The role of branching on the macro and micro structure of hyperbanched polymers, and their use as supports for exotic functional groups and catalyst

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Declaration

I hereby declare that the research discussed has not been submitted, either entirely or partly, for this or any other degree. All the work presented in this thesis is the original work of the author, except where other sources have been acknowledged by references. This work was carried out at the University of Sheffield between April 2011 and April 2015.

Signature: Meshari Alsharif

Date: 20/04/2015

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Abstract

Hyperbranched polymers are polydispersed highly branched dendritic molecules. Due to their properties, their potential for use in many applications is promising. In addition, easy synthesis and purification that is time and cost effective compared to traditional dendrimers adds to their appeal. The similarity between the structure of hyperbranched polymers and many biological systems has highlighted their importance in many biological applications. Copolymerization greatly increases the advantages associated with these polymers, making them even more suitable for use in many applications.

The first part of this research project was an investigation into the effect of the degree of branching on the bulk properties and internal environment of hyperbranched polymers. In terms of the bulk properties, a viscosity study of a series of hyperbranched polymers possessing a relatively constant molecular weight and polydispersity index along with a varied degree of branching was performed. Polymers with a higher degree of branching showed relatively less viscosity than polymers with a lower degree of branching. However, the former could maintain their dendritic structure up to a degree of branching of 37%. The study also assessed the effect of the molecular weight and polydispersity index on these polymers. In the case of the internal environment, the studies were performed by measuring the binding constant of various ligands to hyperbranched polymers with a different degree of branching. The study was carried out on two different molecular weights, one below and one above the dense packing limit. The study revealed an interesting result regarding the steric and electronic effect; polymers with a low degree of branching altered their dense packing limit. For hyperbranched polymers with a molecular weight below the dense packing limit, the association constant decreased as the degree of branching decreased. However, in the case of hyperbranched polymers with a molecular weight above the dense packing limit, the association constant increased as the degree of branching decreased. Finally, a study was carried out to identify the location of co-monomers within the dendritic structure.

The second part of this project involved applying post synthetic methodology to co-polymerise various co-monomers with hyperbranched polymers at room temperature. The use of this method to copolymerise sensitive functional units was successful. This methodology gave the dendritic system many advantages, such as improvement in the molecular weight and the degree of branching.

In the final part of this project, high loaded catalytic sites hyperbranched polymers were examined to determine whether or not they could be used as a soluble catalytic support system, and it was found that they could. A solvent effect study revealed that these polymers could be used to control reactions selectivity.

Abbreviations

Ka - Association constant

^{13}C-NMR - Carbon Nuclear Magnetic Resonance Spectrometry

$CHCl_3$ - Chloroform

DU - Dendritic Unit

DB - Degree of Branching

DCM - Dichloromethane

DMSO - Dimethyl sulfoxide

DMAD - Dimethyl acetylenedicarboxylate

DMAP - Dimethylaminopyridine

DME - Dimethoxyethane

DMF - Dimethylformamide

Et_3N - Triethylamine

FTIR - Fourier Transform Infrared Spectroscopy

GPC - Gel Permeation Chromatography

HBP - Hyperbranched polymer

Co-HBP - Hyperbranched co-polymer

^{1}H-NMR - Proton Nuclear Magnetic Resonance Spectrometry

HOMO - Highest Occupied Molecular Orbital

IR - Infrared Spectroscopy

K_d - Dissociation constant

LU- Linear Unit

LUMO - Lowest Unoccupied Molecular Orbital

M_n - Number Average Molecular Weight

MgO - Magnesium oxide

MS - Mass Spectrometry

M_w - Weight Average Molecular Weight

PDI - Polydispersity Index

SCVP - Self-condensing vinyl polymerisation

TAPP - Tetraacetoxyphenyl porphyrin

THF - Tetrahydrofuran

TU - Terminal Unit

UV/vis - Ultraviolet-Visible Spectroscopy

Zn - TAPP - Zinc functionalised tetraacetoxyphenyl porphyrin

NMR Abbreviations

s – Singlet

d – Doublet

t – Triplet

q – Quartet

m – Multiplet

br – Broad

o – *Ortho*

m – *Meta*

p - *Para*

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Chapter One

Introduction

Chapter One - Introduction

1.1 Preface:

Polymer or macromolecular chemistry can be defined as the field of study concerned with the preparation, classification and modification of macromolecules. The term polymer is derived from the Greek words “poly”, meaning many, and “mers”, meaning parts. A polymer can be defined as a high molecular weight compound containing repeat units, known as monomers, bonded together to form a long chain. Polymers can be classified in several ways based on their structure, type of monomer, synthesis and tacticity.[1,2]

The structure of polymers is key in terms of their classification. Polymers are divided into three groups depending on their structure: linear, branched and cross-linked. In the case of a linear polymer, the monomers are linked together in a chain, for example, polyvinyl chloride and polypropylene. In a branched polymer, the main chain of the polymer, which is comprised of monomers, has one or two branches. Star, comb, graft and dendritic polymers are examples of branched polymers. In the third type of polymer, cross-linked polymers, the monomers of linear polymers are held together at points along the chains by covalent bonds, for example, vulcanised rubber.[1,3]

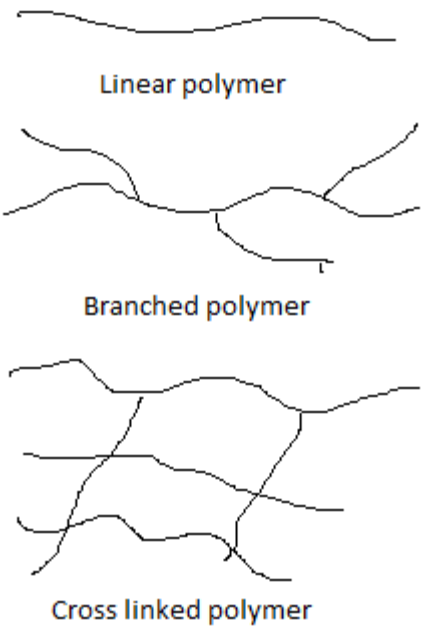


Figure.1.1. Classes of polymers depending upon their structure.[2]

1.2 Introduction to dendritic polymers:

Polymer science has become one of the most interesting areas of study for both industrial and academic researchers due to the advantages of using polymers in many applications, and over the past few years, several materials with complex polymer structures, such as the dendritic structure, have been synthesised. In order to understand dendritic structure, some examples from nature, such as trees and marine coral, should be considered due to their polymer structure being similar to that of dendritic polymers. Dendritic polymers are most commonly described as highly branched polymers with tree-like structures, comprised of multifunctional monomers. This branched structure provides them with remarkably different physical properties when compared with linear polymers. The high degree of branching leads to a large number of functionalised groups, which are responsible for the properties of such a system. Many different branched architectures have dendritic polymers, such as dendrons, dendrimers, star polymers and hyperbranched polymers. The differences between these result from the type of branching.

