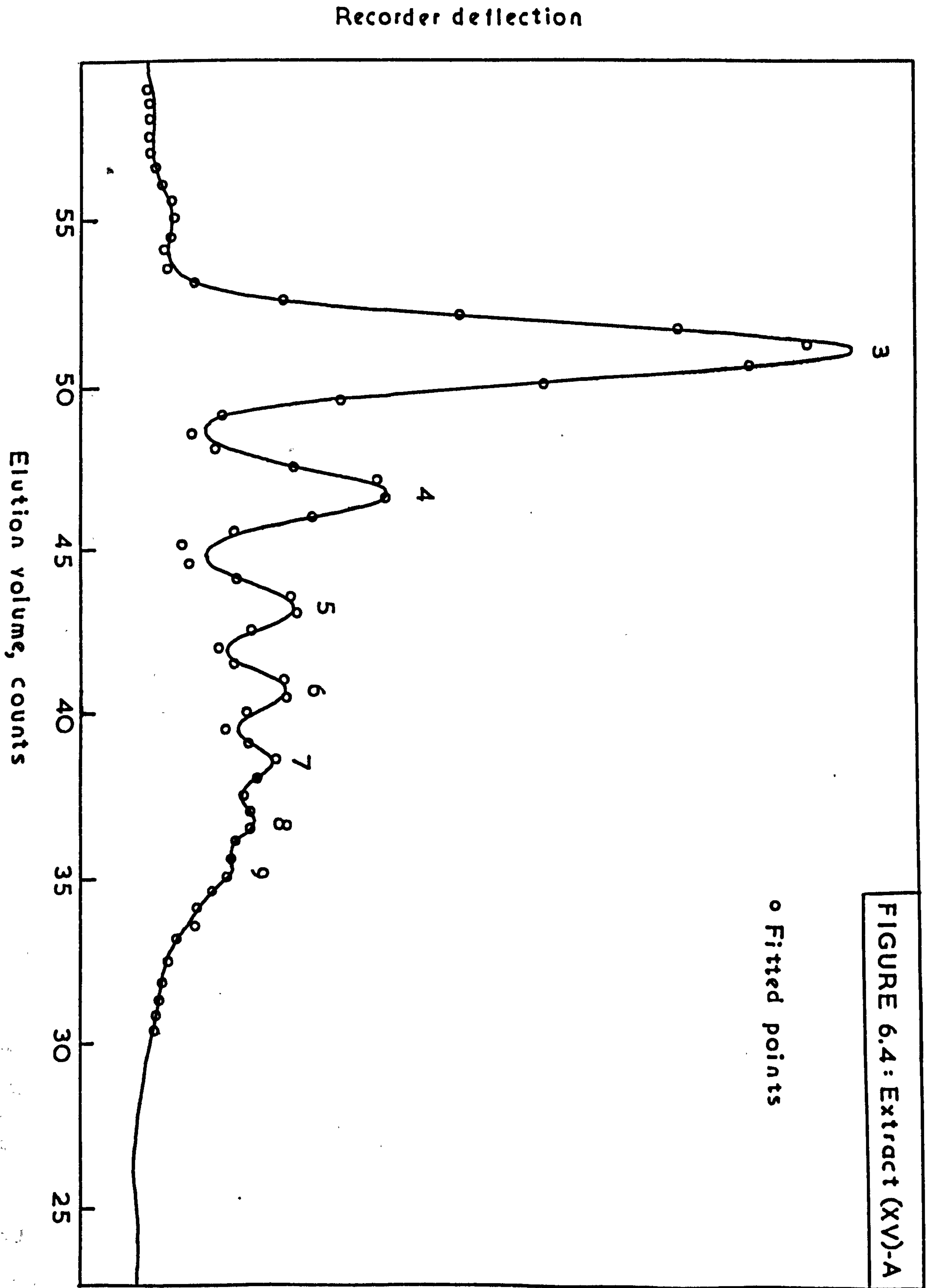


FIGURE 6.4: Extract (XV)-A

exact formalism of Flory³² for type ii polycondensations, whereby \bar{x}_n would be the average number of units of both kinds (viz., acid, and glycol, residues) in the chains. However, the present usage is consistent with the employment of a factor p^x , x being the number of repeat units in the ring; and it may be shown, in any case, that in this context the two schemes are effectively equivalent.

The required values of \bar{x}_n were calculated from number average molecular weights, determined by g.p.c. in m-cresol at 105°C., and by viscometry in o-chlorophenol*. In the former case, reliance was placed upon a g.p.c. calibration based on studies of PET samples with distributions found by other means; in the latter, use was made of the relations of Ward⁷⁸, and of Ravens and Ward⁷⁹, connecting the number average molecular weight of a PET sample with its intrinsic viscosity in o-chlorophenol at 25°C:

$$\text{The relation of Ward: } [\eta] = 1.7 \times 10^{-4} \bar{M}_n^{0.83}$$

$$\text{The relation of Ravens and Ward: } [\eta] = 3.0 \times 10^{-4} \bar{M}_n^{0.77}$$

The two equations give results only very slightly different. Derived initially for commercial melt polymers, they were found to hold equally well for the same samples after partial hydrolysis; it is assumed here that the samples under discussion had distributions of chain lengths sufficiently similar to those of the original polymers to render the equations applicable. Further, it is necessary to assume that the relations hold equally for those of the present samples that fall rather below the range of molecular weight over which the equations were established.

* Thanks are due to members of the Research Department at I.C.I. Fibres for carrying out these determinations.

The data for the three equilibrates are tabulated below. The viscometry result presented was evaluated using the second of the equations.

Equilibrate	\bar{M}_n by g.p.c.	\bar{M}_n by viscometry	x	p
PET(XIV)	7980	7200	40	0.975
PET(XV)	4650		25	0.960
PET(XVII)	3765		20	0.950

Table 6.3

The equilibrated polymers as such were insufficiently soluble for the molecular weight determinations to be made directly on them. Instead, the measurements were made on the chain fractions from the extracted portions. This was disadvantageous, since undoubtedly the extraction process would bring about some further degradation. It is most improbable that the molecular weights of the chains actually in the equilibrates were as low as the values listed, not least because, assuming that Flory's most probable distribution of chain lengths³² holds, the calculated concentrations of linear oligomers are so high that they would utterly swamp the cyclic species. (For $p=0.95$, approximately 10% of the sample will be chains smaller than decamer; for $p=0.98$, approximately 2%; for $p=0.99$, 0.5%). Nevertheless, for the purposes of calculation, the experimental values of p will be adopted: the magnitude of the possible error involved will be discussed presently.

The concentrations of the rings in the starting polymer H2 and the three melt equilibrates, previously given as weight percentages in Table 6.1, are expressed in terms of (molarity/ p^x) in Table 6.4. The same data are plotted logarithmically in Figure 6.5.

(Molarity of x-mer / p^x) $\times 10^2$ for:

x	H2, starting material	PET(XII) (Heated 1hr.)	PET(XIV) (Heated 12 hrs)	PET(XV) (Heated 36 hrs)
3	0.68	1.57	3.17	3.16
4	0.16	0.49	1.00	1.05
5	0.07	0.33	0.49	0.59
6	0.06	0.26	0.36	0.43
7	0.04	0.16	0.24	0.31
8	0.03	0.14	0.19	0.24
9	0.02	0.08	0.10	0.16

Table 6.4

The agreement between the values in the last two columns is excellent for trimer and tetramer; and even beyond these the discrepancies are still quite within the minimum error limits. The additional uncertainty in these results from the introduction of the factor p^x varies with the magnitude of the correction. For PET(XV), the effect of this term is to raise the values by about 12% for trimer, 36% for nonamer. (See Figure 6.6). Modification of the figure for p to 0.98 (a doubling in molecular weight) leads instead to corrections of 6% and 18%. Hence, the error brought in with the function p^x is most unlikely to be greater than 10% for $x=3$, 20% for $x=9$. Bearing in mind the possible presence of small proportions of chain molecules in the extracts, the reliability of the results found from any single run cannot be better than about 20% for trimer, 40% for nonamer.

FIGURE 6.5

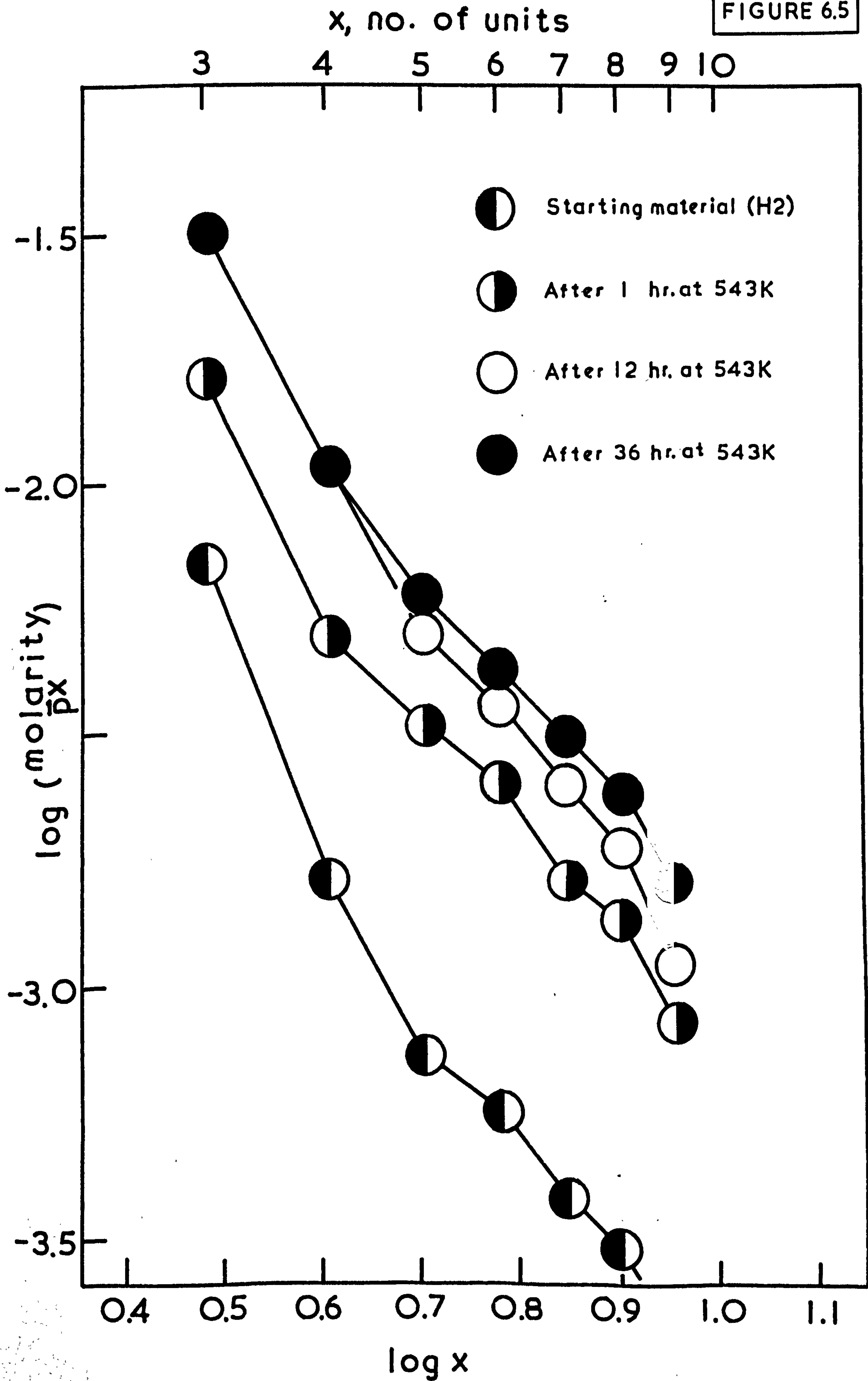
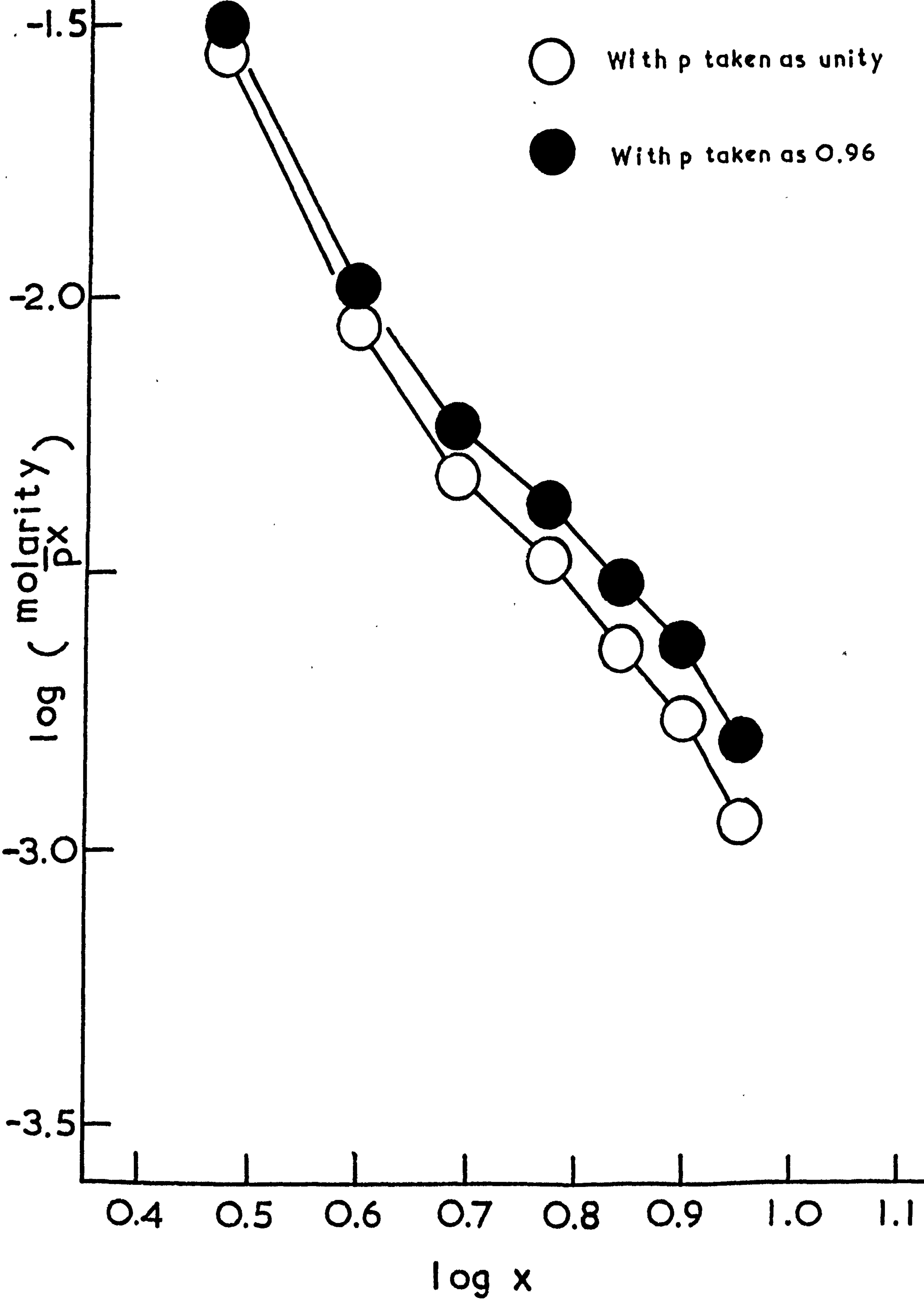


FIGURE 6.6

x, no. of units

3 4 5 6 7 8 9 10



Since it was not possible to definitely attribute the entire differences between the three runs PET(XIV), PET(XV) and PET(XVII) to continued equilibration, rather than to slight contamination with linear species, it will be taken that the equilibrium constants, K_x , are best represented by averages over the first two of these runs. The accepted values, and also the corresponding weight percentages of ring, calculated for a high molecular weight polymer ($p=1$), are given in the final Table 6.5.

x	Molar cyclisation equil ⁿ constants, K_x (Moles/dm ³ , x10 ²)	Equilibrium weight percentages, p = 1
3	3.17	1.50
4	1.03	0.65
5	0.54	0.42
6	0.40	0.38
7	0.28	0.31
8	0.21	0.26
9	0.13	0.18

Table 6.5

The concordance between the two complete sets of results, supported by those from PET(XVII), permits the conclusion that it is improbable that the errors in the final average molar cyclisation equilibrium constants exceed 15% for trimer, rising to 40% for the nonamer.

6.3 EQUILIBRATION IN THE MELT AT 300°C

Initially, the temperature selected for the equilibration of PET was 300°C. The degradation suffered by the polymer at such a high temperature, however, was so severe that, as already described, the main series of experiments was conducted instead at 270°C. The results to be presented here, therefore, are to be regarded as no more than ancillary to those of the previous Section.

Two equilibrates were prepared, in the manner described earlier. The first (PET(VII)) was heated for 7 hours, the second (PET(XVI)) for 15 hours, at 300(+5)°C. The resultant polymer masses, browned, malodorous, and brittle, were broken up and subjected to extraction according to the normal procedure.

For PET(VII), a badly discoloured extract A, comprising 3.6% of the PET, was obtained. In infra-red spectroscopy, it gave carboxyl absorptions more intense than those for the extract from PET(XV). (Figures 4.15 and 4.13, respectively). In g.p.c. the resolution was perceptibly poorer than was normal at that time. Analysis by g.p.c., assuming the sample completely free from linear contaminants, gave the weight percentages of rings in the second column of Table 6.6. To convert these results to those in the third column, they were expressed as molarities, again assuming a melt density of 1.22 kgm./dm³, and corrected for p^x , where p was found from g.p.c. to be 0.943. ($\bar{M}_n = 3380$ for the chain fraction). The accepted equilibrium constants for the bulk at 270° are listed alongside; the comparison is also made in Figure 6.7.

x	Weight %'s of x-meric rings after 7 hrs at 300°	(Molarity/p ^x) at 300° C., x 10 ²	Accepted K _x 's at 270° C., x 10 ²
3	1.24	3.14	3.17
4	0.59	1.19	1.03
5	0.40	0.68	0.54
6	0.37	0.55	0.40
7	0.27	0.36	0.28
8	0.21	0.27	0.21
9	0.15	0.19	0.13

Table 6.6

While the correspondence is excellent for the trimer, and good for the tetramer, the values for the higher rings show systematic discrepancies. Without doubt, the results for these species in the case of the 300° C equilibrate are spuriously high, simply because no account has been taken of the presence of chains in the extract. Nevertheless, the divergences do not exceed the error limits estimated at the end of the last Section.

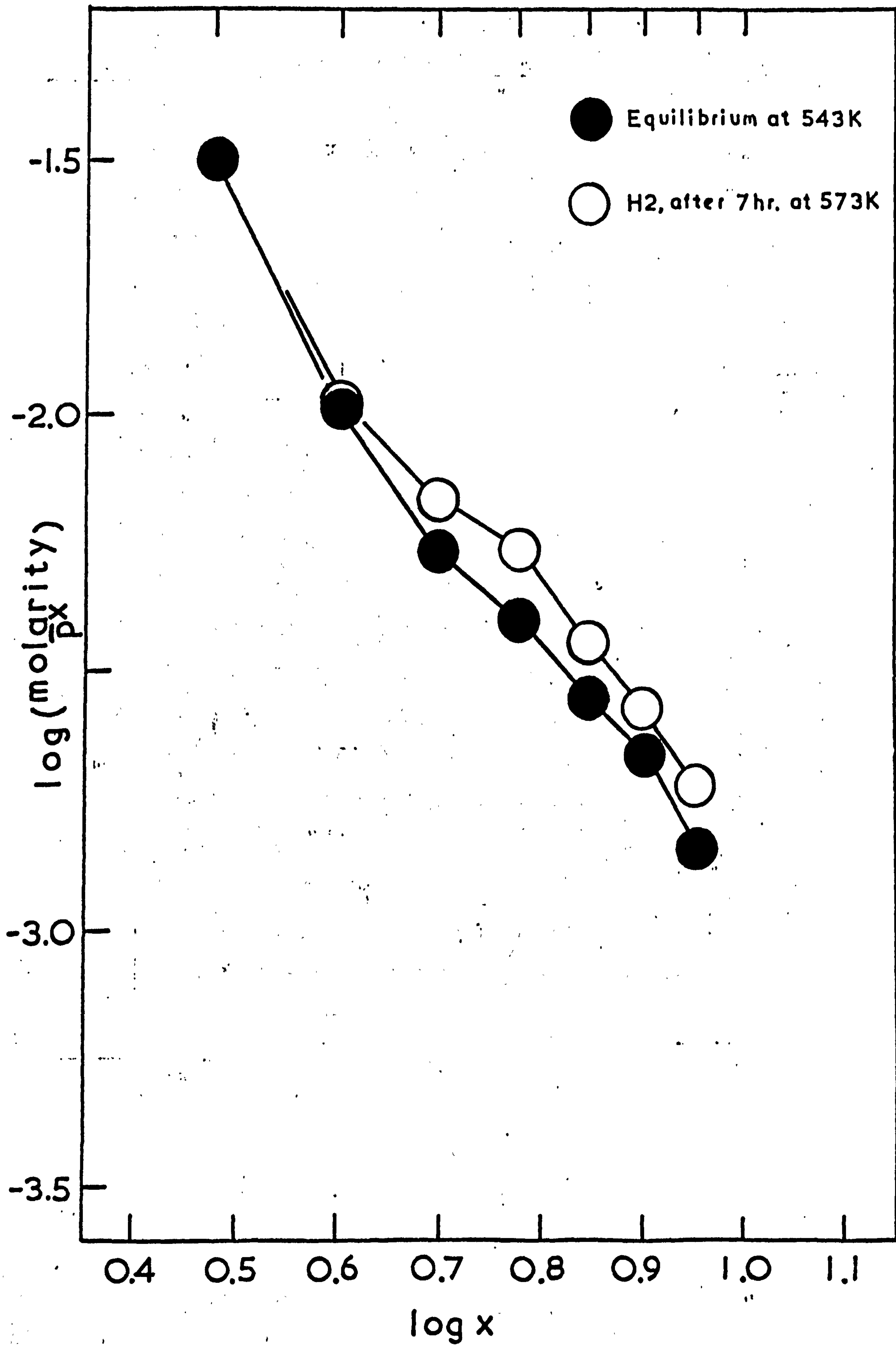
No reliable results were obtained from PET(XVI). Several extracts were taken; their weights varied erratically (3.8 - 8.1%). For all the extracts, the carboxyl absorptions in infra-red spectroscopy were intense (Figure 4.14), and the peaks in g.p.c. were much less well-resolved than usual (Figure 4.20). The polymer was clearly badly degraded, and the extracts heavily contaminated with chain species. It is possible that the irreproducibility in the extract weights resulted from local variations in the concentrations within the melt of substances, catalytic for the degradative processes.

FIGURE 6.7

x, no. of units

3 4 5 6 7 8 9 10

● Equilibrium at 543K
○ H2, after 7hr. at 573K



6.4 EQUILIBRATION IN SOLUTION AT 250°C.

The difficulties encountered in attempting to establish a ring-chain equilibrium in solutions of PET were even greater than those for the case of the melt. The range of possible solvents is limited: phenols, cresols, acids, alcohols, esters, amines and amides are evidently unsuitable. High-boiling aromatic hydrocarbons (.e.g. the methylnaphthalenes) and ethers (e.g. diphenyl ether) represent the alternatives. Unfortunately, the solubility of high molecular weight PET in these solvents is rather limited, and so the absolute rates at which cyclics are generated will be low, even though there should be little change in the concentrations that must finally be produced.

The first two experiments were carried out using 1-methylnaphthalene as solvent and antimony trioxide as catalyst. PET H2, dried for several hours at 60° under vacuum, was weighed into ampoules with freshly distilled 1-methylnaphthalene to make mixtures, 10% by weight. Catalyst was added, as about 0.2% of the total weight. The ampoules were evacuated and sealed; while there was no necessity to freeze the contents prior to sealing, care was taken that they were no longer degassing with any vigour.

The ampoules were put into the heater at 250(± 5)°C and left for 24 hours (PET(V)) and 96 hours (PET(VI)). They were occasionally shaken, with due precautions, to ensure complete dissolution and thorough mixing. Antimony appeared as a grey solid over the course of the heating.

The fixed periods having elapsed, the ampoules were taken from the heater and left to cool. As the solutions cooled, they deposited

PET, in a powdery form, and also a yellow semi-solid. The ampoules being opened, their contents were filtered; the brown filtrates were evaporated down at once, using the short-path distillation apparatus described in the previous Chapter. The solid matter was repeatedly extracted with chloroform, and the residual powder air-dried. The extracts from the solids were combined in each case with those obtained by evaporation of the 1-methylnaphthalene solutions, and evaporated to dryness.

The total extract from PET(V), the 24 hour run, was 2.2% by weight of the solution; from PET(VI), 3.1%. From the spectroscopic and other properties of the extracts it was perfectly clear that they were truly mixtures of ethylene terephthalate cyclics. However, at equilibrium in the melt, the cyclic fraction exceeds 3.2% by weight of the sample; if allowance is made for the difference in density between the melt and the solution (see below) it is predicted that the total concentration of cyclics in solution should be about 4.5% by weight. Evidently, equilibrium had not been reached even after 96 hours at 250°C.

New experiments were therefore conducted, but using zinc acetate as catalyst. Although rather less efficient than antimony trioxide, and also apparently more prone to encourage the degradation of the polymer⁷³, it was more stable and did not seem to decompose in any way upon prolonged heating.

Two 10% mixtures of PET H2 and 1-methylnaphthalene, with 0.5% zinc acetate added, were heated to 250° in sealed ampoules under vacuum. The first (PET(X)) was removed from the heater after 7 hours, the other (PET(XVIII)) after 96 hours. Treated as above, they gave

extracts weighing 1.4% and 3.7% of the solutions, respectively. Both extracts gave carboxyl and hydroxyl absorptions more intense than the cyclics from the previous solution equilibrates, although less so than those from the melts equilibrated at 270° . For the extract from PET(XVIII) it was possible to detect glycol end-groups in the n.m.r. (Figure 4.4); from the intensity of the peaks, it may be estimated that, if these were the only end-groups, the number average degree of polymerisation of the extract would be about fifteen. In g.p.c., the extract from PET(X) gave peaks of normal definition, but that from PET(XVIII) gave a tracing in which there is evidence of significant contamination by linear oligomers. (Figure 6.8). However, no regard was paid to this for the purposes of quantitative analysis.

By weighing aliquots removed with pre-heated pipettes, the density of a 10% PET solution just at its boiling point ($\geq 243^{\circ}$) was determined as $0.86(\pm 0.03)$ kgm/dm³. The molarities of the rings in the starting solution and the two equilibrates, calculated using this density, are given in the table below. For the starting solution and for PET(X), the extent of reaction p will be taken as unity; for the chain fraction of PET(XVIII), a value of 0.935 was found viscometrically. The results for PET(XVIII), modified by the factor p^x , are tabulated; for comparison, the accepted melt molar cyclisation equilibrium constants are also listed. The same comparisons are made graphically in Figures 6.9 and 6.10.

x	Molarities x 10 ² for:			Molarity/p ^x x 10 ² for PET(XVIII)	Melt K values ^x x 10 ²
	Starting solution	PET (X) (heated 7 hrs)	PET(XVIII) (heated 96 hrs)		
3	0.06	0.69	2.55	3.12	3.17
4	0.01	0.23	0.60	0.79	1.03
5	0.01	0.19	0.31	0.43	0.54
6	-	0.13	0.25	0.37	0.40
7	-	0.10	0.16	0.25	0.28
8	-	0.06	0.10	0.16	0.21
9	-	0.03	0.06	0.12	0.13

Table 6.7

The agreement between the values in the last two columns is quite adequate: the departures of the solution values from those of the melt never exceed the error limits for the latter. But it is necessary to view this close correspondence with some caution, both because of the presence of chain in the extract from PET(XVIII) and because of the uncertainties associated with the large corrections necessary for so low a p factor*. These supposed constants for solution equilibrium cannot be regarded as carrying the same weight as those for the melt. and the agreement found cannot justify the firm conclusion that the ring-chain equilibrium in 1-methylnaphthalene solutions of PET replicates that in the melt; but certainly it gives a good indication that this is the case.

* It should be noted that, the chains as a whole being so dilute in solution, there will be a great reduction in the extent to which a cyclic extract will be contaminated with chains as a result of a low value pf p.

Recorder deflection

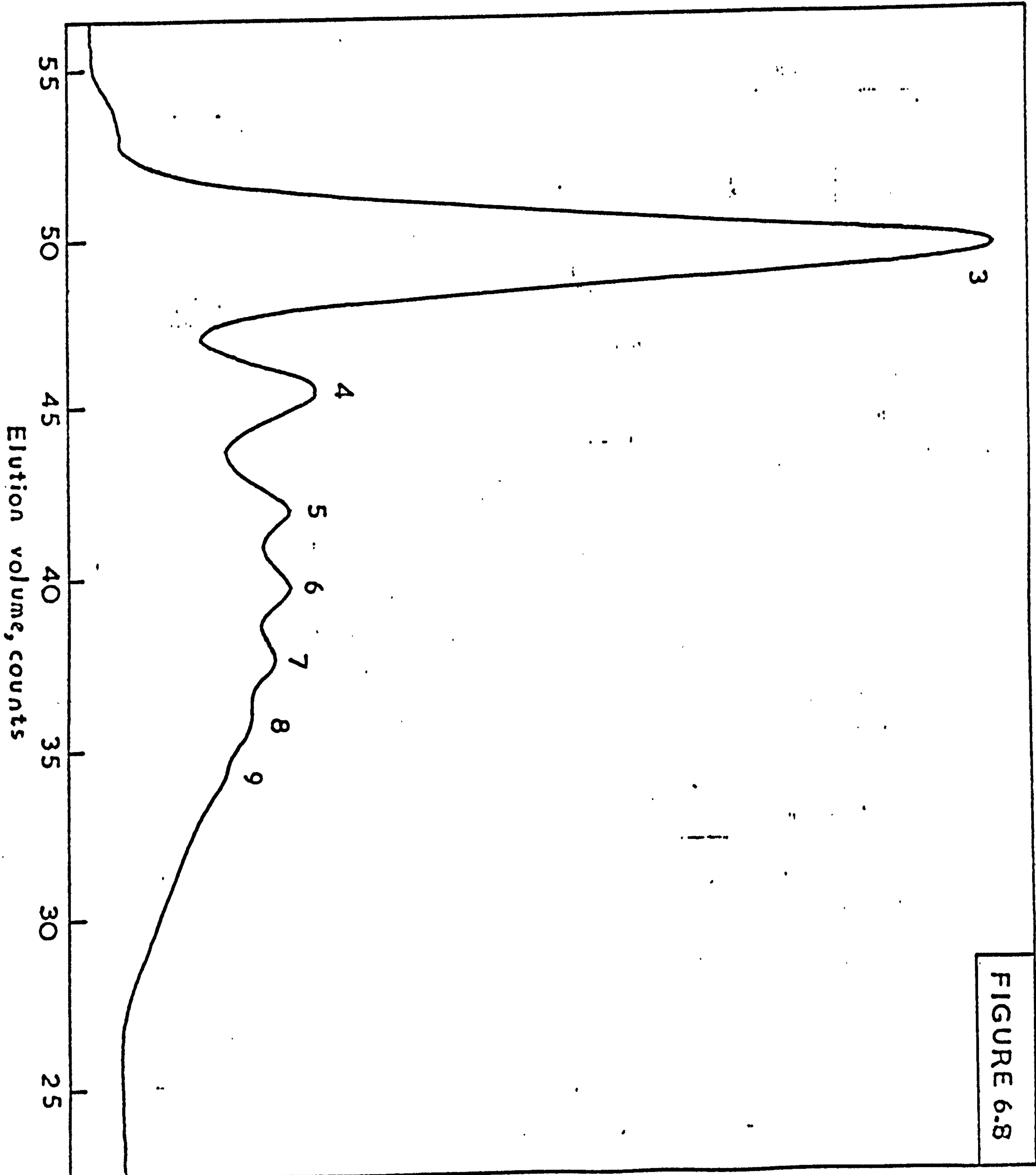


FIGURE 6.8

FIGURE 6.9

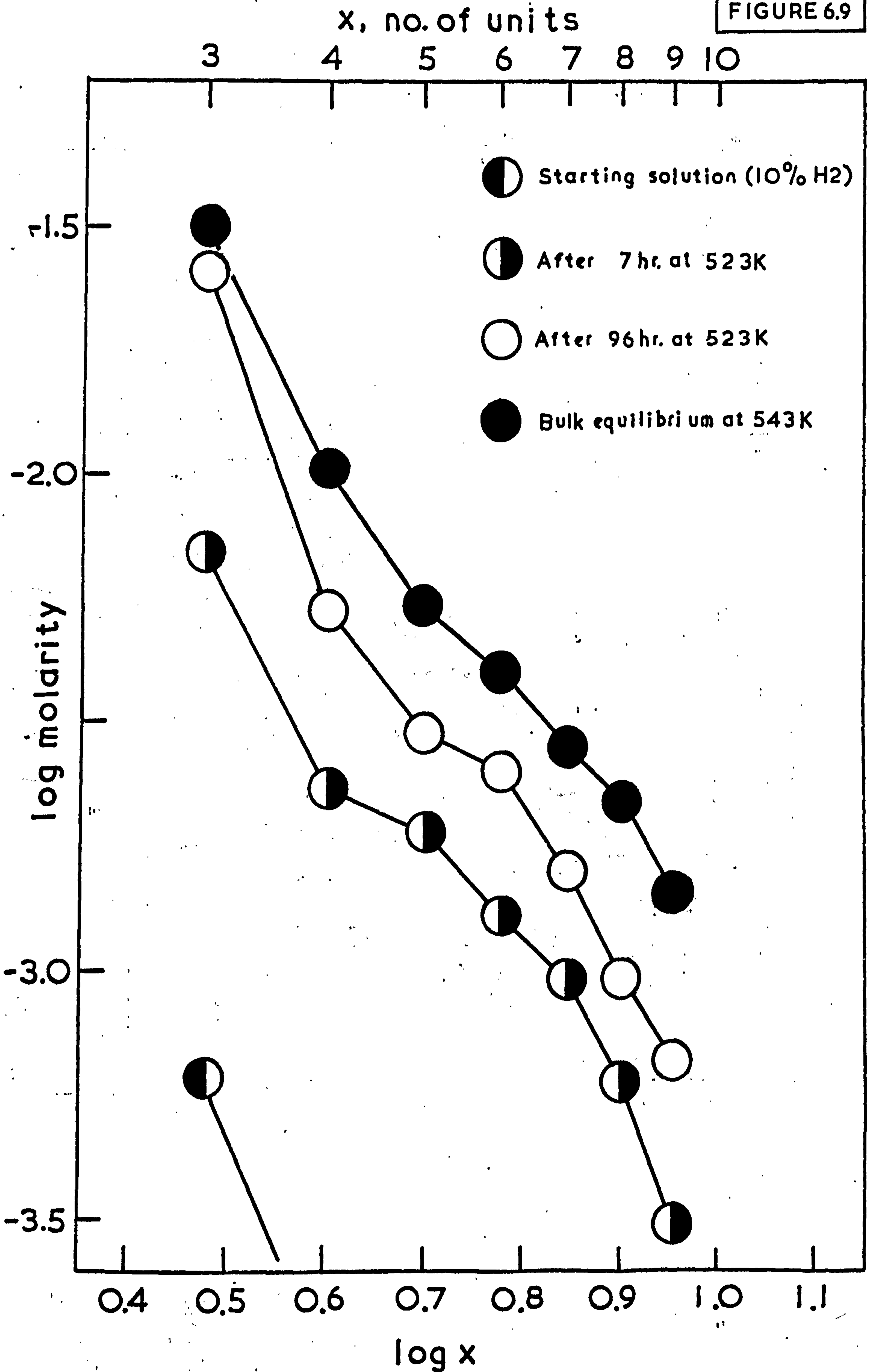
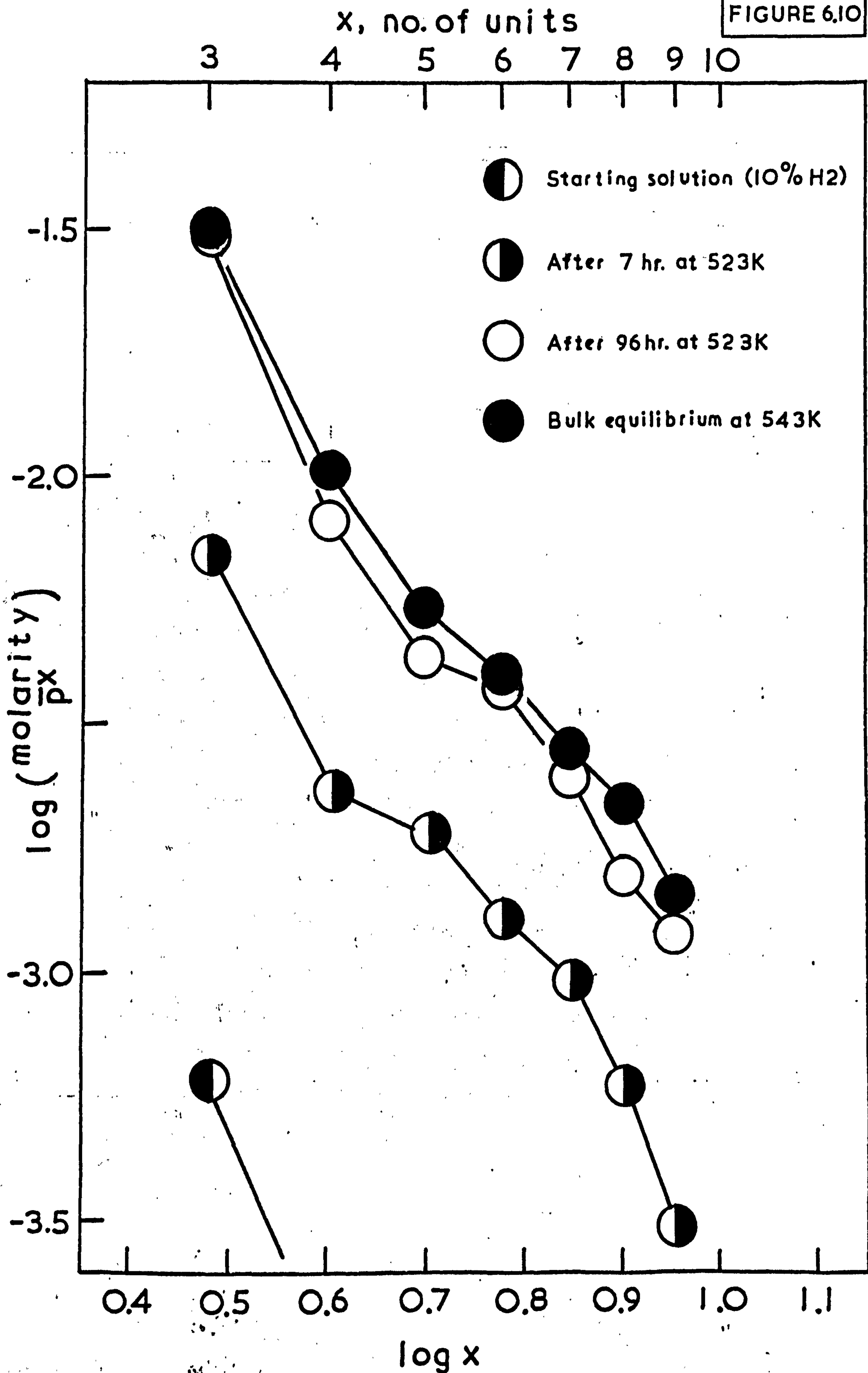


FIGURE 6.10



6.5 EQUILIBRATION FROM RINGS IN SOLUTION AT 250° C

The final equilibration study to be described was an attempt to establish ring-chain equilibrium starting from rings, rather than chains.

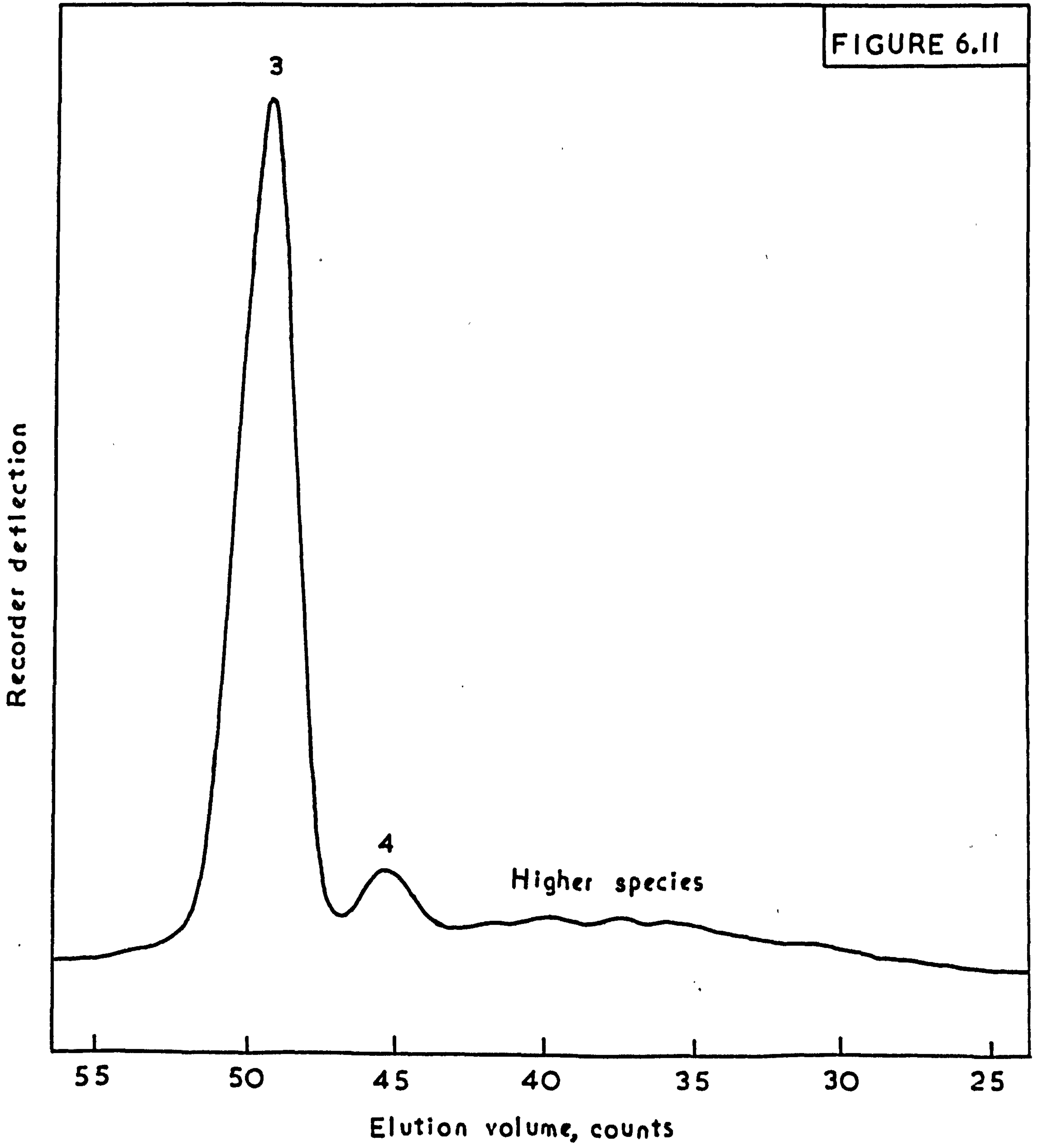
5 gm. ethylene terephthalate cyclics, accumulated from a number of solution re-equilibration experiments, were sealed in an ampoule under vacuum with 45 gm. 1-methylnaphthalene and 0.12 gm. zinc acetate. The ampoule was heated at $250(\pm 5)^{\circ}$ for 96 hours, and then removed from the heater and left to cool. The contents, which cooled to give a powdery deposit and a semi-solid, were treated in the same way as the other solution equilibrates.

The soluble extract comprised 5.3% by weight of the solution, the powder 4.6%. The extract was badly contaminated, in part with the impurities in the original cyclic mixture; it consisted mainly of trimer (3.4%) with smaller amounts of higher species, not necessarily all cyclic. (Figure 6.11). The initial trimer concentration was 5.4%, higher rings making up the residue of the mixture.

The powder was poly(ethylene terephthalate) of rather low molecular weight. ($\bar{M}_n = 1200$, $\bar{M}_w = 3110$, by g.p.c.)

The process of equilibration was clearly incomplete, and the degree of polymerisation of the chain part was, in any case, too low to permit reliable treatment of the higher rings. While furnishing no new information upon the equilibrium concentrations of the cyclics in solution, however, this experiment did serve as a confirmation that all the species discerned in the g.p.c. analysis of the low molecular weight extracts from the poly(ethylene terephthalate) were convertible to the polymer.