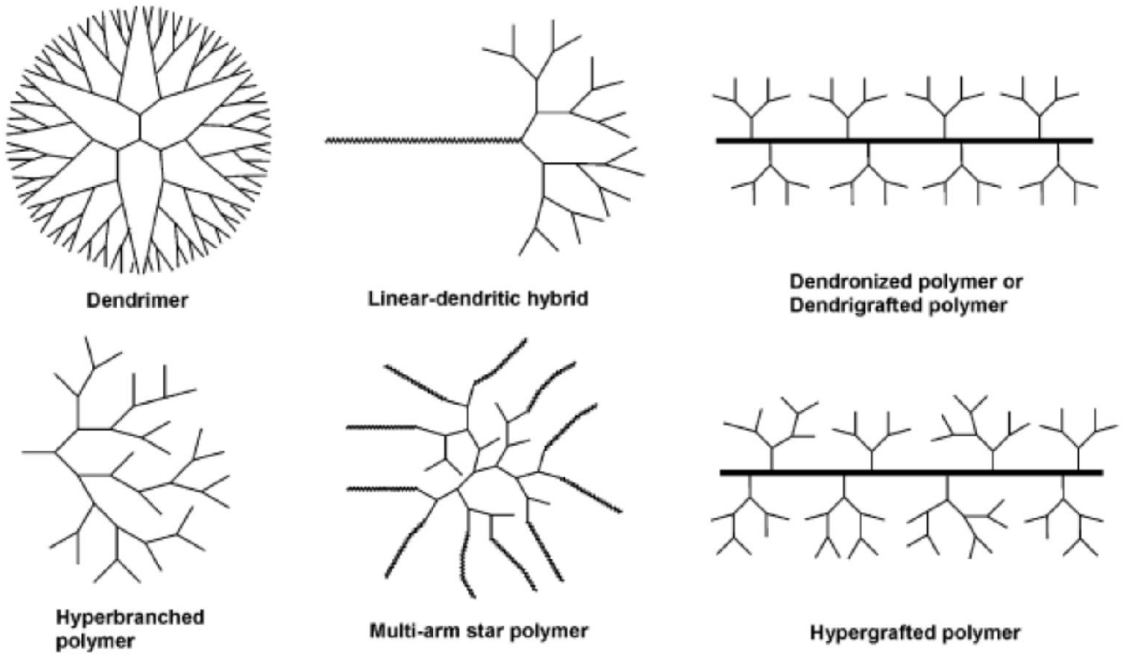


Figure.1.2. Examples of dendritic polymers depending upon their structure, adapted from (Gao, C.; Yan, D. وProgress in Polymer Science **2004**, 29, 1830).[4]

1.3 Introduction to dendrimers:

Due to the structural differences between dendritic and linear polymers, many aspects of dendritic structure cannot be described using conventional polymer chemistry nomenclature. In order to overcome this problem, a specific term has been developed to describe these polymers. The origin of the word 'dendrimer' lies in the Greek word "dendron", meaning tree, and "meros", meaning a part. Dendrimer has a well-defined structure known as complex, monodisperse macromolecule. Based on the AB_2 monomer, repeat units in dendrimers are separated into two parts. The first unit is called a dendritic unit. This is a fully reacted unit. The second unit is called a terminal unit. This is located at the periphery of the molecule. In order to describe the size of a dendrimer, the number of layers of monomers added is used. Each layer in a dendrimer is called a generation. These generations are analogous to a repeat unit in a linear polymer. Therefore, dendrimers consist of three components: core, generation (perfectly branched units) and terminal units. The advantage of dendimers is that they have perfectly branched architecture and a high degree of symmetry.[4-10]

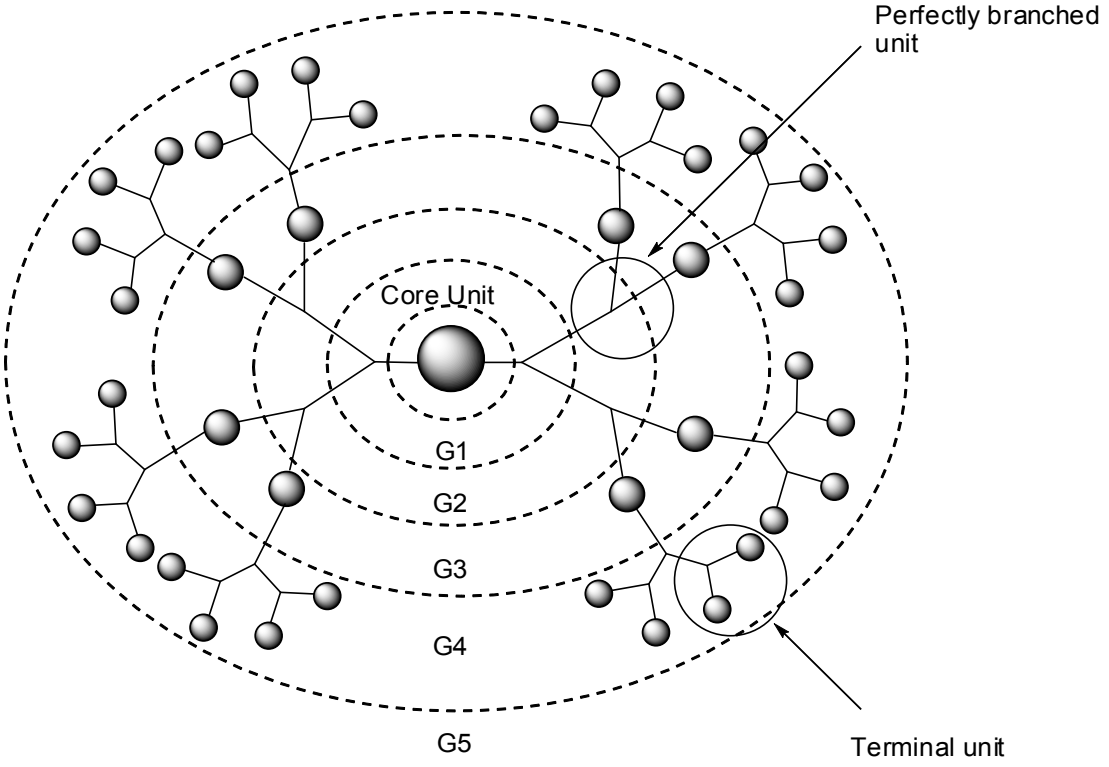


Figure.1.3. Schematic showing the structure of dendrimer.

1.3.1 Synthesis of dendrimers:

The theoretical evidence for the existence of branched 3-dimensional molecules was first presented by Flory in 1952.[11] After that, in the 1970s, Vogtle prepared controlled branched molecules.[12] Many years later, in 1985, Tomalia published a report on the successful synthesis of a series of branched molecules called dendrimers.[13] At the same time, the synthesis of similar macromolecules, named arborols, was reported by Newkome's group. It is worth noting that both reports described the preparation of highly branched macromolecules using multisteps from a central core and containing a well-defined number of generations and end-groups.[14] After the successful synthesis of these polymers, the term dendrimer became the internationally recognised name for this type of molecule.

Dendrimers can be prepared by using two methods: divergent or convergent. There is a fundamental difference between these two methods, as described below.[15]

1.3.1.1 Divergent synthesis:

In this method, the dendrimer is synthesised in steps from a multifunctional core molecule then elaborated to the periphery. The core reacts with the monomer to produce the first generation of dendrimers. Then, the first generation in the new periphery is activated to react with more monomers. This step is repeated for many generations, and layer after layer is added to build a dendrimer. A large scale amount of dendrimers can be prepared using this method. However, this method suffers from structural defects due to side reactions. To overcome this problem, a purification process must be repeated several times. Moreover, the complete reaction of every terminal group is unfavourable. Therefore, a large excess of reactants is required.[15]

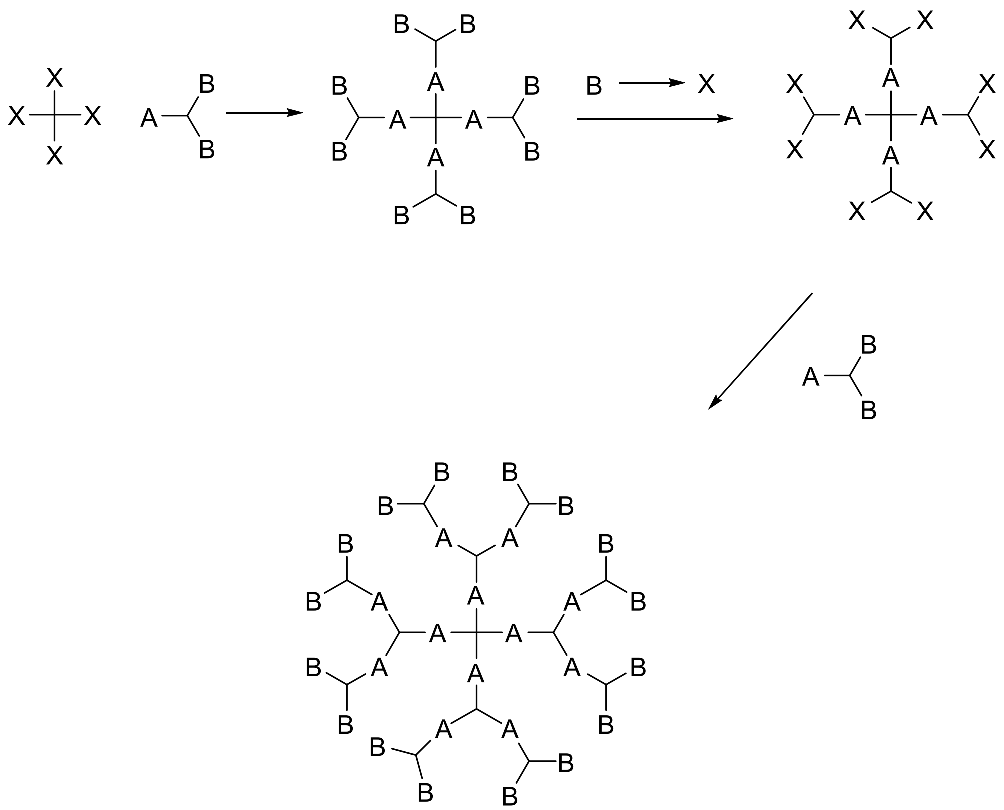


Figure.1.4. Schematic of divergent synthesis.

1.3.1.2 Convergent synthesis:

The weaknesses of divergent synthesis were eliminated by a new method called convergent synthesis. This method was first used in 1990 by Frechet and Hawker.[13] In this method, the synthesis originates from the surface function. Small dendrons react to monomers to produce higher generation dendrons. Then, in the final step, all the dendrons react to a multifunctional core molecule. However, this method is only used to produce small dendrimers; it is difficult to produce large generation dendrimers due to the steric that occurs when the dendrons are attached to the core. [5,15-17]

Therefore, the preparation of dendrimers is difficult and very expensive because they require multistep synthesis and time consuming purifications. For these reasons, hyperbranched polymers have received much attention as they are easier to prepare and have similar properties to dendrimers.[4-10]

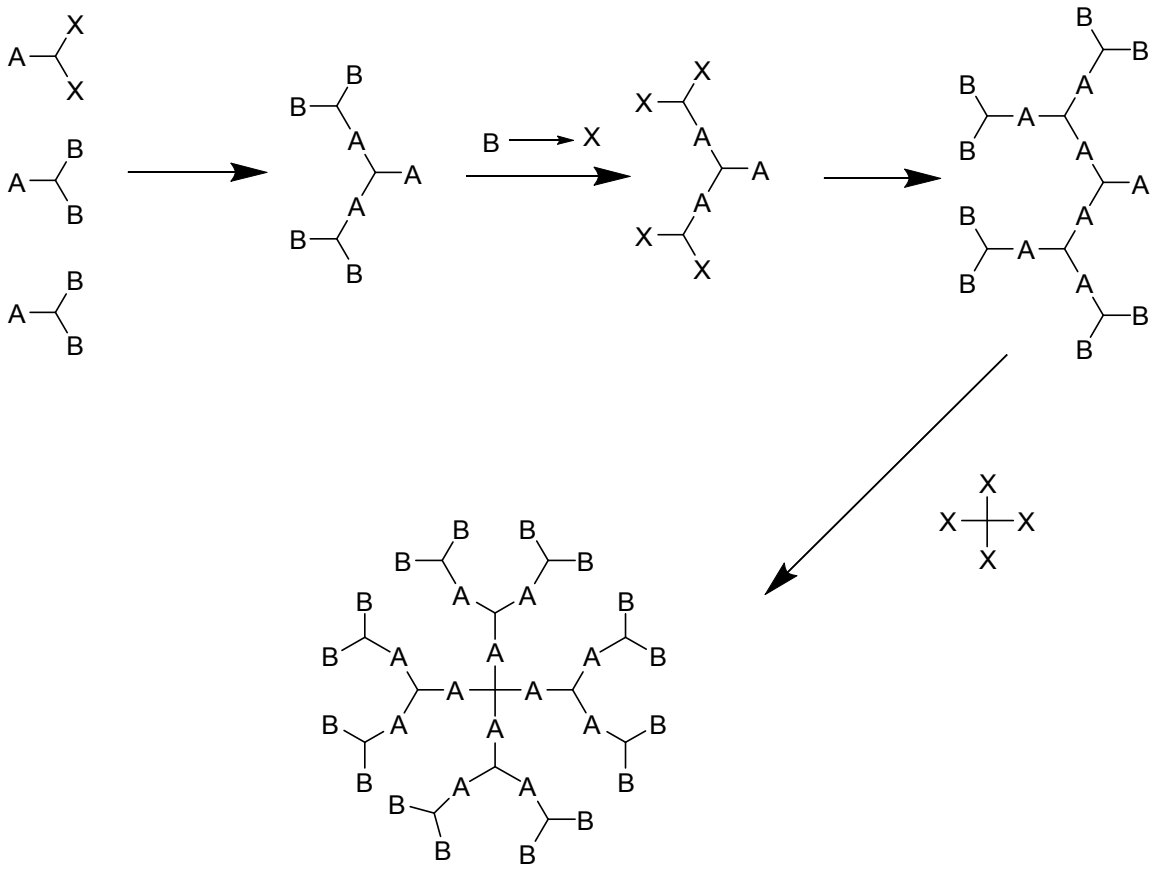


Figure.1.5. Schematic of convergent synthesis.

1.4 Hyperbranched polymers:

Hyperbranched polymers are described as highly branched macromolecules with a random three dimensional dentritic architecture. Although they have a random structure and broad molecular weight distribution, they are more popular than dendrimers because they are easier to prepare. Recently, much research has been conducted in the field of hyperbranched polymers due to their importance in industrial applications as they have unique physical and chemical properties (compared to linear polymers), such as low viscosity, high solubility and the presence of a large numbers of functional end groups.[3,8] These functional end groups are responsible for many features, providing the possibility for furthur modification for various applications in many fields, such as coating, rheological modification, membranes, supermolecule chemistry, drug delivery and nanomaterials, as will be explained later in this chapter.[4]