FIGURE 6.11



CHAPTER 7

THEORETICAL CONCENTRATIONS OF CYCLIC OLIGOMERS
IN POLY(ETHYLENE TEREPHTHALATE)

7.1 INTRODUCTION

In the preceding Chapter, an account was given of the measurement of the equilibrium concentrations of the cyclic oligomers (trimer to nonamer) in poly(ethylene terephthalate) melts and solutions. Here, the concern will be to use the Jacobson-Stockmayer theory (Chapter 1) in attempts to reconcile the experimental molar cyclisation equilibrium constants with the current views on the conformational properties of poly(ethylene terephthalate) chains.

Two rotational isomeric state models of PET chains have been used as bases for the calculations. The first was that initially proposed by Williams and Flory⁸⁷; the second, the later revision of this model by Walker and Semlyen²⁴. For both models, calculations were carried out not only assuming the Gaussian relation between $W_x(\underline{0})$ and $\langle r^2 \rangle$, but also by the systematic generation of the conformations defined by the RISM (Section 1.3). In addition, a further modification to the models will be suggested, and given brief discussion.

There will be no discussion of the necessary computational techniques in this Chapter: it is more convenient that these are dealt with separately, in the Appendices B and C.

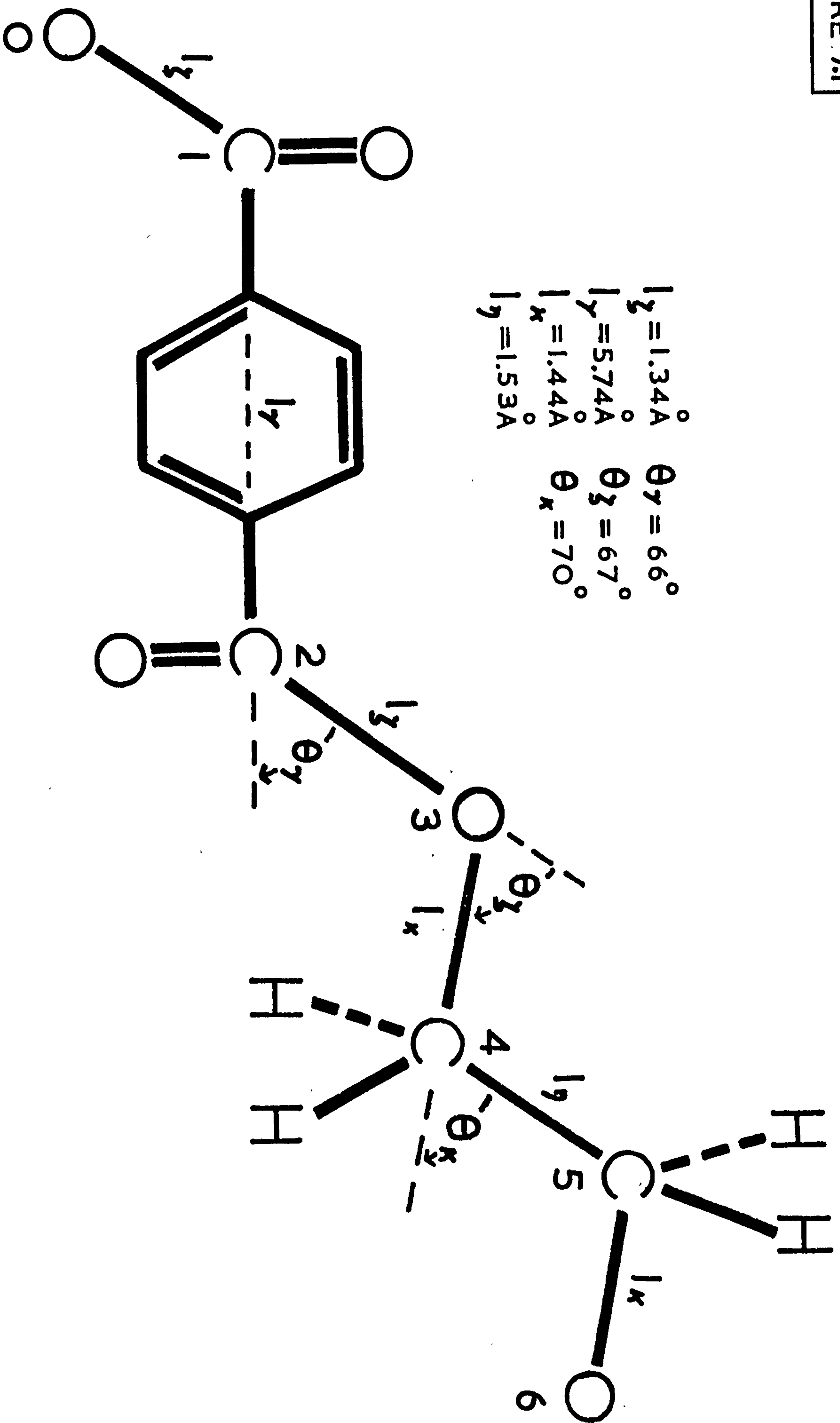
7.2 THE MODEL OF WILLIAMS AND FLORY

The model proposed by Williams and Flory^{87,33} (henceforth the W-F model) may best be described by reference to Figure 7.1, in which is sketched the ethylene terephthalate repeat unit. There are six bonds, of which one is a "virtual bond" of length R_p ($= 5.74 \text{ \AA}$), connecting the carbon atoms of the carbonyl groups of each terephthaloyl residue, and the others are bonds of normal chemical type.

In all polyesters, and polyamides, the partial double-bond character of the $\text{C}=\text{O}$ ester, or $\text{C}-\text{N}$ amide, bonds ensures that they are permanently planar trans. This is a conclusion supported by extensive evidence from crystallography, electron diffraction of gases, and spectroscopy. The mathematical treatment of the chains is greatly simplified by this structural peculiarity, for it implies that there is no interdependence of the rotational states of the bonds on either side; a chain may be considered as a sequence of independent segments. Depending on the type of polyester or polyamide, each segment may span an entire repeat unit, or just the residue of one of the two monomers. For PET, there is an alternation of the independent segments consisting of terephthaloyl virtual bonds, and those consisting of the triads of bonds comprising the glycol parts.

Electron delocalisation requirements restrict the terephthaloyl virtual bonds to two rotational states, cis and trans: there is evidence from the analysis of the dipole moments of dialkyl terephthalates that the states are about equally probable. The bonds in the triads are each assigned three symmetrically disposed states, at bond rotational angles ϕ of 0° , and $\pm 120^\circ$.

FIGURE 7.1



$l_z = 1.34 \text{ \AA}$ $\theta_y = 66^\circ$
 $l_y = 5.74 \text{ \AA}$ $\theta_z = 67^\circ$
 $l_x = 1.44 \text{ \AA}$ $\theta_x = 70^\circ$
 $l_y = 1.53 \text{ \AA}$

Six statistical weight matrices express the probabilities for occupancy of the rotational states of each bond, having regard to the states of the bonds immediately adjacent. (The subscript to each matrix is that of the bond to be rotated, which is determined by the convention that the i 'th bond is that connecting atoms $(i-1)$ and i in the unit).

$$\underline{U}_1 = 1$$

$$\underline{U}_2 = \begin{vmatrix} 1 & \psi \end{vmatrix}$$

$$\underline{U}_3 = \begin{vmatrix} 1 \\ 1 \end{vmatrix}$$

$$\underline{U}_4 = \begin{vmatrix} 1 & \sigma_K & \sigma_K \end{vmatrix}$$

$$\underline{U}_5 = \begin{vmatrix} 1 & \sigma_\eta & \sigma_\eta \\ 1 & \sigma_\eta & \sigma_\eta \omega_{\eta K} \\ 1 & \sigma_\eta \omega_{\eta K} & \sigma_\eta \end{vmatrix}$$

$$\underline{U}_6 = \begin{vmatrix} 1 & \sigma_K & \sigma_K \\ 1 & \sigma_K & \sigma_K \omega_{\eta K} \\ 1 & \sigma_K \omega_{\eta K} & \sigma_K \end{vmatrix}$$

To briefly explain this formulation:

\underline{U}_1 is a single element of unity, because the bond 1 is trans, independently of the state of the preceding bond. (Which will be the bond 6 in the adjoining unit.)

\underline{U}_2 is a row of two elements, because the virtual bond 2 has two states, while 1 has only a single state. ψ weights the cis state relative to the trans.

\underline{U}_3 is a column of two elements, both unity, because bond 3 must again be trans, irrespective of which state bond 2 may occupy.

\underline{U}_4 is a row of three elements, in which σ_k expresses the probability of bond 4 adopting a gauche state, relative to that for it to remain trans.

\underline{U}_5 is a three-by-three matrix. The nine elements give the probability of the bond 5 being in any of its three states, for each of the three states of the preceding bond 4.

\underline{U}_6 is analogous to \underline{U}_5 .

The statistical weight parameters are given values based upon knowledge of the energy of the conformation: which may be estimated, if necessary, from the atomic interactions present.

As noted above, the cis and trans states of the terephthaloyl virtual bond have roughly equal probability: so γ takes a value of unity at normal temperatures.

σ_k is given a value of 0.5 at 303K, since it is found that the carbonyl and methylene groups three bonds apart come into some steric conflict when bonds 4 or 6 are put gauche (bond 5 being trans, in the latter case).

σ_n is given a value of 1.5 at 303K, on the assumption that it resembles the same parameter for similar bonds in poly(oxyethylene).

ω_{jk} is set at 0.1; but this is a more or less arbitrary figure, designed merely to acknowledge that assignment of an adjacent pair of bonds in the triad to the conformations g+g- or g-g+ results in a severe steric overlap (between a carbonyl group, and the ester oxygen four bonds distant).

The mean-square dimensions of a PET chain may now be calculated by the methods of Flory and Jernigan³⁷, appropriately modified to take account of the independence of adjacent segments. The mean-square separation of the ends of a chain comprising x complete units of the kind shown in Figure 7.1 is given by the equation (IV-70 in reference 33):

$$\langle r_x^2 \rangle = 2 \begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 \end{vmatrix} (\underline{G}^{(\xi)})_1 (x) \begin{vmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{vmatrix} \quad (1)$$

where $(\underline{G}^{(\xi)})_1 (x)$ represents the serial product of x -matrices of the type:

$$\underline{G}_k^{(\xi)} = \underline{G}_k^{(\xi)} * \begin{vmatrix} \underline{J} & \underline{0} & \underline{0} \\ \underline{0} & \underline{J} \otimes \underline{E}_3 & \underline{0} \\ \underline{0} & \underline{0} & \underline{J} \end{vmatrix} (z_k^{(\xi)})^{-1} \quad (2)$$

Here, \underline{J} is a column filled with five elements of unity, \underline{E}_3 is the (3 x 3) identity matrix, and the symbol \otimes denotes the operation of taking the "direct", or "Kronecker", product of the two matrices; $\underline{0}$ are null matrices. $z_k^{(\xi)}$ is the partition function for the k 'th unit in the chain, the unit being made up of ξ bonds; in the case of PET, $\xi = 6$, and:

$$z_k^{(6)} = \underline{U}_1 \underline{U}_2 \underline{U}_3 \underline{U}_4 \underline{U}_5 \underline{U}_6 \underline{J} \quad (3)$$

$\underline{Q}_k(\xi)^*$ is itself the serial product of the matrices associated with the ξ bonds in the k'th unit:

$$\underline{Q}_k = \underline{Q}_1 \underline{Q}_2 \underline{Q}_3 \underline{Q}_4 \underline{Q}_5 \underline{Q}_6 \quad (4)$$

Each of these matrices* is formed in this way:

$$\underline{Q}_i = \begin{vmatrix} \underline{U} & (\underline{U} \otimes \underline{t}^T) & \|\underline{T}\| & (\ell^2/2)\underline{U} \\ \underline{0} & (\underline{U} \otimes \underline{E}_3) & \|\underline{T}\| & \underline{U} \otimes \underline{t} \\ \underline{0} & & \underline{0} & \underline{U} \end{vmatrix} \quad (5)$$

In every matrix, $\|\underline{T}\|$ is the pseudo-diagonal matrix containing in diagonal array the ν_i (3 x 3) "transformation matrices", \underline{T}_i , for the i'th bond in its successive ν_i rotational states. For instance, for bond 3 in any PET unit, $\|\underline{T}\|$ will be:

$$\|\underline{T}\| = \begin{vmatrix} \underline{T}_3 \text{ (trans)} & \\ & \underline{T}_3 \text{ (cis)} \end{vmatrix}$$

while for bonds of type 5, with three states:

$$\|\underline{T}\| = \begin{vmatrix} \underline{T}_5 \text{ (trans)} & & \\ & \underline{T}_5 \text{ (gauche+)} & \\ & & \underline{T}_5 \text{ (gauche-)} \end{vmatrix}$$

the elements in the pseudo-diagonal matrices otherwise being zero.

* Save only the matrix \underline{Q}_6 in the last unit of the chain, for which \underline{E}_3 must replace \underline{U} throughout³³.

The fundamental mathematical treatment of the dimensions of chain molecules requires that a system of co-ordinates be attached to each bond in the chain; the function of a transformation matrix \underline{T}_i is to redefine a vector expressed in the frame of reference associated with bond (i+1), in terms of that associated with bond i. If the elements of the (3x1) column \underline{v} represent the x, y, and z components of the vector in the (i+1)'th co-ordinate system, and the elements of the column \underline{v}' likewise express its components in the i'th system, then:

$$\underline{v}' = \underline{T}_i \underline{v} \quad (6)$$

According to the convention to be used here (see Appendix C), \underline{T}_i will be formulated thus:

$$\underline{T}_i = \begin{vmatrix} \cos \theta ; & \sin \theta ; & 0 \\ \sin \theta ; \cos \phi ; & -\cos \theta ; \cos \phi ; & \sin \phi ; \\ \sin \theta ; \sin \phi ; & -\cos \theta ; \sin \phi ; & -\cos \phi ; \end{vmatrix} \quad (7)$$

where $\theta ;$ is the supplement of the angle between the bonds i and i+1, and $\phi ;$ is the rotational angle of bond i.

The column vector \underline{e} that figures in the matrix \underline{E}_i (equation (5) above) represents the bond i expressed as a vector in its own co-ordinate system, and is:

$$\underline{e} = \begin{vmatrix} e \\ 0 \\ 0 \end{vmatrix} \quad (8)$$

where ℓ is the length of the bond i . The transpose of this is the row:

$$\underline{\ell}^T = |\ell \ 0 \ 0| \quad (9)$$

which also appears in the matrix \underline{G}_i .

The original matrices \underline{G}_i are $(5\nu_{i-1} \times 5\nu_i)$ in order; for PET, therefore, the product $\underline{G}^{(6)*}$ is $(5\nu_1 \times 5\nu_6)$, i.e., (5×15) . The effect of post-multiplication of $\underline{G}^{(6)*}$ by the reducing matrix shown in equation (2) is to compress the rows from 15 elements each, to 5; with the result that the order of the final matrix $\underline{G}_k^{(6)}$ will be only (5×5) .

Williams and Flory evaluated $\langle r^2 \rangle$ by means of these equations, using the structural data shown in Figure 7.1, and the statistical weights assigned above: they arrived at a value of 0.93 \AA^2 (gm. molecular weight) $^{-1}$ for the ratio $\langle r^2 \rangle / M$, at the asymptote of very long chains. (M being the molecular weight of the chain with mean-square end-to-end separation of $\langle r^2 \rangle$.)

Now, this prediction takes into account only the interactions between atoms in the chain, separated by no more than a few bonds: but, in solution, "long-range" interactions, between groups sequentially distant in the chain, may "perturb" its dimensions^{32,33}. Specifically, it may be shown that the prohibition of self-intersections in a real polymer chain will result in an increase in its mean-square end-to-end distance in solution; as will, also, the occurrence of enthalpically favourable interactions between the solvent and the polymer segments. On the other hand, if the polymer-solvent interactions are sufficiently unfavourable, the chain expansion arising from the first-named effect may in fact be entirely cancelled out; then so-called " θ -conditions" obtain, under which the actual polymer chains behave as though

"unperturbed" by long-range effects^{32,33}.

Since present experimental techniques for the determination of the dimensions of polymers rely, in the main, upon examination of dilute solutions, care must be taken that theoretical predictions are compared only with results found under, or corrected to,

θ - conditions. In the present case, experimental results adjusted for these effects are available. From the results of Lanka, discussed by Krigbaum⁸⁸, Williams and Flory could deduce a value of 1.05 for $\langle r^2 \rangle / M$ under unperturbed conditions; while Wallach⁸⁹, also, has given a figure of 0.95 (in the units used above).

The agreement between experiment and theoretical prediction vindicates the Williams-Flory rotational isomeric state model, at least insofar as concerns treatment of the average dimensions of PET chains. It becomes of interest, therefore, to ascertain whether it is also capable of accounting for the concentrations of cyclic species in the melts.

7.3 CYCLIC CONCENTRATIONS PREDICTED BY THE W-F MODEL

This Section may immediately be sub-divided:

(a) Calculations assuming Gaussian chain statistics

It will be recalled that, providing the chains conform to a Gaussian distribution of density of end-to-end vectors, the density in the close vicinity of the end serving as origin will be given by:

$$W_x(\underline{0}) = (3/2 \pi \langle r^2 \rangle)^{3/2} \quad (10)$$

for an x-meric chain. (Chapter 1.) Also, the molar cyclisation equilibrium constant for the x-meric ring, K_x , is:

$$K_x = W_x(\underline{0}) / N_A \sigma_{Rx} \quad (11)$$

where N_A is Avogadro's Number, and σ_{Rx} is the symmetry number of the ring, which will equal $2x$ for PET oligomers. (Equation (6) in Chapter 1.)

The average dimensions $\langle r^2 \rangle$ were calculated according to the W-F model for each of the chains from trimer to decamer, and also for occasional higher members of the series, as far as the chain with 577 units. The structural data used were those of Williams and Flory; the statistical weights were those cited earlier, but corrected from 303K to 570K, whereby they became: $\psi = 1$, $\sigma_k = 0.69$, $\sigma_7 = 1.24$, and $\omega_{7k} = 0.29$. (While it is true that the experimental results to

be referred to were obtained at 543K, the small difference in temperature will not significantly affect the validity of the comparison, and certainly will not call into any question the broad conclusions arrived at).

The actual calculations were carried out, not by the equations of Williams and Flory, given above, but instead by the analogous expressions of Walker and Semlyen²⁴, to be discussed in the next Section. These latter expressions resulted from a substantial elaboration of the W-F model, in the course of which many more statistical weight parameters were introduced. To render the later equations equivalent to the earlier, it is necessary merely to set these new parameters to unity; which, indeed, is the value they have by implication, in the W-F model. This procedure had the practical advantage that the same computer programme could be used to perform the calculations for both models. (The programme itself is described in Appendix B).

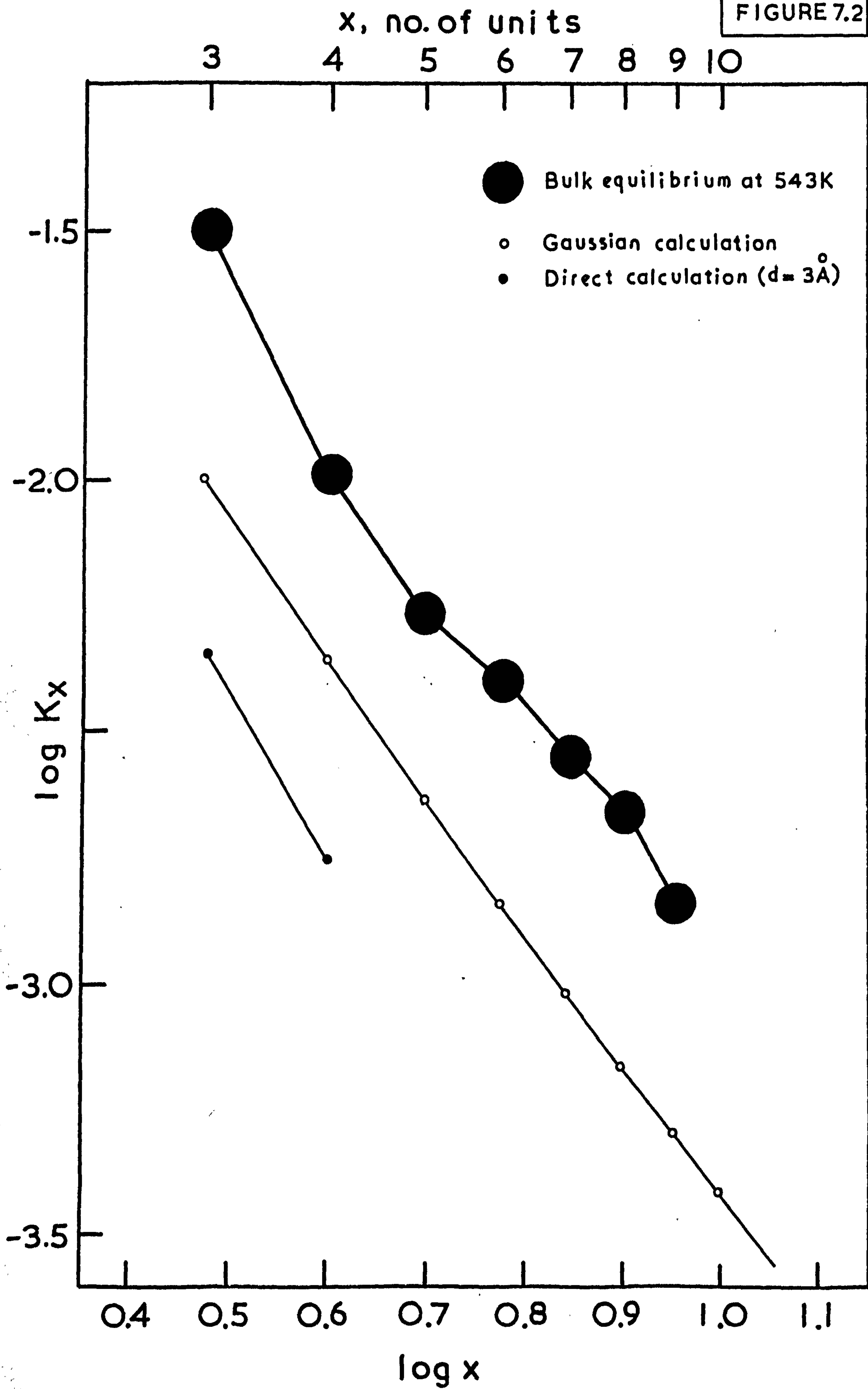
In Table 7.1 the seven experimental equilibrium constants are compared with the predictions of the W-F model at 570K: K_x is again expressed in moles/dm³. The same results are presented graphically in Figure 7.2, where also the theoretical line has been extended to greater ring sizes.

X	$K_x \times 10^2$, found	$K_x \times 10^2$, predicted
3	3.17	0.99
4	1.03	0.44
5	0.54	0.24
6	0.40	0.15
7	0.28	0.10
8	0.21	0.07
9	0.13	0.05

Table 7.1

It will be noted that the predicted values are invariably lower than those found, and by factors of up to three. With the smallest two or three rings, discrepancies of this magnitude are not surprising; for the corresponding chains are unlikely to be long enough to conform to Gaussian statistics, and it is also probable that the chain termini approach each other at non-random angles. (Chapter 1). However, such arguments might not initially be thought to apply for rings larger than, say, the pentamer or hexamer. (The latter possessing 36 bonds, and a molecular weight of over a thousand.) Yet, if the remaining part of the experimental curve is to even converge with the theoretical line, it is necessary that the concentrations of the higher rings were systematically over-estimated by 20 - 30% of their present values; which is just within the maximum experimental error associated with any single one of the concentrations. To bring the experimental points into actual agreement with theory would require that they be subject to

FIGURE 7.2



errors several times greater than those estimated in Chapter 6. The departures of experiment from theory are so large, that it is quite improbable that they are attributable to deficiencies in the former.

On the other hand, unless the experimentally found chain dimensions are badly in error, it is likely that with increasing ring size, the concentrations must eventually come close to the Gaussian line shown. This will be so, almost irrespective of the model actually used to interpret the dimensions: for any other model to give the same results at 303K, but radically different values at 570K, would require a peculiar, and rather improbable, combination of temperature effects. If, indeed, the present trend of the higher ring concentrations is one of divergence from the theoretical line, this must be compensated later by an accelerated convergence. It may well be that certain obscure influences particularly favour formation of rings in the size range investigated: but they cannot continue to have that effect for all ring sizes.

The conclusions to be drawn, therefore, are that the measured concentrations cannot be properly predicted on the basis of Gaussian statistics for the chains, unless their average dimensions are, in fact, much lower than would be expected from the experimental values; and that the amounts of cyclics are being elevated by unknown factors. These factors may simply be connected with a failure of the Gaussian relation, or may involve non-random radial or angular distributions of the density of end-to-end vectors; but whatever their precise nature, the inference must be drawn that they have a specificity that cannot be adequately accounted for in the statistical approach implicit in the Gaussian distribution.

(b) Calculations generating the chain conformations

This is a relatively recent procedure, designed to enable $W_x(\underline{0})$ to be found without recourse to the Gaussian relation. It has already been applied to the cyclic trimer of PET, by Walker and Semlyen²⁴; here, these calculations were repeated, and extended to the tetramer.

The conformations of the chains were generated by means of the computer programme described in Appendix C, run on an Elliot 4130 model computer. In effect, this meant that the computer was instructed to systematically set up separate sequences of numbers, with one such sequence for each conformation, and with the numbers in any sequence representing the rotational angles of the successive bonds in the chain. From knowledge of these angles, together with other input data, it was possible to calculate for each conformation in turn both the end-to-end distance, and the statistical weight.

Since it was desired to probe the distribution of density of end-to-end vectors only in circumstances of close approach of the chain ends, it was not necessary to generate all the conformations. For long chains, considerable savings in computational time resulted from designing the programme to quickly recognise conformations with ends widely separated, since the associated calculations could then be curtailed. The conformational partition function, Z , is required in finding $W_x(\underline{0})$ by the equation

$$W_x(\underline{0}) = z_d / Z \frac{4}{3} \pi d^3 \quad (12)$$

z_x being the total weight of the conformations with ends approaching to within a distance d . It may be found from the sum of the individual

weights, if the whole distribution is treated; but if the distribution is truncated in the manner described, then it must instead be found by multiplication of the U-matrices. For instance, for the PET trimer, Z will be given by:

$$Z = z_{\text{unit}} z_{\text{unit}} z_{\text{terminal}} \quad (13)$$

where z_{unit} is the partition function for a complete unit, given above (equation (3)) and z_{terminal} is the corresponding function for the incomplete terminal unit, given by:

$$z_{\text{terminal}} = \underline{U}_1 \underline{U}_2 \underline{U}_3 \underline{U}_4 \underline{U}_5 \underline{J} \quad (14)$$

Recourse may be had to other devices to speed the calculations. A zero element in any U-matrix will give no weight at all to certain conformations, and these may be at once rejected. (This did not, however, find application in the case of ethylene terephthalate chains). Furthermore, most of the conformations have symmetrical mates. Those in which all the bonds are either trans or cis are planar, and each is unique; but each of the others has a mirror image, in the plane of the non-degenerate conformations. For instance, chains in the conformations:



will have the same end-to-end distance and the same statistical weight. When the calculations have been done for one members of a symmetrical pair, it is only necessary to double the weight to account for the other.

For the trimeric* chain with the same number of bonds as the cyclic, i.e., that comprising three complete units of the type shown in Figure 7.1, the RISM defines 52,488 conformations; for the chain with the same number of atoms, i.e., that with the first bond omitted, there are half as many. In both cases, it is feasible to generate every conformation. (The computer run time was 7 minutes for the first case.) The conformational partition functions and the mean-square dimensions of the chains were found to agree exactly with those calculated by matrix methods.

Results of these calculations are summarised in Tables 7.2 and 7.3, where the numbers of conformations with ends closer than $d \text{ \AA}$, and the K_3 values found by using the sums of their weights as z_d , are listed for $d = 1 - 5$.

d	Number with ends within $d \text{ \AA}$.	K_3 found using $z_d, \times 10^2$
1	0	-
2	78	0.489
3	264	0.436
4	636	0.715
5	1252	0.665

Table 7.2 : 18-bonded chain

* No consideration will be given to the cyclic dimer here. It has already been shown that on the model of Williams and Flory, the ends of the dimeric chain never approach to within 7 \AA .

d	Number with ends within d Å	K_3 found using $z_d, \times 10^2$
1	2	0.023
2	38	0.469
3	120	0.405
4	258	0.353
5	538	0.646

Table 7.3 : 17-bonded chain

These results are in full accord with those found by Walker and Semlyen.

There is a certain dependence of the calculated K_3 values upon the radius of the sphere within which the ends have to meet, d . In these circumstances, it can become difficult to judge which value is the more correct. The number of conformations in the model with their ends approaching very closely may be too small to accurately represent the real probability of the chain adopting a cyclic configuration; conversely, it is always possible that discordant results from the smaller spheres faithfully reflect actual anomalies in the distribution. Attempts to overcome a supposed sampling error by using a sphere large enough for many conformations to contribute to z_d may in fact lead to the masking of such anomalies, and to the acceptance of false equilibrium constants.

In the present instances, the values for any chain show a reasonable consistency, excluding those for $d = 1$; further, the results

are similar for either chain. It will be taken, therefore, that the results with $d = 3\overset{\circ}{\text{A}}$ represent fairly well the cyclisation constant for a trimeric chain conforming to the model of Williams and Flory.

The value for the 18-bond trimeric chain is plotted in Figure 7.2. From this, it is evident that, at least for this species, agreement with experiment is not improved, but considerably worsened, by removal of the Gaussian assumption.

For the tetrameric chain with 24 bonds, there are 2,834,352 conformations in the W-F model: far too many to be fully generated. Discovery and treatment of the 24,882 conformations with ends within $5\overset{\circ}{\text{A}}$, however, required relatively little computational effort. (A run time of 25 minutes). The results for this chain are presented in Table 7.4.

d	Number with ends within $d \overset{\circ}{\text{A}}$	K_4 found using $z_d, \times 10^2$
1	218	0.188
2	1,920	0.163
3	6,208	0.175
4	13,708	0.166
5	24,882	0.178

Table 7.4 : 24-bonded chain.

The chain with 23 bonds was dealt with similarly; the results are summarised in Table 7.5.

d	Number with ends within d A	K_4 found using $z_d, \times 10^2$
1	118	0.179
2	942	0.156
3	3,190	0.167
4	6,902	0.167
5	13,570	0.210

Table 7.5 : 23-bonded chain.

The values show a striking consistency. Nonetheless, they again stand in much poorer agreement with experiment, than does the point calculated assuming a Gaussian distribution. (Figure 7.2).

There are two conclusions from the results presented in this Section. The first is, that it is improbable that any of the measured cyclic concentrations are explicable on the basis of Gaussian behaviour of the corresponding open chains. To obtain agreement on this assumption would require the chains to be so highly-coiled in the melt, that it would almost inevitably follow that their average dimensions at lower temperatures would be very much less than is found experimentally.

The second conclusion is, that even if no reliance is put upon the validity of a Gaussian distribution, simple application of the model of Williams and Flory will not account for the concentrations of the cyclic trimer and tetramer. There may be a number of reasons why this is the case. Some are connected with the model itself, and in particular with the statistical weights it adopts. For the tetramer,

there are many conformations with ends in juxtaposition, and consistent values are obtained for the equilibrium constants. Presumably, the real distribution of end-to-end distances is satisfactorily represented, at least as far as concerns numbers of conformations; part of the depression of the calculated cyclic concentration may arise from the association of unrealistically adverse weights with these highly-coiled conformations. However, it is true that, even giving every chain conformation equal weight, the calculated constants are raised no further than to the Williams-Flory Gaussian line (in Figure 7.2). Clearly, therefore, important factors are involved, other than those immediately connected with the rotational isomeric state model adopted.

7.4 THE MODEL OF WALKER AND SEMLYEN

The published account of this model will not be reproduced in full detail. It depends on treating the bonds not in pairs, but in triads. The specific usefulness of this approach is that every conformation of the complete glycol residue (bonds 4, 5, and 6) may then be assigned an individual statistical weight, directly related to its total energy.

In the model, each bond has a U-matrix in which the rows are indexed by the combined rotational state of the preceding two bonds, and the columns by the combined state of the immediately preceding bond, and the bond itself. The matrices of Williams and Flory are thereby expanded: the largest, U₆, is now (9 x 9).

Matrices $\underline{\mathcal{Q}}_i$ are set up for each bond*:

$$\underline{\mathcal{Q}}_i = \begin{vmatrix} \underline{U} & (\underline{U} \otimes \underline{e}^T) \parallel \underline{T} \parallel & \underline{0} \\ \underline{0} & (\underline{U} \otimes \underline{E}_3) \parallel \underline{T} \parallel & \underline{U} \otimes \underline{e} \\ \underline{0} & \underline{0} & \underline{U} \end{vmatrix} \quad (15)$$

where the symbols retain their earlier meaning, except that $\parallel \underline{T} \parallel$ has been expanded to conform correctly. The order of these matrices varies with that of \underline{U} : the largest is (45 x 45).

Serial products of these matrices are taken for the repeat unit:

$$\underline{\mathcal{Q}}_i^{(6)} = \underline{\mathcal{Q}}_{i1} \underline{\mathcal{Q}}_{i2} \underline{\mathcal{Q}}_{i3} \underline{\mathcal{Q}}_{i4} \underline{\mathcal{Q}}_{i5} \underline{\mathcal{Q}}_{i6} \quad (16)$$

and for the terminal unit:

$$\underline{\mathcal{Q}}_i^{(5)} = \underline{\mathcal{Q}}_{i1} \underline{\mathcal{Q}}_{i2} \underline{\mathcal{Q}}_{i3} \underline{\mathcal{Q}}_{i4} \underline{\mathcal{Q}}_{i5} \quad (17)$$

These products are (15 x 45); they are reduced to (15 x 15) by post-multiplication with the correct (45 x 15) matrix, and also normalised, by division with the appropriate partition function. For the repeat unit:

* In the more recent notation of Flory³³, such a matrix, including a null sub-matrix in the upper right-hand corner, would be represented as \mathcal{F} ; rather than \mathcal{Q} .

$$\underline{G}^{(6)} = \underline{Q}^{(6)} \begin{vmatrix} \underline{J} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \underline{0} \\ \underline{0}^* & \underline{J} & \underline{E}_3 & \underline{0} & \underline{0} & \underline{0} \\ \underline{0}^* & \underline{0}^* & \underline{0}^* & \underline{0}^* & \underline{J} & \underline{0} \end{vmatrix} (\underline{Z}^{(6)})^{-1} \quad (18)$$

Also $\underline{Z}^{(6)} = \underline{J}^* \underline{U}_1 \underline{U}_2 \underline{U}_3 \underline{U}_4 \underline{U}_5 \underline{U}_6$
 $\underline{J}^* = [1 \ 0 \ 0]$

where \underline{J} is now a (9 x 1) column matrix filled with elements of unity, and $\underline{0}^*$ represents a (9 x 3) null matrix.

$\underline{G}^{(5)}$ is formed analogously.

The final equation is:

$$\langle r_x^2 \rangle = n\bar{l}^2 + 2 \begin{vmatrix} 1 & 0 & \dots & 0 \end{vmatrix} (\underline{G}^{(6)})^{x-1} \underline{G}^{(5)} \begin{vmatrix} 0 \\ 0 \\ \bar{l} \\ 6 \\ 0 \\ \dots \\ \dots \\ \dots \\ 0 \\ 1 \\ 0 \\ 0 \end{vmatrix} \quad (19)$$

where \bar{l}^2 is the mean-square bond-length.

The structural data of Williams and Flory were retained, but the bonds 4 and 6 were given different gauche rotational angles, at $\pm 95^\circ$: this was a modification based on information on the states in ethyl formate⁹⁴. The parameters γ and σ_γ were given their original values: σ_γ was assigned values of 0.73 at 303K, and 0.85 at 570K.

ω_{jk} became one of four parameters $\omega_1 \sim \omega_4$, introducing the effect of interactions arising from rotations about pairs of bonds, and nine parameters $\delta_1 - \delta_9$ dealt with the interactions specific to each triad conformation: the values assigned were derived by a close examination of the energies of the relevant interactions.

When the data are appropriately modified, the model reduces to that of Williams and Flory, and their results are exactly reproduced. Furthermore, for the trimer, the partition function and mean square end-to-end distance calculated by these matrix methods agrees precisely with those found by direct generation of all the conformations according to the new data. The validity of the matrix algebra in the model may therefore be regarded as established.

However, the model* does not correctly predict the dimensions of PET chains at normal temperatures, giving an asymptotic value of 0.56 for the ratio $\langle r^2 \rangle / M$, as opposed to the experimental values of 1.05 and 0.95, and the value of 0.93 calculated from the W-F model. (The units being $\text{\AA}^2 (\text{gm. molecular weight})^{-1}$, as earlier). Whatever results are obtained for the calculations of cyclic concentrations, therefore, there will be some doubt about the fundamental realism of the model.

The reasons for this failure may be as follows. It emerges from a numerical examination that the highly-coiled conformations of the triads of bonds forming the glycol residues are weighted much more heavily in the new model than the old, for many of the parameters

ω and δ are favourable to their adoption by the chain. Undoubtedly, the evaluation of these parameters was carried out correctly, and they

* Here, attention will be restricted to the statistical weight scheme derived by Walker and Semlyn²⁴ according to the methods of Scott and Scheraga^{91,95} and will exclude that found by the methods of Brant and Flory^{92,93}.

represent an improvement on the equivalent (explicit and implicit) values in the W-F model. The parameter σ_7 , however, was not adjusted. Now, there are grounds to question the figure given for it in the W-F model; for it was derived by comparison with the case of poly(oxyethylene), which is recognised to have anomalous features. The characteristics of ostensibly similar bonds in the polyester and the polyether may well be quite different. Furthermore, while for poly(oxyethylene) crystallographic evidence supports the conclusion that the gauche states have lower energy than the trans, for PET the evidence is to the contrary. Crystallographic⁹⁰, and also spectroscopic⁵⁸, studies suggest that the preferred conformation of the glycol residue in PET is that with the bonds all-trans.

For this to be recognised in the W-F model, σ_7 would be less than unity. Calculations⁸⁷ show that, other parameters constant, the model would then give $\langle r^2 \rangle / M \approx 1.2$. Through the introduction of modifications to the statistical weight formalism, the new model requires that σ_7 should be no greater than 0.5 at 303K, if the all-trans conformation of the glycol residue is to ^{be} energetically favoured over that with the central bond (5) gauche. The ratio $\langle r^2 \rangle / M$ is then calculated to be 0.82, in better agreement with experiment than followed from continued acceptance of σ_7 as 1.5. Accordingly, it appears that, by correcting this parameter, the experimentally found chain dimensions can be reconciled with the statistical weights provided by detailed analysis of each triad conformation.

In the following Section, the applicability of the model of Walker and Semlyen to the prediction of cyclic concentration shall be investigated, for both the original and the revised values of the parameter σ_7 .

7.5 CYCLIC CONCENTRATIONS PREDICTED BY THE W-S MODEL

(a) Calculations assuming Gaussian chain statistics

The procedure for these calculations exactly paralleled that for the Williams-Flory model: the mean-square separations $\langle r_x^2 \rangle$ for the chains were obtained by equation (19) above, and introduced into the equations (10) and (11). The results are presented below, in Table 7.6, in which the units of the equilibrium constant are again moles/dm³.

X	$K_x \times 10^2$ found.	$K_x \times 10^2$ predicted.
3	3.17	1.43
4	1.03	0.67
5	0.54	0.37
6	0.40	0.23
7	0.28	0.16
8	0.21	0.11
9	0.13	0.08

Table 7.6

These results again correspond to a temperature of 570K, and to the statistical weights found by Walker and Semlyen using the methods of Scott and Scheraga^{91,95}. The equilibrium constants are also plotted in Figure 7.3.

While the agreement is still poor, it is markedly better than for the equivalent results from the model of Williams and Flory. From what has been remarked before, however, it will be apparent that this improvement is gained only at the expense of agreement with the chain dimensions at 303K.

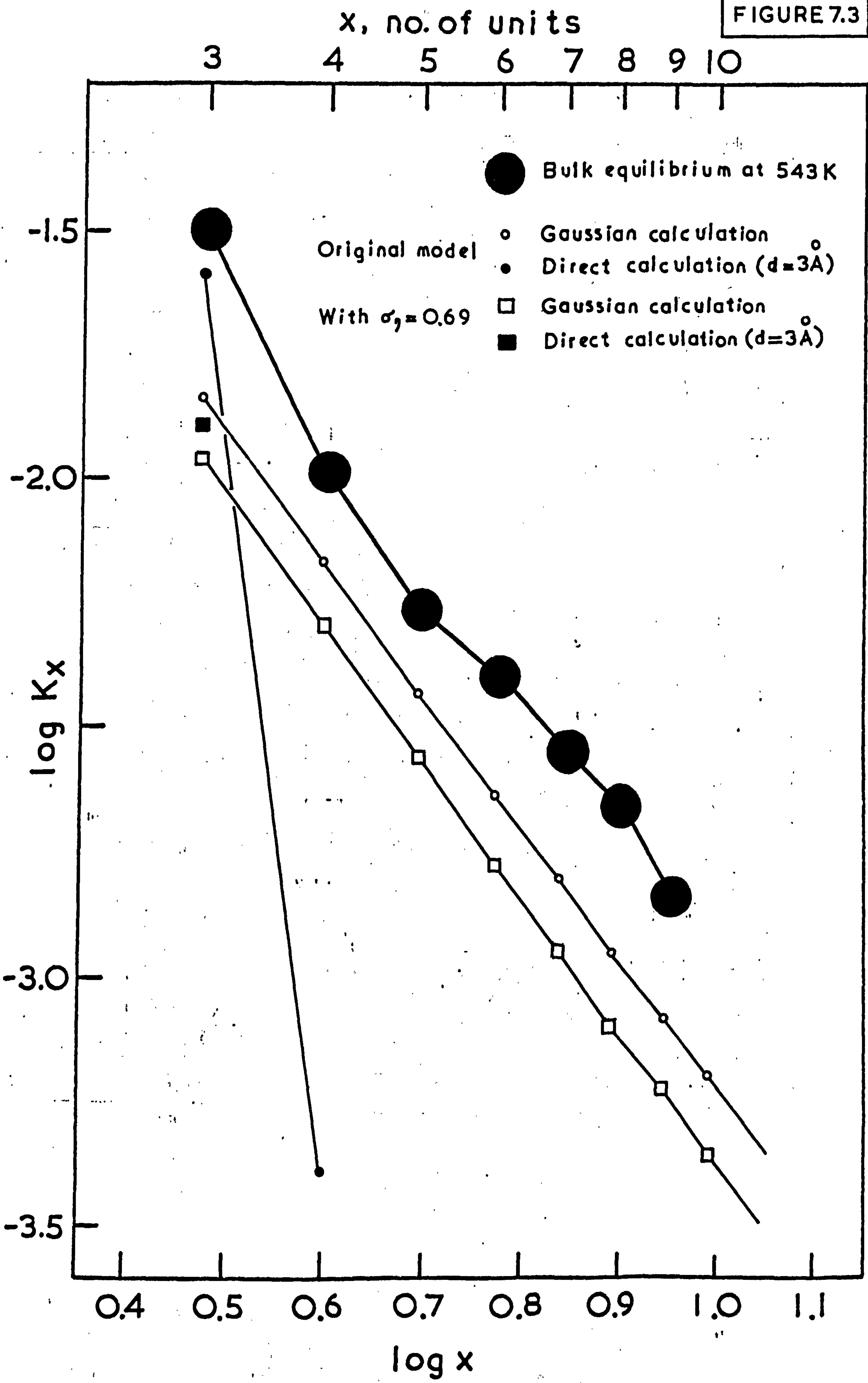
If the parameter σ_p is given the value of 0.69 (i.e. 0.50 corrected to the higher temperature), instead of the value of 1.24 used above, then these results appear:

X	$K_x \times 10^2,$ found	$K_x \times 10^2,$ predicted
3	3.17	1.10
4	1.03	0.50
5	0.54	0.27
6	0.40	0.17
7	0.28	0.11
8	0.21	0.08
9	0.13	0.06

Table 7.7

The correspondence between theory and experiment is now poorer; in fact, reference to Table 7.1 shows that the calculated constants are very close to those found by the W-F model. This accords with expectation, insofar as it has already been noted that with σ_p modified in this way, the new model yields a prediction of the chain dimensions at 303K, similar to that from the model of Williams and Flory. The conclusion is upheld, that it is improbable that any of

FIGURE 7.3



the measured concentrations of rings in the melt can ever be reconciled with the experimentally found chain dimensions, merely by assuming Gaussian behaviour of the linear species.

(b) Calculations generating the chain conformations

These were again largely parallel to those for the W-F model; but two points must be remarked.