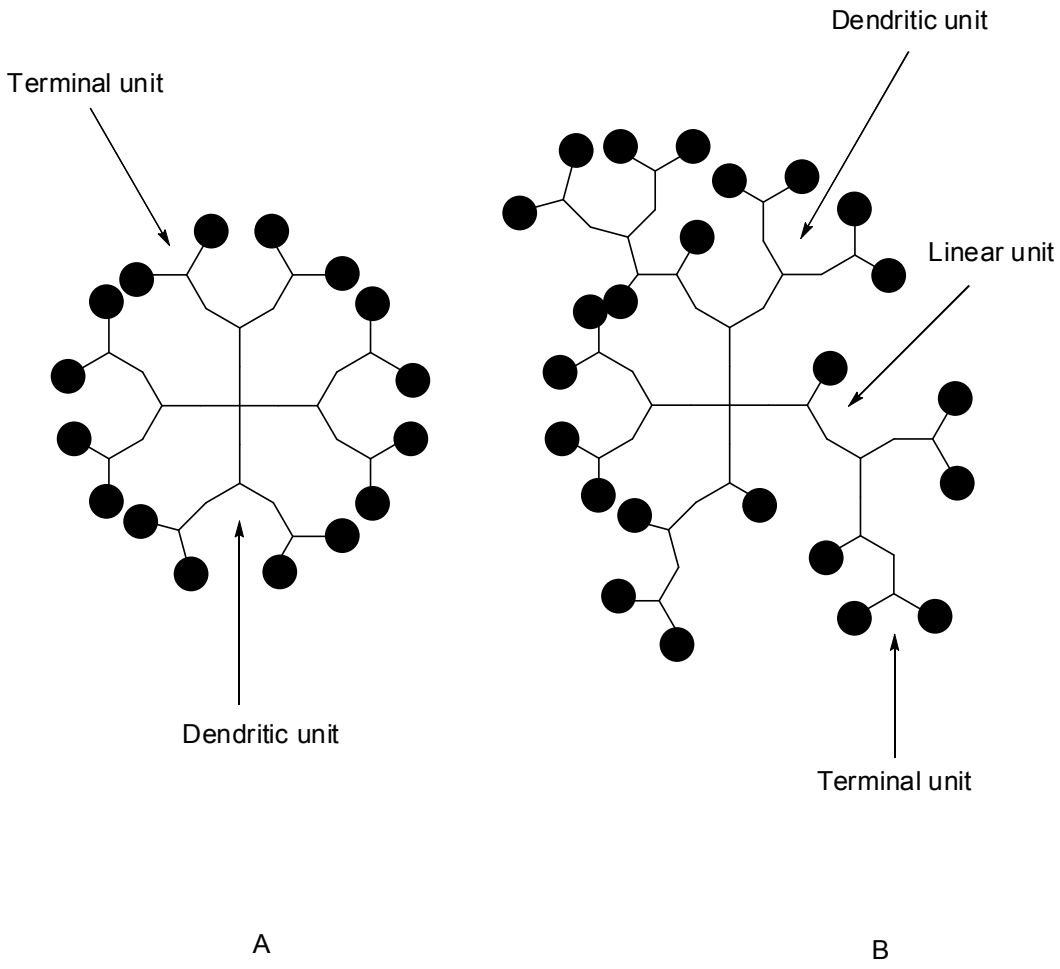


Figure.1.6. Schematic showing the difference of structure of A (dendrimer) vs B (hyperbranched polymer).

1.4.1 History of dendritic polymers:

In 1941, Flory developed a statistical analysis for the "degree of branching" and "highly branched species" concepts. The calculations were based on the poly condensation of A_2 and B_3 monomers. Later, in 1952, Flory reported that hyperbranched polymers can be prepared without gelation by the poly condensation of the AB_2 monomer. Finally, in 1982, Kricheldorf et al. prepared highly branched polyesters by the co-polymerisation of the AB_2 and AB type monomers.[1] The name "hyperbranched polymers" was first used by Kim and Webster when they synthesised soluble hyperbranched polyphenylene in 1988.[18,19]

1.4.2 Synthesis of hyperbranched polymers:

Hyperbranched polymers can be prepared by many methods, including condensation polymerisaiton, self-condensing vinyl polymerisation, such as free radical polymerisation (ATRP, RAFT), and ring opening polymerisation.[6]

1.4.2.1 Condensation polymerisation:

This method is widely used to polymrise AB_x monomers, where x is 2 to 6.[6] A large number of publications have focused on the AB_2 type monomer synthesis. This polymerisation is a one pot reaction. The reaction between a functional A monomer and two functional B monomers produces a branching unit. It is also possible that one functional B monomer reacting with a functional A monomer will produce a linear unit. This method can be used to prepare hyperbranched polymers, for example polyphenylenes,[18] polyester,[20] polyether,[21] polyamide[22] and polyurethanes.[23] It is worth mentioning that this method is the most popular one due to the low cost and the commercial availability of the monomers. However, this method suffers from two major drawbacks. The first is that the polymer gelation caused by an unwanted side reaction makes purification difficult. In addition, an unwanted side reaction in the early stages may limit the molecular weight. Frechet and co-workers demonstrated a hyperbranched polyether with a high molecular weight. This was achieved by polymerising an AB_2 monomer 5-(bromomethyl)-1, 3-diydroxybenzene in the presence of potassium carbonate and 18-crown-6.[24]

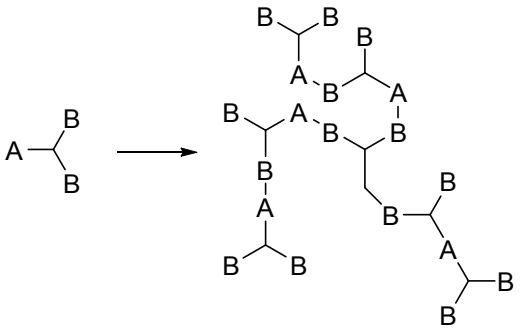


Figure.1.7. Polycondensation polymerisation.

1.4.2.2 Self-condensing vinyl polymerisation:

In 1995, Fréchet [25] and co-workers introduced a second method to prepare hyperbranched polymers. This is known as self-condensing vinyl polymerisation. This method uses a monomer carrying a vinyl group and one initiation moiety. After the activation of the initiation moiety, it reacts with the double bond to form a covalent bond with an active side. The activated species can be an anion, cation or radical. Furthermore, the reaction must be controlled to avoid a reaction between the active moieties of A* and B* themselves and to prevent the polymer from gelation and crosslinking that will affect its solubility in organic solvents.[26]

Gaynor et al.[27] reported that atom transfer radical polymerisation (ATRP) could be used to form hyperbranched polymers. *p*-(chloromethyl)styrene (CMS) was used as a monomer in a one-pot synthesis that was carried out in the presence of Cu(I) and 2, 2′-bipyridyl (bpy).

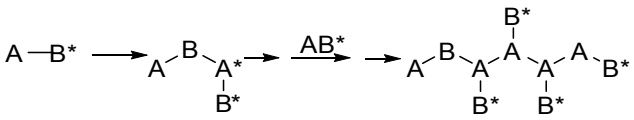


Figure.1.8. Self-condensing vinyl polymerisation.

1.4.2.3 Ring opening polymerisation:

The third method used to prepare hyperbranched polymers is known as ring opening polymerisation. This method was developed by Suzuki in 1992.[28] The monomer does not contain a branching point. This is produced during the propagation reaction. The monomer can be described as a latent AB_X monomer. The terminal function of the polymers acts as a reactive centre, and a further cyclic monomer joins to form a large polymer chain.

Suzuki et al.[28] prepared polyamine hyperbranched polymers by the polymerisation of 5-methyleneperhydro-1,3-oxazin-2-one using a Pd catalyzed ring opening polymerisation at 25 ^{0}C using benzylamine as the initiator.

Liu et al.[29] prepared hyperbranched polymers by polymerising a monomer containing both an *e*-caprolactone ring and a primary alcohol group, which initiated the ring opening polymerisation of *e*-caprolactone .

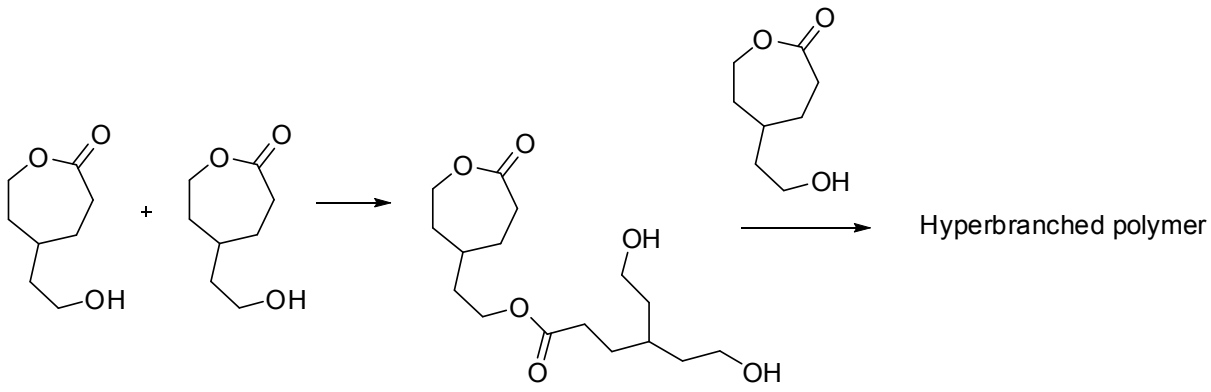


Figure.1.9. Hyperbranched polymer via ring opening polymerisation.