Firstly, the statistical weight formalism of Walker and Semlyen differs from that in general use. As an example of this, it has been intimated already that the probability that a bond of type 5 is in one of the gauche states (both adjacent bonds being trans) is no longer simply σ_7 . Since the computer programme used was designed to deal with the standard formalism, it was necessary to re-interpret the W-S parameters. Care is required in this translation; but that it was made correctly is evinced by the agreement of the results with those of the matrix methods.

Secondly, since the gauche states for bonds 4 and 6 are now at $+95^\circ$, the number distribution of end-to-end distances will obviously differ from those for the W-F model.

The results for the 18-bonded and 17-bonded trimer chains, for the data cited by Walker and Semlyen, are given in Tables 7.8 and 7.9.

d	Number with ends with d A.	K_3 found using $z_d, \times 10^2$
1	28	4.34
2	152	3.59
3	452	2.64
4	988	2.50
5	1776	2.22

Table 7.8 : 18-bonded chain

d	Number with ends within d A	K_3 found using $z_d, \times 10^2$
1	4	2.43
2	58	2.44
3	186	2.06
4	406	1.99
5	762	1.95

Table 7.9: 17-bonded chain

The results show a reasonable constancy, both for an individual chain, and for the pair; the exception to this is the value with $d = 1$ for the 18-bonded chain. Furthermore, they agree well with the measured concentration. (Figure 7.3, where the result for $d = 3$ from Table 7.8 is plotted). However, it has to be acknowledged immediately that this agreement is largely artificial, and stems from the use in the model of statistical weights unduly favourable to cyclisation. When the parameter σ_7 is reduced to 0.69 (at 570K) the calculated equilibrium constants are lower, although still representing an improvement over those found by the W-F model:

d	Number with ends within d Å	K_3 found using $z_d, \times 10^2$
1	4	1.48
2	58	1.50
3	186	1.29

Table 7.10 : 17-bonded chain.

The last value is also plotted in Figure 7.3.

Before proceeding to further discussion of these results, the outcome of the calculations for the tetramer chains will be revealed. (The values are those for the original statistical weights of Walker and Semlyen).

d	Number with ends within d Å	K_4 found using $z_d, \times 10^2$
1	0	-
2	58	0.023
3	424	0.041
4	2276	0.088
5	8294	0.155

Table 7.11 : 24-bonded chain

d	Number with ends within d Å	K_4 found using $z_d, \times 10^2$
1	0	-
2	38	0.021
3	400	0.066

Table 7.12 : 23-bonded chain

There is a surprising lack of consistency in the values; but they are all extremely low. The remarkable circumstance has arisen, also, of a chain possessing nearly three million defined conformations, without a single one bringing the ends to within 1 Å.

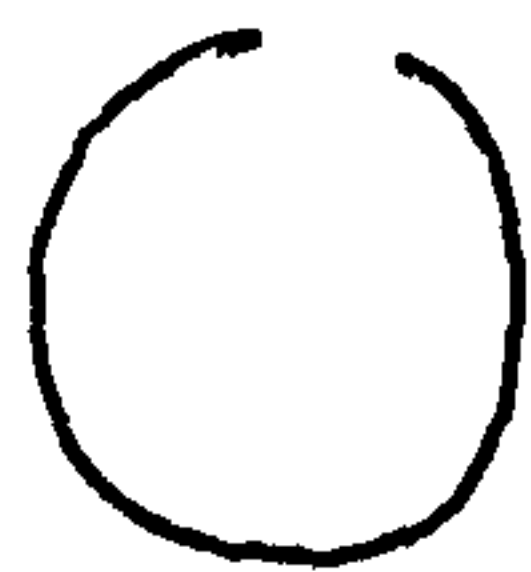
The results of the direct generation method for both models may now be reviewed. Since the statistical weights of the conformations are probably unreliable, attention will be focussed on their distribution by number across the different categories of end-to-end distance. There are certain prominent features. Firstly, for the W-F model the ends of the trimeric chains never properly meet: the 17-bonded chain has only two conformations with ends within 1 Å of each other, the 18-bonded chain has none. For the tetramer, however, the conformations are smoothly distributed in number, right to the least end-to-end separation.

This situation is reversed for the model of Walker and Semlyen.

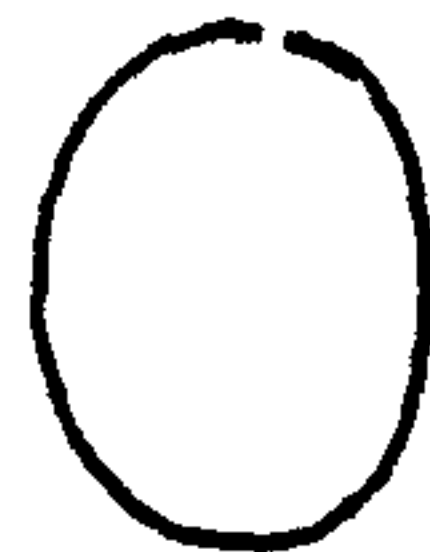
For the trimer, the number distribution is smooth up to the lowest distance category for the 17-bonded chain, and for the 18-bonded there is actually an increase in the density of conformations as the distance decreases; but for the tetramer, the ends fail to encounter each other.

Since attention is being restricted to numbers of conformations, and no regard is being paid to their statistical weights, the difference between the models reduces to that in the gauche rotational angles assigned to the bonds 4 and 6 in each unit. Allocation of angles of $\pm 95^\circ$ rather than $\pm 120^\circ$ might be expected to lead to more rapid coiling of the chain. If this is so, then the observed distributions may be rationalised in this way:

For the trimer, the chain ends do not meet for the rotational states of Williams and Flory, but just meet for those of Walker and Semlyen. Diagrammatically:

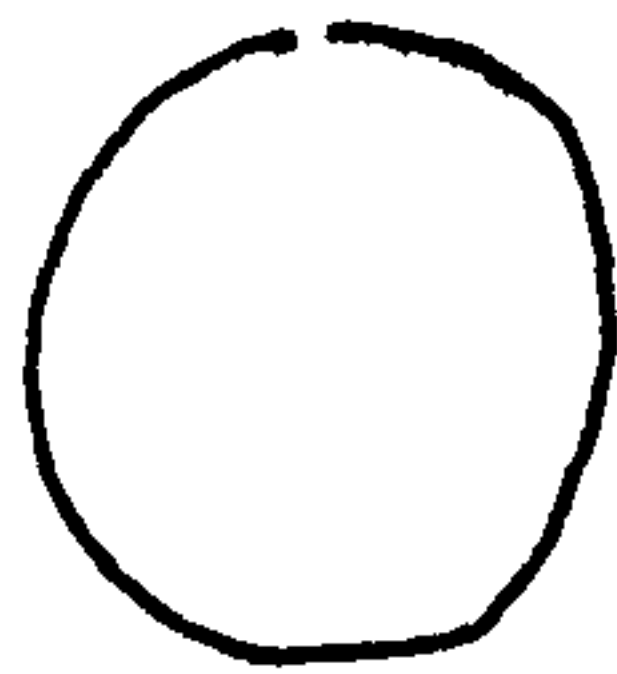


Williams-Flory



Walker-Semlyen

For the tetramer, the chain ends just meet for the rotational states of Williams and Flory, but for those of Walker and Semlyen, highly-coiled conformations correspond to self-intersection of the chain and projection of the termini away from each other.



Williams-Flory



Walker-Semlyen

If this is an accurate representation, then it is apparent that the ring concentrations will be much affected by the non-random manner in which the ends approach each other; but, irrespective of whether this precise interpretation is valid, the sensitivity of the results to changes in the details of the calculations affords a clear demonstration, that the factors responsible for the elevation of the ring concentrations are highly specific, and do not readily lend themselves to statistical treatment.

CHAPTER 8.

CYCLIC OLIGOMERS IN ALIPHATIC POLYESTER SYSTEMS

8.1 INTRODUCTION

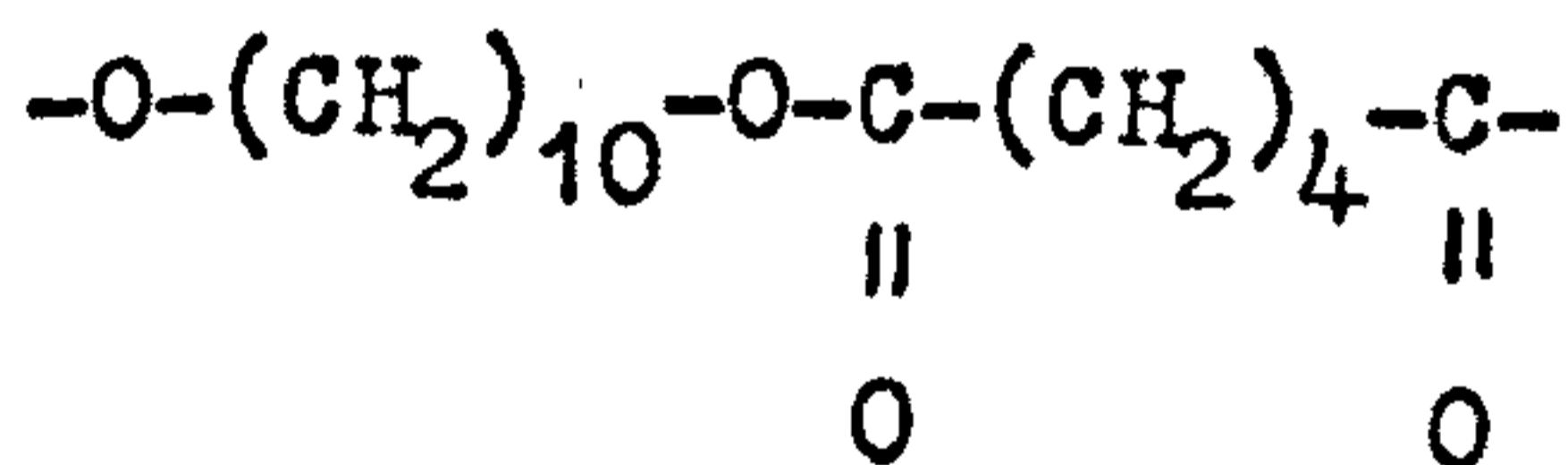
Although the investigations by Stoll and Rouvé¹ of the cyclisation behaviour of aliphatic hydroxyl-acids have been succeeded by many studies of intramolecular condensation in aliphatic polyester systems, all except one must be excluded from considerations for the others^{80,81,82} concerned the effect of intramolecular linkages upon the gelling of systems with polyfunctional reactants, while the polymers to be dealt with here are derived from bifunctional reactants, only, and will be free from branches.

The single research of relevance is that which was undertaken by Jacobson, Beckmann and Stockmayer¹⁸ to test the theoretical predictions of Jacobson and Stockmayer²⁹. They heated high molecular weight poly(decamethylene adipate) in chlorobenzene solution with an ester-exchange catalyst, and followed the conversion from chains to rings by noting the fall in intrinsic viscosity. The fraction of the polymer that was consumed during the generation of the cyclics at their final, equilibrium, concentrations could be related to the conformational properties of the polymer chains, and in particular the length of their "effective links". It was clearly not possible, however, to directly determine the equilibrium concentrations of individual rings by this method.

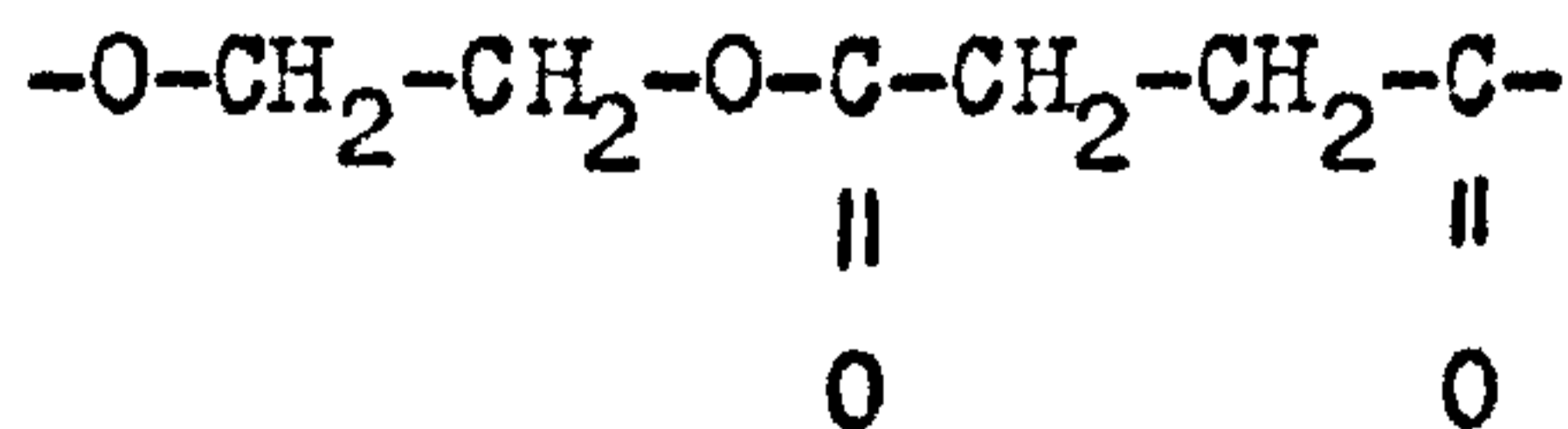
The paucity of information on the cyclic concentrations in aliphatic polyesters undoubtedly reflects a certain lack of interest in the polymers as a class: for, unlike poly(ethylene terephthalate), they have found only limited practical application. Indeed, general methods are available for their preparation; but only in a few cases have the relationships permitting the viscometric determination of molecular weights been established, and there is relatively little guidance upon methods for their analysis. Again, there is a dearth of experimental information on the conformations of their chains.

On the other hand, they present one advantage: that the lower cyclics may be readily obtained by Carother's^{2,3} method of pyrolytic cyclic depolymerisation, and in many cases can also be partially characterised on the basis of his published data.

The studies to be described here were of two aliphatic polyesters: poly(decamethylene adipate) (henceforth PDA), and poly(ethylene succinate)(PES). The first, of course, has a repeat unit of eighteen bonds:



the second, one of eight bonds:



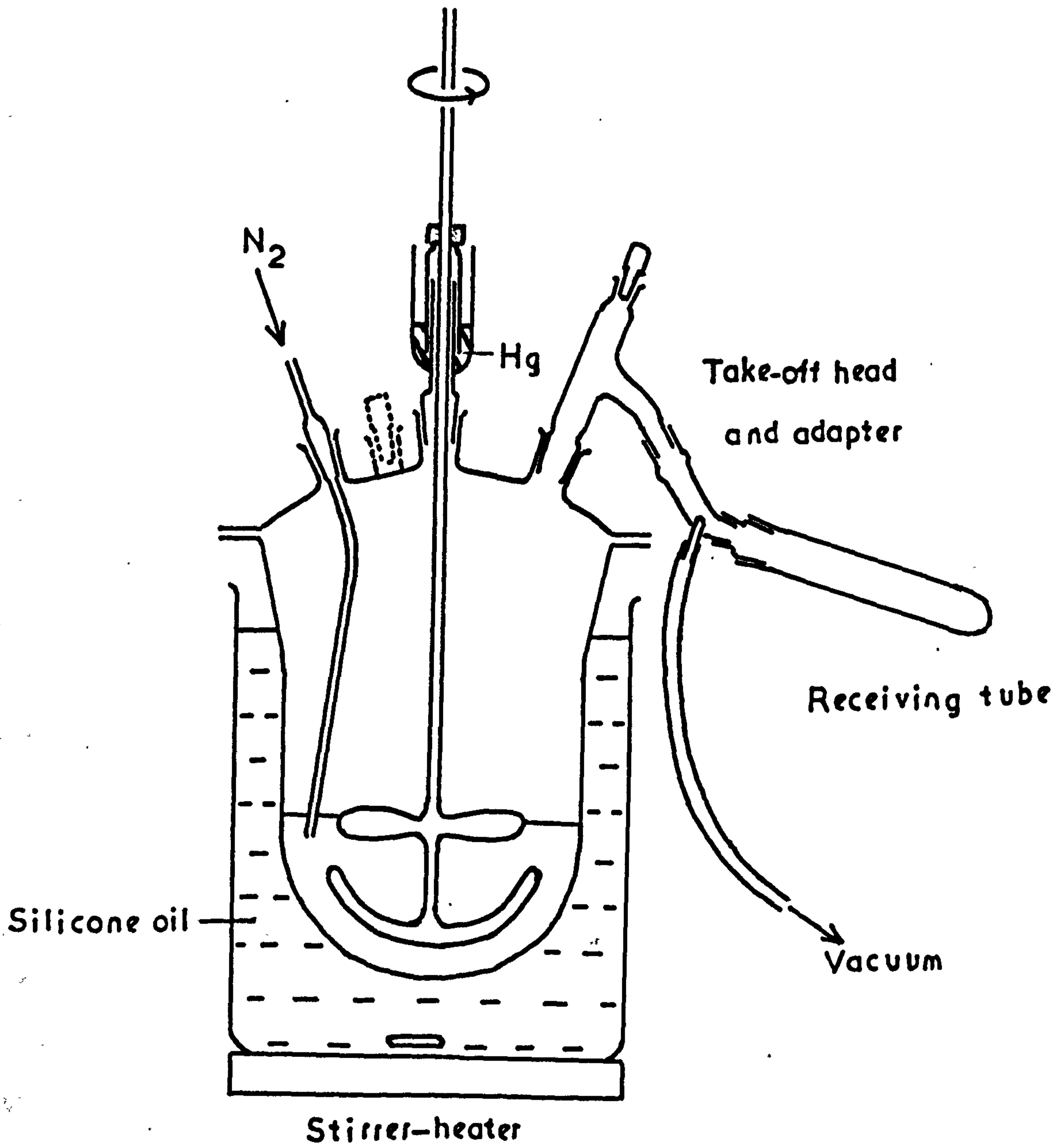
The polymers were made by direct esterification of the diol and the diacid. From each of the prepared samples, there was obtained a low molecular weight fraction with the properties of a mixture of the cyclic oligomers of the polymer; and, further, it was found possible to resolve these mixtures into individual rings by means of gel permeation chromatography. (As has been described in Chapter 3). Unfortunately, however, attempts to prepare samples in which a proper ring-chain equilibrium had been attained met with little success. The original aims have therefore only been incompletely realised.

8.2 PREPARATION OF ALIPHATIC POLYESTERS

Preparation of the polyesters was carried out by the direct esterification method of Zavaglia, Mosher and Billmeyer⁸³. In their procedure, the reaction is driven close to completion by use of tetraisopropyl titanate as polyesterification catalyst, coupled with vigorous agitation of the melt under vacuum.

The apparatus used is shown in Figure 8.1. The polymerisation vessel was a 700 ml. flanged flask, since this made it possible to use a large stirrer, as well as facilitating the removal of the final product. It fitted conveniently into the shortened 2000 ml. beaker that served as a (silicone) oil bath. The lid of the flask carried four ground-glass sockets. That placed centrally permitted the insertion of the stirrer, fitted into a "Tru-Bore" guide, lightly lubricated with silicone oil and sealed with mercury. Another carried a nitrogen bleed, long enough to dip into the melt; while a third was provided with a take-off head leading to a collecting trap, and also

FIGURE 8.1



to a vacuum connection. The last was available for the addition of catalyst to the mixture.

The flask and its lid were dried in the oven, and cooled in a desiccator; then purified diol and diacid were weighed in. For the preparation of poly(decamethylene adipate), exactly equimolar quantities were used; but for the poly(ethylene succinate), 5% extra ethylene glycol was added, to allow for that lost during the early stages of the reaction. The total charge was 250 - 280 gm..

The contents of the flask were rapidly stirred under nitrogen, and heated steadily, until completely liquid. (120° - 160° , after about an hour). 1 ml. of the catalyst (supplied by Pfaltz and Bauer, and distilled before use under vacuum) was then added dropwise; whereupon, the melt would bubble vigorously, and distillation of water would commence. The temperature was raised over an hour to 170° - 175° , and maintained there for about 15 hrs.: over this period, most of the water to be produced in the polyesterification distilled into the trap. The flask was now taken to 190° - 200° , and held there for 6 - 10 hrs., by when a little more water would have been evolved.

The heating was now lowered, and the temperature allowed to drop to 165° . The receiving trap was emptied, and the nitrogen bleed replaced by a stopper. Vacuum was carefully applied, and then the trap was cooled in liquid nitrogen. The melt was vigorously agitated at 165° , under 0.3 mm., for some 6 - 10 hrs. During this time, a very little condensate would collect in the trap: when preparing PDA, this would also be water, but for PES it would in part be ethylene glycol (since this was present in slight stoichiometric excess).

The heating and stirring were discontinued, and the coolant was removed from around the trap. The flask was disconnected from vacuum, back-filled with nitrogen, and left to cool.

To remove the polymer from the flask, and convert it from a lump to a manageable form, it was dissolved out, and precipitated from solution.

PDA dissolved quite readily in about 2000 ml. chloroform at room temperature; the solution was passed through a sintered glass filter, concentrated to 750 ml. by rotary evaporation at 30° , and poured with very rapid mechanical stirring into an ice-cold mixture of diethyl ether (4400 ml.) and petroleum ether (40° - 60° boiling range, 1100 ml.). The creamy product was further stirred in an ice-bath, for 10 mins., and left overnight at 0° . The polymer was then filtered off, using a large Büchner funnel, washed with a little petroleum ether, sucked dry, and afterwards dried under vacuum with progressive increase of temperature, up to 40° . The material that remained in solution during the precipitation was concentrated into a weighed flask and evaporated to dryness.

PES was treated similarly, save that it was necessary to use warm chloroform, or, in one case, sym-tetrachloroethane, to dissolve it.

Of particular importance in this preparation is effective agitation of the polymer melt. First attempts to reproduce the published results on a larger scale were unsuccessful, simply because there was inadequate provision for the agitation. In one such case, for PES, it was necessary to resort to bubbling nitrogen through the melt at 165° , for some 24 hours, to achieve a reasonably high molecular weight; indeed, the mixture of oligomers used in testing the gel permeation

chromatograph (Chapter 3) derived from this polymer sample. Once the apparatus had been modified to permit proper stirring however, this difficulty was overcome, and the results were satisfactory.

High purity of the starting materials is also important, since if high molecular weights are to be attained, there must be a close equivalence of the amounts of the two reagents in the initial mixture. (Except in the instances of polymers derived from the relatively volatile ethylene glycol). The reactants used here were purified by these means:

Ethylene glycol: the glycol, of S.L.R. grade, was shaken with one-tenth its volume of toluene in a separating funnel. The lower layer, of glycol saturated with toluene, was run off into a flask containing a trace of anhydrous sodium carbonate. It was distilled at atmospheric pressure to remove first a toluene-water azeotrope, then any remaining hydrocarbon; then it was distilled under vacuum, using a grease-free apparatus without a bleed, and an oil-pump. A small first fraction was rejected; the main fraction (b. about 60° at 0.5 mm.) was collected, and redistilled in the same way.

Succinic acid: this was doubly-recrystallised from hot distilled water; the solutions were approximately 25% in acid at 70° . The final product was dried under vacuum at 70° . It represented 70% of the starting material and melted at $183.75^{\circ} - 184.25^{\circ}$. (Literature⁸⁴: 182°).

Decamethylene glycol: as obtained from Koch-Light, Ltd., this reagent was contaminated with traces of an unpleasantly smelling, yellowish, oil, which could not be removed by normal recrystallisation procedure, nor by treatment with active carbon. However, it was found that slow cooling of a hot solution in acetone would give large

crystals that were of improved purity. The glycol was therefore recrystallised three times in this way. The final solid, 60% of the starting material, m. 72.5° - 74.5° was odourless, and gave a colourless solution in acetone. (Literature⁸⁴ melting point: 71.5°).

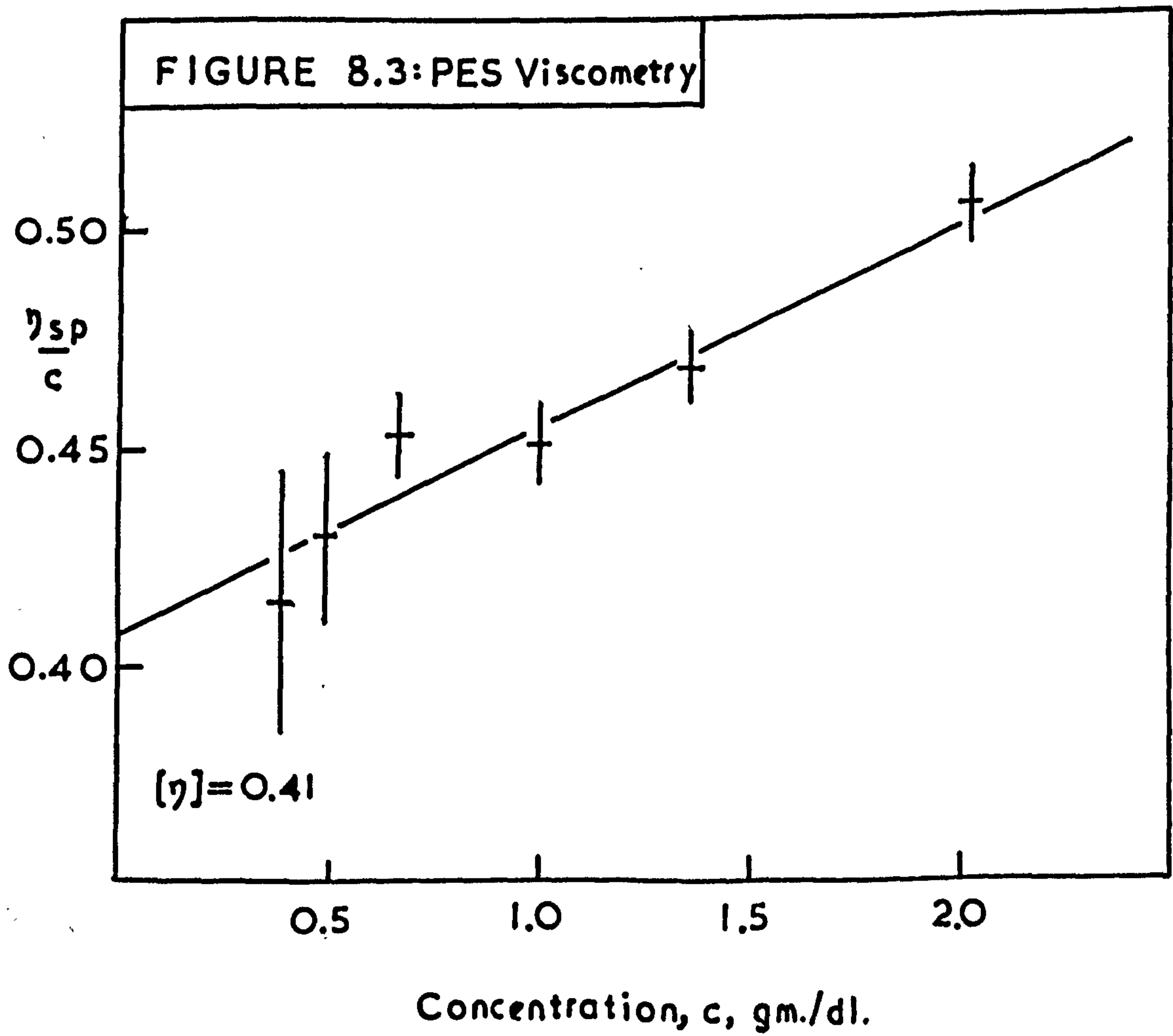
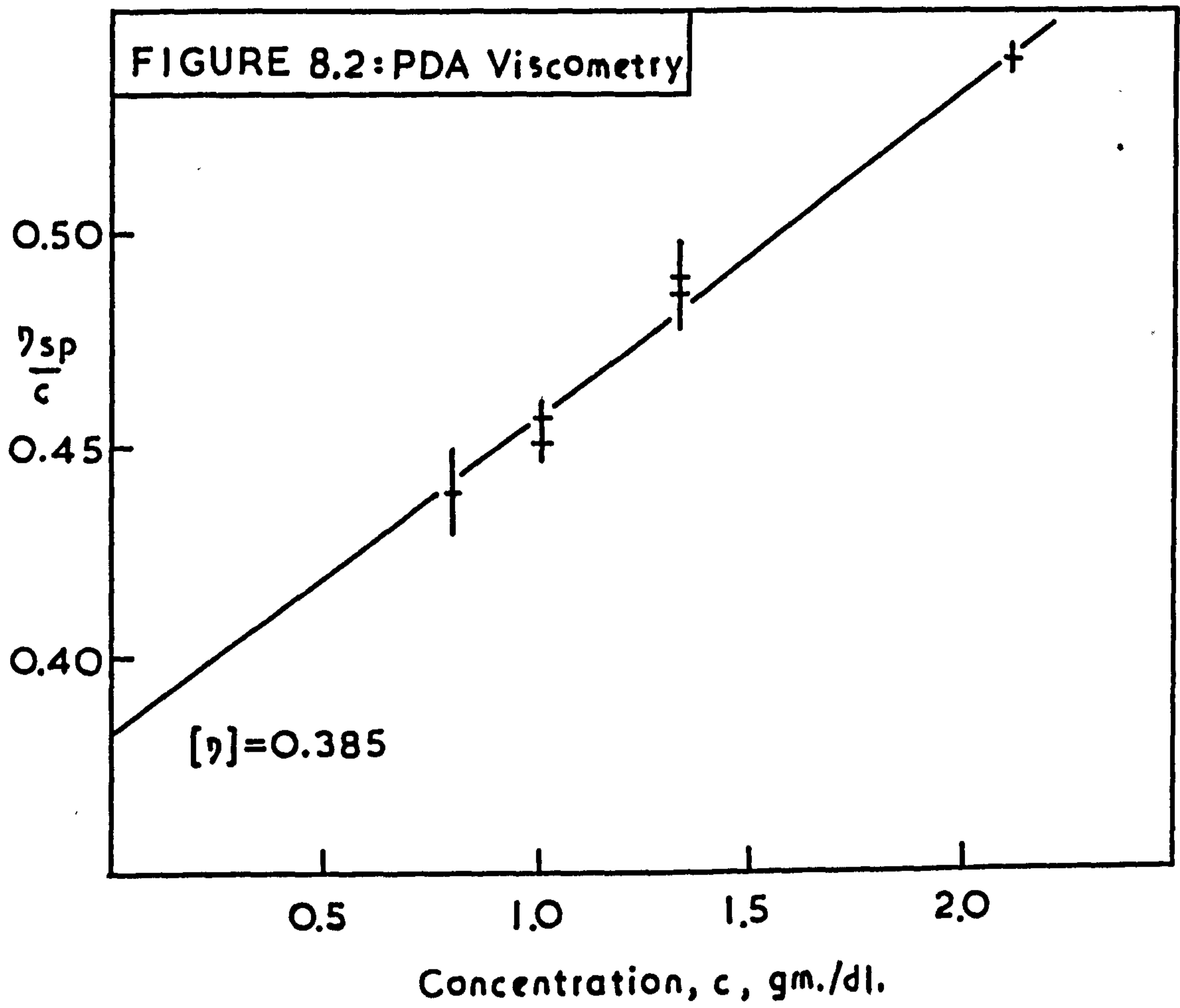
Adipic acid: the acid was recrystallised twice from water, with cooling in ice. The product, dried at 60° under vacuum, represented 88% yield, and melted at 152° - 153° (Literature⁸⁴: 153°).

The molecular weights of the prepared polymers were estimated viscometrically. For FDA, the solvent used was chlorobenzene, and the intrinsic viscosity was related to the weight average molecular weight by the equation of Flory and Stickney⁸⁵.

$$\log_{10} [\eta] = 2.295 + 0.655 \log_{10} \bar{M}_w$$

For PES, the solvent was chloroform: there is no exact relation of the above kind available, but Chang, Zavaglia and Billmeyer⁸⁶ have established equations for other aliphatic polyesters, and it was possible to obtain approximate results from these.

The intrinsic viscosity of the FDA sample was found to be $0.385 (\pm 0.010)$ dl./gm., corresponding to a weight average degree of polymerisation of $95 (\pm 5)$. (Figure 8.2). The intrinsic viscosity of a sample of PES prepared by the described method was $0.41 (\pm 0.02)$ dl./gm. (Figure 8.3). From tables of $[\eta]$ and weight average molecular weight given by Chang et al., it may be estimated that the polymer had a weight average degree of polymerisation of 100 - 170. These values compared rather unfavourably with those given by Zavaglia, Mosher and Billmeyer⁸³ for many of their polymers; nevertheless, they were high enough to permit the polyesters to be used in the subsequent studies.



8.3 PROPERTIES OF THE SOLUBLE RESIDUES

It was noted in the last Section that there were small amounts of material left in solution after the precipitation of the prepared polymers, and that these soluble residues were carefully preserved. There was one such residue from the preparation of PDA, constituting 1.3% of the polymer, and two from those of PES, comprising 3.3% and 2.4%. In this Section, their properties will be reviewed.

(a) Physical properties

The residue from PDA was a white solid, soft, and slightly sticky, even after complete removal of the solvents; it had a definite odour. One of the PES residues, that obtained from the preparation where passage of nitrogen was necessary to force up the molecular weight, was brownish and initially syrupy, but later setting to a waxy, and rather adhesive, mass. The second was only slightly green-yellow, and was at first a viscid liquid, but set overnight to a firm lump; it was, however, only semi-solid. All the residues were freely soluble in chloroform, and soluble to lesser extents in other solvents, but not in diethyl or petroleum ethers.

(b) Elemental analysis

The analysis for the residue from PDA is compared below with that expected for an empirical formula of $C_{16}H_{28}O_4$:

	% carbon	% hydrogen	% oxygen, by difference
FOUND	66.98	9.93	23.09
CALCULATED	67.57	9.92	22.51

Table 8.1

FIGURE 8.4: PDA Residue

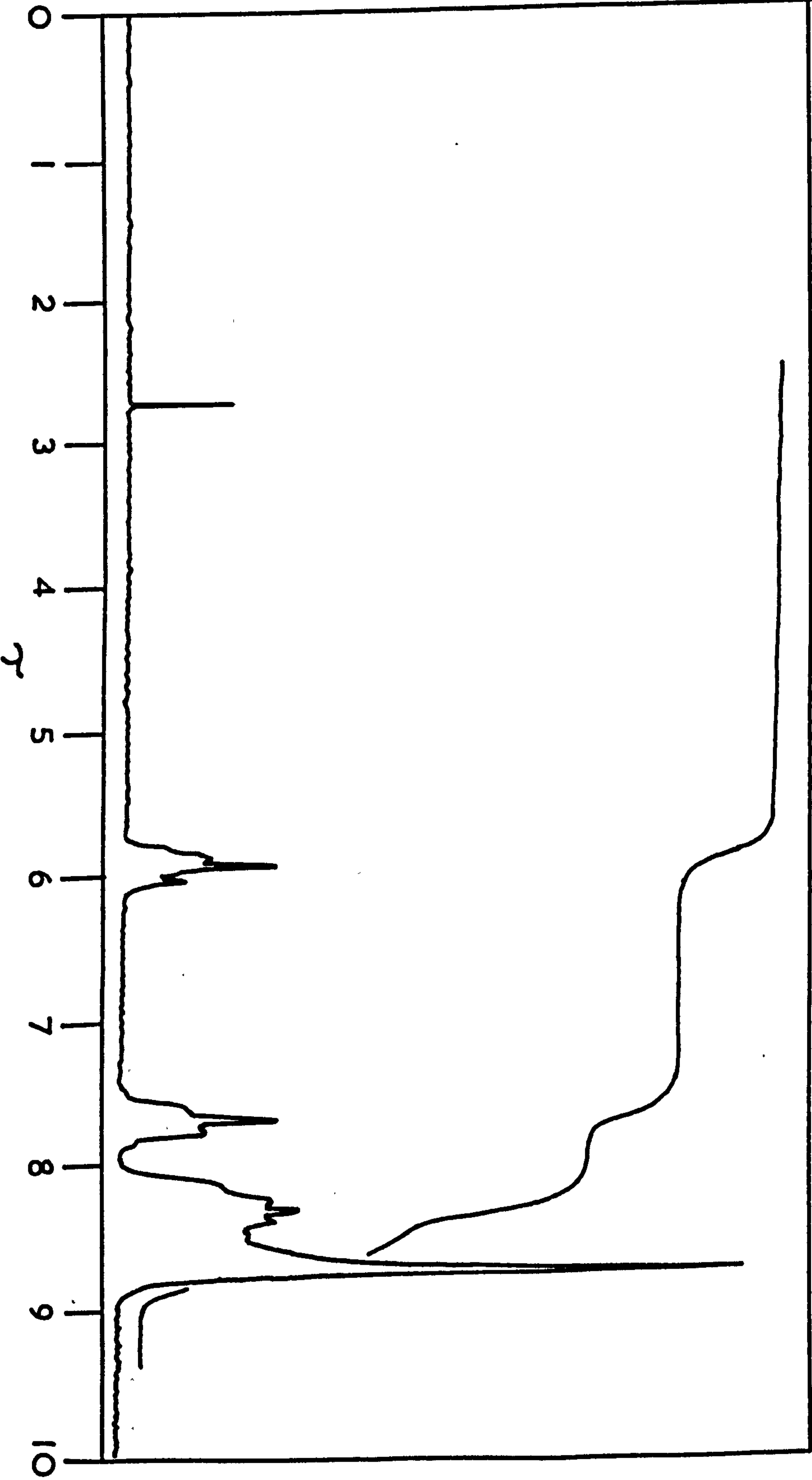


FIGURE 8.5: PDA

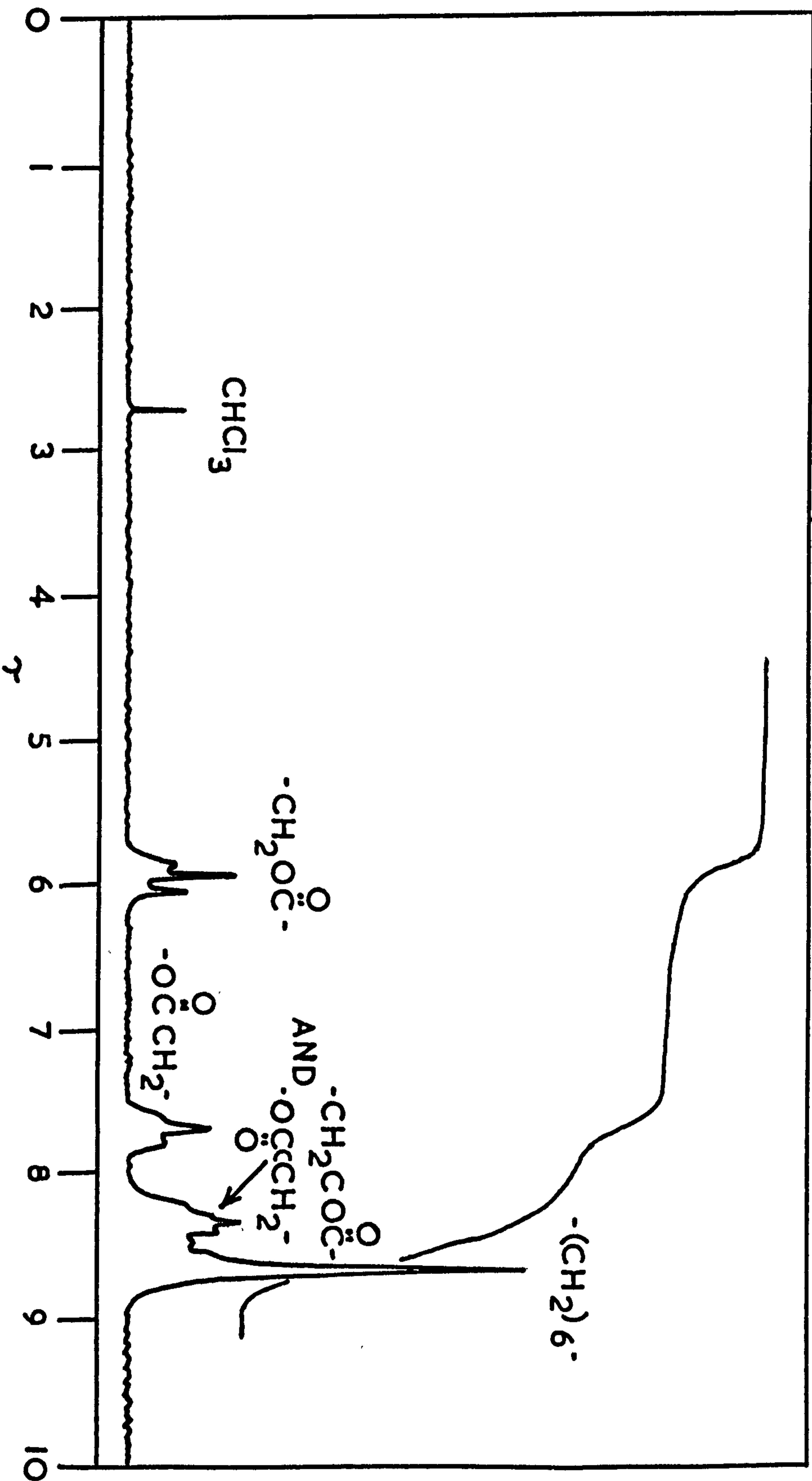


FIGURE 8.6: PDA Monomer

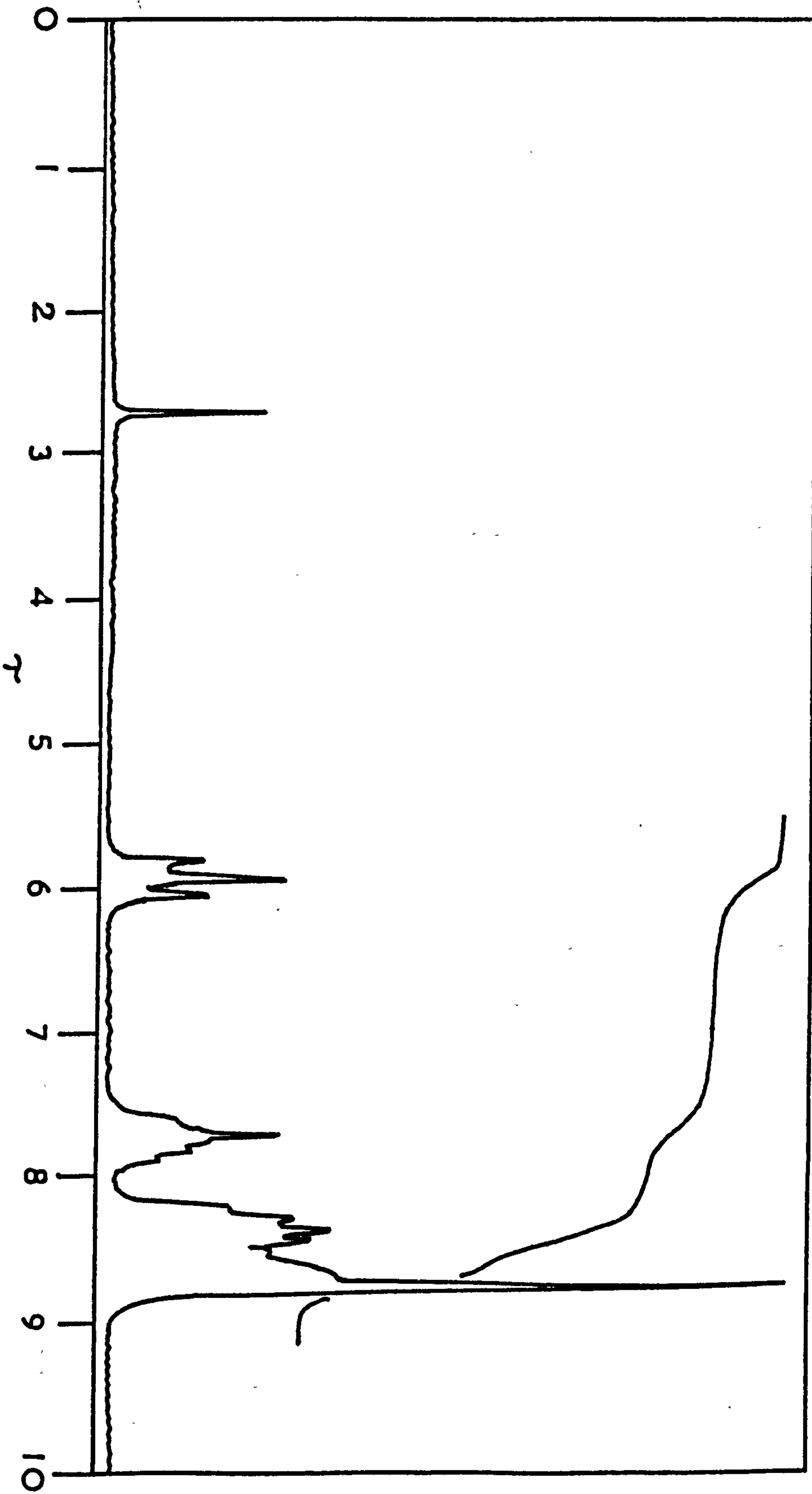


FIGURE 8.7: PES Residue

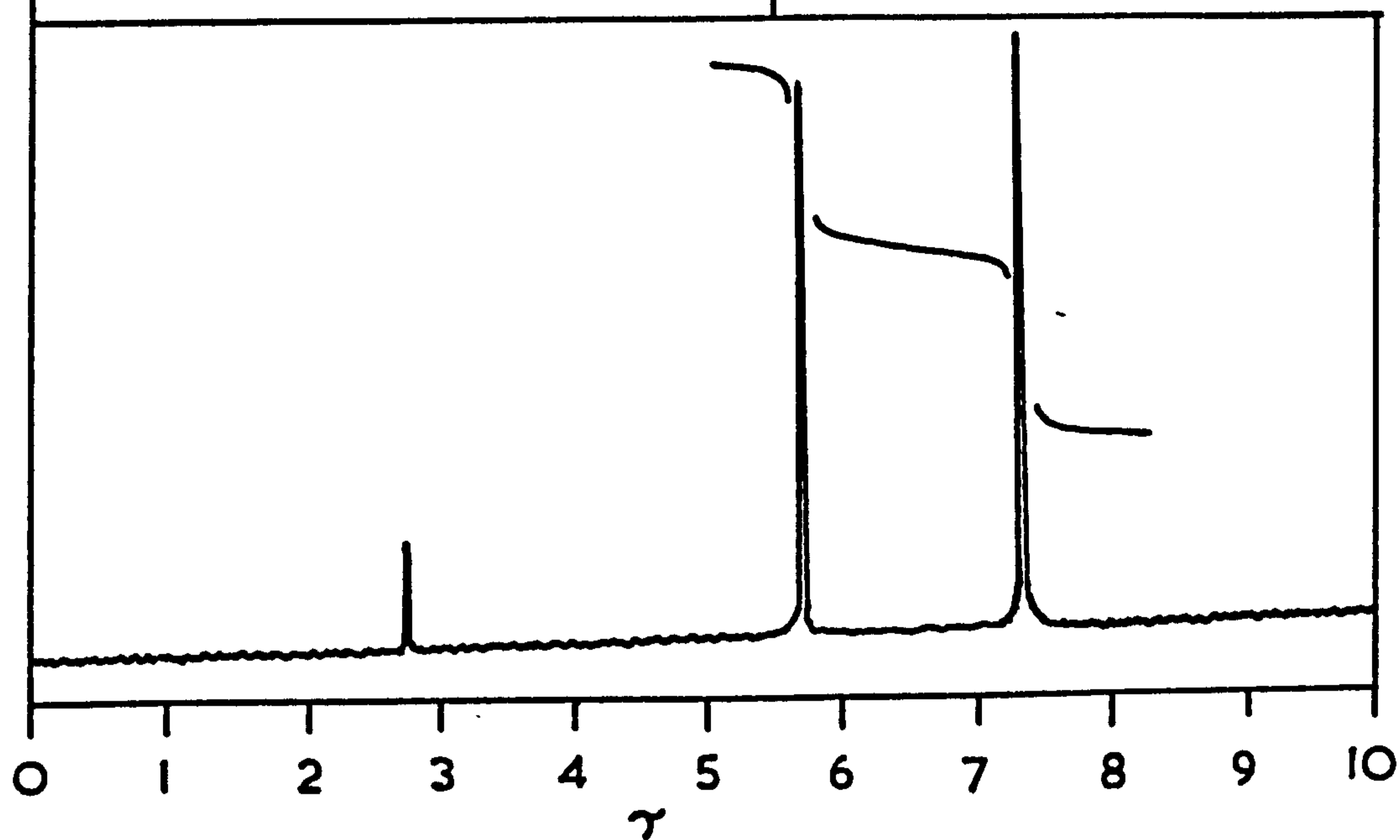
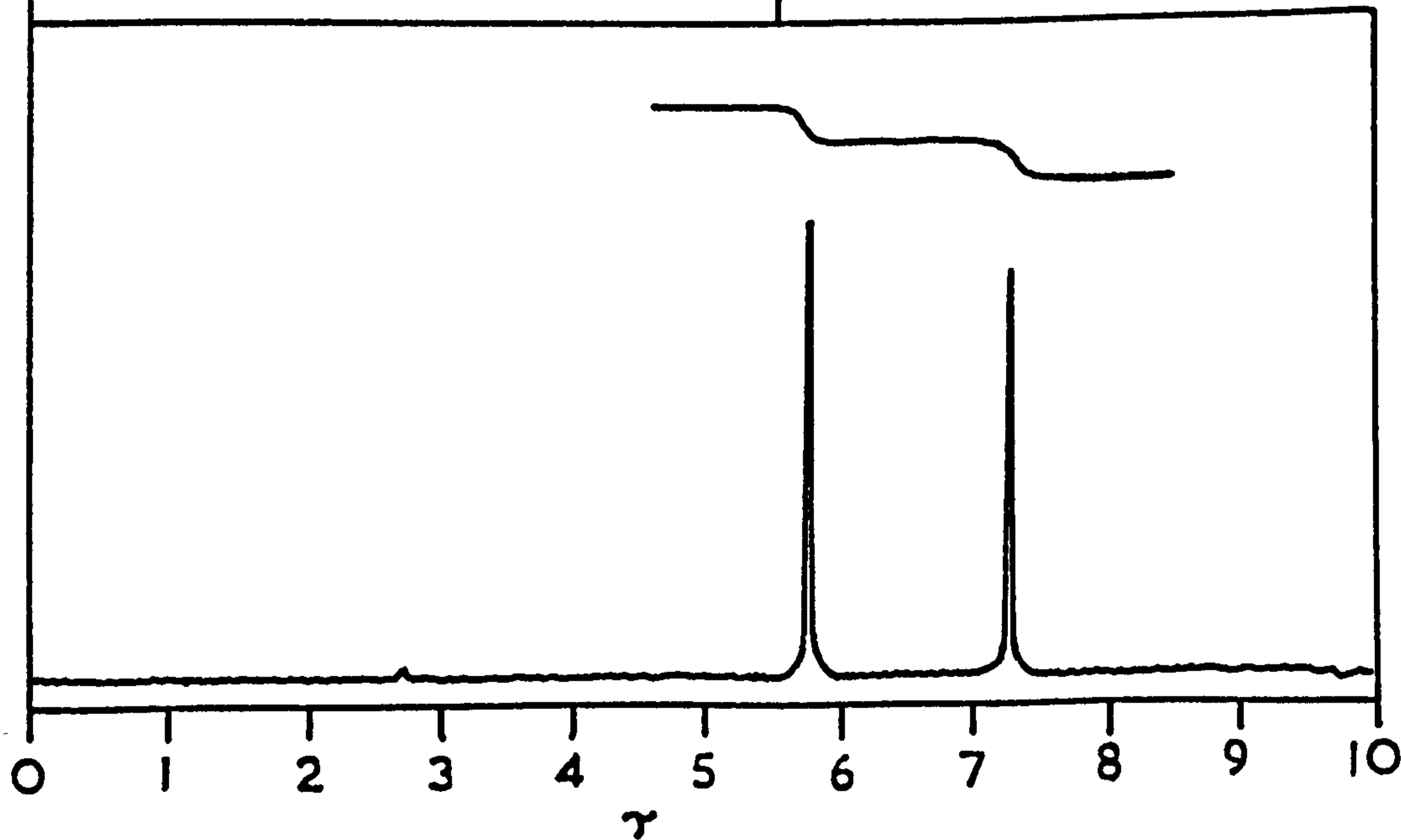


FIGURE 8.8: PES Dimer



(c) Nuclear magnetic resonance spectroscopy

In Figures 8.4, 8.5 and 8.6 the proton resonance spectra of respectively the residue from FDA, high molecular weight FDA, and the cyclic monomer of FDA are shown; the preparation of the last material is described in Section 8.4. Assignments for the bands are given on the second spectrum. The three spectra are closely similar: the only differences being in slight extraneous absorptions between the main bands, for the monomer, and in the superposition of weak absorptions on the band centred at 5.95, in the trace for the soluble residue.

In Figures 8.7 and 8.8 there are presented the spectra for a soluble residue from PES and the cyclic dimer of PES, obtained as detailed in Section 8.4. They are identical, and both conform to the expectation of two equally intense absorptions, at the τ values for methylene groups adjacent to an ester linkage ($\tau = 5.7$) and to a carbonyl group ($\tau = 7.3$).

(d) Infra-red absorption spectroscopy

In Figures 8.9, 8.10 and 8.11, there are presented the spectra of, respectively, high molecular weight FDA, the soluble residue from FDA, and the cyclic monomer of FDA. The spectrum of the polymer was obtained from a potassium bromide disc¹; that of the residue, from a paste; that of the monomer, from a liquid film.

The three spectra are very similar below 6500 nm.: changes in the breadth and complexity of the carbonyl stretching band at 5900 nm. might be due to the different sampling techniques used. None of the spectra show strong hydroxyl or carboxyl absorptions in this region. Above 6500 nm., there are marked variations in the band intensities.

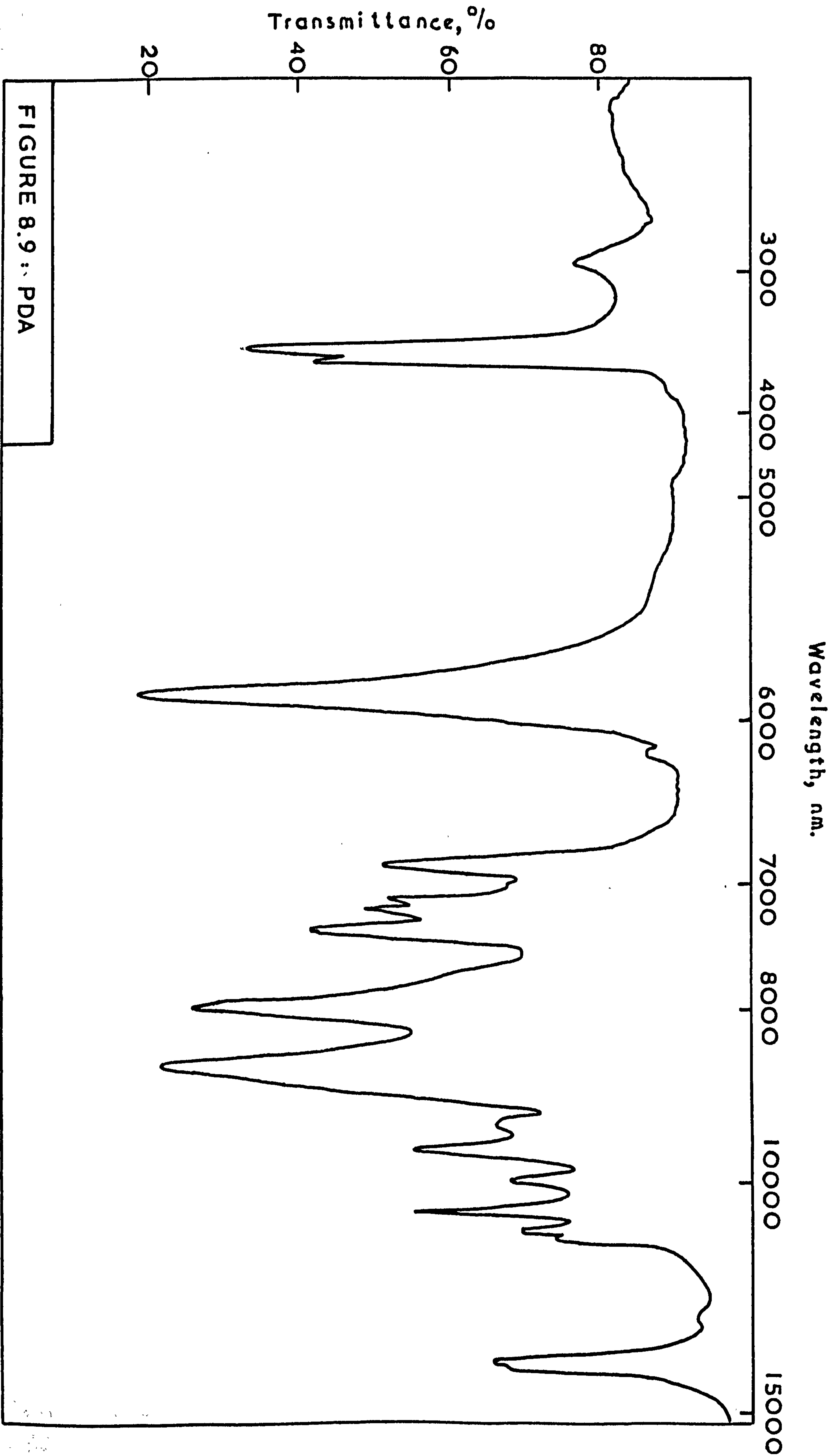


FIGURE 8.9 : PDA

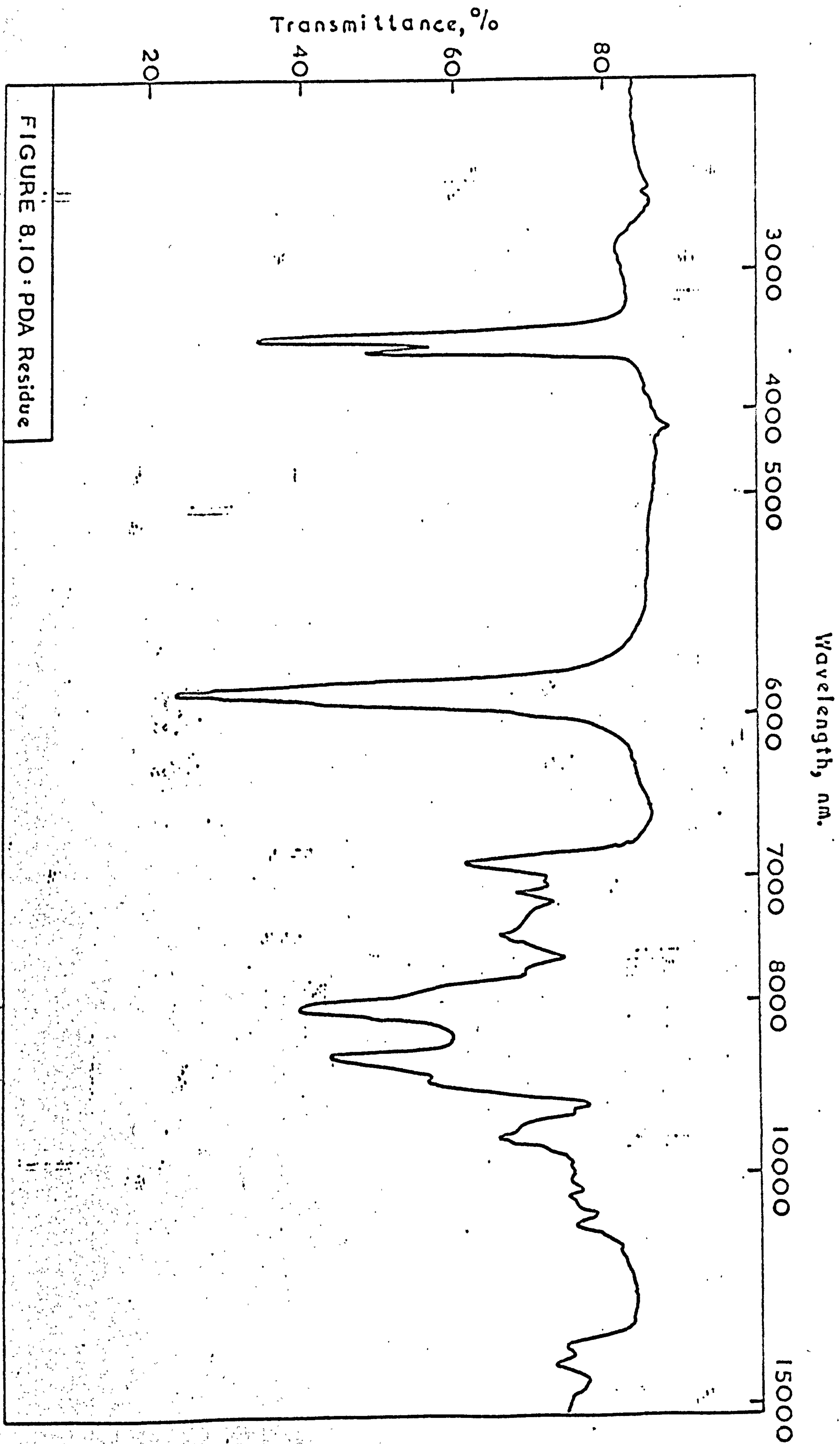


FIGURE 8.10: PDA Residue

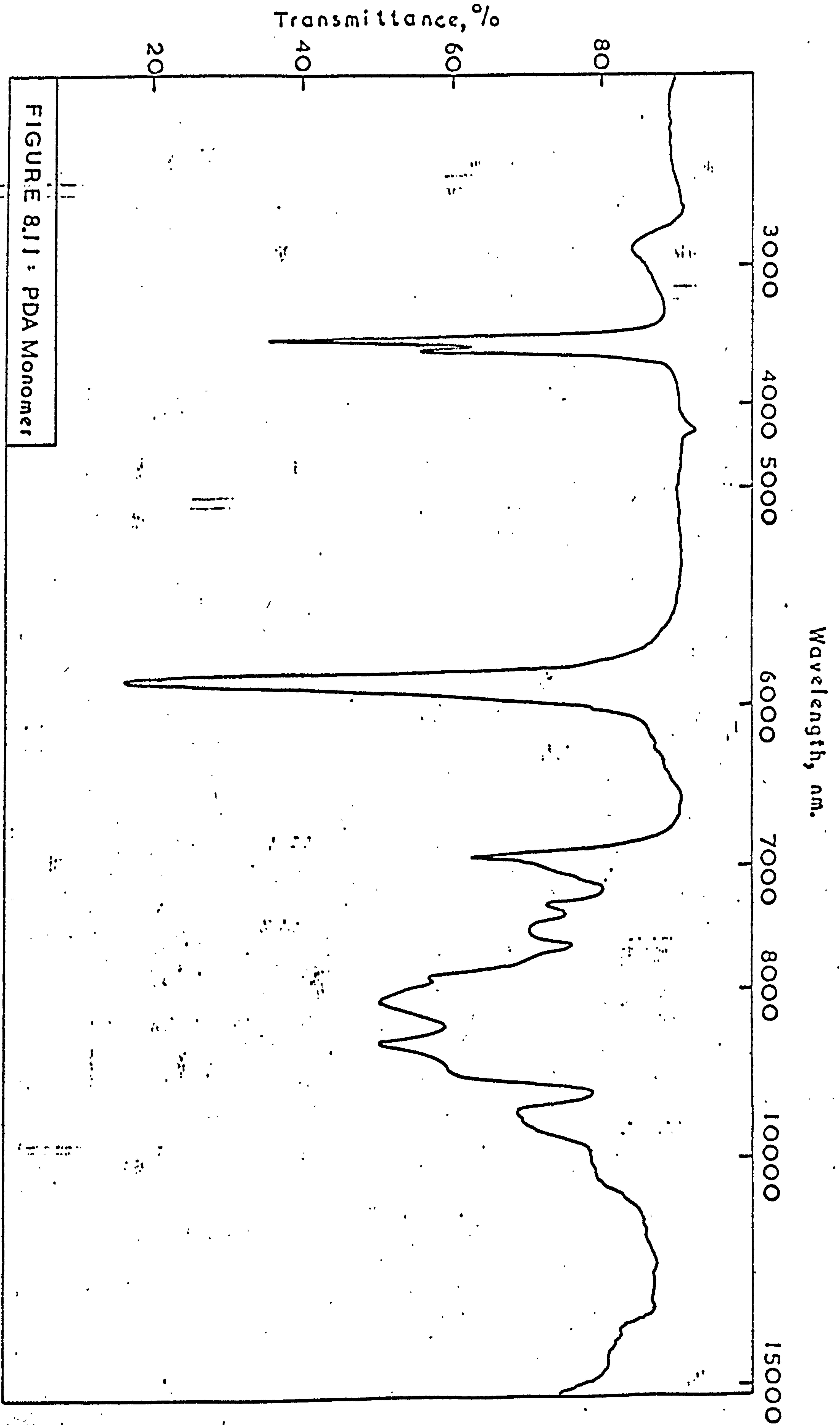


FIGURE 8.11 : PDA Monomer

Some of these disparities may be due to genuine chemical differences: for instance, the weak bands at 9250 and 9600 nm. may arise from traces of primary alcohol groups, and those at around 10000 and 11000 nm. from carboxyls⁶⁵. Such arguments do not, however, apply to the broad bands at 8000 nm. and 8600 nm. (probably attributable to CH₂ wagging modes⁶⁵). These absorptions appear in the spectrum of adipic acid, but not all in that of decamethylene glycol. Their striking growth (from monomer, to residue, to polymer) is very probably the result of conformational differences in the adipic acid residue, analogous to those already discussed for the ethylene glycol residues in the ethylene terephthalates (Chapter 4). The band at 7100 nm., which may be assigned to a CH₂-C=O deformation mode⁶⁵, also appears only in the spectrum of the acid, and is showing similar effects. Most of the other bands, too, are subject to parallel increases; but they cannot be so readily attributed to one residue, rather than the other.

The spectra shown in Figures 8.12, 8.13 and 8.14 are those for high molecular weight PES, a soluble residue, and the cyclic dimer. The residue was examined as a paste, the other compounds as discs. In all three cases there are only very slight hydroxyl or carboxyl absorptions. Once again, there are differences between the spectra above 6500 nm., possibly attributable to conformational factors.

The two soluble residues showed different degrees of absorption in the 2700 - 3800 nm. region. The first residue mentioned in (a) above gave rather intense carboxyl absorptions (Figure 8.15) while the second showed much lower intensities (Figure 8.16). For comparison, the spectrum of the cyclic dimer is presented over the same region. (Figure 8.17). The two residues behaved similarly in other respects, however.

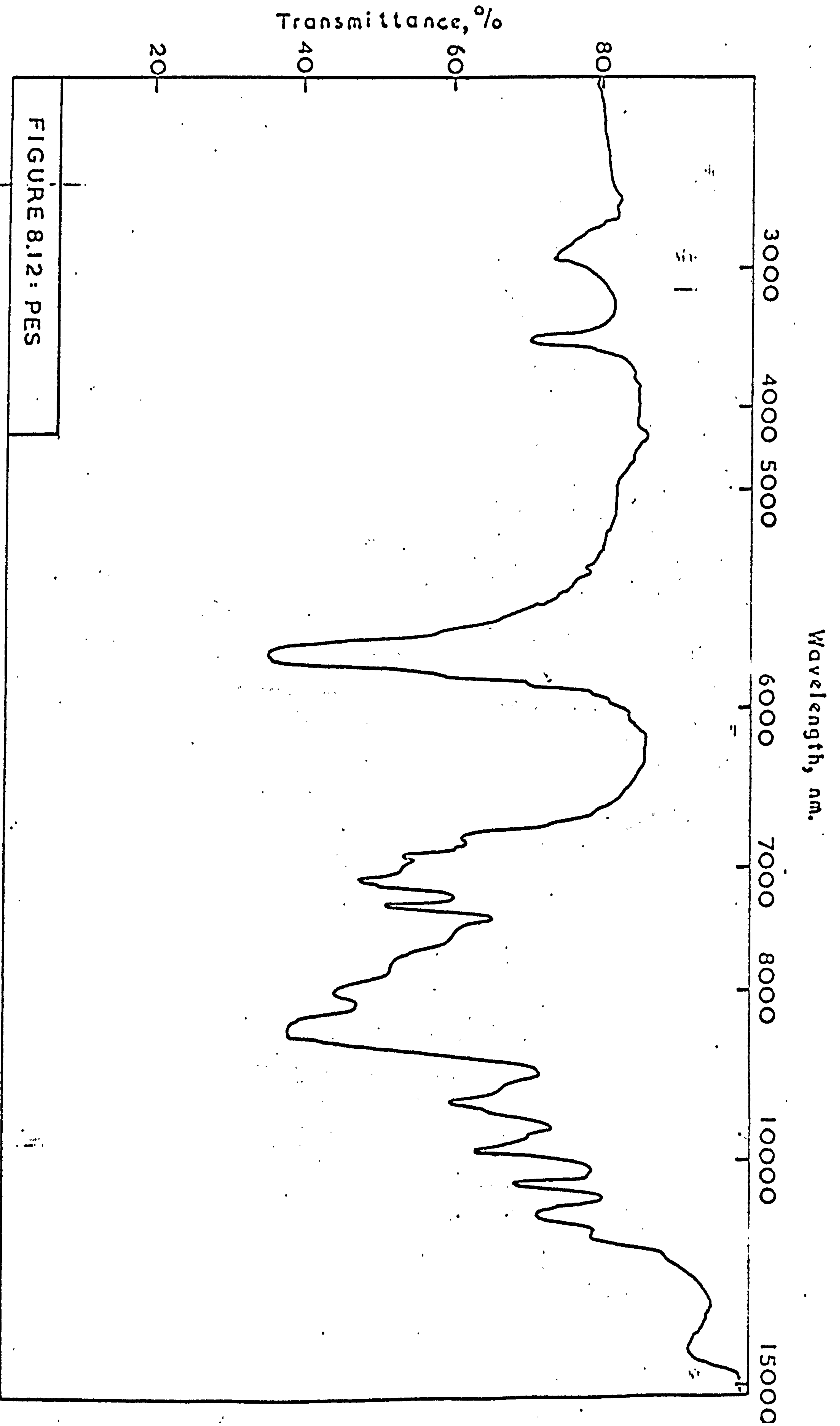


FIGURE 8.12: PES

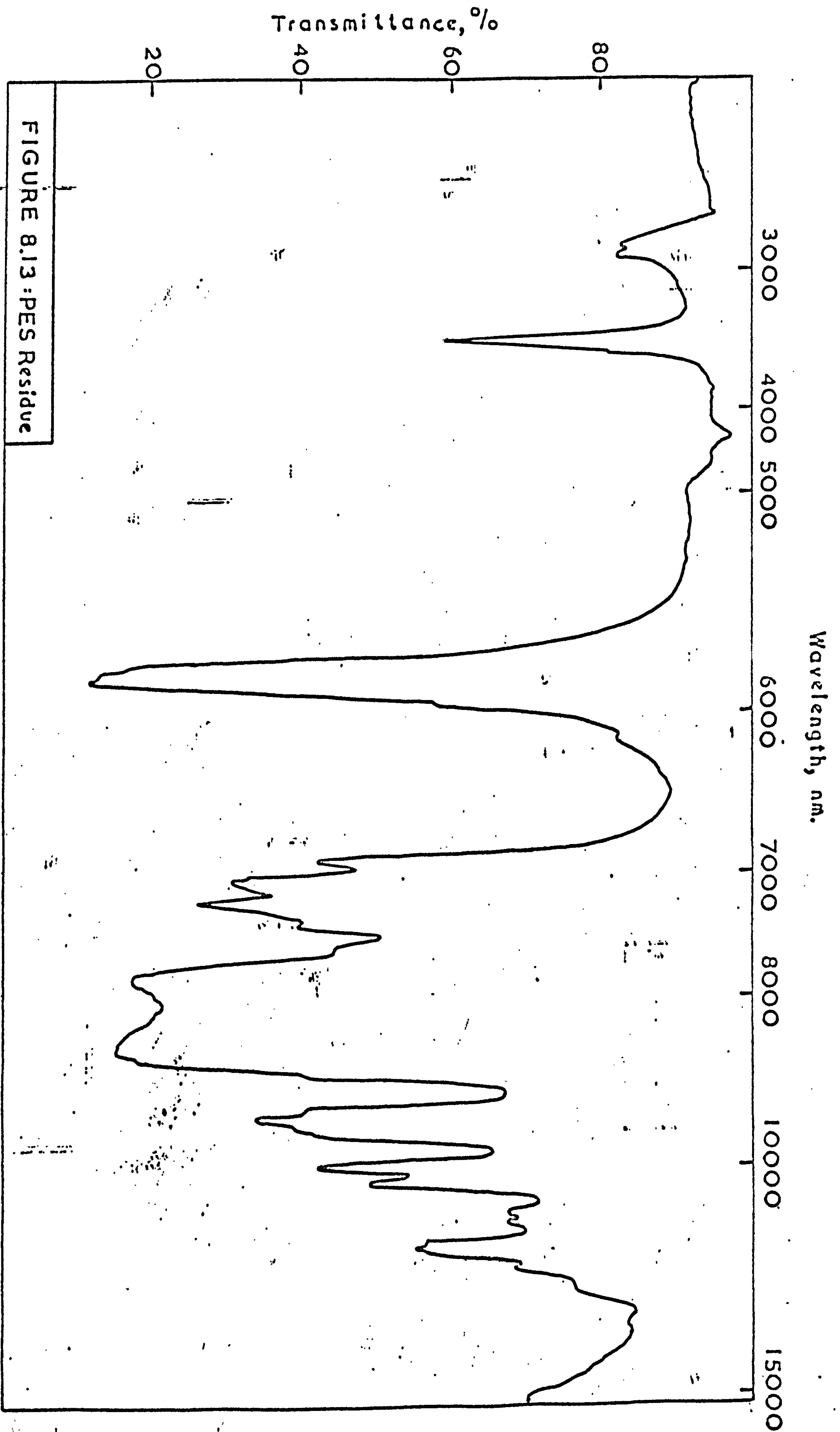


FIGURE 8.13 : PES Residue

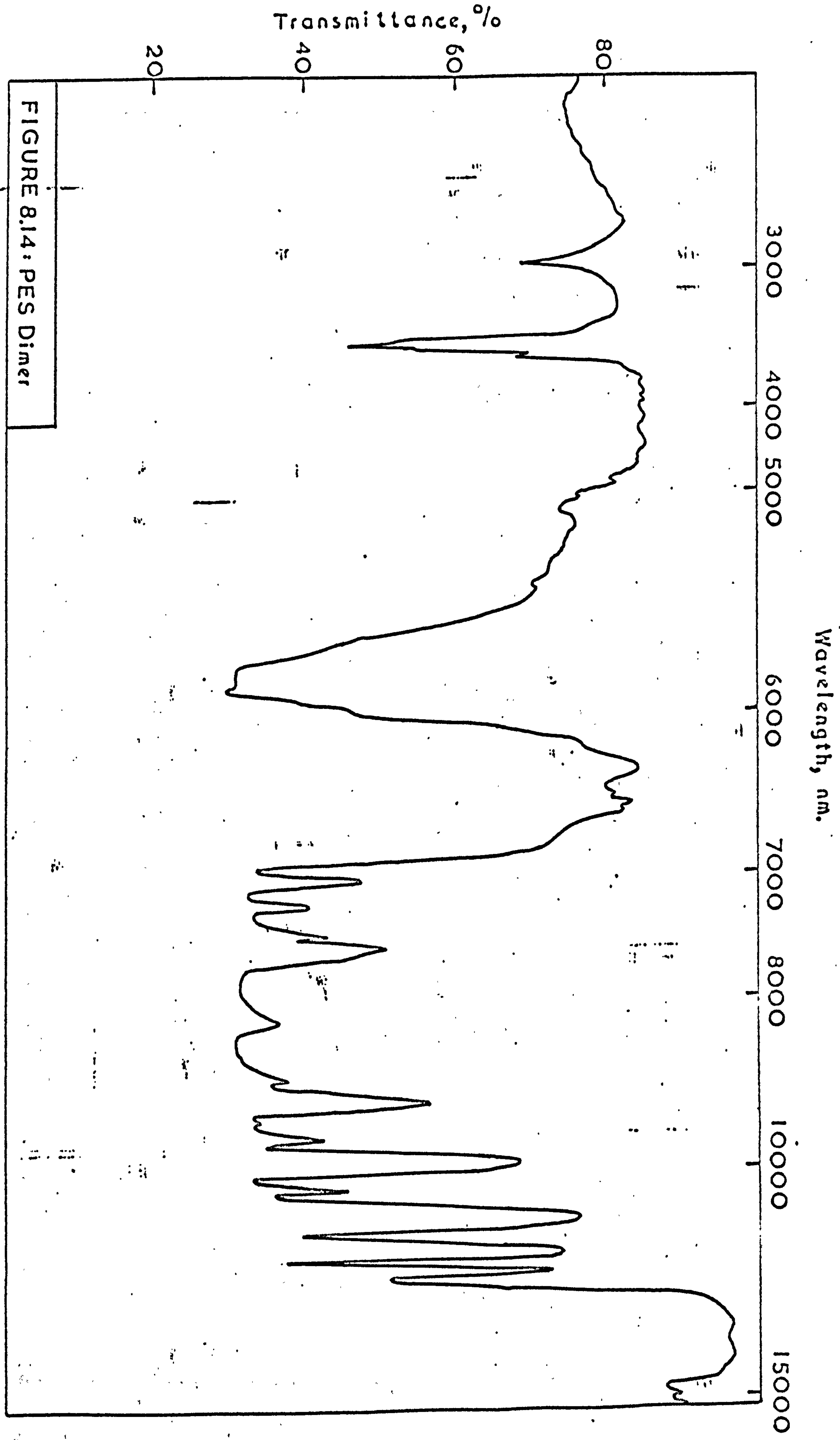


FIGURE 8.14: PES Dimer

% transmittance

20

40

60

80

2500

3000

3500

4000

5000

6000

wavelength, nm.

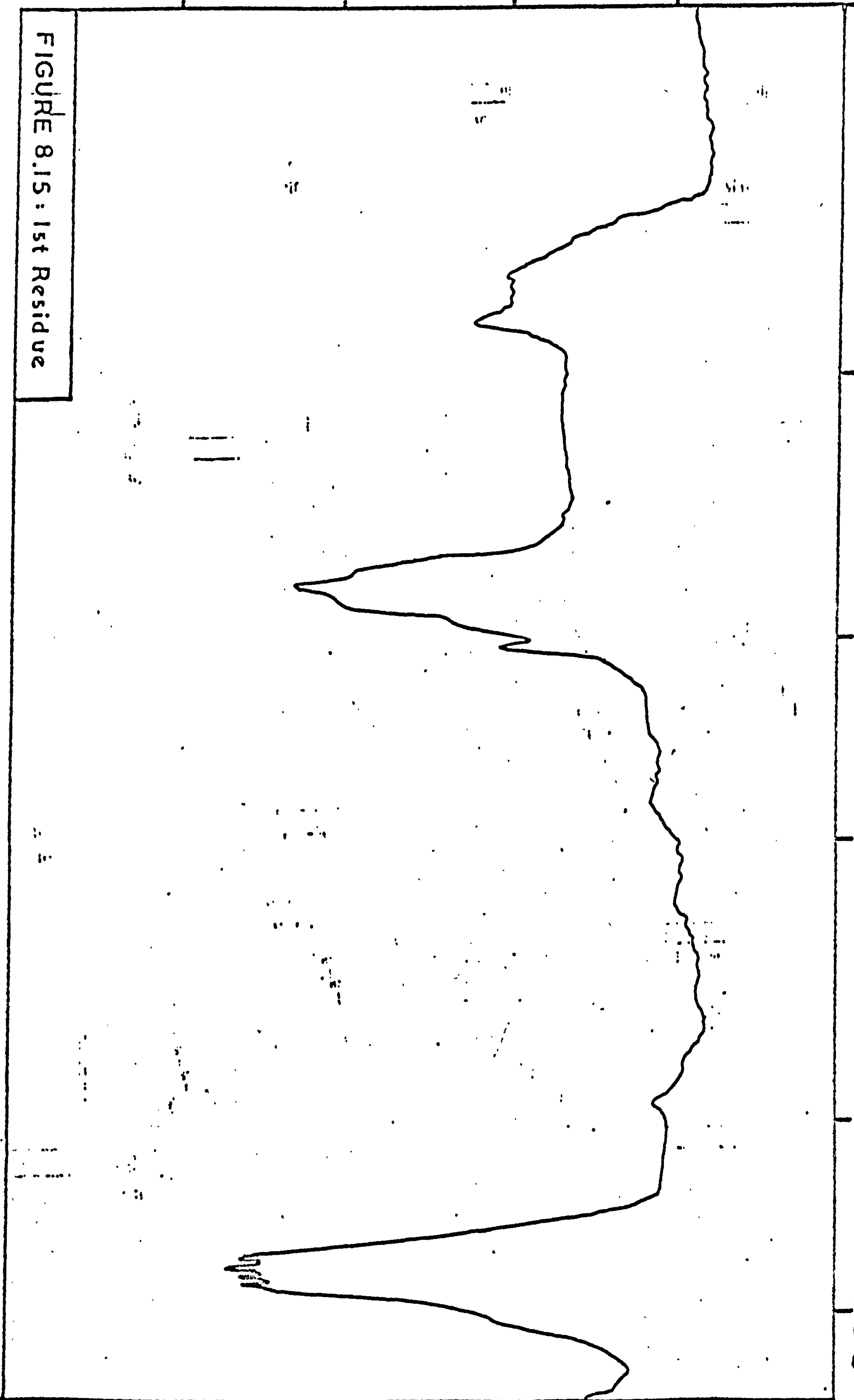


FIGURE 8.15 : 1st Residue

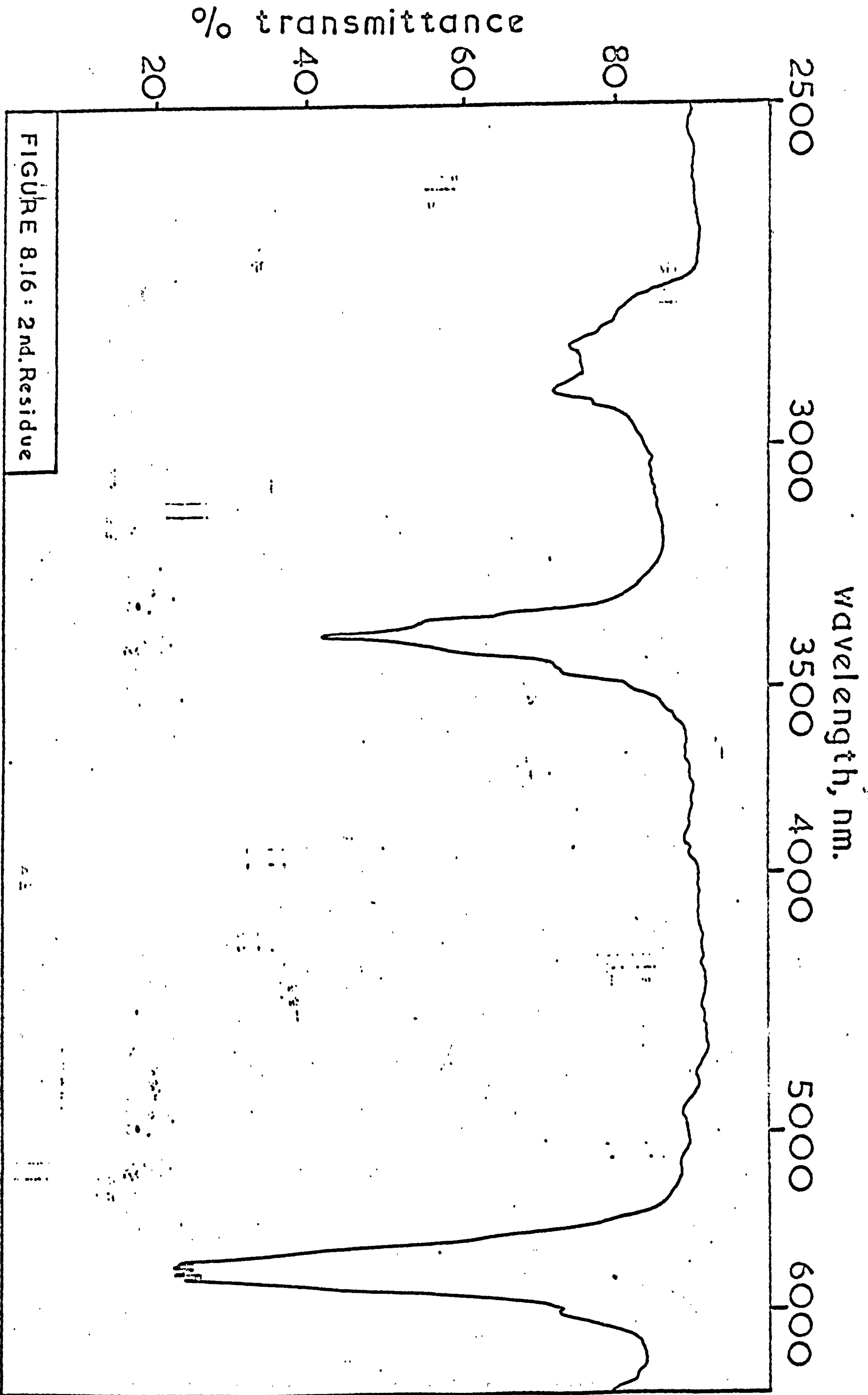


FIGURE 8.16: 2nd. Residue

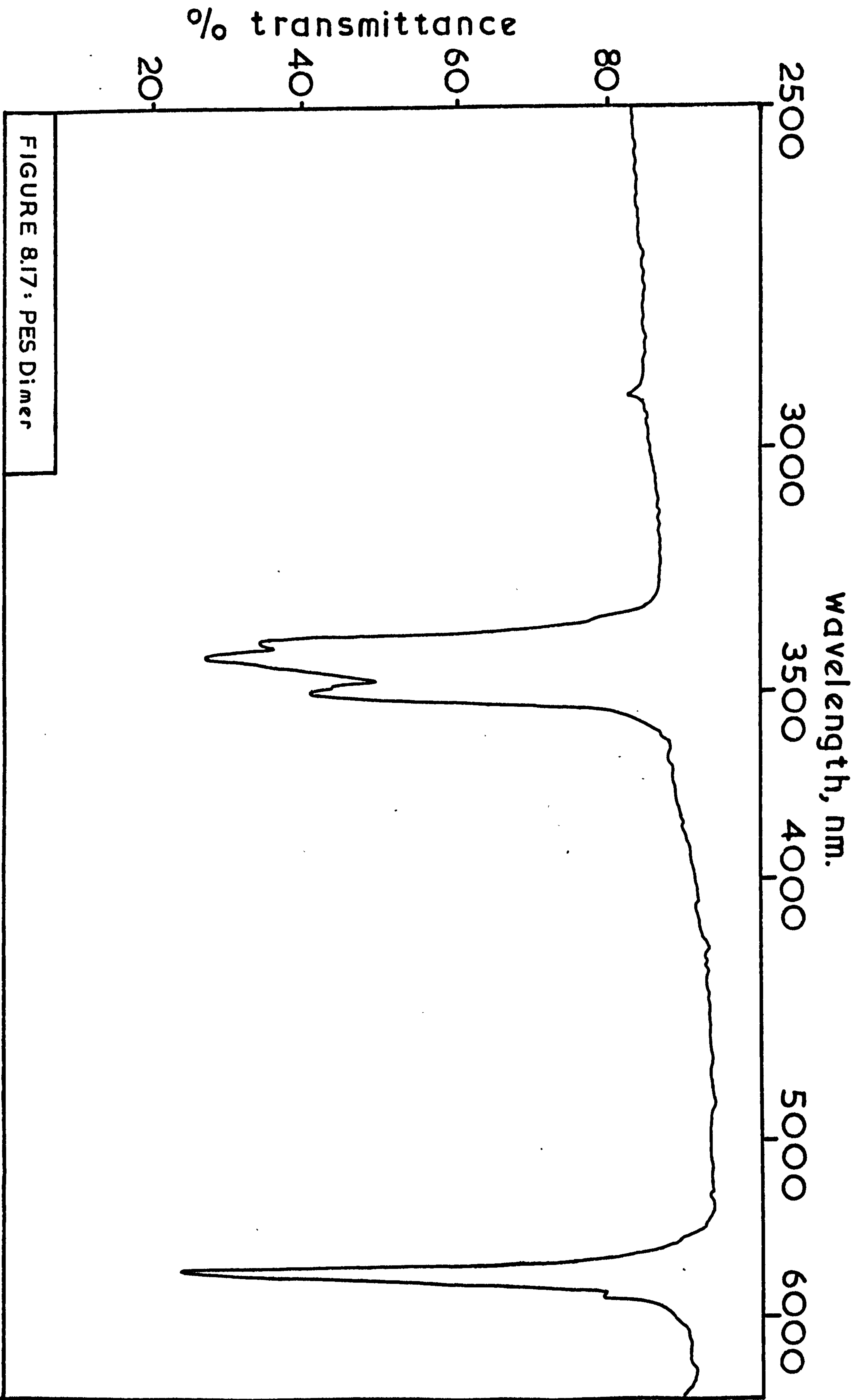


FIGURE 8.17: PES Dimer

(e) Gas-liquid chromatography

Injection of solutions of the PDA residue onto a 4' column packed with silanized Embacel carrying a 2% coating of OV-17, with the temperature programmed to start at 80° and increase at 4 deg./min., resulted in the emergence of two peaks, at 200° and 330°. With a higher programming rate, or using methyl silicone gum coatings, the peaks emerged later.