1.4.3 Properties of hyperbranched polymers:

The highly branched three dimensional structure of hyperbranched polymers provides them with specific physical properties when compared with linear polymers. These properties, which include solubility, viscosity, mechanical and rheological properties, are an important aspect of hyperbranched polymers in their applications.[8]

The solubility of hyperbranched polymers is one of their most important physical properties. The terminal groups of hyperbranched polymers play an important role in the solubility of these polymers. This is because the presence of a large number of terminal groups on the surface could shift the interior environment. Therefore, the solubility can be controlled via the modification of the terminal groups.

Low viscosity is another positive property of hyperbranched polymers. It is widely known that the viscosity of linear polymers increases in tandem with the molecular weight increasing due to the chain entanglement increasing. However, hyperbranched polymers have a lower viscosity in solution compared with linear analogue polymers. This is because the globular structure that is a result of the branching in the polymers limits the formation of long chains. Reduced chain entanglement at a higher molecular weight leads to a decrease in viscosity. Mark, Houwink and Sakurada's equation describes the relationship between intrinsic viscosity and molecular weight.[30]

$$[\eta] = kM^{\alpha}$$

Where [η] is the intrinsic viscosity, M is the molecular weight and k and α are specific constants for the polymer solvent system.

As can be seen in the figure below, Mark, Houwink and Sakurada's equation has been used to study the relationship between molecular weight and the intrinsic viscosity of dendrimers, hyperbranched polymers and linear polymers. Hyperbranched polymers exhibit lower solution viscosity than linear polymers, whereas dendrimers exhibit the lowest solution viscosity.

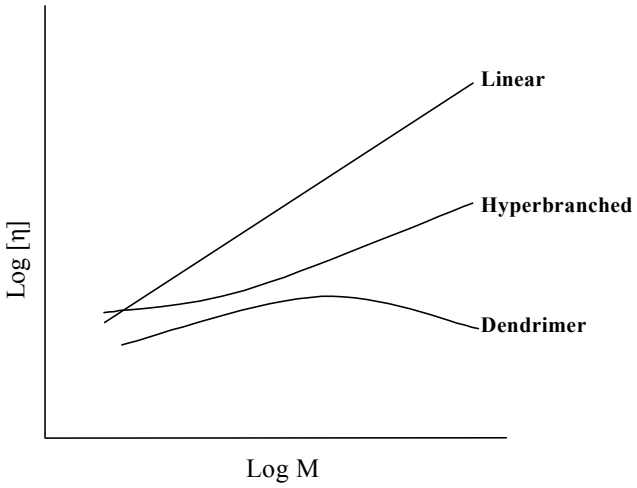


Figure.1.10. Comparison of intrinsic viscosities vs. molecular weight for dendrimers, linear, and hyperbranched polymers, Adapted from (Higashiara, T.; Segawa, Y.; Sinananwanich, W.; Ueda, M., Polymer **2012**, 44, 14).[31]

It is indicated that hyperbranched polymers have high reactivity. This is the result of many features, such as their globular structure, high solubility and low viscosity as well as the presence of a large amount of end groups. Due to all these properties, hyperbranched polymers are likely to be reactive with other components, depending mainly on the end groups.[11]

In order to study the uses of hyperbranched polymers, their mechanical and rheological behaviour must be examined. The Newtonian behaviour in the molten state is used to charaterise hyperbranched polymers, and it is indicated that the limited entanglements of these polymers leads to their poor mechanical properties. As a result of this study, hyperbranched polymers are understood to have only minor uses in the applications of thermoplastics polymers. On the other hand, hyperbranched polymers can be suitable as

thermosets when they require high mechanical strength due to the amorphous structure of these polymers being affected by the large amount of branching.[11]

Finally, it is worth mentioning that the hydrodynamic volume of hyperbranched polymers is smaller than the the hydrodynamic volume of linear polymers of a similar molecular weight. This is due to the difference in the conformation of these polymers. Linear polymers exhibit linear comformations, whereas hyperbranched polymers exhibit compact conformation in the solution. This leads to difficulty in measuring the molecular weight of hyperbranched polymers in GPC as it provides a lower molecular weight than expected.

1.4.3 Degree of branching:

The degree of branching is classified as the most important parameter as it is the indicator of many dendritic properties.[32]

As mentioned perviously, dendritic polymers are built from different repeating units. In perfectly branched dendrimers, only two types of repeating units can be recognised: dendritic and terminal. In the case of hyperbranched polymers, their random growth provides a random structure caused by the presence of a linear unit. Therefore, the physical properties of these polymers might be effected.[32]

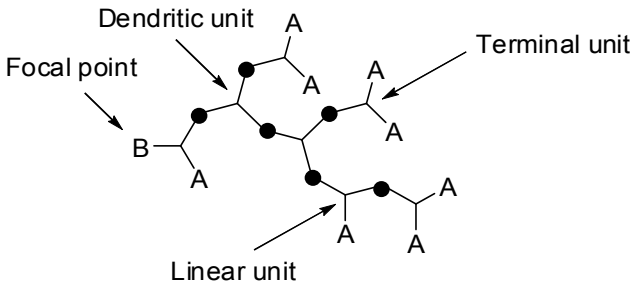


Figure.1.11. Schematic architecture of hyperbranched polymers from AB_2 monomers.

In order to describe this feature, the term "degree of branching" (DB) was used by Fréchet[33] (equation 1) and Fery[34] (equation 2). Fréchet included the number of non linear units in the total unit, whereas Fery defined the degree of branching by the actual amount of growth direction. DB can be caculated by using one of the equations below, where D is the number of dendritic units, T is the number of terminal units and L is the number of linear units.

$$(1)\ \text{Degree of branching (DB)} = \frac{\text{D+T}}{D+T+L} \qquad \textbf{Equation 1}$$

$$(2)\ \text{Degree of branching (DB)} = \frac{\text{2D}}{2D+L} \qquad \textbf{Equation 2}$$

Using either one of the above equations, it is clear that the DB for hyperbranched polymers is somewhere between zero and one. It is worth mentioning that the DB of a dendrimer is one, whilst the DB of a linear polymer is zero. However, some polymers have a degree of branching equal to one but do not necessarily have a dendrimer structure, such as an isomer of polyphenylene.[31]

Two different techniques are used to determine the degree of branching. The first of these is NMR spectroscopy. From the ^{1}H-NMR spectra, the degree of branching can be calculated by the use of a peak area. The second less common method is via the degradation of the hyperbranched backbone.[31]

1.4.4 Dense packing:

Dendrimers usually possess a high symmetrical structure. The molecular structure is displayed with all terminal groups that are located at the surface pointing outward, suggesting that the dendrimer is a spherical entity. Early studies revealed that dendrimers have a dense shell structure, with the core of a dendrimer being less dense than the periphery.[35] This is because of the nature of growth of dendrimers; as the size of the dendrimer increases, the molecular weight also increases and more globular conformation occurs. However, according to De Gennes, at maximum molecular weight, there is a limitation occur by the steric saturation, which implies that the dendrimers should not exceed a specific molecular weight.[35] The dendrimers may continue to grow after this limit is reached, but this growth can cause structural flaws. Mathematical analysis has shown that the terminal groups can be back folded into the core of the dendrimer and not appear at its surface.[36] Back folding relieves the steric crowding at the dendrimer surface when there is a high generation of the dendrimer. This makes the dendrimer core have a very high density and gives rise to the dense core model.

The size and nature of the dendrimer determines whether the dense shell model or the dense core model is correct. A large number of dendrimers are flexible because the terminal groups occur throughout the entire volume of the dendrimer. This is consistent with the dense core model. Sometimes, the units are repeated inside the dendrimer and the terminal units collect at the periphery. In this case, the shell model can be used.