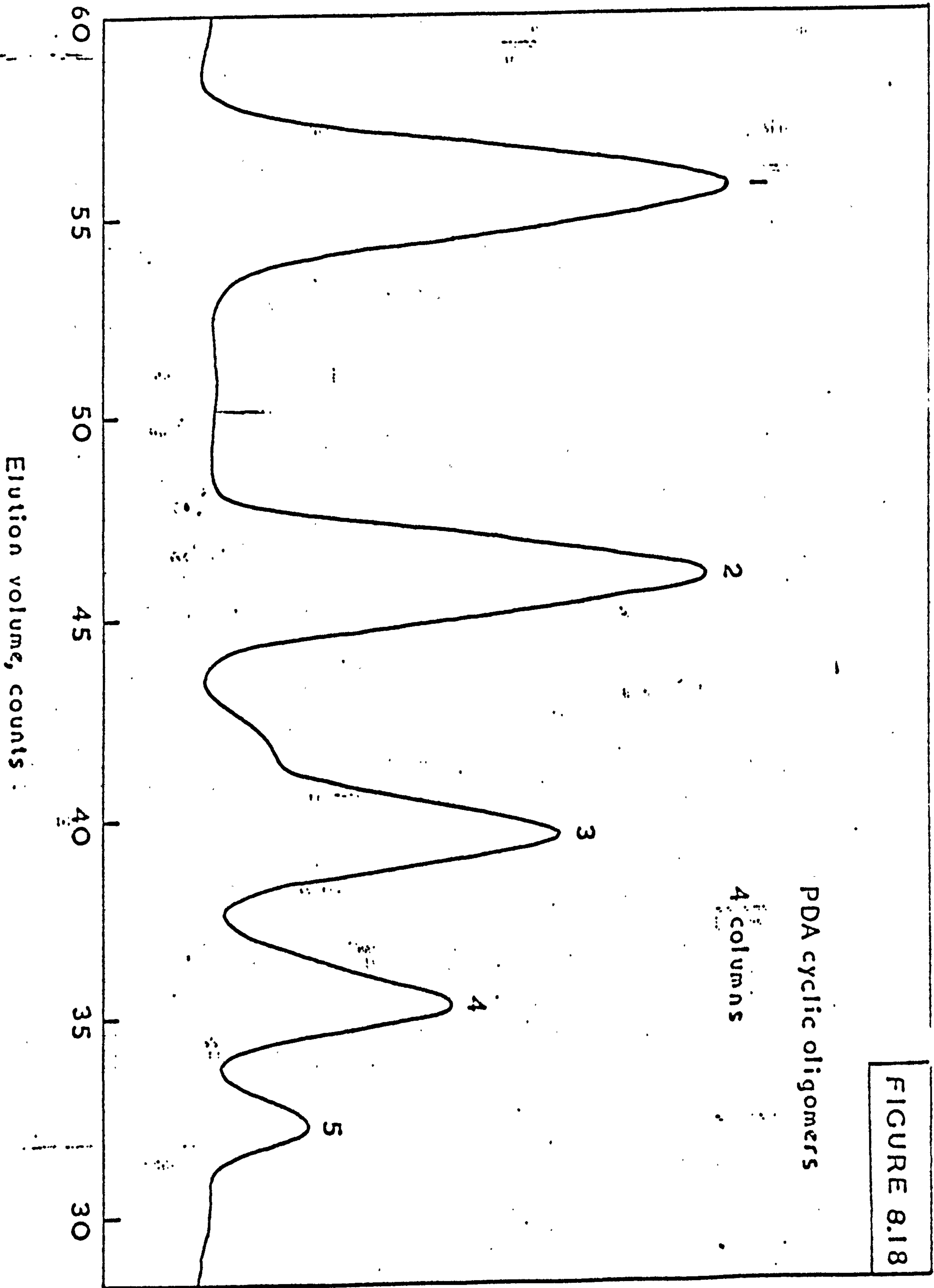
The residues from PES were not themselves analysed by g.l.c.; but in the following Section, references will be made to the use of this method to detect the components of a similar sample.

(f) Gel permeation chromatography

The analysis of two of the mixtures has been described fully in Chapter 3: they could be resolved completely into their component species. The final tracings obtained are reproduced in Figure 8.18 and 8.19. The chromatogram for the second of the PES residues, which was not discussed earlier, is given in Figure 8.20.

By injection of the pure substances, the peaks eluting last, other than the solvent impurity peaks, could be identified as the cyclic monomer, for the PDA residue, and the dimer, for the residues from PES. As noted before (Section 3.6, and also Section 4.2), straight-line calibration curves are obtained if it is assumed that the other peaks extend the series of oligomers. (Except for the slight curvature at the ends, shown also by the calibration for the PET oligomers.)

Recorder deflection



PDA cyclic oligomers

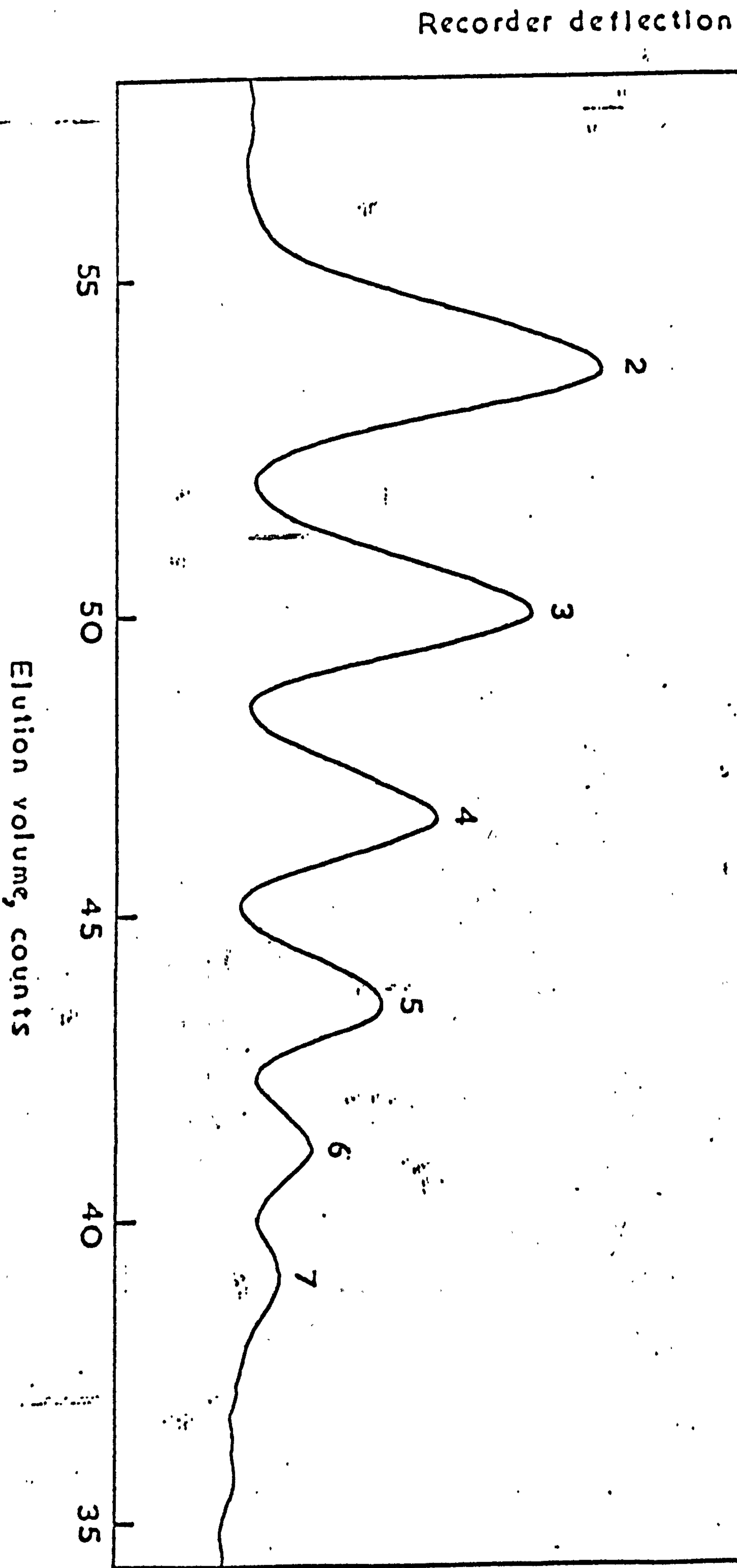
4 columns

FIGURE 8.18

Elution volume, counts

FIGURE 8.19

PES cyclic oligomers
4 columns



It must be acknowledged that the evidence available, to support the view that the residues consisted of mixtures of the cyclic oligomers, is less complete than that for the extracts from poly(ethylene terephthalate), presented in Chapter 4. Nevertheless, it was strong enough to act as a basis for further investigations.

Knowing the weight fractions of their polymers comprised by the residues, and assuming each species to be equally responsive, it is now possible to calculate the weight percentage of each cyclic in the original melts. Further, taking the densities of the melts to be $0.94(\pm 0.03)$ Kgm/dm^3 , for the PDA, and $1.06(\pm 0.02)$ Kgm/dm^3 , for the PES (see Section 8.5 below), these values may be converted to molarities. The results are given in Tables 8.2 and 8.3, and the molarities are also plotted logarithmically in Figures 8.21 and 8.22. It must immediately be emphasised, however, that these concentrations are not necessarily those at equilibrium between the rings and the chains; not only because of too slow a generation of cyclics during the polymerisation, but also because of sublimation of the lower members in the vacuum stage. Further, the concentrations themselves and especially those of the higher range, may be in error through incomplete extraction from the polymer.

X	Amount of x-meric cyclic:	
	Weight %	Molarity, $\times 10^2$
1	0.44	1.47
2	0.36	0.61
3	0.28	0.31
4	0.17	0.14
5	0.06	0.04

Table 8.2

X	FIRST RESIDUE		SECOND RESIDUE	
	Amount of x-meric cyclic:		Amount of x-meric cyclic:	
	Weight %	Molarity, $\times 10^2$	Weight %	Molarity, $\times 10^2$
2	1.24	4.57	0.73	2.69
3	0.88	2.16	0.72	1.76
4	0.53	0.98	0.46	0.86
5	0.35	0.52	0.30	0.45
6	0.20	0.25	0.10	0.13
7	0.12	0.13	0.05	0.05

Table 8.3

Apart from the values for the dimer, probably affected by sublimation losses, the results for the two PES residues are quite close to each other; this may indicate that they are in fact not very distant from the equilibrium case.

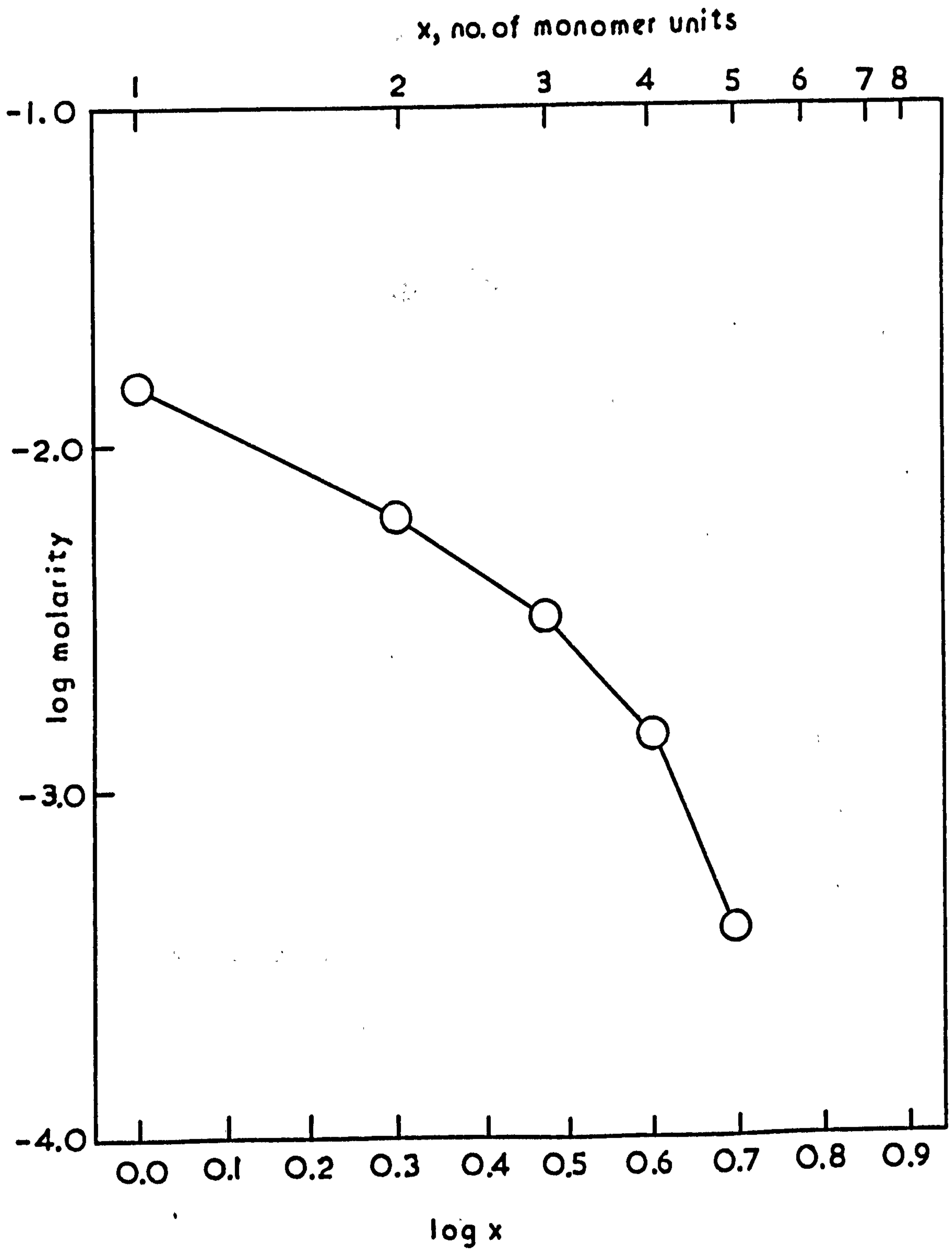


FIGURE 8.21

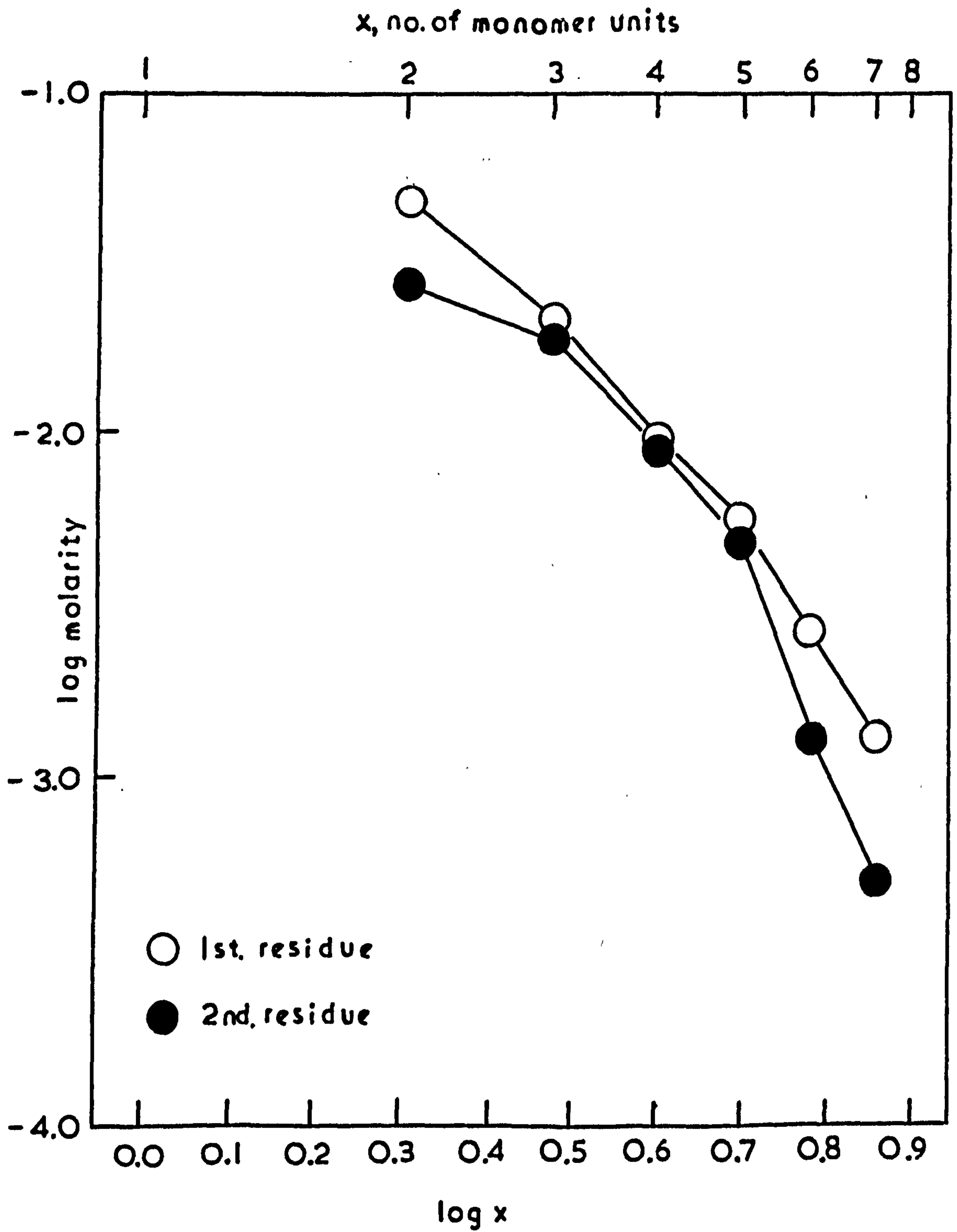


FIGURE 8.22

8.4 PREPARATION OF PURE CYCLIC OLIGOMERS

The cyclic dimer of PES, and the cyclic monomer of PDA, both referred to previously, were obtained by pyrolysis of the polymers by the method of Carothers^{2,3}. The reaction was carried out in the large-scale molecular still represented in Figure 8.23.

20 - 30 gm. polymer, mixed with 2.5% magnesium chloride hexahydrate, to act as catalyst, were put in the still, and it was set up as shown. The apparatus was evacuated to below 0.05 mm., and slow heating was applied; care was necessary to prevent the polymer from bubbling up onto the cooled probe. The temperature was raised over 8 - 12 hours to 270°, and held there for 30 - 40 hours, during which period sticky, yellow sublimate collected on the probe. The heating was discontinued, and the still allowed to cool; then the vacuum lead was closed off, and air re-admitted. The sublimate was removed from the probe, and the charred mass in the still was dissolved out by heating with strong nitric acid.

The sublimates were treated as follows:

(a) For poly(ethylene succinate)

The sublimate, comprising 60% of the polymer, gave two peaks during g.l.c. under the conditions mentioned in (e) in Section 8.3: the first emerged at 210°, the second at 320°. It was made up as a 5% solution in chloroform, and washed several times with water, to remove any traces of catalyst: residual moisture was removed as azeotrope by rotary evaporation at room temperature. To decolourise the solution,

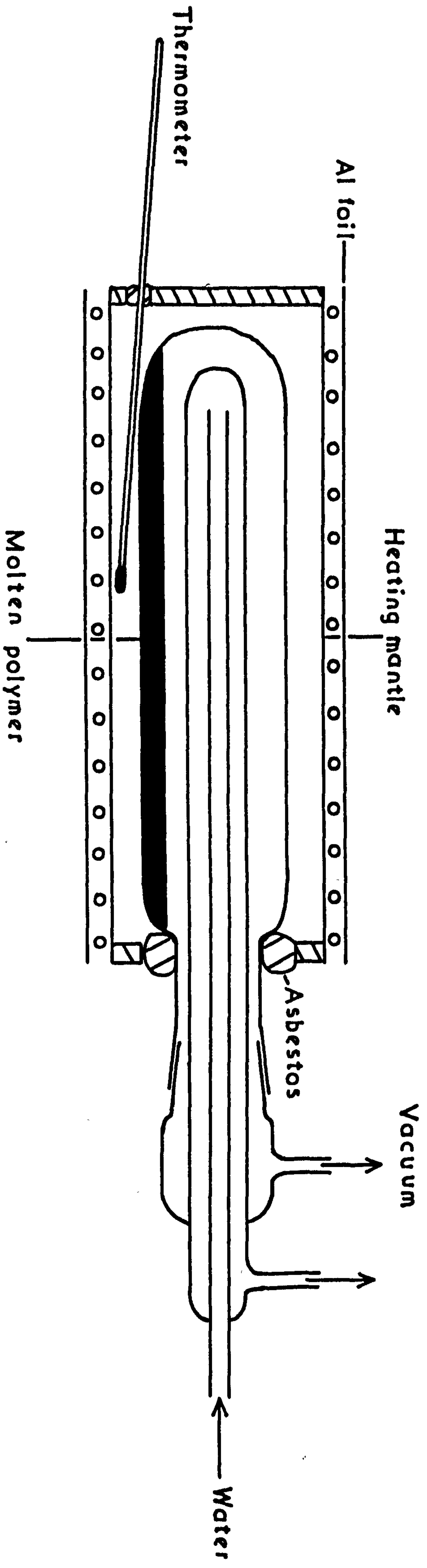
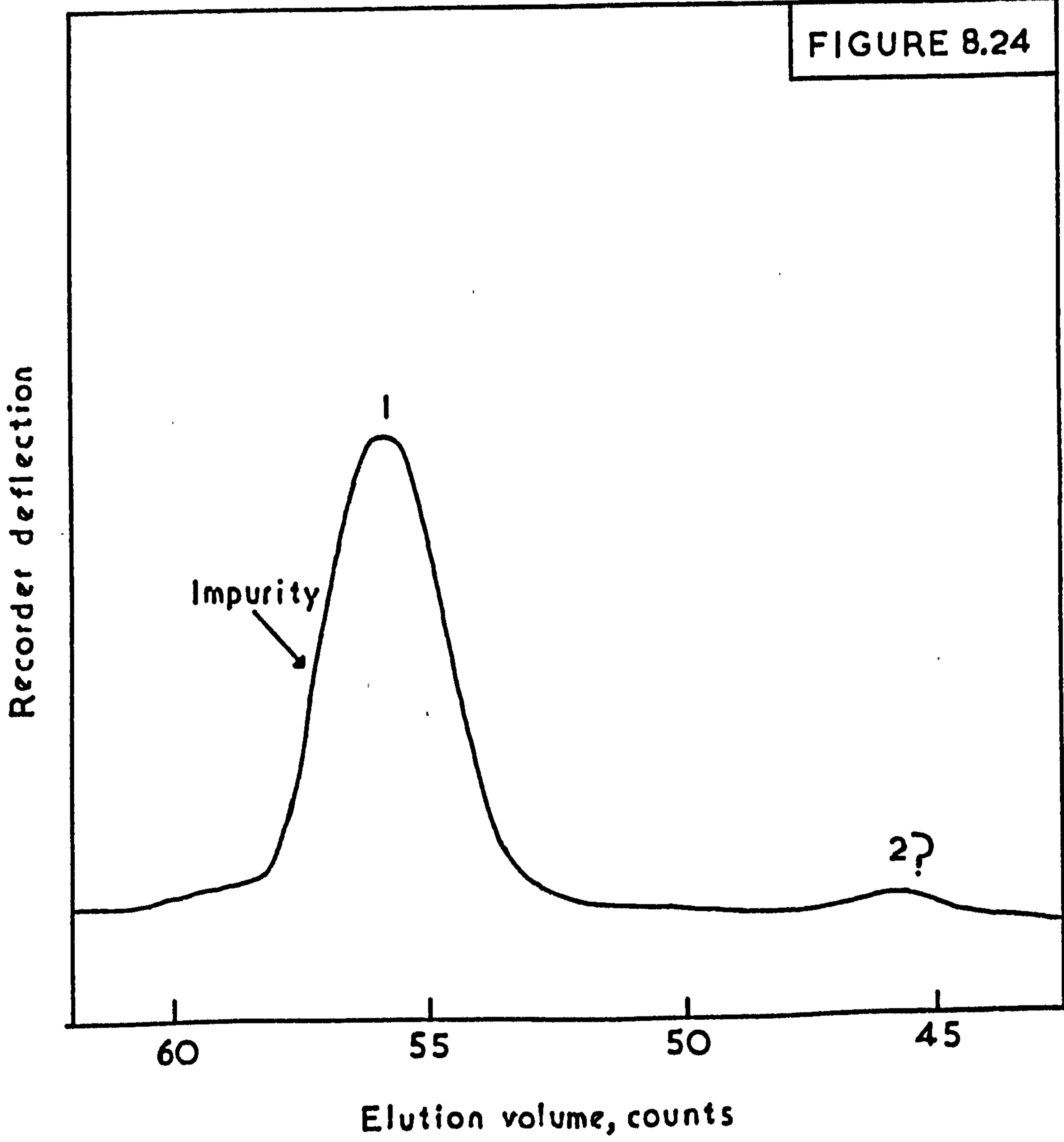


FIGURE 8.23

FIGURE 8.24



it was stood overnight with active carbon; but this was not found to be effective. The solution was filtered, and rotary evaporated at 30° , almost to dryness; when methanol was added, and the remaining chloroform taken off as azeotrope. After sufficient concentration, the solution was cooled, first on the bench, then in ice; large, well-formed crystals appeared, were filtered off, washed with a little ice-cold methanol, and air-dried. The mother-liquors were concentrated further, but gave only a yellow syrup which would not crystallise unless left to stand for some weeks.

The solid deposited from solution gave only the first peak in g.l.c., and melted at 127° . A further recrystallisation from methanol gave attractive white plates, melting at $129.0^{\circ} - 129.5^{\circ}$ (Carothers' melting point for the cyclic dimer of PES: 130°). It was pure by g.l.c. and g.p.c. Elemental analysis gave: carbon, 50.10%, hydrogen 5.45%. (Calculated: 50.00% and 5.56%) The molecular weight was 266 (± 15). (Calculated: 288). The solid gave the infra-red and n.m.r. spectra discussed in Section 8.3. Yield was about 20% of the starting polymer.

The yellow syrup gave the second peak in the g.l.c. (probably that of the cyclic trimer), but many other smaller peaks as well. It was not examined further.

(b) For poly(decamethylene adipate)

Again, the sublimate, 50% of the polymer, was dissolved in chloroform and washed, and the solution then evaporated down. The semi-solid material was dissolved in warm methanol, and the solution was concentrated: on cooling, a small amount of white solid appeared. This was filtered off; its properties suggested that it was low

molecular weight polymer. The solution would not immediately crystallise upon further concentration, and so was evaporated to dryness: on brief standing it turned to a fairly fluid semi-solid. It was left overnight, and then filtered. The white solid left in the filter (about an eighth of the mixture) was thoroughly washed with methanol, and air-dried. From its infra-red spectrum and melting point it was identified as α decamethylene glycol. The yellow filtrate, 35% of the polymer, was formulated as a cyclic decamethylene adipate on the basis of its spectroscopic properties (see Section 8.3); the supposition that it was the monomer is supported by the findings of Carothers^{2,3} on the favoured sizes of the rings formed by his method. It was shown by g.p.c. to be pure, except for a small amount of a low molecular weight material (probably decamethylene glycol) and also of another substance, probably cyclic dimer. (Figure 8.24).

8.5 EQUILIBRATION OF ALIPHATIC POLYESTERS

For both of the aliphatic polyesters under discussion, attempts were made to prepare samples in which proper ring-chain equilibria had been set up: but none were successful.

(a) Poly(decamethylene adipate)

The polymer, mixed with 0.5% p-toluene sulphonic acid catalyst, was sealed in ampoules under vacuum. The ampoules were heated at 130°: one for 48 hours, a second for 96 hours, a third for 120 hours. At the end of the set periods, the ampoules were removed from the heater: the

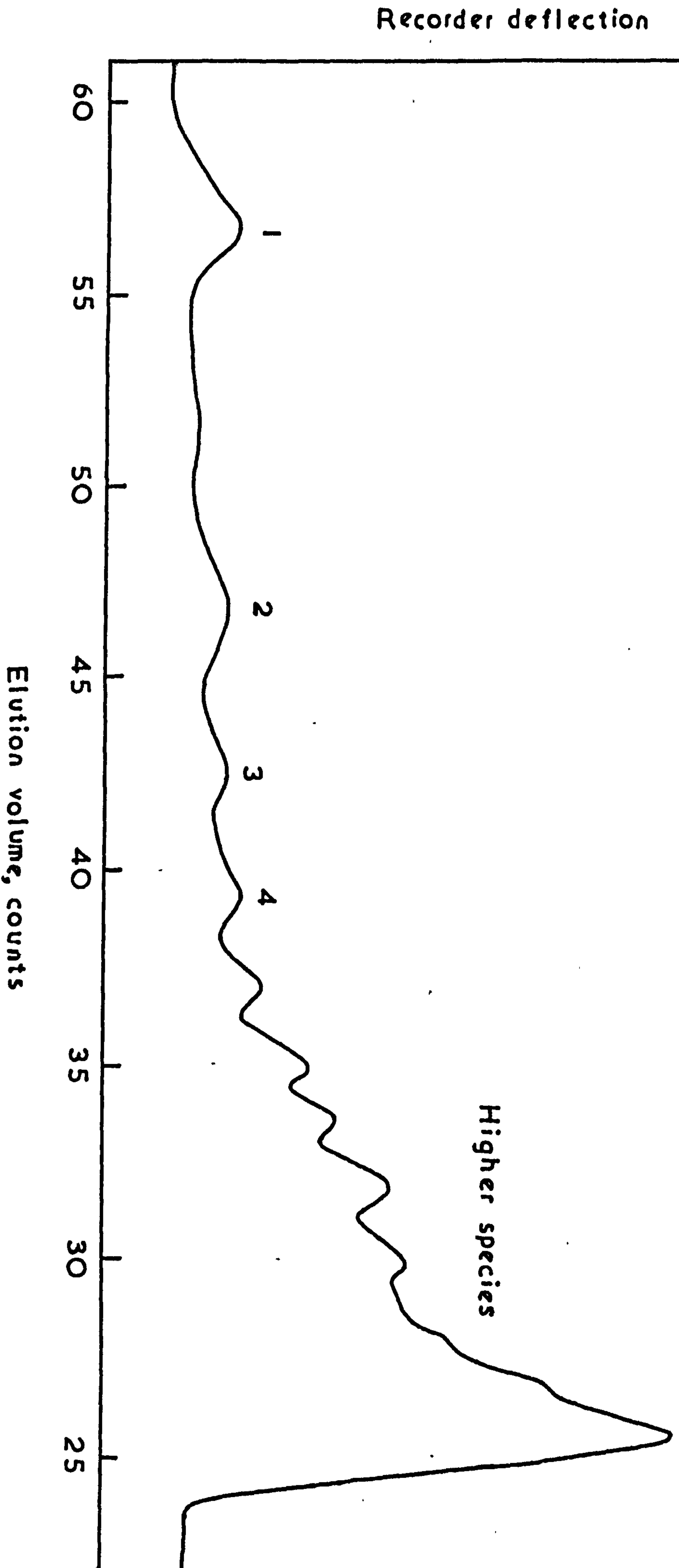


FIGURE 8.25

level of the melt in each was at once marked. The ampoules were left to cool, and were then opened, and weighed. The polymer lump in each was dissolved out with chloroform over 1 - 2 days, the resulting solutions having concentrations of around 10%; they were poured into three times the volume of ice-cold diethyl ether, stood at 0° overnight, and then filtered. The solid polymer was redissolved, and precipitated again; this was repeated twice more. The filtrates from the four precipitations were combined, and evaporated down to give low molecular weight extracts from each sample. The weights of the polymer were found by difference, by weighing the empty ampoules; the density of the melts was determined by weighing the volume of water at room temperature needed to fill the ampoules to their marks. (It was 0.94 (\pm 0.03) Kgm/dm³).

The extracts comprised 3.2%, 3.4% and 4.7% of the polymers for the 48, 96 and 120 hour runs, respectively. Examination by g.p.c. however, at once revealed that they contained only very small amounts of the cyclics observed in the residue from the polymer preparation, and seemed to consist largely of chain species. The tracing for the extract from the 120 hour run is given in Figure 8.25; those for the other extracts were similar.

(b) Poly(ethylene succinate)

The procedure used in trying to equilibrate the polymer in the melt was closely similar to that described above. Two samples, heated for 48 and 96 hours, gave extracts of 3.75% and 3.29% by weight. The g.p.c. tracings for the extracts are given in Figures 8.26 and 8.27. For

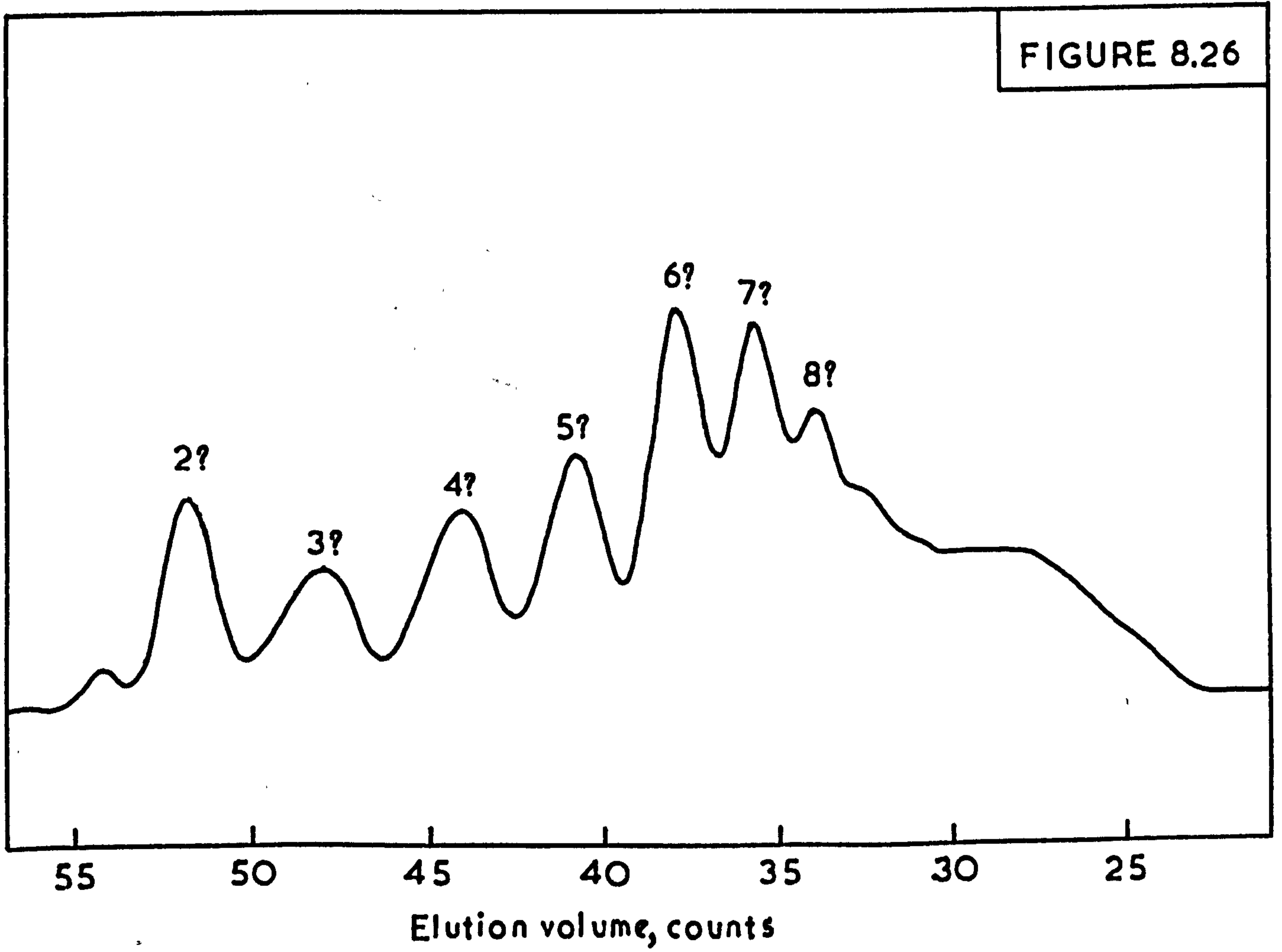
this polymer, substantial proportions of the cyclics were formed; assuming, that is, that the main peaks are indeed those of the rings. The distributions of species are curious: even allowing for apparent elevation of the amounts of the higher rings through the simultaneous elution of short chains, they are greater than would be expected, relative to the lower cyclics (trimer, tetramer, etc.). Changes had clearly taken place between the two runs, and so neither can be regarded as having reached equilibrium; the results are therefore quite inconclusive.

The density of the melts had been determined as $1.06(\pm 0.02)$ kgm/dm^3 .

A number of experiments were performed to bring this polymer to ring-chain equilibrium in sym-tetrachloroethane solution, at 130° . These met with no greater success than those for the melts: many of the extracts contained considerable amounts of chain, and gave g.p.c. tracings resembling those for PDA heated in the bulk, discussed above; others gave distributions like those of the soluble residues dealt with in the earlier Section, but invariably showing contamination with extraneous materials. The concentrations of the rings found for each sample are subject to such large uncertainties, and show such a lack of consistency, that they do not merit detailed presentation: but it will be noted that, on the whole, the amounts of the rings were less than those for the soluble residues. (Although the concentrations of the higher rings could certainly appear greater, if the extract was contaminated with linear species). These observations are compatible with the view that all the samples had incompletely equilibrated.

FIGURE 8.26

Recorder deflection



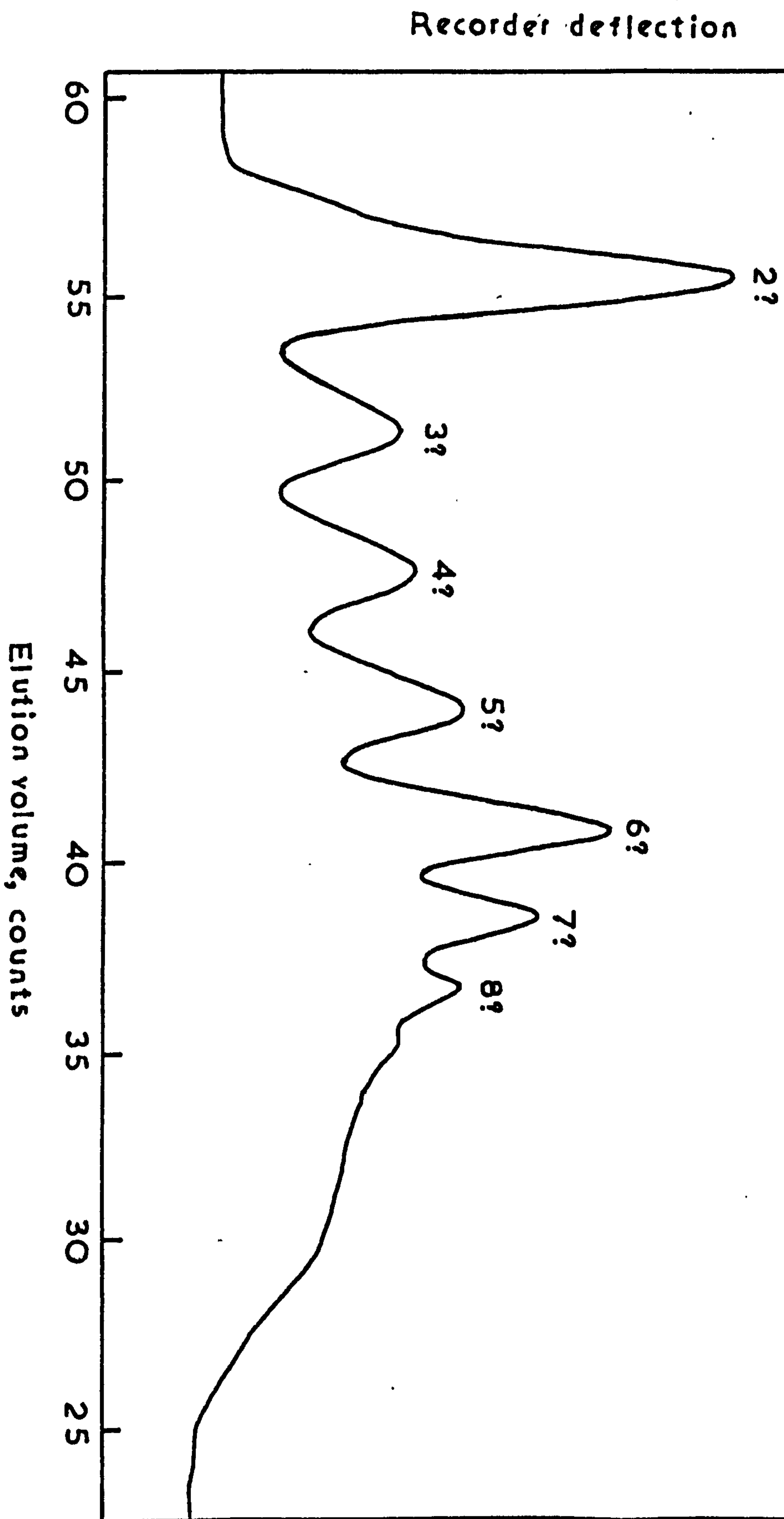


FIGURE 8.27

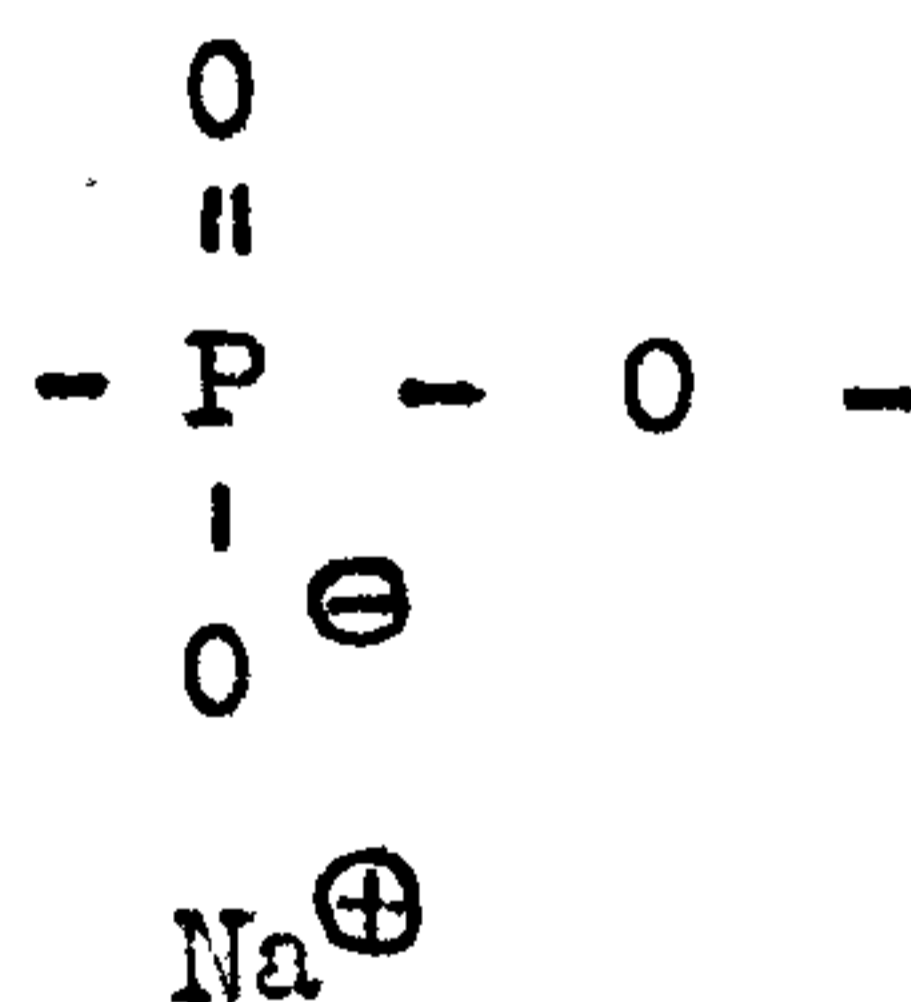
These findings are in complete contradiction to those of Jacobson, Beckman and Stockmayer¹⁸ on the equilibration of PDA, successfully carried out at the same temperature, and using the same catalyst; they found that, even though working with solutions, equilibrium was attained within far shorter periods than those employed here, and furthermore state that the process was readily reversible. It is possible that the particular batch of catalyst used here was faulty; or perhaps there were differences in the polymer itself, and especially in the end-groups it carried, arising from the use of tetraisopropyl titanate as polyesterification catalyst, rather than the p-toluene sulphonic acid upon which the earlier workers relied. Again, all the previous studies were of chlorobenzene solutions; it is at least conceivable that the bond interchange rates are higher in this solvent. Even having regard to all such considerations, however, the reasons for this persistent failure of the aliphatic polyesters to properly equilibrate remain unclear.

CHAPTER 9.