The hyperbranched polymers have dendritic and terminal units. This feature is also found in dendrimers. The entire polymeric volume contains terminal units. The partially reacted (linear) units, like irregularities in branching, can also cause the polymer structure to assume a linear nature. As a result of this, the generations cannot be used to determine for the size of the hyperbranched polymer and molecular weights are used for the size description. Many analytical methods can be used to assess the hyperbranched polymer's molecular weight. These methods include NMR, UV/Vis and GPC. Furthermore, there are various molecular weight definitions, the main ones being Mn and Mw.

1.4.5 Application of hyperbranched polymers:

The development of dendritic polymers is of primary importance in polymer science. Although the preparation of dendrimers is time consuming and expensive, a huge amount of work has been carried out in this area with massive success. However, there has been little successful work in relation to hyperbranched polymers due to the difficulty in controlling their random structure. Nevertheless, their advantages, namely the low cost of their synthesis and their unique properties when compared with linear polymers, have made the research in the field of hyperbranched polymers invaluable. Interest in this area has increased dramatically of late and has led to improvements in the synthesis of hyperbranched polymers and in their applications.[10]

One of the area in which hyperbranched polymers have been widely used is drug delivery.[37, 44] This is due to the controlling of the functionality on the periphery. The functional groups can undergo further modifications to be attached to a drug in order to solubilise the drug or control the delivery rate in the body.

In addition to drug delivery, the use of hyperbranched polymers in gene delivery has been approved. This is because the large number of functional groups on the surface can act as an

ideal vector for DNA binding. Thurecht and co-workers reported the synthesis and characterisation of hyperbranched dimethylaminoethyl methacrylate (DMAEMA) polymers using reversible addition fragmentation chain transfer polymerisation as a model for gene delivery. The work indicated that there is a remarkable difference between the interaction of these polymers with DNA and that of linear or block co-polymers. These hyperbranched polymers were shown to effectively bind and condense oligonucleotides (ODNs).[45] Many other examples have been found in the literature, including coating,[46] catalysts,[47,48] nanocompsites [11] and additives.[11]

Chapter Two

Aims and Objectives

Chapter Two – Aims and Objectives

2.1 Aims and project outline:

One of the problems of using functional linear polymers in many applications is the location of their functional group, where these functional groups can interact with solvent due to their flexibilitey and facile dynamics.Therefore, It is difficult to control the microenviroment surrounding the functional groups. As dendritic polymers are rigid and do not really undergo chain entanglement, they have many advantageous uses, such as controlling the microenviroment around the functional groups and the large number of end groups on the surface.[49] Dendritic polymers have attracted much attention as a consequence of this, and they have been well researched due to their unique properties. Dendrimers require multi step synthesis and a tedious purification process, as explained previously. Thus, the preparation of dendrimers is costly and time consuming. Furthermore, functional dendrimers are even more difficult to synthesis. However, they are widely addressed in the literature.[49-53] Although the rigidity of hyperbranched polymers is less than that of dendrimers, due to their non-defined structure, they have been shown to have similar properties to dendrimers and can take the place of dendrimers in many applications. It is worth mentioning that the synthesis of a hyperbranched polymer is much easier than that of a dendrimer and the former can be prepared in view hours.[54] The main aim of my project is to synthesis hyperbranched polymers with interior functionality that could be used for encapsulation and controlled environment applications.

The three dimensional branched nature of dendritic molecules makes them suitable for use in several applications that mimic nature. These applications include: site isolation, encapsulation and catalysis.[55,56] The local controlled environment provided by the arrangement of the dendritic polymers allows chemical and physical reactions to take place under specific condition. This is because the branched structure provides a different internal environment than the bulk solution. Therefore, such a system can be used to control the microenvironment and isolate a specific molecule from the external bulk environment. Several publications have claimed that dendritic polymers are a promising possibility for use in such applications. Encapsulation is a phenomenon that refers to the incorporation of an active substance, such as a drug or catalyst, in a carrier component.[57] The structure of

dendritic polymers allows them to encapsulate a molecule within their interior. This is due to either the electronic or steric effect. Work by the Twyman group that involved encapsulation of a hydrophobic drug in the interior of hyperbanched polymers indicated that hyperbranched polymers could be used to solubilise hydrophobic drugs. Water soluble hyperbranched polyglycerols were prepared for use in this study. Many drugs were used, for example, naphthalene, porphyrin and ibuprofen. All the drugs were encapsulated into hyperbranched polymers, and the solubility of the drugs was detected using UV-vis spectroscopy. The effect of different concentrations and the molecular weights of the hyperbranched polymers on the solubility of the drugs were also investigated in this study.[56]

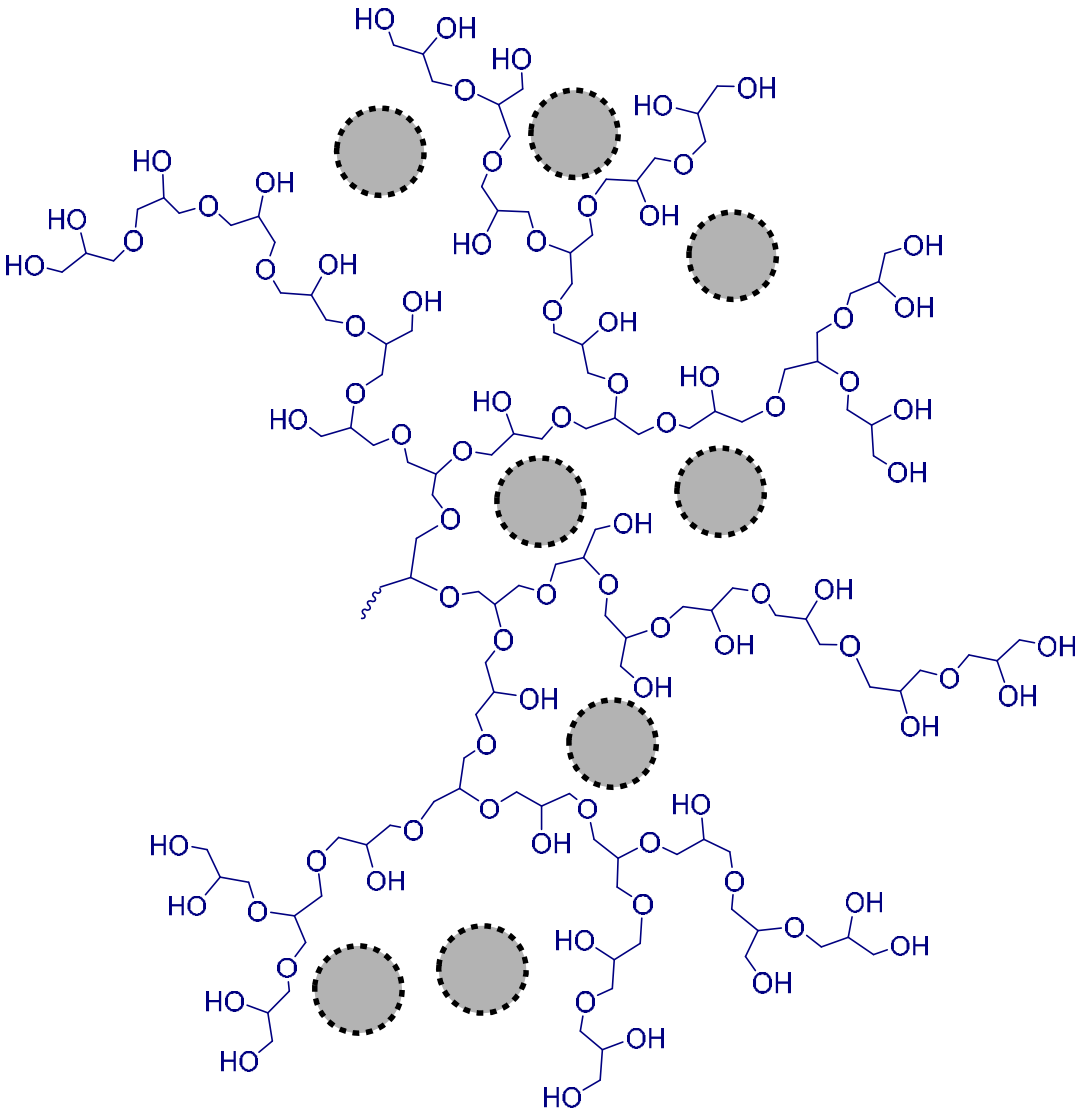


Figure.2.1. A water soluble hyperbranched polymer solublising hydrophopic drug within the interior of the architecture.