ROTATIONAL ISOMERIC STATE MODEL OF POLYPHOSPHATE
CHAINS IN SODIUM PHOSPHATE MELTS

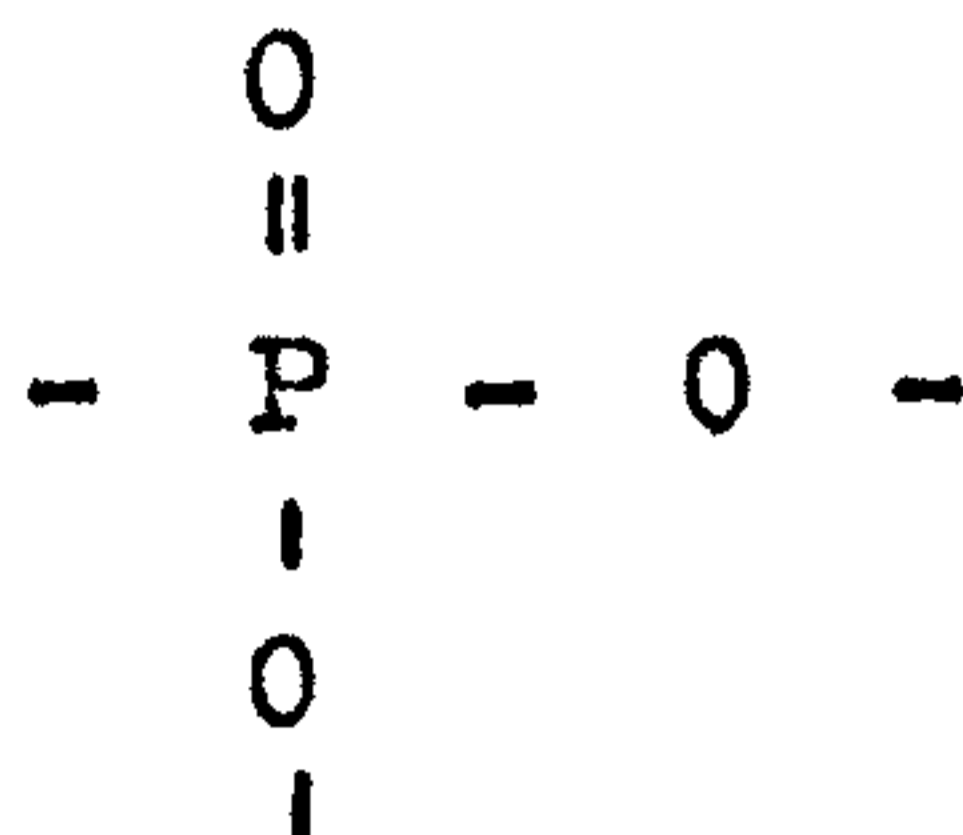
9.1 INTRODUCTION

If sodium dihydrogen phosphate, NaH_2PO_4 , is heated for many hours at just below 1000K, and the molten mass is then rapidly chilled between metal plates, there results a glass-like product of empirical formula NaPO_3 , known as "Graham's Salt"^{96,97,98}. Similar products, but with a range of composition, can be obtained by the use of such mixtures as those of sodium carbonate and phosphoric acid, or sodium oxide and phosphorus pentoxide⁹⁷. In both cases, many investigations⁹⁹⁻¹⁰² have shown the glasses to consist of polyphosphate chains of repeat unit:



together with small amounts of cyclic "metaphosphates", $(\text{NaPO}_3)_x$, $x \gg 3$. For Graham's Salt, the chains are terminated with - OH and - H groups, derived from the residual traces of water, and the number average degree of polymerisation often exceeds a hundred. In glasses where the mole ratio phosphorus : sodium is less than unity, the chains are shorter, and are terminated with - ONa and - Na ; while in those where

the ratio is greater than unity, the chains possess occasional branches:



and the material is a cross-linked matrix⁹⁷.

Measured concentrations of the trimeric to heptameric metaphosphates in polyphosphate glasses have been reported^{27,28}. Also, an attempt has been made to account for the experimentally determined unperturbed dimensions of polyphosphate chains^{103,104} by a rotational isomeric state model¹⁰⁵. The calculations presented here were undertaken with the purpose of reconciling the known ring concentrations with the structural and conformational characteristics of the polyphosphate chains. For this to be possible, it was first necessary to modify the rotational isomeric state model to pay regard to (amongst other things) the differences between the chemical environment in the phosphate melt, and that in which the dimensions had been determined. This revision of the model is presented in this Chapter. In the succeeding Chapter, the application of the adjusted model to the calculation of the metaphosphate concentrations will be described.

9.2 THE MODEL OF SEMLYEN AND FLORY

Strauss and his co-workers^{103,104} have examined the chain dimensions of linear polyphosphates in aqueous solution. The cations dissociate from the phosphate units, and in pure water long-range electrostatic repulsions between the units cause the chain to adopt highly extended conformations. In the presence of the correct concentrations of supporting electrolyte, however, the long-range interactions may be eliminated, so that the dimensions of the chains come under the exclusive control of local conformational factors. Such θ - conditions were selected for the measurement of the characteristic ratios, $\langle r^2 \rangle / n\ell^2$, of several polyphosphates. (Where $\langle r^2 \rangle$ is the mean square end-to-end distance of a chain of n bonds, each of length ℓ , taken in the limit of high molecular weight). The ratio was found to be 6.6 for sodium polyphosphate in 0.415 M sodium bromide at 298K, and 7.1 and 7.2 for two lithium polyphosphates in 1.80 M lithium bromide at the same temperature.

The rotational isomeric state model of Semlyen and Flory¹⁰⁵ was intended to give a theoretical interpretation to these results. In the model, account is taken of the effect upon chain conformation of both steric and electrostatic factors.

It is assumed that the polyelectrolyte is fully dissociated, and that the presence of the counter-ions in no way affects the conformations. A segment of the chain may then be represented simply as in Figure 9.1. The atoms carry different partial electronic charges, given by Pauling¹⁰⁶ as +0.9 for a phosphorus, -0.3 for a skeletal oxygen, and -0.8 for a pendant oxygen. From X-ray crystallographic

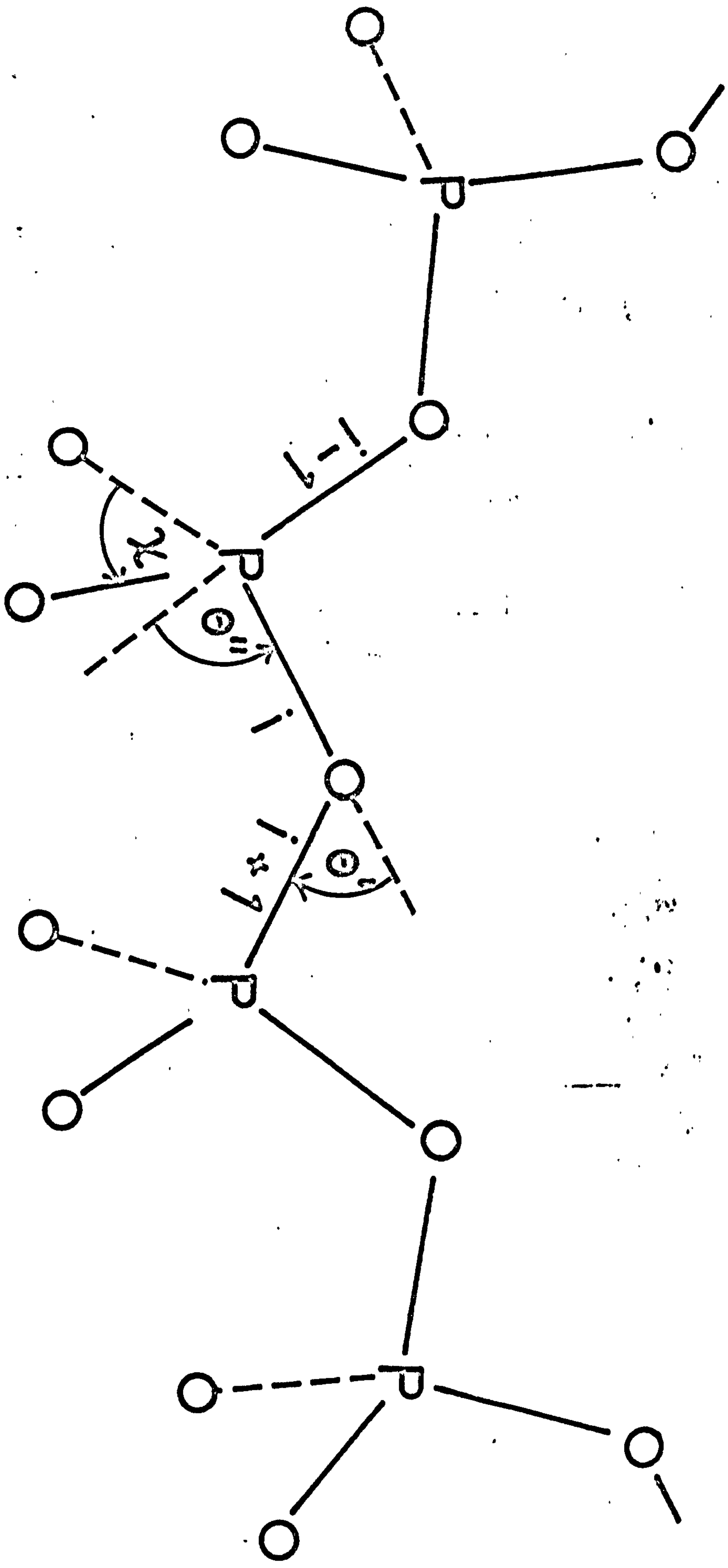


FIGURE 9.1

studies, the following data are available:

The skeletal bond length, ℓ , is 1.62 Å.

The bond angle supplement at oxygen, θ' , is 50° .

The bond angle supplement at phosphorus, θ'' , is 78.5° .

The length of a bond connecting a pendant oxygen to its phosphorus, ℓ_p , is 1.48 Å.

The angle, χ , between two such bonds is 121° .

Each bond is attributed three rotational states: trans (at rotation angle = 0°) and gauche \pm (at $\pm 120^\circ$). There are some reasons for believing that the intrinsic rotational potentials for this chain are so low that they hardly define discrete physical states; the intention in assigning three states to each bond is that they should serve as a mathematical representation of the real continuum of rotational angles.

There will be two (3 x 3) statistical weight matrices, one for each type of bond in the chain. For phosphorus-oxygen bonds (such as i in Figure 9.1):

$$\underline{U}^i = \begin{vmatrix} 1 & \sigma & \sigma \\ 1 & \alpha/\sigma & \beta/\sigma \\ 1 & \beta/\sigma & \alpha/\sigma \end{vmatrix}$$

For oxygen-phosphorus bonds (such as $i + 1$ in Figure 9.1):

$$\underline{U}^{i+1} = \begin{vmatrix} 1 & \sigma & \sigma \\ 1 & \gamma/\sigma & \delta/\sigma \\ 1 & \delta/\sigma & \gamma/\sigma \end{vmatrix}$$

The elements of these matrices were evaluated by estimation of the total energy associated with the conformation. The steric contributions were found by conventional semi-empirical methods, taking the Van der Waals radius of phosphorus to be 1.80 \AA , and that of oxygen to be 1.50 \AA . Electrostatic energies were calculated according to Coulomb's Law; since most of the interactions considered were between atoms separated by only $3 - 6 \text{ \AA}$, it was assumed that the correct local dielectric constant would be closer to the square of the refractive index of the polyphosphate glass, than to the bulk constant for water.

It was found that rotation of any one bond in an all-trans segment to a gauche state neither precipitated steric conflicts nor greatly modified the electrostatic energy: σ was accordingly assigned a value of unity. Simultaneous rotation of two bonds such as $i-1$ and i to opposite gauche states was found to result in an intolerable overlap ($> 1 \text{ \AA}$) of one of the pairs of oxygen atoms separated by six bonds, for all possible rotations about the bonds on either side ($i-2$ and $i+1$), and so steric factors alone demanded that the parameter β be zero. For simultaneous rotations of the same bonds into gauche states of the same sign, the increase in electrostatic energy was found to be sufficiently great to warrant setting α to zero also. Similarly, for rotations about bond-pairs such as i and $i+1$, the increases in energy were so large that δ would have to be close to zero, and γ could not exceed 0.1 at 298K. The matrices therefore became:

$$\underline{U}' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 0.1 & 0 \\ 1 & 0 & 0.1 \end{vmatrix}$$

These matrices are employed in the calculations of the characteristic ratio by the methods of Flory and Jernigan³⁷. The ratio is given by the equation:

$$\frac{\langle r^2 \rangle}{n \ell^2} = 1 + \frac{2}{Zn \ell^2} \begin{vmatrix} 1 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 \\ \underline{J} \otimes \underline{\ell} \\ \underline{J} \end{vmatrix} (\underline{G}' \underline{G}'')^{x-1} \quad (1)$$

where

$$\underline{G}'' = \begin{vmatrix} \underline{E}_3 & (\underline{E}_3 \otimes \underline{\ell}^T) & \|\underline{T}''\| & 0 \\ 0 & (\underline{E}_3 \otimes \underline{E}_3) & \|\underline{T}''\| & \underline{E}_3 \otimes \underline{\ell} \\ 0 & 0 & \underline{E}_3 & \end{vmatrix} \quad (2)$$

$$\underline{G}' = \begin{vmatrix} \underline{U}' & (\underline{U}' \otimes \underline{\ell}^T) & \|\underline{T}'\| & 0 \\ 0 & (\underline{U}' \otimes \underline{E}_3) & \|\underline{T}'\| & \underline{U}' \otimes \underline{\ell} \\ 0 & 0 & \underline{U}' & \end{vmatrix} \quad (3)$$

and \underline{G}'' is formulated analogously to \underline{G}' : the symbols here have the same meanings as in Chapter 7.

These equations, in conjunction with the structural data listed earlier, and the above \underline{U} -matrices, were found to give a value for the characteristic ratio of 7.0, in good agreement with experimental findings.

9.3 MODIFICATION OF THE MODEL OF SEMLYEN AND FLORY

There are several reasons for undertaking a re-examination of the rotational isomeric state model, prior to attempting to calculate the ring concentrations. Firstly, statistical weights of acceptable accuracy for prediction of the chain dimensions may require refinement for rationalisation of the equilibrium cyclisation constants. Again, there are differences between the polarity of the melt and that of the medium in which the chain dimensions were originally measured, and the magnitude of certain electrostatic interactions may differ accordingly. Finally, the possibility arises of incomplete dissociation of the cations in the melt.

There emerges, indeed, another question, but one which cannot be considered in detail. The argument has been put forward³² that the conformational properties of chains in undiluted polymers resemble those under θ -conditions, inasmuch as they are unaffected by both the presence of other molecules, and the long-range interactions between sequentially remote parts of the same chain; in fact, the effect of the one is precisely cancelled by the other. For poly(dimethylsiloxane), at least, this has been shown true³⁴; but this does not establish its universal validity. It is found that many of the Coulombic interactions in polyphosphate chains involve very considerable energies, and it cannot be certain in these circumstances that there is sufficient thermal disordering in the melt to prevent co-operative disposition of neighbouring chains in low-energy configurations. Intermolecular ordering of this sort would be expected to substantially modify the conformational behaviour of the chains. In the absence of further information, however,

it shall be assumed that the conformation of any chain is effectively independent of that of its neighbours.

In a detailed examination of the interactions in any given chain section, interatomic distances may be calculated by expressing atomic positions in terms of vectors in co-ordinate systems attached to consecutive skeletal bonds, and interrelated by the transformation matrices discussed in Chapter 7. According to the conventions adopted here (Appendix C), a skeletal atom has components represented by:

$$\begin{vmatrix} \ell \\ 0 \\ 0 \end{vmatrix}$$

in the co-ordinate system of the preceding bond (which is of length ℓ).

To be invariant upon bond rotation, the positions of the pendant oxygens must be defined in the frame of reference attached to the succeeding bond, when they are represented by:

$$\begin{vmatrix} -\ell_p \cos \frac{\chi}{2} & \cos \left(\frac{\pi - \theta''}{2} \right) \\ \ell_p \cos \frac{\chi}{2} & \sin \left(\frac{\pi - \theta''}{2} \right) \\ \pm \sin \frac{\chi}{2} & \end{vmatrix}$$

where the sign to be given to the z-component depends not only upon which of a pair of pendant oxygens is concerned, but also upon the position of the parent phosphorus atom in the chain.

To estimate the energy of different conformations, systematic account was taken of all the electrostatic interactions between the atoms in an eight-bond chain segment. (Such as that in Figure 9.1). The energy associated with a pair of atoms i and j , carrying partial electronic charges q_i and q_j , and separated by a distance of r_{ij} Å, was found by the Coulombic equation:

$$Q_{ij} = 1389 \cdot q_i q_j / \epsilon r_{ij}$$

where Q_{ij} is expressed in kJ/mole.

As an immediate modification of the model of Semlyen and Flory, the statistical weight parameters were re-evaluated at 1000K, assuming the atoms to retain the partial charges cited by Pauling¹⁰⁶, and using a dielectric constant, ϵ , of 5. (The dielectric constants of sodium polyphosphate glasses having been found to lie in the range $4 - 6^{97}$.) The results are presented in Table 9.1, below.

Segment conformation	Desired parameter	ΔE , kJ/mole	Parameter at 1000K
tttg+tttt	σ	4.34	0.596
tttg+g+ttt	γ	10.91	0.272
tttg+g-ttt	δ	15.17	0.164
ttg+g+tttt	α	33.46	0.018

Table 9.1

In this Table, the terminal bonds of the segment are represented as trans, even though their conformations are technically undefined. The quantity ΔE for each conformation is the difference between its energy

and that of the all-trans conformation. The ttg+g-tttt conformation is not included in the Table, for the severity of the six-bond steric interaction is such that the parameter β must be close to zero even at elevated temperatures.

With these parameters, the statistical weight matrices become:

$$\underline{U}' = \begin{vmatrix} 1 & 0.60 & 0.60 \\ 1 & 0.03 & 0.00 \\ 1 & 0.00 & 0.03 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 0.60 & 0.60 \\ 1 & 0.45 & 0.27 \\ 1 & 0.27 & 0.45 \end{vmatrix}$$

If it is desired, to investigate the effects of variation in the dielectric constant, ϵ , then it might be halved, to 2.5, when the parameters must be squared:

$$\underline{U}' = \begin{vmatrix} 1 & 0.36 & 0.36 \\ 1 & 0.01 & 0.00 \\ 1 & 0.00 & 0.01 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 0.36 & 0.36 \\ 1 & 0.20 & 0.07 \\ 1 & 0.07 & 0.20 \end{vmatrix}$$

Or, ϵ might be doubled, when the original parameters must be raised to the power of one-half.

$$\underline{U}' = \begin{vmatrix} 1 & 0.77 & 0.77 \\ 1 & 0.17 & 0.00 \\ 1 & 0.00 & 0.17 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 0.77 & 0.77 \\ 1 & 0.68 & 0.51 \\ 1 & 0.51 & 0.68 \end{vmatrix}$$

The changes in the calculated equilibrium constants resulting from these variations will receive discussion in the next Chapter.

In the use of Pauling's partial charges, it has so far been assumed that the polyphosphate chain may be regarded as fully dissociated in the melt. The case at the opposite extreme to this might be considered to be a chain in which each pair of pendant oxygens has a cation in close association. Then, the partial charge on each of them would be reduced, in effect, to -0.3: it shall be considered that the charges on the other atoms are unaltered. It is found then that the differences in electrostatic energy from one conformation to another becomes slight, and the chain may be thought of as possessing free rotation about each of its bonds, with the sole exception that no bond pair about a phosphorus atom can occupy gauche states of opposite sign. The corresponding matrices are:

$$\underline{U}' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{vmatrix}$$

These matrices, too, will be employed in calculation of the cyclic concentrations.

9.4 FURTHER CONSIDERATION OF THE ROTATIONAL ISOMERIC STATE MODEL

In the last Section, the statistical weights were derived on the consistent assumption that attention might properly be restricted to just an eight-bond segment of the chain; this was an assumption that originated in the work of Semlyen and Flory. Here, the first concern will be to investigate the limitations of the procedure. A brief discussion of the general applicability of the fundamental bond-pair approach to the polyphosphate chain will then follow.

As part of a study of the first question, the parameter σ was evaluated for the central bonds in otherwise all-trans (oxygen-terminated) chain segments of differing lengths, taking the temperature as 1000K and ϵ as 5. The results are summarised in Table 9.2.

Number of bonds in segment	Calculated value of σ
6	0.69
8	0.60
10	0.15
12	0.15

Table 9.2

Clearly, the value of σ accepted could depend upon the choice of segment to be examined. Perhaps just as significantly, there emerge "end-effects", in that the value to be associated with a bond tends to vary systematically with its position within the segment:

Number of bonds in segment	σ , for bond number:				
	2	3	4	5	6
8	1.81	0.26	0.60	-	-
10	1.72	0.10	0.60	0.15	-
12	1.60	0.05	0.66	0.04	0.15

Table 9.3

These end-effects may be eliminated, by rotating bonds within sufficiently long segments, while restricting attention to interactions

between atoms separated by no more than a specified number of chemical bonds. Different values of σ , again, arise:

Permitted range of interaction (in bonds)	6	6	10	12	14	16
Calculated value of σ	0.32	0.11	0.04	0.03	0.02	0.06

Table 9.4

Interactions between atoms separated by 14 or 16 bonds are almost certainly "long-range": by which is meant, in effect, that in the undiluted polymer, they may not be distinguished from the great mass of intermolecular interactions, simply because they chance to be between sequentially remote parts of the same chain; while under θ - conditions they are counteracted by polymer-solvent interactions. In neither case, should they be taken into account in determining the chain conformation. If the atoms are only 6 bonds apart, on the other hand, their interaction will probably be "short-range", insofar as its effect will persist under all conditions, and must always be taken into account. The uncertainty in the dividing line between the two sorts of interaction must inevitably imply that the previous selection of particular values of the statistical weight parameters must be somewhat arbitrary.

It may be remarked that this difficulty does not seem to arise in the instances of chains for which the conformational properties are dominated by steric interactions, since then most of the conformations that precipitate interactions of intermediate range are in any case

forbidden by short-range factors³³. Indeed, the uncertainties for the polyphosphate chain might be expected to be less in solution, for there the absolute magnitude of the medium-range electrostatic interactions will be diminished, through the progressive increase in dielectric constant accompanying the intrusion of solvent molecules between the more distant atoms. For the sodium phosphate melt, however, no such mechanism can be relied upon for the simplification of the analysis.

In view of the foregoing, it is somewhat surprising that the bond-pair approximation appears to hold quite well for polyphosphate chains. Information on this became available from studies to be described in the next Chapter, whereby the conformations of short phosphate chains were systematically generated, and each was attributed a statistical weight determined by a direct calculation of the total electrostatic energy.

When an eight-bonded segment was examined in this way, it was found that the total weight of the conformations with the second bond in the chain trans was 31.3, whereas the total for those with bond 2 in a specified gauche state was 51.9. From this, it may be deduced that σ for this bond has an average over all chain conformations of 1.66. That this agrees so well with the value found by just rotating the same bond in an all-trans segment (1.81, from Table 9.3) indicates that the conformation of this bond depends little upon those of bonds not immediately adjacent. The equivalent result for a ten-bonded segment was 1.59, compared to the 1.72 found earlier.

Average values of σ may also be derived for bonds nearer the middle of chain sections. For instance, figures of 0.08 and 0.19 were found for bonds 5 and 6 in a twelve-bonded segment, in comparison to 0.04 and 0.15 calculated when the rest of the chain was retained trans.

Finally, a comparison may be made, for the generation of all the conformations of an eight-bonded segment, between the overall results obtained by direct calculation of the weight of each complete chain conformation, and those predicted by the bond-pair approach. For the bond-pair model, the statistical weight parameters for any bond gave regard to its position in the segment; and since in the direct analysis, about 15% of the conformations were rejected, on the grounds of steric hindrances that went undetected in the bond-pair approach, the results in the fourth column of Table 9.5 have been proportionately corrected for these losses.

Separation of the chain ends, in Å.	Total statistical weight for the conformations with their ends in that range of separation, for:		
	Bond-pair model.	Direct analysis	Direct analysis, corrected.
0 - 1	0.002	0.000	0.000
1 - 2	0.000	0.000	0.000
2 - 3	1.767	0.609	0.739
3 - 4	0.729	0.322	0.391
4 - 5	3.477	0.375	0.455
5 - 6	11.070	7.743	9.392
6 - 7	18.109	17.194	20.856
7 - 8	35.517	29.363	35.617
8 - 9	60.552	52.707	63.934
9 - 10	32.602	26.756	32.455
0 - ∞	163.825	135.069	162.083

Table 9.5

Thus, the overall conformational partition function is closely replicated by the bond-pair model, and the distribution of end-to-end distances is accurately described for separations greater than 5 Å, although less well for those below that figure. Examination of the weights ascribed to individual conformations by the two models reveals that the agreement is usually good; save for those conformations of very low weight, for which major discrepancies may arise.

To summarise the results presented in this Section, it appears that the conformations of polyphosphate chains in sodium phosphate melts may be adequately described in terms of a bond-pair approach, but at the same time the values of the relevant parameters must be regarded as being subject to some uncertainty.

CHAPTER 10.

CONCENTRATIONS OF THE METAPHOSPHATES
IN SODIUM PHOSPHATE MELTS.

10.1 EXPERIMENTAL CONCENTRATIONS

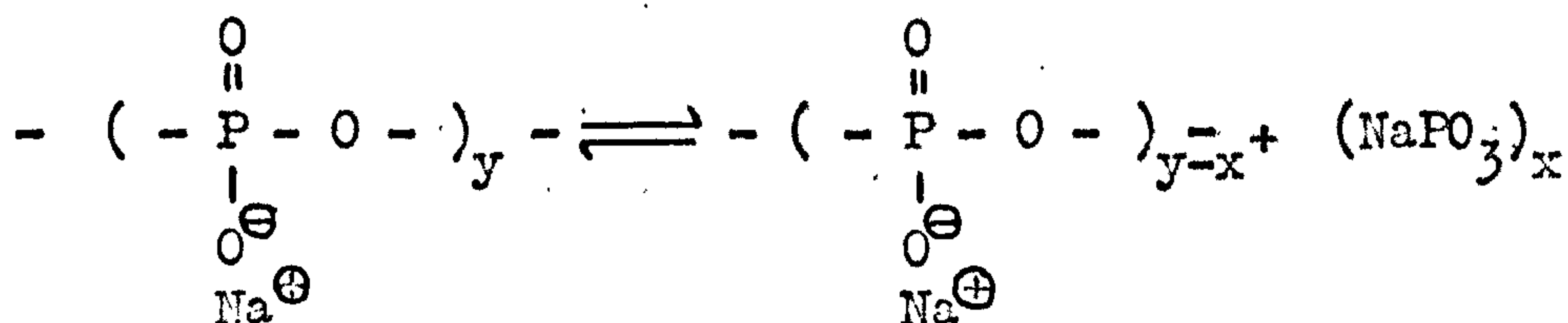
The concentrations of the trimeric to hexameric metaphosphates in Graham's Salt have been measured by McCullough, Van Wazer and Griffiths²⁷, and Thilo and Schülke²⁸ have extended the measurements to heptamer, both for Graham's Salt and for a glass with a mole ratio phosphorus : sodium of 0.8. The results are given in Table 10.1 below.

Value of x in (NaPO ₃) _x	Graham's Salt, prepared by heating NaH ₂ PO ₄ at 973K for 1½ days (27)		Graham's Salt, prepared by heating NaH ₂ PO ₄ at 1073K for 1 day (28)		Glass with r = 0.8 (28)	
	Wt%	K _x	Wt%	K _x	Wt%	K _x
3	3.9	0.280	4.3	0.308	2.4	0.238
4	2.5	0.135	2.6	0.140	1.2	0.102
5	0.75	0.032	0.8	0.035	0.5	0.037
6	0.5	0.018	1.0	0.036	0.35	0.025
7	-	-	0.5	0.015	0.13	0.009

Table 10.1

There can be little doubt that these weight percentages represent those at equilibrium between the cyclic metaphosphates and the

phosphate chains:



The interconvertibility of the rings and the chains in the melt is readily confirmed by the observation that at melt temperatures sufficiently low to permit the trimetaphosphate to crystallise out, the entire sample may be converted to the cyclic; wherefore, it is necessary to rapidly quench the melt if a vitreous product is to be obtained¹⁰¹.

The constants describing the equilibria are given by the formula:

$$K_x = \left[(\text{NaPO}_3)_x \right] / p^x$$

where p is the fractional extent of reaction; the relevant reaction in this case is the formation of a bond between (just) one of the oxygens of a PO_3^- structural unit and the phosphorus of another such unit, resulting in the extension of the chain. For high molecular weight Graham's Salt, p may be taken as unity, for rings of up to moderate size; for glasses where r , the mole ratio phosphorus : sodium, is less than unity, it may be shown that p is correctly given by the expression: $(3r - 1)/2r$. For the purposes of converting weight percentages to concentrations, a value of 2.2 kgm./dm^3 may be taken for the melt density.^{97,107} The resulting molar cyclisation equilibrium constants, in units of moles/ dm^3 , are presented in Table 10.1 alongside the weight percentages from which they were deduced.

The differences between the concentrations found for the two samples of Graham's Salt probably stem from the limitations of the paper

chromatography employed in their determination. Mean values will be taken for the trimer, tetramer and pentamer, while for the hexamer, reliance shall be put upon the more recent result of Thilo and Schülke: these values will appear in subsequent plots. The equilibrium constants for the third glass do not accord particularly well with the others, and they shall be given no further attention.

10.2 CONCENTRATIONS CALCULATED FOR THE DISSOCIATED CHAIN

In this Section, there will be a description of calculations of the metaphosphate concentrations according to the model for the fully dissociated polyphosphate chain, that is, the chain where the pendant oxygens carry partial electronic charges of -0.8, and the statistical weight matrices are:

$$\underline{U}' = \begin{vmatrix} 1 & 0.60 & 0.60 \\ 1 & 0.03 & 0.00 \\ 1 & 0.00 & 0.03 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 0.60 & 0.60 \\ 1 & 0.45 & 0.27 \\ 1 & 0.27 & 0.45 \end{vmatrix}$$

and also these matrices, with the elements modified to take account of variation in the dielectric constant, ϵ , used in their derivation. Following the pattern of analogous studies presented in Chapter 7., there will be a sub-division according to the method used to find $W_x(\underline{0})$, the density of end-to-end vectors under circumstances of close approach of the chain ends.

(a) Calculations assuming a Gaussian relation: once again: it is known that, for long chains, the density of end-to-end vectors, $W_x(\underline{r})$ is given in the region of $\underline{r} \rightarrow \underline{0}$ by the equation:

$$W_x(\underline{0}) = (3/2 \pi \langle r^2 \rangle)^{3/2} \quad (1)$$

Also, from the Jacobson-Stockmayer theory, the molar cyclisation equilibrium constant is given by:

$$K_x = W_x(\underline{0}) / N_A \sigma_{R_x} \quad (2)$$

where N_A is Avogadro's Number, and σ_{R_x} is the symmetry number of the x-meric ring (equal to $2x$ for the metaphosphates).

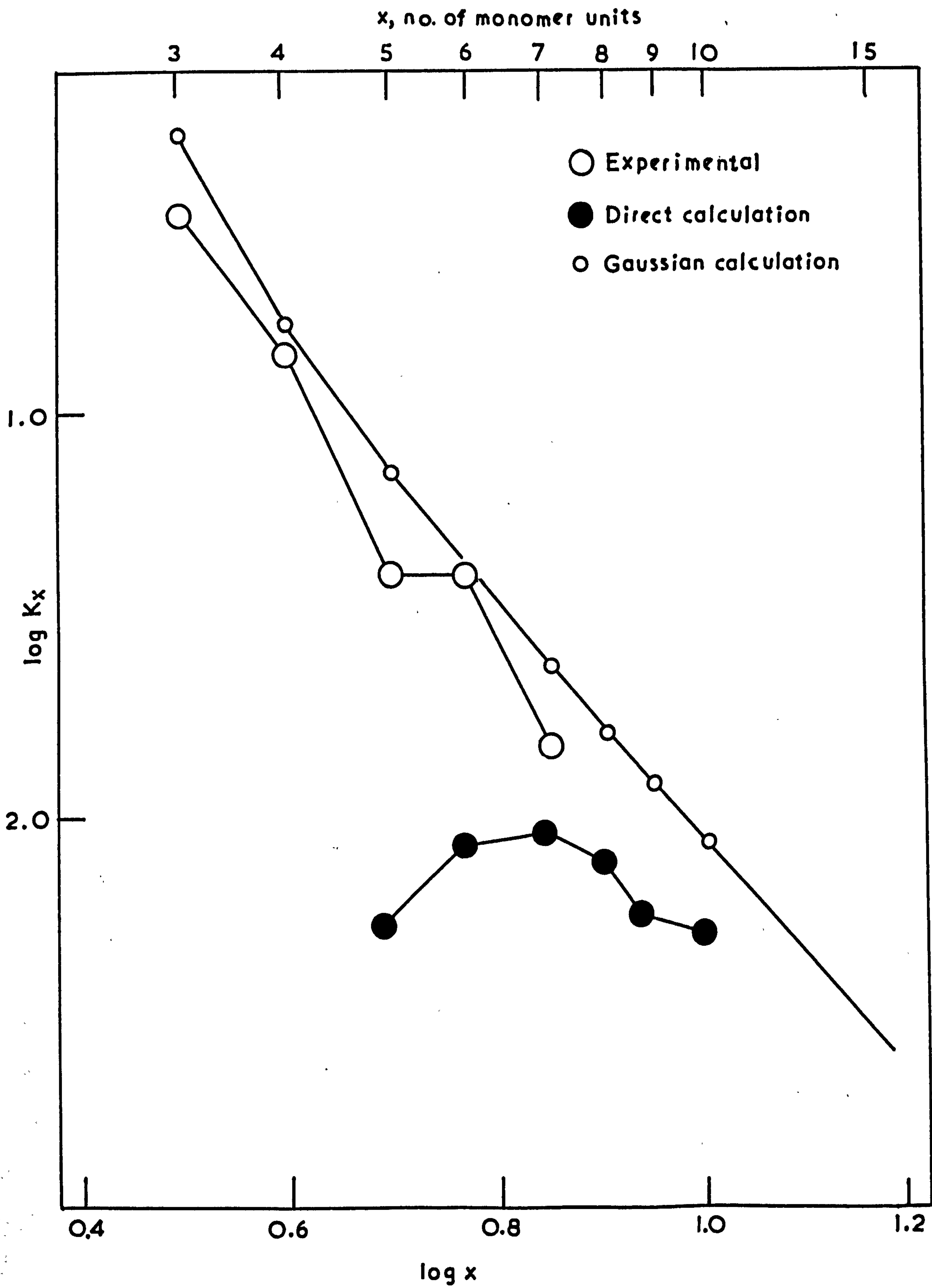
The procedure for these calculations in no way differed from those described in Chapter 7: for a succession of chains, the mean-square end-to-end separation $\langle r^2 \rangle$ was found, by means of the equations cited in the last Chapter, then the values were substituted into equations (1) and (2) above.

The results for the structural data listed in the previous Chapter, together with the statistical weight matrices derived for a temperature of 1000K and a dielectric constant of 5, are compared in Table 10.2 with the experimental findings: the same values are plotted logarithmically in Figure 10.1.

X	Calculated K_x , moles/dm ³ .	Experimental K_x , moles/dm ³ .
3	0.477	0.294
4	0.161	0.138
5	0.074	0.034
6	0.041	0.036
7	0.025	0.015

Table 10.2

FIGURE 10.1



Broadly speaking, the calculated concentrations are about 50% too high; however, even this limited agreement must be regarded as fortuitous. It would not be expected that Gaussian behaviour would be shown by chains as short as those corresponding to the cyclics with measured concentrations; and, indeed, the results to be presented below tend to conform that their distributions are quite radically non-Gaussian, especially in the region of low end-to-end separation. On the other hand, it is of interest to note that there is a rough similarity between the trend of the experimental curve and that of the theoretical line, which suggests that it is possible that at increased ring sizes they will come into a genuine coincidence.

(b) Calculations generating the chain conformations: the methods used here were precisely like those for corresponding calculations in Chapter 7: z_d , the sum of the statistical weights of the conformations with their ends within $d \text{ \AA}$ of each other, was introduced into the equation:

$$w_x(\underline{0}) = z_d / Z \frac{4}{3} \pi d^3 \quad (3)$$

where Z , the conformational partition function, was found either as the sum of the individual statistical weights, or from the matrix methods outlined earlier. In one practical respect, however, the present calculations differed from those in the former Chapter: for the presence of zero elements in one of the \underline{U} -matrices meant that many conformations could automatically be rejected. This device could be used to even greater advantage at long chain lengths, when it was found permissible to replace the element of 0.03 in \underline{U}' with a zero. Indeed, treatment of

the decamer, nominally possessing 129,140,163 conformations, was possible only because it could be shown that this substitution had negligible effect on the results for the octamer and nonamer.

The overall results of these calculations, employing the statistical weights cited above, are summarised in the Table below.

Value of x in the chain -(-O-PO ₂ -)-x	Total number of conformations for the chain	Kx, in moles/dm ³ x 10 ² calculated for d =			
		2Å	3Å	4Å	5Å
3	27	0.00	0.00	0.15	0.28
4	243	0.00	0.00	0.73	1.34
5	2,187	0.02	0.55	0.47	0.85
6	19,683	0.67	0.86	0.86	0.62
7	177,147	1.34	0.92	-	-
8	1,594,323	0.92	0.80	-	-
9	14,348,907	0.54	0.59	-	-
10	129,140,163	0.54	0.53	-	-

Table 10.3

In the succeeding eight Tables, more detailed results for each chain are presented; these comprise in each case the distribution (by number) of the conformations over the distance categories, together with the equilibrium constants found assuming values of the radius d varying from 1 up to 5 Å.

d	Number with ends within d Å	K_3 found using $z_d, \times 10^2$
1	0	-
2	0	-
3	2	0.00
4	6	0.15
5	10	0.28

Table 10.4 : trimeric chain

d	Number with ends within d Å	K_4 found using $z_d, \times 10^2$
1	2	-
2	10	0.00
3	22	0.00
4	42	0.73
5	74	1.34

Table 10.5 : tetrameric chain

d	Number with ends within d Å	K_5 found using $z_d, \times 10^2$
1	0	-
2	38	0.02
3	156	0.55
4	342	0.47
5	554	0.85

Table 10.6 : pentameric chain

d	Number with ends within d Å	K_6 found using $z_d, \times 10^2$
1	40	0.72
2	370	0.67
3	976	0.86
4	2,228	0.86
5	4,196	0.62

Table 10.7 : hexameric chain

d	Number with ends within d Å	K_7 found using $z_d, \times 10^2$
1	254	3.14
2	2,342	1.34
3	7,566	0.92

Table 10.8 : heptameric chain

d	Number with ends [≡] within d Å	K_8 found using $z_d, \times 10^2$
1	312 (28*)	1.43 (1.46*)
2	2,462 (230*)	0.92 (0.92*)
3	7,798 (770*)	0.80 (0.80*)

Table 10.9 : octameric chain

* These values were calculated with α set equal to zero in \underline{U}
[≡] For these chains only conformations with non-zero weight were enumerated.

d	Number with ends Ξ within d Å	K_9 found using $z_d, \times 10^2$
1	1,644 (84*)	0.32 (0.30*)
2	14,712 (900*)	0.54 (0.54*)
3	46,638 (2,984*)	0.59 (0.59*)

Table 10.10: nonameric chain

d	Number with ends Ξ within d Å	K_{10} found using $z_d, \times 10^2$
1	490 *	0.52 *
2	3,866 *	0.54 *
3	12,520 *	0.53 *

Table 10.11 : decameric chain

In the discussion of the Jacobson-Stockmayer theory in Chapter 1, it was made clear that its application presumes that the distribution of end-to-end vectors in the vicinity of the chain end acting as origin is uniform, both radially and angularly. Insight into the radial distribution may readily be gained from inspection of these Tables.

For the trimer and tetramer, the three-state model defines no acceptable conformations with the chain ends approaching to within 3 Å, and the distributions even outside this range show variability. No values will be cited for the equilibrium constants of these rings. The

* These values were calculated with α set equal to zero in U' .

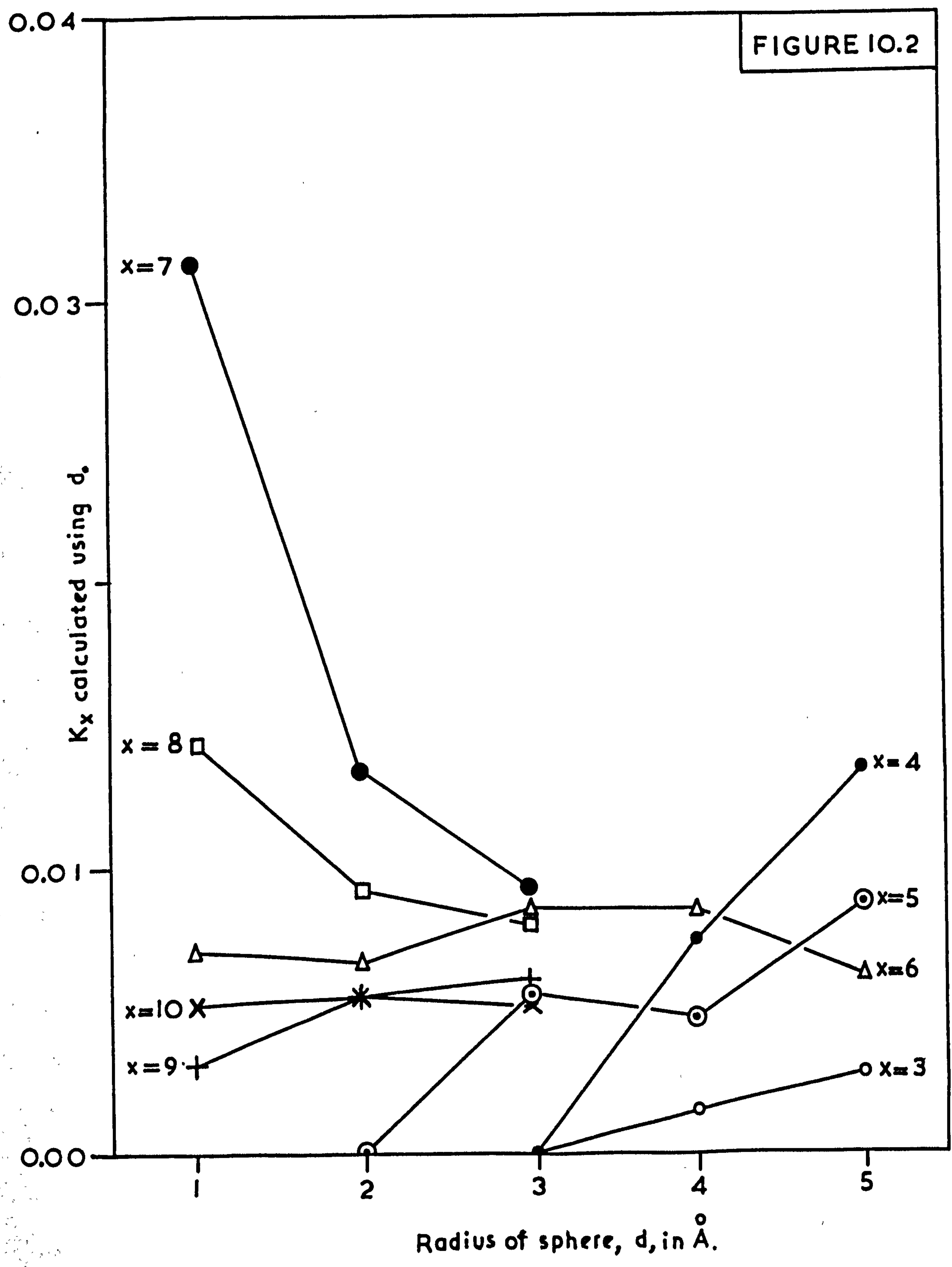
Ξ For these chains only conformations with non-zero weight were enumerated.

case of the pentamer is similar, although somewhat improved; the value for a test sphere of radius 3 \AA will be accepted, but only as a tentative result. For the other chains, serious non-uniformity of the radial distributions is restricted to the sphere with $d = 1 \text{ \AA}$, and the constants calculated for $d = 3 \text{ \AA}$ may justifiably be selected for the sake of consistency with the pentamer.

The accepted results are plotted in Figure 10.1, so that they may be compared with both the experimental points, and the Gaussian line (for the identical statistical weight scheme). From this diagram, it may be seen that, while agreement between the known experimental concentrations and those predicted by theory is not improved by removing the assumption of a Gaussian distribution, at least it appears that, at slightly higher ring sizes, there would be good agreement; it would be of considerable interest to determine the concentrations of such metaphosphates. Further, it is instructive to note that, even for the decamer, with very many defined conformations with ends approaching closely, and a fairly smooth radial distribution, the result does not coincide with that found by the Gaussian equation. From the plot it would seem that, as far as concerns cyclisation, the polyphosphates cannot be regarded as conforming to Gaussian statistics until, perhaps, the 20-meric chain.