The functionalisation of hyperbranched polymers could occur at the core or in the branching units.[54] In the case of functionalising the core, the loading is limited to one group. However, the addition of a core to a hyperbranched polymer system provides many significant advantages to their synthesis, such as controlling the molecular weight and the degree of branching.[58-62]

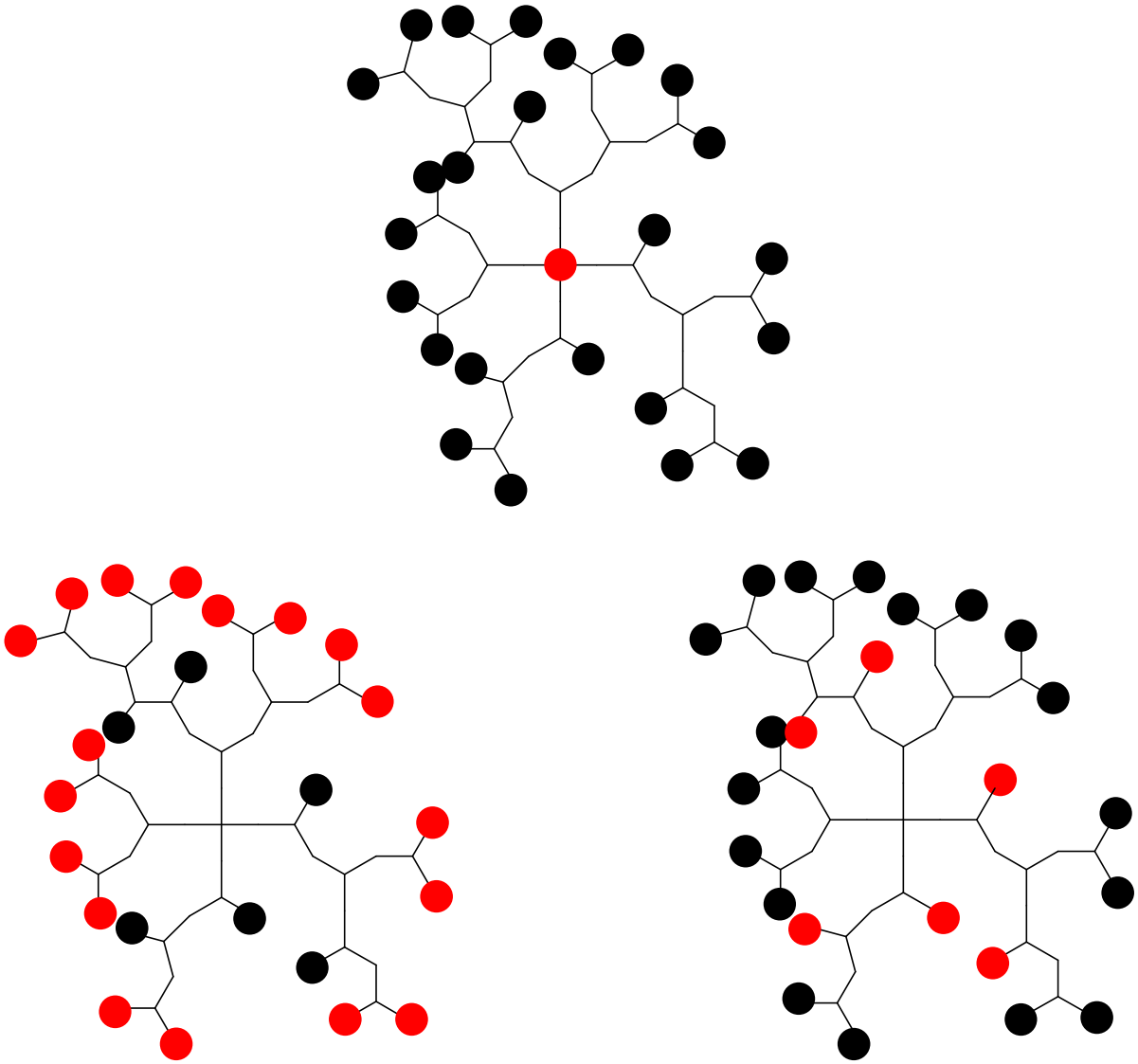


Figure.2.2. Figure to show core functional hyperbranched polymer (top), periphery functional hyperbranched polymer (below left), interior functional hyperbranched polymers (below right).

Twyman et al.[63] synthesised hyperbranched polymers via poly condensation polymerisation, using 3,5 diacetoxybenzoic acid as a monomer and p-nitrophenyl acetate as a reactive core. The molecular weight was 4100 Da and the polydispersity was 1.92. In other work, Twyman used the same hyperbranched system based on 3,5 diacetoxybenzoic acid with one porphyrin unit at the core. The molecular weight was 20000 and the PDI was 1.19.[64] Zaho and co workers[65] studied the effect of adding a multifunctional core to an AB_2 monomer on the molecular weight distribution of hyperbranched polymers. They indicated that the presence of a small amount of multifunctional core in the polymerisation system of AB_2 reduced the polydispersity index of the polymer. Wang and his team examined the average molecular weight, polydispersity, structural units and degree of branching of hyperbranched polymers made from AB_2 monomers with trifunctional cores of different reactivity.[66] A highly reactive core can decrease the polydispersity index of hyperbranched polymers. When 0.05 molar ratio of the reactive core is added to the AB_2 monomer, the polydispersity index decreases to about two. Cheng et al.[67] explained the effect of feed rate on the structure of hyperbranched polymers prepared via the slow addition of AB_2 monomers into the multifunctional core. He investigated the kinetics of the co-polymerisation of AB_2 monomers slowly added into the trifunctional core under various feed rates. The PDI was found to be broad when the monomer was fed quickly, with lower concentration of the core. In the case of slow addition, the PDI was narrow. However, the addition of a core to a hyperbranched polymer will not negatively affect the degree of branching. Indeed, many reports have been published indicating that the method using slow addition of the monomer to the core improves the degree of branching. The kinetics of the slow monomer addition technique were examined by ZhiPing et al. [58] This method is used in the production of hyperbranched polymers. The slow monomer addition technique was compared with one pot polymerisation. It was found that the distribution of the molecular weight is enhanced by the slow monomer addition technique and the polymer's degree of branching is also improved. The results of further research by Satoh were similar.[62] However, many researchers have proved that hyperbranched polymers with a degree of branching of 50 % keep their dendritic structure and are capable of replacing dendrimers in specific biological applications, such as enzyme mimic and drug delivery.[54-56]

Pervious work carried out by the Tywman group indicated that a cored porphyrin hyperbranched polymer with a degree of branching of 50% is suitable for use in applications involving controlled and selective environments as dendrimers. The work involved the preparation of a range of different molecular weight hyperbranched polymers from 3, 5 diacetoxybenzoic acid with porphyrin cores. In this study, the binding of three different sized ligands to three differently structured cored porphyrin hyperbranched polymers was examined using UV-vis spectroscopy.[5] The work postulated that these polymers exhibit dense packing at 8000 Da and that satirically hindered porphyrin cored hyperbranched polymers possess shape selective catalytic properties.[5]