Direct quantitative analysis of the angular distribution is not yet possible: but information may be obtained indirectly, from a careful re-examination of the radial distributions. For it is found that the fluctuations in the density of end-to-end vectors in the region of zero separation of the chain ends are far from random. This is made more clear if the calculated constants tabulated above are instead

FIGURE 10.2



plotted out, as in Figure 10.2; when it may readily be recognised that there are systematic oscillations in the density.

Now, the appearance of these trends has rather subtle implications. Consider, firstly, the instance of the hexameric chain, for which the radial distribution is reasonably uniform. To progress to the heptamer, it is merely necessary to extend the chain by two bonds, in each of the conformations. But if there were both radial and angular uniformity of the density for the hexamer, it would be extremely improbable that addition of the two bonds could generate the radically non-uniform density distribution found for the heptamer. The same arguments must apply to the other chains: the failure of the radial distributions to show a steady and monotonic approach to a perfect uniformity with increasing chain length, is totally incompatible with random orientation of the chain termini. In short, the systematic re-appearance of radial non-uniformity as the chain length increases does not merely suggest that the angular distributions, also, are perceptibly non-random, but furnishes an unassailable proof that this is the case.

It is not, of course, possible to give quantitative expression to these findings. Indeed, it might be questioned whether the observed oscillations in calculated density are a feature of the real chains, or whether they arise as an artifice of a three-state model. In the case of polymethylene chains, for which similar sorts of effects have recently been noted¹⁰⁷, this is less open to doubt: since for this polymer, the attribution of three states to each bond is intended to reflect the physical reality, whereas pronounced intrinsic energy barriers to bond rotation ^{appear to be} absent in the polyphosphates, and the three

states assigned to each bond are meant merely to represent the continuum of rotational angles. (Chapter 9). But the evidence of non-random approach of the termini in no way contradicts the qualitative expectation for such short chains, and it cannot be doubted that such factors significantly affect the concentrations of, at the least, the smaller of the rings dealt with.

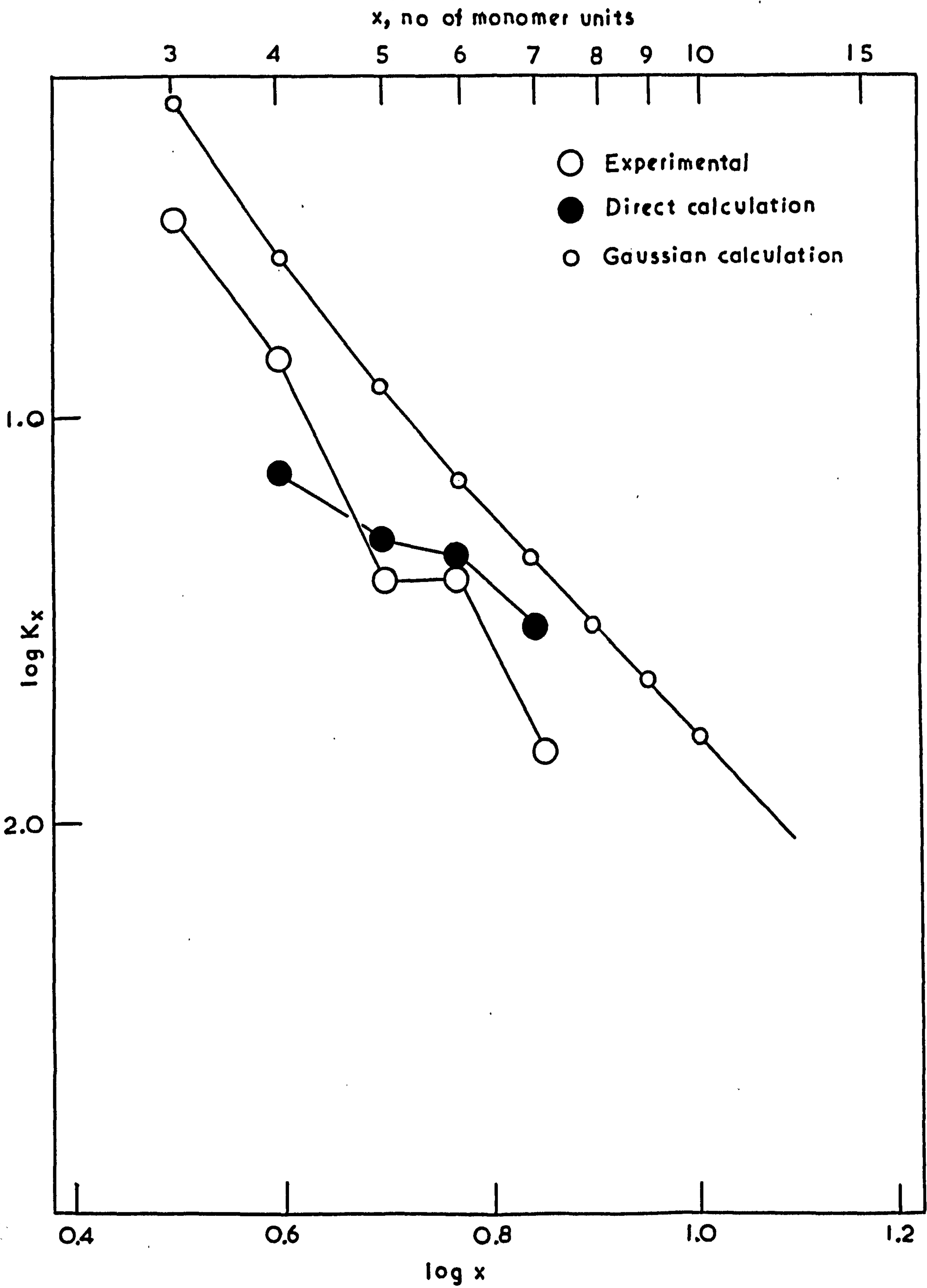
In view of these uncertainties, coupled with those relating to the fundamental bases of the rotational isomeric state model, which were discussed in the preceding Chapter, there could be little point in pursuing in detail the dependence of the calculated results upon the magnitude of the melt dielectric constant, ϵ . It shall be remarked, however, that if use is made of the revised U-matrices set up earlier, it is found that a change in ϵ of a factor of two in either sense modifies the calculated concentrations by approximately the same factor, in the same sense.

10.3 CONCENTRATIONS CALCULATED FOR THE ASSOCIATED CHAIN

The testing of this variation of the rotational isomeric state model requires little description, for it followed exactly the same scheme as that in the last Section. It will be recalled that the statistical weight matrices become:

$$\underline{U}' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{vmatrix} \quad \underline{U}'' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{vmatrix}$$

FIGURE 10.3



The results of the calculations with these matrices are presented graphically in Figure 10.3. It may be seen from this plot that the points found by direct generation of all the chain conformations stand in quite good agreement with experiment, even though no account has been taken of non-random angular distributions of the density of end-to-end vectors, which would be expected to elevate the concentrations of such small rings. Furthermore, these points are coming smoothly, and quite rapidly, to the line predicted on the basis of the Gaussian relation, which itself is overestimating the cyclic concentrations by factors of about three. In sum, it is apparent that the statistical weights derived for this modification of the model are altogether too favourable for cyclisation.

10.4 CALCULATIONS INDEPENDENT OF THE BOND-PAIR APPROXIMATION

The final Section of this Chapter is concerned with certain calculations, already referred to; those in which no reliance was placed on the bond-pair approximation. (That is, the approximation that the rotational state of a bond in a chain is independent of the states of the other bonds, beyond its nearest neighbours.) Instead, the statistical weight of each complete chain conformation was determined from its total energy. Apart from the uncertainty in the applicability of the bond-pair approach itself, there were two other considerations suggesting that the new method might be fruitful. The first was, that it would obviate the use of long-chain statistical weights, possibly inappropriate for shorter chains. Secondly, it would facilitate the

assignment of many states to each bond rotated, and would thereby present opportunities for improved descriptions of the conformations of the smaller rings.

Development of the computational techniques required for this approach presented no great difficulty: some details of the programmes employed are to be found in Appendix C. It was possible to generate conformations, and examine them for both electrostatic and steric interactions, at about a thousand a minute; so a six-bonded trimer chain was accessible to treatment, even with twelve states to each bond, and a total of 20,736 conformations.

For the small rings, and for the trimer in particular, it appeared initially that excellent results could be obtained by assigning six or twelve states to the bonds. No values will be presented here, however; for it emerges that they are in fact entirely spurious. The reason for this is not necessarily immediately evident. It is related to the discussion given in Chapter 1, to the perturbation of the Jacobson-Stockmayer theory by differences between the environment at the junction of the two ends of the hypothetical cyclising chain, and that at the corresponding junction of this short chain with a longer. Explicitly, in the present case, the statistical weights of the conformations with proximate chain ends were determined in large part by interactions across this junction, i.e., between atoms situated near the two ends of the chain: indeed, for the shortest chain there could hardly be a distinction between the "ends" and the "middle" in this respect. But although the statistical weights of the "cyclising" conformations were modified in this way, those of the remaining conformations underwent no parallel, and compensatory, modification

to account for the interactions that were removed when the hypothetical short chain was detached from the longer polyphosphate chain. Expressed differently, the conformations with proximate ends may well represent quite accurately the conformations of the actual cyclic, and the other conformations may equally well represent those of a hypothetical chain of that length; but that which is ultimately required is a comparison of the opportunities for conformational diversity open to the ring, and those open to an equivalent segment in a long chain. The "non-cyclising" conformations of the conjectured short chain will not adequately represent the latter because their statistical weights are derived without reference to the necessity for the chain to be extended on either side, and to the concomitant interactions. Only by undertaking an ancillary analysis, of the interactions between the termini of the hypothetical short chain, and the longer chain to which it is originally attached, could the results from these calculations be given any sort of validity. This would prove a formidable task.

The usefulness of these calculations, therefore, reduces to revealing that, with six or twelve states to each bond, there are very many conformations for the trimer and tetramer with the chain ends in close juxtaposition, and to establishing, by the way, that the bond-pair approximation indeed holds quite well for short polyphosphate chains (Chapter 9).

APPENDIX A.

LEAST MEAN SQUARES ANALYSIS OF CHROMATOGRAPHIC TRACINGS

Consider an experimental chromatographic tracing that is a composite of N individual peaks, of which the j 'th alone would have a height h_j . Let the height of the tracing at the i 'th of M positions along its length be H_i , to which the contribution of the j 'th component peak is given by: $\alpha_{i,j} \cdot h_j$. So the predicted height at the i 'th position, S_i , is given by:

$$S_i = \sum_{k=1}^{k=N} \alpha_{i,k} h_k$$

The M predicted heights must be fitted as closely as possible to the experimental heights H_i . This is achieved by minimising the sum of the deviations, $\sum_{i=1}^{i=M} (S_i - H_i)^2$, with respect to each of the h_j . So;

$$\therefore \frac{\partial}{\partial h_j} \sum_{i=1}^{i=M} (H_i - S_i)^2 = 0 \quad \text{for all } j$$

$$\therefore \sum_{i=1}^{i=M} 2 (H_i - S_i) \frac{\partial S_i}{\partial h_j} = 0$$

$$\therefore \sum_{i=1}^{i=M} (H_i - \sum_{k=1}^{k=N} \alpha_{j,k} h_k) \alpha_{i,j} = 0$$

$$\therefore \sum_{i=1}^{i=M} \alpha_{i,j} \sum_{k=1}^{k=N} \alpha_{j,k} h_k = \sum_{i=1}^{i=M} H_i \cdot \alpha_{i,j}$$

$$\begin{aligned} \therefore \sum_{i=1}^{i=M} \sum_{k=N}^{k=N} \alpha_{ij} \cdot \alpha_{ik} \cdot h_k &= \sum_{i=1}^{i=M} H_i \cdot \alpha_{i,j} \\ \therefore \sum_{k=1}^{k=N} \sum_{i=M}^{i=M} \alpha_{ij} \cdot \alpha_{ik} \cdot h_k &= \sum_{i=1}^{i=M} H_i \cdot \alpha_{i,j} \\ \therefore \sum_{k=1}^{k=N} h_k \sum_{i=1}^{i=M} \alpha_{ij} \cdot \alpha_{ik} &= \sum_{i=1}^{i=M} H_i \cdot \alpha_{i,j} \end{aligned}$$

If : $\sum_{i=1}^{i=M} \alpha_{ij} \cdot \alpha_{ik} = A_{j,k}$ and $\sum_{i=1}^{i=M} H_i \cdot \alpha_{i,j}$

then: $\sum_{k=1}^{k=N} A_{j,k} \cdot h_k = B_j$, which is the j'th of a set of N simultaneous equations.

In matrix notation: $|A| |h| = |B|$ whence: $|h| = |A|^{-1} |B|$

The proportionality factors $\alpha_{i,j}$ may be found in whatever way is appropriate to the problem. For gel permeation chromatography, provided the peaks shown no significant asymmetry, the Gaussian formula can be applied:

$$\alpha_{i,j} = \exp\left(-\frac{(V_i - V_j)^2}{2 \sigma_j^2}\right)$$

where σ_j is the standard deviation of the peak about the mean, i.e. = $\frac{1}{2}$ the width at half-height of the peak, and V_i and V_j are the elution volumes at the i'th point taken from the trace and at the peak of the j'th component, respectively. The area of such a peak is given by:

$h_j \cdot \sigma_j \cdot (2\pi)^{1/2}$, and the area fraction by: $h_j \cdot \sigma_j / \sum_{j=1}^{j=n} h_j \cdot \sigma_j$. For

an already fairly well resolved peak V_j will be close to the apparent peak on the tracing, while σ_j may be found from tracings on which components of similar elution volumes are perfectly resolved. In the case of the cyclic oligomers of poly(ethylene terephthalate), reliance was placed upon the values found for the cyclic oligomers of poly(decamethylene adipate).

The computer programme employed for the calculations is listed, with the omission of the library PROCEDURE MALINCH2, which inverts a symmetric matrix.

The other PROCEDURES have these functions:

INPUT reads in identifying strings, the trace heights and elution volumes for M positions, and the elution volumes and σ values for N components.

GAUSS calculates the coefficients $\alpha_{i,j}$, represented by the array ALPHA.

FILLA calculates the elements of the matrix of cross-products $A_{j,k}$. (Denoted as such).

FILLB calculates the corresponding elements for the column B_j . (Denoted as such).

MULTCB multiplies the inverse of the symmetric matrix A with the column B to obtain the fitted peak heights PEAKH[I].

FIT uses the fitted peak heights to derive the overall fitted tracing.

AREAS calculates the area and area fraction for each component.

OUTPUT outputs the experimental and also the fitted data.

RESOLVE is a master PROCEDURE calling the other PROCEDURE in turn. For itself, it is called once, after values of M and N have been read in.

The data needed for the operation of this programme is: the integer M, the integer N; three strings giving the date, the sample, and the conditions of the run; M pairs of trace heights and elution volumes; N peak elution volumes, each at once followed by the value of σ_j and by an identification of the component.

ANALYSIS OF GPC TRACINGS;

"BEGIN"

"LIBRARY" LINALG;

"INTEGER" M,N;

"PROCEDURE" INPUT(TRACEV,TRACEH,PEAKV,SIGMA,M,N,DATE,SAMPLE,CONDNS,
LABEL,DATEM,SAMPLM,CONDNM,LABELM);

"REAL""ARRAY" TRACEV,TRACEH,PEAKV,SIGMA;

"INTEGER" M,N;

"INTEGER""ARRAY" DATE,SAMPLE,CONDNS,LABEL;

"INTEGER" DATEM,CONDNM,SAMPLM,LABELM;

"BEGIN"

"INTEGER" I,J;

DATEM:=SAMPLM:=CONDNM:=LABELM:=1;

INSTRING(DATE,DATEM); INSTRING(SAMPLE,SAMPLM); INSTRING(CONDNS,CONDNM);

"FOR" I:= 1 "STEP" 1 "UNTIL" M "DO"

"READ" TRACEV[I],TRACEH[I];

"FOR" J:= 1 "STEP" 1 "UNTIL" N "DO""BEGIN"

"READ" PEAKV[J],SIGMA[J];

INSTRING(LABEL,LABELM);

"END";

"END" INPUT;

"PROCEDURE" GAUSS(ALPHA,SIGMA,TRACEV,PEAKV,M,N);

"REAL""ARRAY" ALPHA,SIGMA ,TRACEV,PEAKV; "INTEGER" M,N;

"BEGIN"

"INTEGER" I,J;

"FOR" I:= 1 "STEP" 1 "UNTIL" M "DO"

"FOR" J:= 1 "STEP" 1 "UNTIL" N "DO"

ALPHA[I,J]:=EXP(-((TRACEV[I]-PEAKV[J])*(TRACEV[I]-PEAKV[J]))/
(2.0 * SIGMA[J] * SIGMA[J]));

"END" GAUSS ;

"PROCEDURE" FILLA(A,ALPHA,M,N);

"REAL""ARRAY" A, ALPHA; "INTEGER" M,N;

"BEGIN"

"INTEGER" I,J,K;

"FOR" J := 1 "STEP" 1 "UNTIL" N "DO"

"FOR" K := 1 "STEP" 1 "UNTIL" N "DO""BEGIN"

AC[J,K]:=0.0; "FOR" I :=1 "STEP" 1 "UNTIL" M "DO"

AC[J,K]:=AC[J,K] + ALPHA[I,J]*ALPHA[I,K]; "END";

"END" FILLA;

"PROCEDURE" FILLB(B,ALPHA,TRACEH,M,N);

"REAL""ARRAY" B, ALPHA,TRACEH; "INTEGER" M,N;

"BEGIN""INTEGER" I,J;

"FOR" J:= 1 "STEP" 1 "UNTIL" N "DO""BEGIN"

BC[J]:=0.0; "FOR" I:= 1 "STEP" 1 "UNTIL" M "DO"

BC[J]:=BC[J] + TRACEH[I]*ALPHA[I,J]; "END";

"END" FILLB;

```
"PROCEDURE" MULTCB(C,B,PEAKH,N);  
"REAL""ARRAY" C,B,PEAKH;  
"INTEGER" N;  
"BEGIN""INTEGER" I,J;  
"FOR" I:= 1 "STEP" 1 "UNTIL" N "DO""BEGIN"  
PEAKHC[I]:=0.0;  
"FOR" J:= 1 "STEP" 1 "UNTIL" N "DO"  
PEAKHC[I]:=PEAKHC[I] + C[I,J]*B[J]; "END";  
"END" MULTCB;
```

```
"PROCEDURE" FIT(TRACEV,TRACEH,CALCDH,ALPHA,PEAKH,RMS,M,N);  
"REAL""ARRAY" TRACEV,TRACEH,CALCDH,ALPHA,PEAKH;  
"REAL" RMS; "INTEGER" M,N;  
"BEGIN"  
"INTEGER" I,J; "REAL" ERROR,SUMSQ;  
SUMSQ:=0.0;  
"FOR" I:= 1 "STEP" 1 "UNTIL" M "DO""BEGIN" CALCDHC[I]:=0.0;  
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"  
CALCDHC[I]:=CALCDHC[I] + ALPHA[I,J]*PEAKH[J];  
ERROR:=TRACEH[I] - CALCDHC[I];  
SUMSQ:=SUMSQ + ERROR*ERROR; "END";  
RMS:=SQRT(SUMSQ/M);  
"END" FIT;
```

```
"PROCEDURE" AREAS(PEAKH,SIGMA,AREA,FRAREA,SUMARE,N);  
"REAL""ARRAY" PEAKH,SIGMA,AREA,FRAREA; "REAL" SUMARE; "INTEGER" N;  
"BEGIN"  
"INTEGER" J;  
SUMARE:=0.0;  
"FOR" J:= 1 "STEP" 1 "UNTIL" N "DO""BEGIN"  
AREAC[J]:=PEAKH[J]*SIGMA[J]*SQRT(6.2832);  
SUMARE:=SUMARE + AREAC[J]; "END";  
"FOR" J:= 1 "STEP" 1 "UNTIL" N "DO"  
FRAREAC[J]:=AREAC[J]/SUMARE;  
"END" AREAS;
```

```
"PROCEDURE" OUTPUT(TRACEV,TRACEH,CALCDH,PEAKV,SIGMA,PEAKH,FRAREA,AREA,
SUMARE,RMS,M,N,DATE,SAMPLE,CONDNS,LABEL,DATEM,SAMPLM,CONDNM,LABELM);
"REAL""ARRAY" TRACEV,TRACEH,CALCDH,PEAKV,SIGMA,AREA,FRAREA;
"REAL""ARRAY" PEAKH;
"INTEGER" M,N; "REAL" RMS,SUMARE;
"INTEGER""ARRAY" DATE,SAMPLE,CONDNS,LABEL;
"INTEGER" DATEM,SAMPLM,CONDNM,LABELM;
"BEGIN"
"INTEGER" I;
"PRINT" 'F','L','S10' DECOMPOSITION OF A GPC TRACING INTO ITS',
' CONSTITUENT PEAKS BY THE METHOD OF LEAST SQUARES.';
DATEM:=SAMPLM:=CONDNM:=LABELM:=1;
"PRINT" 'L5','S8' DATE: '; OUTSTRING(DATE,DATEM);
"PRINT" 'L2','S6' SAMPLE: '; OUTSTRING(SAMPLE,SAMPLM);
"PRINT" 'L2','S2' CONDITIONS: '; OUTSTRING(CONDNS,CONDNM);
"PRINT" 'L10','S12' INPUT AND CALCULATED DATA FOR TRACING.',
'S13' INPUT AND CALCULATED DATA FOR CONSTITUENT PEAKS. ', 'L3',
'S19' ELUTION'S4' TRACE'S5' FITTED'S10' ELUTION'S5' PEAK 'S4' FITTED',
'S4' FITTED'S5' AREA'S9' IDENTITY'L', 'S19' VOLUME'S5' HEIGHT'S4',
' HEIGHT'S10' VOLUME'S6' SIGMA'S4' HEIGHT'S4' AREA'S5' FRACTION'S7' OF PEAK';
I:=0;
NEXT: I:=I + 1; "IF" I > M "AND" I > N "THEN""GOTO" FINISH;
"IF" I < M+1 "THEN""PRINT" 'L','S20',SAMELINE,ALIGNED(2,1),
TRACEV[I],'S5',ALIGNED(2,1),TRACEH[I],'S5',ALIGNED(2,1),
CALCDH[I] "ELSE""PRINT" 'L','S45';
"IF" I<N+1 "THEN""BEGIN"
"PRINT" 'S12',SAMELINE,ALIGNED(2,1),PEAKV[I],
'S4',ALIGNED(1,2),SIGMA[I],'S5',ALIGNED(2,1),PEAKH[I],'S4',
ALIGNED(2,2),AREA[I],'S5',ALIGNED(1,3),FRAREA[I],'S5';
OUTSTRING(LABEL,LABELM);
"END";
"GOTO" NEXT;
FINISH: "PRINT" 'L5','S40' RMS DEVIATION OF FITTED CURVE ',
' FROM EXPERIMENTAL POINTS = ',SAMELINE,ALIGNED(1,2),RMS,' UNITS.';
"PRINT" 'L5','S40' TOTAL CALCULATED AREA = ',SAMELINE,ALIGNED(2,1),
SUMARE,' UNITS';
"PRINT" 'L5','S40' (VOLUME UNIT = COUNT ON CHART, HEIGHT UNIT = ',
'1 CM.)';
"END" OUTPUT;
```

```
"PROCEDURE" RESOLVE(M,N);
"INTEGER" M,N;
"BEGIN"
"REAL" "ARRAY" TRACEV[1:M], TRACEH[1:M], CALCDH[1:M], PEAKH[1:N],
PEAKV[1:N], SIGMA[1:N], AREA[1:N], FRAREA[1:N], ALPHA[1:M, 1:N],
A[1:N, 1:N], B[1:N], C[1:N, 1:N];
"REAL" RMS, LIMIT, SUMARE;
"INTEGER" "ARRAY" DATE[1:10], SAMPLE[1:50], LABEL[1:(N*15)];
"INTEGER" "ARRAY" CONDNS[1:50];
"INTEGER" DATEM, SAMPLM, CONDNM, LABELM;
LIMIT:=1;
INPUT(TRACEV, TRACEH, PEAKV, SIGMA, M, N, DATE, SAMPLE, CONDNS, LABEL, DATEM,
SAMPLM, CONDNM, LABELM);
GAUSS(ALPHA, SIGMA, TRACEV, PEAKV, M, N);
FILLA(A, ALPHA, M, N);
FILLB(B, ALPHA, TRACEH, M, N);
RETURN: LIMIT:=LIMIT * 1.0e-5;
MALINCH2(A, C, N, LIMIT, FAIL);
MULTCB(C, B, PEAKH, N);
FIT(TRACEV, TRACEH, CALCDH, ALPHA, PEAKH, RMS, M, N);
AREAS(PEAKH, SIGMA, AREA, FRAREA, SUMARE, N);
OUTPUT(TRACEV, TRACEH, CALCDH, PEAKV, SIGMA, PEAKH, FRAREA, AREA, SUMARE, RMS,
M, N, DATE, SAMPLE, CONDNS, LABEL, DATEM, SAMPLM, CONDNM, LABELM);
"GOTO" SOLVED;
FAIL: "PRINT" "'S' FOR LIMIT = ", SAMELINE, SCALED(1), LIMIT;
"IF" LIMIT > 1.0e-35 "THEN" "GOTO" RETURN;
SOLVED: "END" RESOLVE;
```

```
"READ" M,N;
RESOLVE(M,N);
"END";
```


APPENDIX B.

GAUSSIAN CALCULATIONS OF EQUILIBRIUM CONSTANTS

Only slight computational difficulties were encountered in these calculations, for their requirements in terms of run time and computer store are very moderate. The only possible problem that arises is that, in treating long chains, certain of the numbers generated as matrix elements may be larger than the computer can handle; but this may easily be circumvented.

The different programmes for the variants of these calculations inevitably had many parts in common, and that which is listed here is chosen as an example. It is for the calculation of the mean-square end-to-end distance of oxygen-terminated polyphosphate chains, and so also of the molar cyclisation constants of the corresponding ring phosphates.

The first part of the programme is concerned with declarations of the variables common to the entire programme, including U and G matrices. This is followed by the five PROCEDURES MULT, FILL, CLEAR, KRONE and VALUT, the functions of which are made clear in the listing itself. These PROCEDURES were of very general usefulness and appeared in all programmes of this type.

The PROCEDURE GFILL, which follows, also has great generality: it fills the G-matrix* for a bond with three states. In doing this it makes calls to the preceding PROCEDURES.

* It has been noted already (Chapter 7) that such a generator matrix, with a null sub-matrix in the upper right-hand corner, would nowadays be denoted F_i rather than G_i .

PROCEDURE DIVIDE, which divides every element in a matrix by a constant, is required to prevent the generation of excessively large numbers. It is called for this purpose in the master PROCEDURE CRAT1 that appears later.

PROCEDURE CALC extracts elements from the serial products of the U-matrices and the G-matrices, and calculates the characteristic ratio for the chain. PROCEDURE WRITE outputs the characteristic ratio at each chain length, and statements may also be inserted so that it calculates and outputs the equilibrium constant for the equivalent ring. Both these PROCEDURES are specific to the polyphosphate chains, and to those closely related, such as the polysiloxanes.

The PROCEDURE that follows, CRAT1, is specific not only to polyphosphate chains, but, further, to those in which both ends are oxygens, or both are phosphoruses. As presented, it is used for those terminated with oxygens; the other case may be dealt with by consistent interchange of the data for oxygen-phosphorus and phosphorus-oxygen bonds. Another PROCEDURE, CRAT2, was used to treat chains in which one end was a phosphorus atom, and the other an oxygen.

The overall calculation is performed in stages, with the chain length extended at each; the function of CRAT1 is to post-multiply the serial matrix products for the existing chain with the matrices for the bonds being added. This is done for both the U-matrices and the G-matrices; in the latter case, the product is afterwards pre-multiplied by a constant G-matrix, that for the first bond. (GD) The final matrix products are referred to CALC and WRITE in turn.

Once the chain has reached twenty bonds, by successive additions of single units, it is rapidly increased by doubling its length, excluding the terminal bonds: this requires a squaring of matrices. At this stage, CRAT1 assumes an additional function: it prevents the growth of excessively large numbers, by the division of the matrices to be squared by the existing partition function, Z^* . The G-matrices and U-matrices appear in the equation for the characteristic ratio on the top and bottom, respectively, of a fraction, and the answer obtained is unaffected by this device.

The next sections of the programme are concerned with input and output of the data employed, setting up bond vector and identity matrices, and filling the G-matrices. Finally, there is a succession of calls to CRAT1, firstly to build up and treat chains with 4, 6, 8, etc., bonds, and then, having reached 20 bonds, to increase by matrix squaring to 38, 74, 146 etc., The longest chain dealt with was of nearly five million bonds; and even here the limitation was in the capacity of the computer to hold the integer representing the number of bonds, and not in the generation of excessively large numbers during the calculation of the characteristic ratio, or in the time required. However, there was little virtue in extending the calculations so far, since by 500,000 bonds the characteristic ratio was constant to within 1 part in 10^5 .

The programme for performing the equivalent calculations for poly (ethylene terephthalate) chains differed somewhat from this. It was necessary to input information upon the number of states assigned to

* The same purpose may be served by normalising the initial U matrices, by dividing each by its greatest eigenvalue.³³

to each bond in the unit, and also upon the order and the indexing of its U-matrix; this information had later to be transferred to the PROCEDURE GFILL used. Again, it was necessary to set up the reducing matrix discussed earlier, prior to the calculations; and during them, there was no stage at which the matrices were divided by the partition function, for the G-matrix for the unit was already normalised. The PROCEDURES CALC and WRITE were combined into a single PROCEDURE OUTPUT, that also incorporated new features.

In both cases, the programme was checked by reference to previous results, as well as by comparison with the results of the direct calculations described in Appendix C.

CHARACTERISTIC RATIO OF POLYPHOSPHATE CHAINS;

"BEGIN"

"REAL" THET,L; "REAL" LAST,AVSQL;

"INTEGER" X,I,J;

"REAL""ARRAY" PHIC[1:3],LROW[1:1,1:3],LCOL[1:3,1:1],EC[1:3,1:3],
UA[1:3,1:3],UR[1:3,1:3],UC[1:3,1:3],GA[1:15,1:15],GB[1:15,1:15],
GC[1:15,1:15],GD[1:15,1:15];

"REAL" 7;

"REAL""ARRAY" UD[1:3,1:3];

"PROCEDURE" MULT (A,B,C,L,M,N);

"COMMENT" THIS PROCEDURE TAKES THE MATRIX PRODUCT OF A(L*M) AND B(M*N)
AND PUTS IT IN C(L*N);

"INTEGER" L,M,N; "REAL""ARRAY" A,B,C; "BEGIN"

"INTEGER" X,Y,Z;

"FOR" X:=1 "STEP" 1 "UNTIL" L "DO"

"FOR" Y:= 1 "STEP" 1 "UNTIL" N "DO""BEGIN"

C[X,Y]:=0.0;

"FOR" Z:= 1 "STEP" 1 "UNTIL" M "DO"

C[X,Y]:=C[X,Y]+(A[X,Z]*B[Z,Y]); "END";

"END" MULT;

"PROCEDURE" FILL(A,B,I,J,K,L);

"COMMENT" THIS PROCEDURE INSERTS MATRIX B(K*L) INTO MATRIX A ,
STARTING AT THE(I,J) LOCATION;

"INTEGER" I,J,K,L; "REAL""ARRAY" A,B; "BEGIN"

"INTEGER" X,Y;

"FOR" X:= 1 "STEP" 1 "UNTIL" K "DO"

"FOR" Y:= 1 "STEP" 1 "UNTIL" L "DO"

A[(I+X-1),(J+Y-1)]:=B[X,Y];

"END" FILL;

"PROCEDURE" CLEAR(A,I,J);

"COMMENT" THIS PROCEDURE FILLS A (I*J) MATRIX A WITH ZEROES;

"INTEGER" I,J; "REAL""ARRAY" A; "BEGIN"

"INTEGER" X,Y;

"FOR" X:= 1 "STEP" 1 "UNTIL" I "DO"

"FOR" Y:= 1 "STEP" 1 "UNTIL" J "DO"

A[X,Y]:=0.0;

"END" CLEAR;

```
"PROCEDURE" KRONE(A,B,C,I,J,K,L);  
"COMMENT" THIS PROCEDURE TAKES THE KRONECKER PRODUCT OF MATRICES  
A(I*J) AND B(K*L) AND PUTS IT INTO MATRIX C;  
"INTEGER" I,J,K,L; "REAL" "ARRAY" A,B,C; "BEGIN"  
"INTEGER" W,X,Y,Z;  
"FOR" W:=1 "STEP" 1 "UNTIL" I "DO"  
"FOR" X:=1 "STEP" 1 "UNTIL" J "DO"  
"FOR" Y:=1 "STEP" 1 "UNTIL" K "DO"  
"FOR" Z:= 1 "STEP" 1 "UNTIL" L "DO"  
C[(K*(X-1)+Y),(L*(X-1)+Z)]:=A[W,X]*B[Y,Z];  
"END" KRONE;
```

```
"PROCEDURE" VALUT(T,THET,PHI,J);  
"COMMENT" THIS PROCEDURE FILLS THE T-MATRICES;  
"INTEGER" J; "REAL" THET; "REAL" "ARRAY" T,PHI; "BEGIN"  
"REAL" RAD; RAD:=57.2958;  
T[1,1]:=COS(THET/RAD);  
T[1,2]:=SIN(THET/RAD);  
T[1,3]:=0.0;  
T[2,1]:=SIN(THET/RAD)*COS(PHI[J]/RAD);  
T[2,2]:=-COS(THET/RAD)*COS(PHI[J]/RAD);  
T[2,3]:=SIN(PHI[J]/RAD);  
T[3,1]:=SIN(THET/RAD)*SIN(PHI[J]/RAD);  
T[3,2]:=-COS(THET/RAD)*SIN(PHI[J]/RAD);  
T[3,3]:=-COS(PHI[J]/RAD);  
"END" VALUT;
```

```
"PROCEDURE" GFILL(G,U,E,LROW,LCOL,THET,PHI);  
"COMMENT" THIS PROCEDURE FILLS THE G-MATRIX WITH ITS PARTS;  
"REAL" THET; "ARRAY" G,U,E,LROW,LCOL,PHI; "BEGIN"  
"INTEGER" I,J; "REAL" "ARRAY" T[1:3,1:3],PSEUD[1:9,1:9],DPROD1[1:3,1:9],  
DPROD2[1:9,1:9],DPROD3[1:9,1:3],PROD1[1:3,1:9],PROD2[1:9,1:9];  
CLEAR(G,15,15);  
CLEAR(PSEUD,9,9);  
"FOR" J:=1,2,3 "DO" "BEGIN"  
VALUT(T,THET,PHI,J);  
FILL(PSEUD,T,(1+3*(J-1)),(1+3*(J-1)),3,3); "END";  
KRONE(U,LROW,DPROD1,3,3,1,3);  
MULT(DPROD1,PSEUD,PROD1,3,9,9);  
KRONE(U,E,DPROD2,3,3,3,3);  
MULT(DPROD2,PSEUD,PROD2,9,9,9);  
KRONE(U,LCOL,DPROD3,3,3,3,1);  
FILL(G,U,1,1,3,3);  
FILL(G,PROD1,1,4,3,9);  
FILL(G,PROD2,4,4,9,9);  
FILL(G,DPROD3,4,13,9,3);  
FILL(G,U,13,13,3,3);  
"END" GFILL;
```

```
"PROCEDURE" DIVIDE(A,DIV,L,M);  
"COMMENT" THIS PROCEDURE DIVIDES A MATRIX A BY A NUMBER DIV;  
"REAL" "ARRAY" A; "REAL" DIV; "INTEGER" L,M;  
"BEGIN" "INTEGER" X,Y;  
"FOR" X:=1 "STEP" 1 "UNTIL" L "DO"  
"FOR" Y:=1 "STEP" 1 "UNTIL" M "DO"  
A[X,Y]:=A[X,Y]/DIV;  
"END" DIVIDE;
```

```
"PROCEDURE" WRITE(X,NBONDS,Z,RATIO);  
"COMMENT" THIS PROCEDURE PRINTS OUT THE CALCULATED DATA;  
"INTEGER" X,NBONDS; "REAL" Z,RATIO; "BEGIN"  
"PRINT" ' (L2)FOR X=',SAMELINE,DIGITS(7),X,' 'S2'(',DIGITS(7),NBONDS,  
' BONDS)',', Z=',ALIGNED(6,3),Z,  
' , CHARACTERISTIC RATIO =',ALIGNED(2,3),RATIO;  
"END" WRITE;
```

```
"PROCEDURE" CALC(A,B,X,NBONDS,LAST,AVSQL,Z,RATIO);  
"COMMENT" THIS PROCEDURE CALCULATES THE CHARACTERISTIC RATIO;  
"INTEGER" NBONDS,X; "REAL" LAST,Z,RATIO,AVSQL; "ARRAY" A,B; "BEGIN"  
Z:=A[1,1]+A[1,2]+A[1,3];  
RATIO:=1.0+(LAST*(B[1,4]+B[1,7]+B[1,10])+B[1,13]+B[1,14]+B[1,15])  
/(Z*NBONDS*0.5*AVSQL);  
"END" CALC;
```

"COMMENT" THE FOLLOWING CARDS ONLY DEPEND UPON THE CASE;

"COMMENT" POLY(PHOSPHATE) CHAINS TERMINATED WITH OXYGENS;

```
"PROCEDURE" CRAT1 (U1,U2,U3,G1,G2,G3,G4,X,L,Z);  
"COMMENT" THIS PROCEDURE COMBINES ALL THOSE NEEDED TO CALCULATE  
THE CHARACTERISTIC RATIO ;  
"REAL" Z;  
"REAL" "ARRAY" U1,U2,U3,G1,G2,G3,G4; "REAL" L; "INTEGER" X; "BEGIN"  
"REAL" RATIO; "REAL" "ARRAY" G5[1:15,1:15]; "INTEGER" NBONDS;  
"REAL" LAST,AVSQL;  
NBONDS:=2*X;  
LAST:=L; AVSQL:=L*L;  
"IF" X>10 "THEN" "BEGIN" DIVIDE(U1,Z,3,3);  
DIVIDE(G1,Z,15,15); "END";  
MULT(U1,U2,U3,3,3,3);  
MULT(G1,G2,G3,15,15,15);  
MULT(G4,G3,G5,15,15,15);  
CALC(U5,G5,X,NBONDS,LAST,AVSQL,Z,RATIO);  
WRITE(Z,NBONDS,Z,RATIO);  
"END" CRAT1;
```

"DO NOT" 'L5' CHARACTERISTIC RATIOS OF POLY(PHOSPHATE) CHAINS ',
' WITH X PHOSPHORUS ATOMS AND TERMINATED WITH OXYGENS. ';

"READ" E:

"PRINT" 'L5', 'S20 BOND LENGTH= ', SAMELINE, ALIGNED(3,2), L,
' ATOMS: ';

"COMMENT" SET UP BOND VECTOR AND IDENTITY MATRICES;

CLEAR(LROW,1,3); LROW[1,1]:=L;
CLEAR(LCOL,3,1); LCOL[1,1]:=L;
CLEAR(E,3,3); E[1,1]:=E[2,2]:=E[3,3]:=1.0;

"PRINT" 'L5', 'S20 ELEMENTS OF MATRIX UA: ';
"FOR" I:=1,2,3 "DO" "BEGIN" "PRINT" 'L3', 'S18';
"FOR" J:=1,2,3 "DO" "BEGIN"
"READ" UACI,J]; "PRINT" SAMELINE, ALIGNED(3,3), UACI,J], 'S3'; "END";
"END";

"READ" THET; "PRINT" 'L5', 'S20 THETA(0)= ', SAMELINE, ALIGNED(3,1),
THET, ' DEGREES';

"FOR" I:=1,2,3 "DO" "BEGIN" "READ" PHIC[I];
"PRINT" 'L2', SAMELINE, 'S20 PHIC', DIGITS(1), I, '] FOR A= ',
ALIGNED(3,1), PHIC[I], ' DEGREES'; "END";

GFILL(GA,UA,E,LROW,LCOL,THET,PHI);

"PRINT" 'L5', 'S20 ELEMENTS OF MATRIX UB: ';
"FOR" I:=1,2,3 "DO" "BEGIN" "PRINT" 'L3', 'S18';
"FOR" J:=1,2,3 "DO" "BEGIN"
"READ" UB [I,J]; "PRINT" SAMELINE, ALIGNED(3,3), UB[I,J], 'S3'; "END";
"END";

"READ" THET; "PRINT" 'L5', 'S20 THETA(P)= ', SAMELINE, ALIGNED(3,1),
THET, ' DEGREES';

"FOR" I:=1,2,3 "DO" "BEGIN" "READ" PHIC[I];
"PRINT" 'L2', SAMELINE, 'S20 PHIC', DIGITS(1), I, '] FOR B= ',
ALIGNED(3,3), PHIC[I], ' DEGREES'; "END";

GFILL(GR,UB,E,LROW,LCOL,THET,PHI);

GFILL(GD,E,E,LROW,LCOL,THET,PHI);

"PRINT" 'F', 'Z IS PARTITION FUNCTION AT THIS STAGE';

X:= 2; CRAT1 (UA,UB,UC,GA,GB,GC,GD,X,L,Z);

X:= 3; CRAT1 (UC,UC,UA,GC,GC,GA,GD,X,L,Z);

X:= 4; CRAT1 (UA,UC,UB,GA,GC,GB,GD,X,L,Z);

X:= 5; CRAT1 (UB,UC,UA,GB,GC,GA,GD,X,L,Z);

X:= 6; CRAT1 (UA,UC,UB,GA,GC,GB,GD,X,L,Z);

X:= 7; CRAT1 (UB,UC,UA,GB,GC,GA,GD,X,L,Z);

X:= 8; CRAT1 (UA,UC,UB,GA,GC,GB,GD,X,L,Z);

X:= 9; CRAT1 (UB,UC,UA,GB,GC,GA,GD,X,L,Z);

X:= 10; CRAT1 (UA,UC,UB,GA,GC,GB,GD,X,L,Z);

"PRINT" 'L5' FROM THIS POINT Z IS (NEW PARTITION FUNCTION) / ',

' (OLD PARTITION FUNCTION) + 2 ';;

"FOR" I:=1 "STEP" 2 "UNTIL" 21 "DO" "BEGIN"

X:=(9*(2+I)+1); CRAT1 (UB,UB,UA,GB,GB,GA,GD,X,L,Z);

X:=(9*(2+(I+1))+1); CRAT1 (UA,UA,UB,GA,GA,GB,GD,X,L,Z); "END";

"END" PROG.;

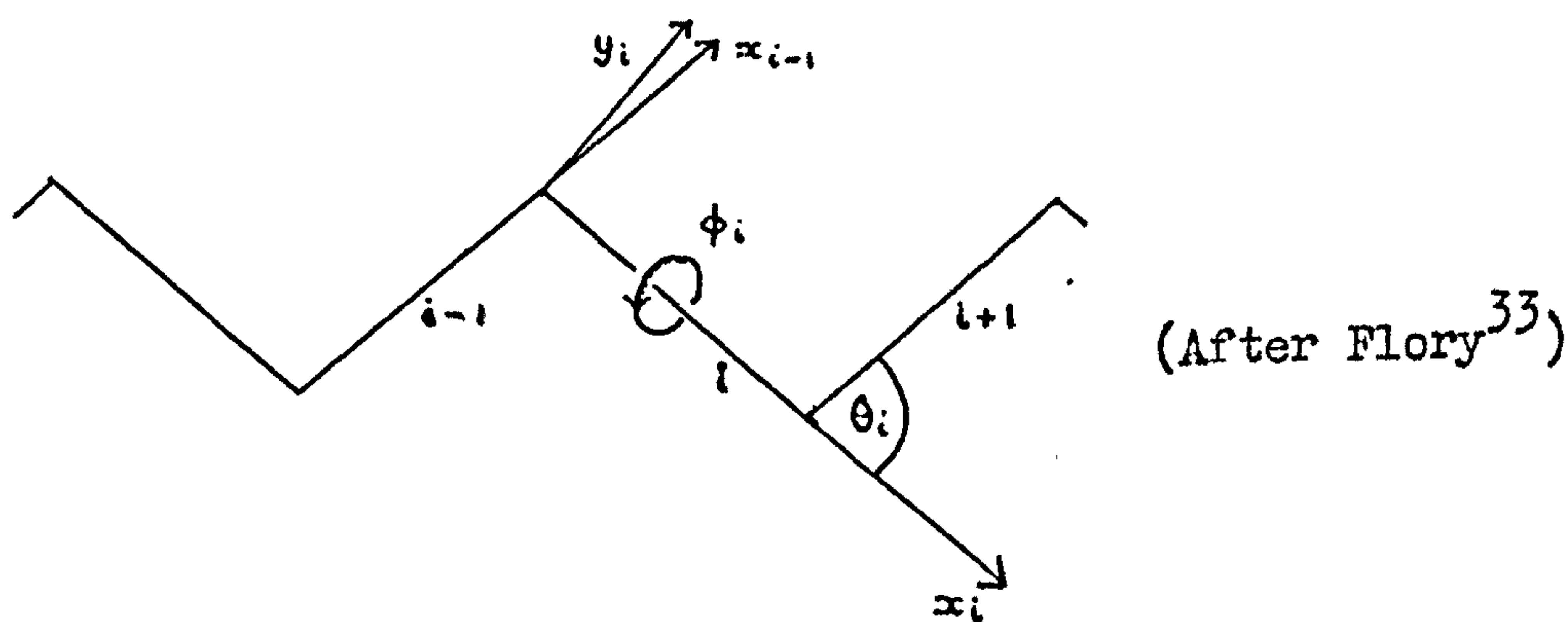
APPENDIX C.

DIRECT CALCULATION OF EQUILIBRIUM CONSTANTS

Before presenting the programme and discussing it in detail, a summary of the principles involved will be given.

(a) Calculation of the end-to-end distance of a chain molecule

The first step in this calculation is to attach a system of co-ordinates to each bond in the chain. According to the conventions adopted here³³, the rectangular co-ordinate system for bond i is defined with the x-axis lying along the bond, the y-axis lying at right angles to it so as to make an acute angle with the preceding bond, and the z-axis completing a right-handed system:



With this convention, the matrix that transforms a vector in the co-ordinate system attached to the $(i + 1)$ 'th bond into that of the i 'th is:

$$\underline{T}_i = \begin{vmatrix} \cos \theta_i & \sin \theta_i & 0 \\ \sin \theta_i \cos \phi_i & -\cos \theta_i \cos \phi_i & \sin \phi_i \\ \sin \theta_i \sin \phi_i & -\cos \theta_i \sin \phi_i & -\cos \phi_i \end{vmatrix}$$

For an n-bonded chain, the end-to-end vector \underline{d} is given by the sum of the vectors representing the n bonds, but with the provision that the vectors are expressed in a common frame of reference. If this common frame is that of the first bond, it follows that:

$$\underline{d} = \underline{l}_1 + \underline{T}_1 \underline{l}_2 + \underline{T}_1 \underline{T}_2 \underline{l}_3 + \dots + \underline{T}_1 \underline{T}_2 \dots \underline{T}_{n-1} \underline{l}_n$$

where \underline{l}_i is the vector representing the bond i in its own system of co-ordinates, and is given by:

$$\underline{l}_i = \begin{vmatrix} l_i \\ 0 \\ 0 \end{vmatrix}$$

If the components of \underline{d} are expressed by:

$$\underline{d} = \begin{vmatrix} d_x \\ d_y \\ d_z \end{vmatrix}$$

then the scalar end-to-end distance is given by:

$$d = \underline{d} \cdot \underline{d} = \begin{vmatrix} d_x & d_y & d_z \end{vmatrix} \begin{vmatrix} d_x \\ d_y \\ d_z \end{vmatrix}$$

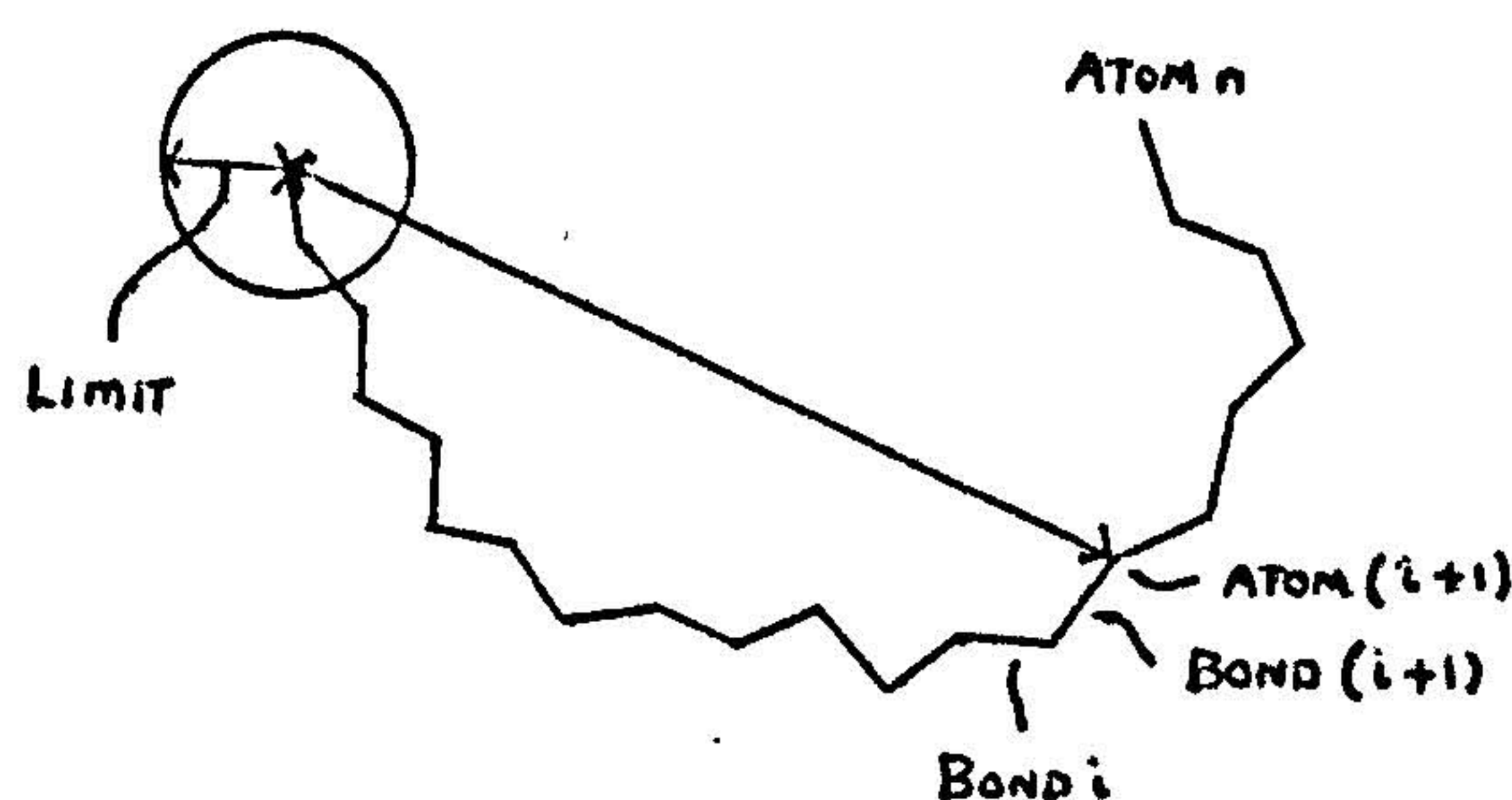
or
$$d = (d_x^2 + d_y^2 + d_z^2)^{1/2}$$

In the programme, \underline{T} becomes a four-dimensional array, with the first index denoting the number of the bond in the chain and the

second its rotational state (1 for trans, 2 for gauche+, 3 for gauche-). \underline{d} is represented for each of the skeletal atoms by elements in the two-dimensional array D, for which the second index is the number of the bond leading to the atom.

(b) "Rejection by distance"

By this is meant, the early identification of conformations for which the chain ends could not possibly come within a specified distance, and truncation of their associated calculations. The mechanism of this is clear from the diagram:



If the atom (i + 1) is so remote from the chain end acting as origin, that the remaining bonds in the chain could not possibly bring the ends to within the specified distance (LIMIT in the programme), then all the conformations with atom (i + 1) in that position may automatically be rejected, and it may immediately be relocated, by rotation of bond i into a new state. In the programme, an element in the array SQRAD is allocated to each atom: it contains a test number, formed by taking the total of the lengths of the bonds succeeding the atom in the chain, adding on the values of LIMIT, and squaring. Whenever during the generation of the conformations the position of the atom is altered, the permissibility of its new location is determined by comparing its SQRAD value with the square of the new distance separating it from the origin.

(d) Statistical weights of conformations

The statistical weight of a complete chain conformation is simply the product of the appropriate elements of the U-matrices for the successive bonds. In the programme, the matrices are formalised as:

$$\underline{U}_i = \begin{vmatrix} 1 & \sigma_i & \sigma_i \\ 1 & \sigma_i \psi_i & \sigma_i \omega_i \\ 1 & \sigma_i \omega_i & \sigma_i \psi_i \end{vmatrix}$$

and are held within a three-dimensional array U, for which the first index is the number of the bond in the chain. They are filled from input values of σ_i , ψ_i , and ω_i (denoted as such in the programme).

(d) "Rejection by statistical weight"

If a bond is rotated into a state such that with the preceding bond it forms a pair attributed zero weight in the model, it is immediately subjected to a further rotation.

(e) "Rejection by symmetry"

It will be recalled that this depends on the observation that most of the conformations may be grouped in pairs of mirror images, with the exception of those that have all bonds in either a cis or a trans state, which are planar and unique. Duplication of the calculations

may readily be avoided by the simple rule that attention is given to those conformations with the leftmost non-trans bond in the gauche+ state, but is withheld from those with the leftmost non-trans bond gauche-. For instance, the conformation:

t t t g+ t t g+ g+ t g- t g+ t

would be explicitly treated, but its mirror image:

t t t g- t t g- g- t g+ t g- t

would not be dealt with separately. The system by which the conformations are generated particularly facilitates the application of this rule, provided only that special provision be made for the treatment of the few conformations such as:

t t t t t t t t g+ t

that are planar as far as the penultimate atom. (Here, the terminal bonds are represented as trans, even though their states are technically undefined.)

(f) Computational economy

The main difficulty in these calculations is that the programme must operate with great rapidity if chains of reasonable length are to be accessible to treatment. It is essential that the labour required for each conformation be minimised, and wherever possible re-calculation of data must be avoided by its storage. For instance, the T-matrices for each bond in each of its states are permanently stored, as are the

components of each bond vector in the co-ordinates of the preceding bond, for each state of the latter. The matrix products $\underline{T}_1 \underline{T}_2 \underline{T}_3 \dots$ are stored for as long as they are useful (in the arrays PROD). The vector components of the position of each skeletal atom are recorded. The statistical weight is not entirely re-calculated for each conformation, but instead the weight for the unmodified chain segment is preserved, and new factors for the rest are multiplied in. (The weight of the chain up to the I'th atom being stored as WT [I].) The end-to-end separation of the chain is retained as the square when the conformation is being put into its distance category. Finally, the PROCEDURE format is avoided if it entails frequent transfers of control, or constant re-assignment of fresh values to the variables in a long parameter list.

A fairly detailed description of the programme used will now be given. The programme itself is listed at the end of this Appendix, including the statements designed to effect rejections by distance and weight, but excluding certain optional output statements.

It may be noted, firstly, that the main programme is a PROCEDURE. It was cast in this form to permit automatic adjustment of the array dimensions to those suitable for the length of the chain being treated. It is called once for each chain, by the statement CONFMS(NBONDS): that appears at the end of the programme; the argument NBONDS is an input integer representing the number of bonds in the chain.

The other two PROCEDURES are RITIT and RITALL. RITIT outputs the results of the calculations for a single conformation. It is rarely used, other than as a test routine. RITALL outputs the overall

results of the calculation, that is: the total number of conformations treated, and their total statistical weight; the number and the weight of the conformations in each distance category, and the equilibrium constants calculated assuming the different sphere radii; the root-mean-square end-to-end separation of the chain; the average conformational energies of the conformations as a whole, and in their distance categories (calculated from the input statistical weight parameters). It is framed as a PROCEDURE to facilitate intermittent dumping of the calculated data during the course of the run, but is entered no more than a few times.

Proceeding to the main body of the programme, there follows a section mainly concerned with clearing arrays. Some of these variables were introduced at an earlier stage, and are no longer relevant; those of importance are NOS[I] , WTS[I] , and, to a lesser extent, WTDENS[I] . NOS[I] , I = 1 - 10, stores the number of conformations with ends between (I - 1) and I Å apart; NOS[11] stores the number with ends more distant than 10 Å; NOS[12] stores the total number of conformations. WTS[I] and WTDENS[I] perform analogous functions for the weights, and for the statistically weighted conformational energies.

The next section inputs and outputs the data for each bond, namely: bond length and angle, rotational angles, statistical weight parameters; and also an integer HOLD[I] . The value assigned to this variable distinguishes rotatable bonds from non-rotatable (such as ester bonds): it is 0 for the first, 1 for the second, kind.

The following section fills statistical weight matrices. It also converts the parameters back into terms of conformational energies (EN). On the same page, the row SQRAD[I] , discussed in (b) above, is set up.

On page 219, the T-matrices are filled, and the vector components of each bond in the co-ordinate system of that preceding are evaluated. The two integers MARK and SYM are important in the mechanism for rejection by symmetry. MARK contains the number of the left-most bond to have been rotated away from trans. SYM is 2 for conformations dealt with as pairs of mirror images, 1 for those dealt with individually; the values they are given here are in preparation for entry into the block starting at statement GENO on the next page. Similarly, the weight of the first bond, $WT[I]$, is set at 2.0 so that all subsequent weights are automatically doubled.

The calculation is initiated with the chain set all-trans, and the next section prepares for this by calculating the data for that conformation. The integer $IND [I]$, recording the number (1, 2 or 3) associated with the state of bond I, is set to 1 for all I. There follows a natural lead to the statement GENO, on page 220. The statements between GENO and DONEO perform the calculations for the conformations planar as far as atom (NBONDS - 1), i.e.:

```
t t t ..... t t t t
t t t ..... t tg+ t
t t t ..... t tg- t
```

These conformations are dealt with individually, and so the doubling of the statistical weights must be temporarily counteracted; this is achieved by the statement GENO itself. Correct enumeration is ensured if SYM has already been set to 1 whenever GENO is entered. The actual calculation is carried out by means of a do-loop that puts the penultimate bond into its three states (denoted 1, 2 and 3) in turn.

For each state, the first check is on the statistical weight of the bond-pair generated; then the end-to-end distance squared is evaluated, and compared with the input value of LIMIT. ($SQRAD[NBONDS] = LIMIT.$) If the ends are too widely separated, the conformation is rejected. The cards effecting these checks may be omitted if desired. If the conformation is acceptable, its weight is fully evaluated and it is assigned to its correct distance category.

After treatment of these conformations, SYM is returned to its normal value of 2. The conformational weight needs no re-adjustment, since GEN0 affects only the last two members of the row WT [I], which are now in any case irrelevant. Control is passed to the statement GEN2, which is described below.

The block starting with the statement GEN1 (page 221) is closely analogous to that of GEN0, except that it deals with conformations as symmetrical pairs, and so the doubling of weights is retained. This block in fact completes the calculation for each of the remaining conformations successively; and in normal use no further transfers are made to GEN0.

The statement GEN2 starts a sequence that systematically adjusts the conformations of bonds further back down the chain, and re-calculates the variables it modifies in doing so. It takes account of the HOLD value of each bond, and will not alter the state of a bond designated as fixed trans. It will not attempt to rotate a bond already in the last of its states into a further state. It will reject a bond rotation that produces a conformation that has already been treated in mirror image. In all three cases, control is passed to GEN3 (page 223) which ensures that the bond in question is set to trans, and refers back to

GEN2 for adjustment of bond states even further back down the chain. This process continues until an acceptable conformation is found for the entire chain segment running from the first bond to that numbered as (NBONDS - 2), when return may be made to GEN1 for the penultimate bond, (NBONDS - 1), to be set in each of its states in turn and for the calculation for each conformation to be completed.

The following will clarify the system upon which the conformations are generated. Entry is made to GEN2 from GEN0 with the numbers in the row IND[I] corresponding to the conformation:

t t t t t t g- t

where the terminal bonds are denoted as trans. Provided bond (NBONDS - 2) is rotatable, return is made to GEN1 with the partial conformation:

t t t t t g+ ? t

where the penultimate bond is in an undefined state. GEN1 now operates to put this bond through its three states and to deal with the resulting chain conformations:

t
t t t t t g+ g+ t
g-

successively. Transfer having been made to GEN2 after the last with

t t t t t g+ g-tt

the partial conformation:

t t t t t g- ? t

will be considered, but rejected by the symmetry rule. Return will therefore be made to GEN1 on:

t t t t g+ t ? t

provided bond (NBONDS -3) is rotatable; here, GEN2 has detected the exhaustion of the states of bond (NBONDS -2), and GEN3 has set it back trans. The next transfer to GEN2 will be at:

t t t t g+ t g- t

and return to GEN1 will be with:

t t t t g+ g+ ? t

Subsequent transfer to GEN2 is at :

t t t t g+ g+ g- t

which will return the symmetry-permitted partial conformation:

t t t t g+ g- ? t

On the next transfer to GEN2, the bond (NBONDS - 2) has again exhausted its three states:

t t t t g+ g- g- t

while the partial conformation:

t t t t g- t ? t

that comes next is not allowed by the symmetry tests. Return to GEN1 must therefore be on:

t t t g+ t t ? t

provided that bond (NBONDS - 4) is rotatable.

The calculations proceed in this manner until the conformations of the chain are completely exhausted, which, in the case of a chain with all bonds rotatable, occurs after GEN1 has treated the conformation:

t g+ g+ g+ g+ g+ g- t

for the next conformation:

t g- t t t t ? t

is unacceptable on grounds of symmetry. In the programme, the end of the calculations is detected when GEN3 sets bond 2 back on trans.

The statements in GEN2 relating to the rejection of conformations by statistical weight and distance are extremely powerful. They test the partial conformations as they are built up, and by detecting unsatisfactory combinations of bond states at an early stage they may achieve the elimination of many conformations at once. For instance, simple recognition that the partial conformation:

t g+ g-

(say) has zero weight may permit the immediate rejection of literally millions of chain conformations in which it appears. Similarly, the discovery that conformations starting:

t t t t t

cannot possibly have their ends within a distance LIMIT may lead to the automatic rejection of many tens of thousands of conformations featuring this sequence.

The programme as presented is in a form appropriate for a chain in which all rotatable bonds have three states. For poly(ethylene terephthalate) chains, where the terephthaloyl virtual bonds have only two, certain modifications are required. These consist of giving the virtual bonds a HOLD value of -1, so that they can be recognised at later stages, and adapting the symmetry rejection statements and the assignments of MARK and SYM to allow for conformations with all bonds in either the trans or cis states. Such conformations are also planar, and use is made of GENO at the correct times to deal with them. The statistical weight scheme also requires some minor adaptations.

For the phosphate calculations in which the bonds were assigned more than three states, similar provision had to be made for the appearance of planar conformations during the course of the calculation. The statistical weights were not, of course, found from input parameters as here, but calculated directly from the total energy of the conformation. This involved the insertion of a PROCEDURE ENERGY, derived from the programme for the systematic evaluation of all the electrostatic interactions, and the detection of steric overlaps, which was used for the calculation of the statistical weights presented in Section 9.3.

POLYPHOSPHATE SHORT CHAIN CONFORMATIONS;

```
"COMMENT" THIS PROGRAM HAS BEEN WRITTEN TO HAVE FEW PROCEDURES AND NO
ARGUMENTS IN THOSE IT HAS;
"BEGIN"
"INTEGER" NBONDS;

"PROCEDURE" CONFMS(NBONDS);
"COMMENT" CONFMS IS IN FACT THE MAIN PROG. IN PROCEDURE FORM;
"INTEGER" NBONDS; "BEGIN"

"REAL""ARRAY" EC[1:3];
"REAL" DIST,SUMSQ,RAD,SQDIST,WTDEN,COSIN1,COSIN2;
"REAL""ARRAY" DC[1:3,1:NBONDS];
"INTEGER" SYM;
"INTEGER" START; "REAL" LIMIT; "REAL""ARRAY" SQRAD[1:NBONDS];
"INTEGER" I,J,M,N,K,KOUNT;
"INTEGER""ARRAY" NOS[1:12],CUTNOS[1:3,1:7],CUT[1:3],IND[1:NBONDS],
HOLD[1:(NBONDS-1)];
"REAL""ARRAY" TC[1:NBONDS-1,1:3,1:3,1:3],COMPON[2:NBONDS,1:3,1:3];
"REAL""ARRAY" PRODC[1:NBONDS-1,1:3,1:3],
THET[1:(NBONDS-1)],PHI[1:(NBONDS-1),1:3],L[1:NBONDS],
CTHET[1:(NBONDS-1)],STHET[1:(NBONDS-1)],CPHI[1:(NBONDS-1),1:3],
SPHI[1:NBONDS-1,1:3],SIGMA[1:NBONDS-1],OMEGA[1:NBONDS-1],
WTSC[1:12],WTDENS[1:12],
CUTWTSC[1:3,1:7],CWTDEN[1:3,1:7],WTANG1[1:6,1: 9],
WTANG2[1:6,1: 9],CTANG1[1:3,1:6,1: 9],CTANG2[1:3,1:6,1: 9],CTSMSQ[1:3],
COSINC0: 9],SINE[1: 9];
"REAL""ARRAY" PSIC[1:(NBONDS-1)];
"REAL""ARRAY" WTC[1:(NBONDS-1)],TOTENC[1:(NBONDS-1)],
UC[1:(NBONDS-1),1:3,1:3],ENC[1:(NBONDS-1),1:3,1:3];
"INTEGER" MARK;
"INTEGER" X,Y;
"INTEGER" Merno,SYMNO;
"REAL""ARRAY" SQUARE[1:11];

"PROCEDURE" RITIT;
"COMMENT" PROCEDURE RITIT PRINTS A CONFORMATION AND ITS DATA;
"BEGIN"
"PRINT" 'L';
"FOR" X:= 1 "STEP" 1 "UNTIL" NBONDS "DO""BEGIN"
"IF" INDC[X] = 1 "THEN""PRINT" 'T ';
"IF" INDC[X] = 2 "THEN""PRINT" 'G+';
"IF" INDC[X] = 3 "THEN""PRINT" 'G-'; "END";
"PRINT" SAMELINE,'S5'DIST= ',ALIGNED(3,3),DIST,'S5'WT.= ',
ALIGNED(3,3),WTENBONDS-1]/2.0,'S'(',DIGITS(1),SYM,')';
"END" RITIT;
```

```
"PROCEDURE" RITALL;
"COMMENT" PROCEDURE RITALL PRINTS THE OVERALL DATA;
"BEGIN"
"REAL" "ARRAY" K[1:10]; "REAL" TOTWT;
"REAL" RMS;
WTSC[12]:=WTDENS[12]:=0.0; NOS[12]:=0;
TOTWT:=0.0;
"FOR" X:= 1 "STEP" 1 "UNTIL" 11 "DO" "BEGIN"
WTSC[12]:=WTSC[12] + WTSC[X]; NOS[12]:=NOS[12] + NOS[X];
WTDENS[12]:=WTDENS[12] + WTDENS[X];
"END";
"PRINT" 'F';
"PRINT" 'L2' TOTAL NO. CONFIGURATIONS TREATED = ', SAMELINE, DIGITS(7),
NOS[12], 'S2' TOTAL STATISTICAL WT. = ', ALIGNED(6,3), WTSC[12], 'S2';
"IF" WTSC[12]>0.0 "THEN" "PRINT" SAMELINE,
'MEAN CONFORMATIONAL ENERGY = ', ALIGNED(3,3), (WTDENS[12]/WTSC[12]),
' RT'L2'
"ELSE" "PRINT" 'MEAN CONFORMATIONAL ENERGY UNDEFINED.';
"FOR" X:= 1 "STEP" 1 "UNTIL" 11 "DO" "BEGIN"
"PRINT" 'L' NO. WITH ENDS BETWEEN ', SAMELINE, DIGITS(2), (X-1), ' AND ' ;
"IF" X=11 "THEN" "PRINT" ' INFINITY = ' "ELSE" "PRINT" SAMELINE,
DIGITS(2), X, ' ANGSTROMS = ' ;
"PRINT" SAMELINE, DIGITS(7), NOS[X], 'S1' WITH WT. = ',
ALIGNED(6,3), WTSC[X], 'S1';
"IF" WTSC[X]>0.0 "THEN" "PRINT" 'ENERGY = ',
SAMELINE, ALIGNED(3,3), (WTDENS[X]/WTSC[X])
"ELSE" "PRINT" 'ENERGY UNDEFINED.';
"IF" X< 11 "THEN" "BEGIN"
TOTWT:=TOTWT + WTSC[X];
"IF" WTSC[12] > 0.0 "THEN" "BEGIN"
K[X]:=(3.0*TOTWT*10000)/(WTSC[12]*4.0*3.1416*X*X*X*SYMNO*6.023);
"PRINT" ' K( ', SAMELINE, DIGITS(1), MERN0, ' ) = ', ALIGNED(1,6), K[X],
' MOLES/LITRE.';
"END";
"END"; "END";
"IF" WTSC[12] > 0.0 "THEN" "BEGIN"
RMS:=SQRT(SUMSQ/WTSC[12]);
"PRINT" 'L5', 'RMS SEPARATION = ', SAMELINE, ALIGNED(2,3), RMS;
"END";
"END" RITALL;
```

"COMMENT" THE MAIN BODY OF THE PROGRAM FOLLOWS;

```
RAD:=57.2958;
SUMSQ:=CTSMSQ[1]:=CTSMSQ[2]:=CTSMSQ[3]:=0.0;
"FOR" I:= 1 "STEP" 1 "UNTIL" 12 "DO""BEGIN"
NOSC[I]:=0; WTSC[I]:=WTDENSC[I]:=0.0;
"IF" I<7 "THEN" "BEGIN"
"FOR" K:= 1 "STEP" 1 "UNTIL" 9 "DO"
WTANG1[I,K]:=WTANG2[I,K]:=0.0;
"FOR" J:= 1 "STEP" 1 "UNTIL" 3 "DO""BEGIN"
CUTNOSC[J,I]:=0; CUTWTSC[J,I]:=CWTDENSC[J,I]:=0.0;
"FOR" K:= 1 "STEP" 1 "UNTIL" 9 "DO"
CTANG1[J,I,K]:=CTANG2[J,I,K]:=0.0;"END";
"END";
"END";
```

"COMMENT" THE NEXT SECTION INPUTS AND OUTPUTS BOND DATA;

```
"PRINT" ''L5'', ''S1' BOND NO.'S2' THETA'S6' LENGTH'S5' SIGMA'S7' OMEGA',
''S4' PSI'S16' PHIS';
"FOR" I:= 1 "STEP" 1 "UNTIL" (NBONDS-1) "DO""BEGIN"
"READ" THETC[I],LC[I],SIGMAC[I],OMEGAC[I],PSIC[I],HOLDC[I];
CTHETC[I]:=COS(THETC[I]/RAD); STHETC[I]:=SIN(THETC[I]/RAD);
"FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO""BEGIN"
"READ" PHIC[I,J]; CPHIC[I,J]:=COS(PHIC[I,J]/RAD);
SPHIC[I,J]:=SIN(PHIC[I,J]/RAD);
"END";
"PRINT" ''L'', SAMELINE, ''S3'', DIGITS(2), I, ''S6'', ALIGNED(2,1), THETC[I],
''S6'',
ALIGNED(1,2), LC[I], ''S6'', ALIGNED(1,2), SIGMAC[I], ''S6'', ALIGNED(1,3),
OMEGAC[I], ''S2'', ALIGNED(1,3), PSIC[I], ''S2'', ALIGNED(3,1), PHIC[I,1],
''S5'', ALIGNED(3,1), PHIC[I,2], ''S5'', ALIGNED(3,1), PHIC[I,3];
"IF" HOLDC[I] = 1 "THEN""PRINT" ''S5' NO ROTATION ABOUT THIS BOND';
"END";
"READ" L[NBONDS];
"PRINT" ''L'', SAMELINE, ''S3'', DIGITS(2), NBONDS, ''S17'', ALIGNED(1,2),
L[NBONDS], ''L2'';
```

```
"READ" Merno, SYMNO;
"PRINT" ''L2' THE CHAIN CORRESPONDS TO A ', SAMELINE, DIGITS(2), Merno,
'-MERIC RING, WITH SYMMETRY NO. = ', DIGITS(2), SYMNO, ''L5'';
```


"COMMENT" THIS SECTION FILLS STATISTICAL WEIGHT MATRICES FOR LATER USE;

```
"FOR" I:= 1 "STEP" 1 "UNTIL" (NBONDS-1) "DO""BEGIN"  
UCI,1,1]:=UCI,2,1]:=UCI,3,1]:=1.0;  
UCI,1,2]:=UCI,1,3]:=SIGMACI];  
UCI,2,2]:=UCI,3,3]:=SIGMACI]*PSICI];  
UCI,2,3]:=UCI,3,2]:=SIGMACI]*OMEGACI];  
"FOR" J:=1,2,3 "DO""FOR" K:=1,2,3 "DO"  
"IF" UCI,J,K]>0.0 "THEN" ENCI,J,K]:=-LN(UCI,J,K])  
"ELSE" ENCI,J,K]:=0.0; "END";
```

"COMMENT" A CAPTION CAN BE INSERTED HERE IF REJECTION BY STATISTICAL WEIGHT IS BEING OPERATED;
"PRINT" 'L2'', 'CONFORMATIONS WITH ZERO STATISTICAL WT. HAVE BEEN ',
'REJECTED';

```
"FOR" I:= 0 "STEP" 1 "UNTIL" 9 "DO""BEGIN"  
COSINCI]:=COS((20.0*I)/RAD);  
"IF" I>0 "THEN" SINECI]:=SIN((20.0*(I-0.5))/RAD); "END";
```

"COMMENT" THE FOLLOWING CARDS SET UP SQRADS FOR REJECTION BY DISTANCE;
"COMMENT" ALTERNATIVELY , IF NO REJECTION IS TO TAKE PLACE, LIMIT IS GIVEN THE VALUE OF 11;

```
"READ" LIMIT;  
"PRINT" 'L'ALL CONFORMATIONS WITH END-TO-END DISTANCES >',  
SAMELINE,ALIGNED(2,1),LIMIT,' ANGSTROMS HAVE BEEN REJECTED.'L2'';  
"PRINT" 'THEREFORE THE OVERALL STATISTICAL WEIGHT IS INCORRECT AND ',  
'THE K(X) VALUES ARE WITHOUT MEANING.'L2'';
```

```
SQRAD[NBONDS]:=LIMIT;  
"FOR" I:= NBONDS-1 "STEP" -1 "UNTIL" 3 "DO"  
SQRADCI]:=SQRADCI+1]+LCI+1];  
"FOR" I:= 3 "STEP" 1 "UNTIL" NBONDS "DO"  
SQRADCI]:=SQRADCI]*SQRADCI];  
"IF" LIMIT > 11 "THEN" LIMIT:=11;
```

"COMMENT" SQUARE[X] IS USED TO CLASSIFY DISTANCES IN THE RECORDING SEQUENCES;

```
"FOR" X:= 1 "STEP" 1 "UNTIL" LIMIT "DO"  
SQUARE[X]:=(X-1)*(X-1);
```

"COMMENT" THE T-MATRICES ARE FILLED FOR EACH BOND IN ALL ITS STATES AND THE VECTOR COMPONENTS OF EACH BOND IN THE COORDINATES OF THE PRECEDING BOND ARE CALCULATED, FOR EVERY STATE OF THE LATTER;

```
"FOR" I:= 1 "STEP" 1 "UNTIL" NBONDS-1 "DO"  
"FOR" J:= 1,2,3 "DO" "BEGIN"  
T[I,J,1,1]:=CTHET[I];  
T[I,J,1,2]:=STHET[I];  
T[I,J,1,3]:=0.0;  
T[I,J,2,1]:=STHET[I]*CPHI[I,J];  
T[I,J,2,2]:=-CTHET[I]*CPHI[I,J];  
T[I,J,2,3]:=SPHI[I,J];  
T[I,J,3,1]:=STHET[I]*SPHI[I,J];  
T[I,J,3,2]:=-CTHET[I]*SPHI[I,J];  
T[I,J,3,3]:=-CPHI[I,J];  
COMPON[I+1,J,1]:=L[I+1]*T[I,J,1,1];  
COMPON[I+1,J,2]:=L[I+1]*T[I,J,2,1];  
COMPON[I+1,J,3]:=L[I+1]*T[I,J,3,1];  
"END";
```

"COMMENT" MARK CONTAINS THE NUMBER OF THE MOST LEFT-HAND BOND THAT HAS BEEN PUT INTO A STATE OTHER THAN TRANS- OR CIS-. THIS MEANS THAT THE MOLECULE IS PLANAR AS FAR UP AS THE ATOM NUMBERED MARK;
"COMMENT" SYM CONTAINS 1 IF THE CONFORMATION IS ENTIRELY PLANAR, 2 OTHERWISE;

```
MARK:= NBONDS-2; SYM:=1;
```

"COMMENT" AS ONLY ONE OF A SYMMETRICAL PAIR OF CONFORMATIONS IS TREATED IT IS NECESSARY TO DOUBLE THE STATISTICAL WEIGHTS CALCULATED BY SETTING WTC[1] = 2.0 AT THE START;

```
WTC[1]:=2.0; TOTENC[1]:=0.0;
```

"COMMENT" THE FOLLOWING SECTION SETS THE CHAIN UP IN THE ALL-TRANS CONFORMATION, AND CALCULATES THE VECTOR COORDINATES OF THE CHAIN ATOMS AND THE TOTAL STATISTICAL WT. IT ALSO CALCULATES MATRIX PRODUCTS PROD [I,X,Y], WHERE PROD [I.. IS THE PRODUCT OF THE T-MATRICES FROM 1 TO I;
"COMMENT" FINALLY IT JUMPS TO THE TREATMENT OF PLANAR CONFORMATIONS;

"COMMENT" INDC[I] CONTAINS AN INTEGER ASSOCIATED WITH THE STATE OF BOND [I]. FOR EFFICIENCY J IS GIVEN THE VALUE OF INDC[I], K THAT OF INDC[I-1], AND M AND N THE VALUES I-1 AND I+1, FOR USE IN LATER OPERATIONS;

```
"FOR" X:= 1,2,3 "DO" "FOR" Y:= 1,2,3 "DO"  
PROD[1,X,Y]:=T[1,1,X,Y];  
D[1,1]:=L[1]; D[2,1]:=D[3,1]:=0.0;
```

```
J:=INDC[1]:=1;  
"FOR" X:= 1,2,3 "DO"  
D[X,2]:=D[X,1] + COMPON[2,J,X];  
INDC[NBONDS]:=1;
```

```
"FOR" I:= 2 "STEP" 1 "UNTIL" NBONDS-1 "DO""BEGIN"  
J:=IND[I]:=1; M:=I-1; N:= I+1;  
"FOR" X:= 1,2,3 "DO""BEGIN"  
D[X,N]:=D[X,I];  
"FOR" Y:= 1,2,3 "DO""BEGIN"  
D[X,N]:=D[X,N]+COMPON[N,J,Y]*PROD[M,X,Y];  
PROD[I,X,Y]:=PROD[M,X,1]*T[I,J,1,Y] + PROD[M,X,2]*T[I,J,2,Y]  
+ PROD[M,X,3]*T[I,J,3,Y]; "END"; "END";  
K:=IND[M];  
TOTEN[I]:=TOTEN[M] + EN[I,K,J];  
WT[I]:=WT[M]*UCI,K,J];  
"IF" I = NBONDS - 1 "THEN""GOTO" GEN0;  
"END";
```

"COMMENT" GEN0 DEALS WITH THOSE CONFORMATIONS WHICH ARE PLANAR AS FAR AS BOND [NBONDS];

```
GEN0: WTC[M]:=0.5*WTC[M];  
"FOR" J:= 1,2 ,3 "DO""BEGIN"  
"COMMENT" THE FOLLOWING CARD REJECTS CONFORMATIONS WITH ZERO WEIGHT;  
"IF" UCI,K,J] > 0.0 "THEN""BEGIN"
```

"COMMENT" THE NEXT SECTION CALCULATES THE END-TO-END DISTANCE;

```
"FOR" X:=1,2,3 "DO""BEGIN"  
D[X,N]:=D[X,I];  
"FOR" Y:= 1,2,3 "DO"  
D[X,N]:=D[X,N] + COMPON[N,J,Y]*PROD[M,X,Y];  
E[X]:=D[X,N]*D[X,N];  
"END"; SQDIST:= (E[1] + E[2] + E[3]);  
"COMMENT" THE FOLLOWING CARD REJECTS CONFORMATIONS WHOSE ENDS DO NOT  
COME WITHIN LIMIT ANGSTROMS OF EACH OTHER;  
"IF" SQDIST > SQRAD[NBONDS] "THEN""GOTO" DONE0;
```

"COMMENT" THE NEXT SECTION CALCULATES THE STATISTICAL WEIGHT;

```
WTC[I]:=WTC[M]*UCI,K,J];  
TOTEN[I]:=TOTEN[M] + EN[I,K,J];  
WTDEN:= TOTEN[I] * WTC[I];
```

"COMMENT" THIS SEQUENCE RECORDS THE DISTRIBUTION OF WEIGHT OVER THE DISTANCE CATEGORIES;

```
"FOR" X:= LIMIT "STEP" -1 "UNTIL" 1 "DO"  
"IF" SQDIST > SQUARE[X] "THEN""BEGIN"  
WTSC[X]:=WTSC[X]+WTC[I];  
WTDENS[X]:=WTDENS[X]+WTDEN;  
NOS[X]:=NOS[X]+SYM; "GOTO" OUT0; "END";  
OUT0:SUMSQ:=SUMSQ + SQDIST*WTC[I];  
"COMMENT" THE NEXT CARD IS CONNECTED WITH REJECTION BY STATISTICAL WT.;  
"END";
```

DONE0:"END" GEN0;

```
SYM:=2;  
"GOTO" GEN2;
```

"COMMENT" GEN1 DEALS WITH THOSE CONFORMATIONS THAT HAVE A SYMMETRICAL MATE, WHICH IS NOT TREATED;

GEN1: "FOR" J:= 1,2,3 "DO""BEGIN"
"COMMENT" THE FOLLOWING CARD REJECTS CONFORMATIONS WITH ZERO WEIGHT;
"IF" UCI,K,J] > 0.0 "THEN""BEGIN"

"COMMENT" THE NEXT SECTION CALCULATES THE END-TO-END DISTANCE;

"FOR" X:= 1,2,3 "DO""BEGIN"
DCX,N]:=DCX,I];
"FOR" Y:= 1,2,3 "DO"
DCX,N]:=DCX,N] + COMPONENT,J,Y]*PRODCM,X,Y];
ECX]:=DCX,N]*DCX,N];
"END"; SQDIST:= (EC[1] +EC[2] + EC[3]);
"COMMENT" THE FOLLOWING CARD REJECTS CONFORMATIONS WHOSE ENDS DO NOT COME WITHIN LIMIT ANGSTROMS OF EACH OTHER;
"IF" SQDIST > SQRADENBONDS] "THEN""GOTO" DONE1;

"COMMENT" THE NEXT SECTION CALCULATES THE STATISTICAL WEIGHT;

WTCI]:=WTCM]*UCI,K,J];
TOTENCI]:=TOTENCM] + ENCI,K,J];
WTDEN:=TOTENCI]*WTCI];

"COMMENT" THIS SEQUENCE RECORDS THE DISTRIBUTION OF WEIGHT OVER THE DISTANCE CATEGORIES;

"FOR" X:= LIMIT "STEP" -1 "UNTIL" 1 "DO"
"IF" SQDIST > SQUARE[X] "THEN""BEGIN"
WTSC[X]:=WTSC[X]+WTCI];
WTDENS[X]:=WTDENS[X]+WTDEN;
NOSC[X]:=NOSC[X]+SYM; "GOTO" OUT1; "END";
OUT1:SUMSQ:=SUMSQ + SQDIST*WTCI];
"COMMENT" THE NEXT CARD IS CONNECTED WITH REJECTION BY STATISTICAL WT.;
"END";

DONE1: "END" GEN1;

"COMMENT" GEN2 ADJUSTS THE CONFORMATIONS OF BONDS FURTHER BACK DOWN THE CHAIN, AND RECALCULATES THE CORRESPONDING QUANTITIES. IT ALSO SELECTS THE CONFORMATIONS ADMISSIBLE ON SYMMETRY GROUNDS;

"COMMENT" I-1 IS USED IN GEN2 RATHER THAN M BECAUSE M RETAINS AN OUTDATED VALUE WHEN RETURN TO GEN2 FROM GEN3 IS MADE;

```
GEN2:I:=I-1;
CHANGE:("IF" HOLD[I] > 0 "THEN""GOTO" GEN3;
"IF" INDC[I] > 2 "THEN""GOTO" GEN3;
INDC[I]:=INDC[I] + 1;
```

"COMMENT" THE NEXT CARD ENSURES THAT A PLANAR SECTION OF CHAIN IS NOT TERMINATED ON THE RIGHT BY A BOND IN A STATE WHOSE MIRROR IMAGE HAS ALREADY BEEN TREATED. IN THIS CASE, THE MOST LEFT-HAND BOND TO HAVE BEEN ROTATED AWAY FROM THE TRANS- STATE CANNOT BE SET G-, SINCE ALL THE CONFORMATIONS DERIVED FROM THIS SETTING HAVE ALREADY BEEN TREATED IN MIRROR IMAGE WHEN THE BOND WAS SET G+;

```
"IF" I > MARK "THEN""GOTO" ALLOW "ELSE""BEGIN"
"IF" INDC[I] > 2 "THEN""GOTO" GEN3;
"END";
```

"COMMENT" THE LOOP STARTING WITH STATEMENT BACK WILL RECALCULATE THE ATOMIC POSITIONS, THE STATISTICAL WEIGHTS, AND THE MATRIX PRODUCTS, THAT HAVE BEEN ALTERED THROUGH THE ACTION OF GEN2;

```
ALLOW: M:=I-1; N:=I+1;
BACK: J:=INDC[I]; K:=INDC[M];
"COMMENT" THE NEXT CARD REJECTS CONFORMATIONS WITH ZERO WEIGHT;
"IF" UCI,K,J] > 0.0 "THEN""BEGIN"

"FOR" X:= 1,2,3 "DO""BEGIN"
D[X,N]:=D[X,I];
"FOR" Y:= 1,2,3 "DO"
D[X,N]:=D[X,N] + COMPO[N,J,Y]*PRODC[M,X,Y];
"COMMENT" THE NEXT CARD IS CONNECTED WITH REJECTION BY DISTANCE;
E[X]:=D[X,N]*D[X,N];
```

```
"END";
"COMMENT" THE NEXT CARD REJECTS CONFORMATIONS WHOSE ENDS COULD NOT POSSIBLY COME WITHIN LIMIT ANGSTROMS OF EACH OTHER;
"IF" SQRAD[N] < (E[1] +E[2] +E[3]) "THEN""GOTO" CHANGE;
```

```
"FOR" X:= 1,2,3 "DO""FOR" Y:= 1,2,3 "DO""BEGIN"
PRODC[I,X,Y]:=PRODC[M,X,1]*TC[I,J,1,Y] + PRODC[M,X,2]*TC[I,J,2,Y]
+ PRODC[M,X,3]*TC[I,J,3,Y]; "END";
WTC[I]:=WTC[M]*UCI,K,J];
TOTEN[I]:=TOTEN[M] + ENCI,K,J];
"COMMENT" THE NEXT CARD IS CONNECTED WITH REJECTION BY STATISTICAL WT.;
"END""ELSE" "GOTO" CHANGE;
```

```
I:=I+1; M:=M +1; N:=N +1;
"IF" N < NBONDS "THEN""GOTO" BACK-"ELSE""BEGIN"
K:=INDC[M]; "GOTO" GEN1; "END";
```

"COMMENT" PRIOR TO THE RETURN TO GEN1, I IS SET TO NBONDS-1, M TO I-1, N TO I+1, K TO INDC[I-1]. J WILL BE ASSIGNED IN GEN1;

"COMMENT" GEN3 SETS A BOND BACK TO TRANS- AFTER THE EXHAUSTION OF ITS STATES, RELOCATES MARK AND ALSO TERMINATES THE PROGRAM, OR ENABLES IT TO BE INTERRUPTED FOR DUMPING;

GEN3:IND[I]:=1;

"IF" (I-1) < MARK "THEN" MARK := (I-1);

"COMMENT" OPTIONAL DUMPING CARDS CAN BE INSERTED HERE;

"IF" I = 2 "THEN""GOTO" DUMPER;

"GOTO" GEN2;

DUMPER: RITALL;

"COMMENT" A RETURN AFTER DUMPING CAN BE INSERTED HERE;

FINISH: "END" CONFMS;

"READ"NBONDS;

"PRINT" 'F', ' CONFORMATIONAL ANALYSIS OF A ',SAMELINE,DIGITS(2), NBONDS,'-BONDED PHOSPHATE CHAIN, TERMINATED WITH PHOSPHORUS AND ', 'OXYGEN.';

CONFMS(NBONDS);

"END";

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