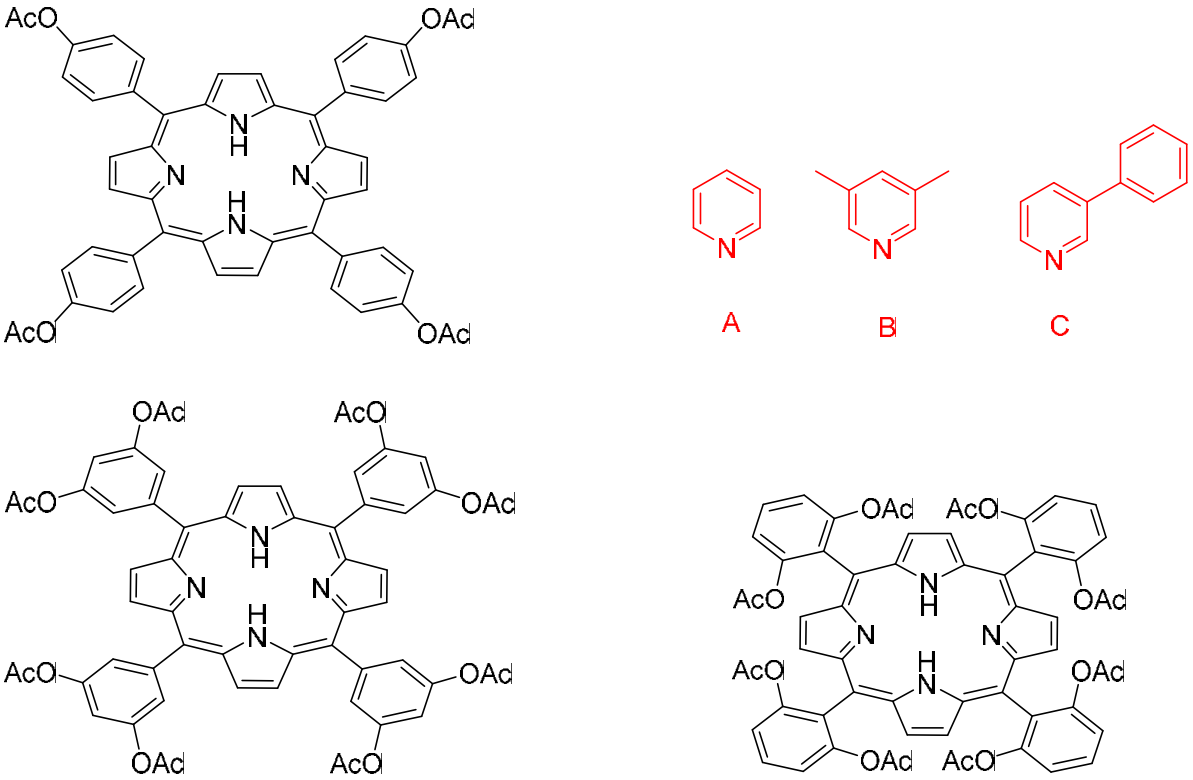


Figure.2.3. Figure to show three different structures of porphyrin cores and three different sizes ligands A) pyridine B) 3, 5- Lutidine B) 3-phenyl pyridine were used in study carried in Twyman group.

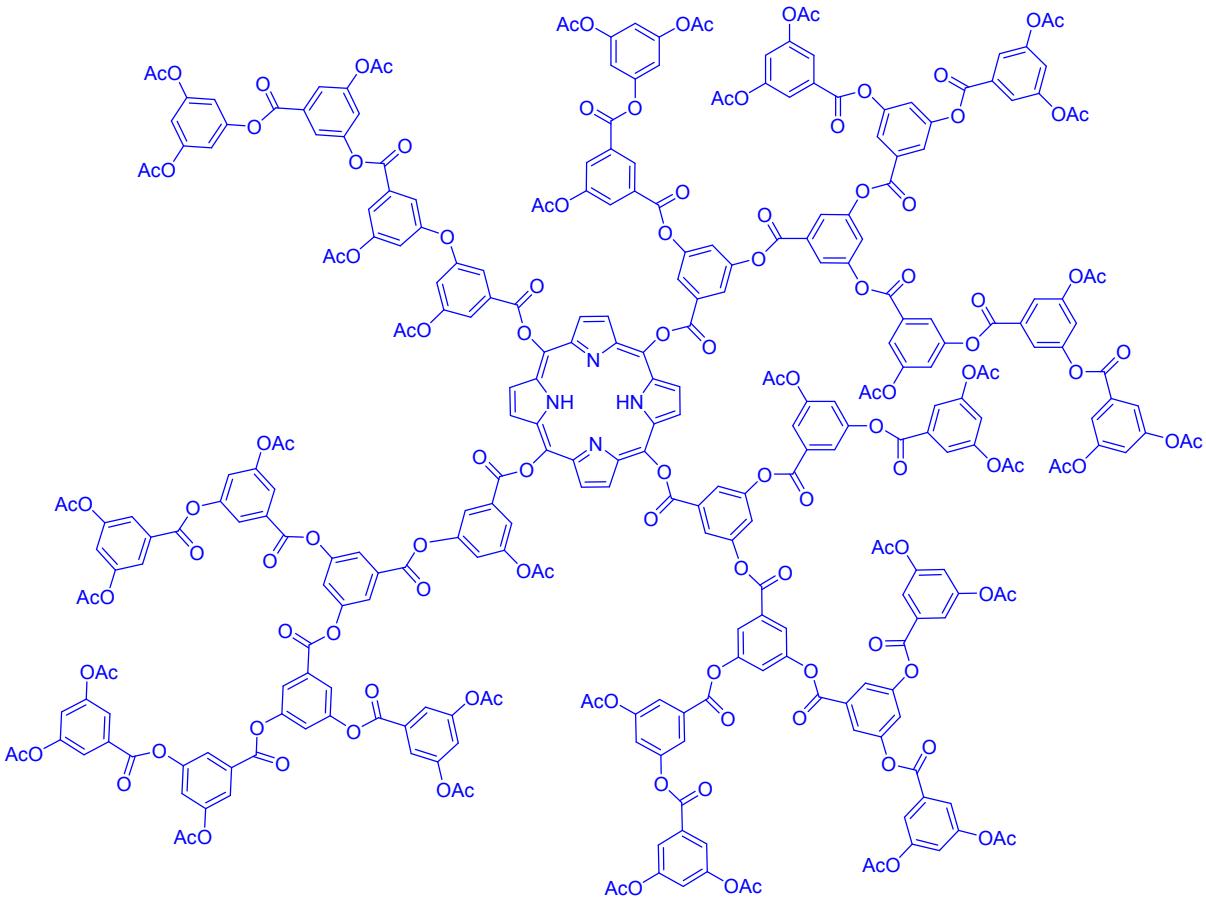


Figure.2.4. Porphyrin cored hyperbranched polymers.

Considering that the area of cored functionalised hyperbranched polymers is well researched, it is surprising that the field of interior functionalised hyperbranched polymers has not been reported upon to the same extent since they are undoubtedly beneficial. For some applications, the addition of many functional groups to the dendritic polymers might be beneficial, whilst in others it might even be necessary.[68-83] This could be achieved by the co-polymerisation of hyperbranched polymers, which can occur in two possible ways. The first possibility is that the co-polymerisation takes place in the periphery of the polymer after polymerisation of the monomer. In this case, the system will have limited use in some applications, such as controlled environments and site isolation. This is due to the location of the functional group. The second possibility is direct co-polymerisation; the co-polymerisation of the functional group takes place in the interior of the hyperbranched polymer. Therefore, the direct co-polymerisation method is the only method that can be used to provide hyperbranched polymers with many functional groups in the interior phase.

However, the degree of branching associated with this type of co-polymerisation needs to be taken in consideration. The addition of co-monomers will result in a decrease in the number of dendritic units and an increase in the number of linear units; therefore, the degree of branching will be affected. Many studies have demonstrated that the properties of hyperbranched polymers are strongly correlated with their branched structure. Defining and determining the dendritic structure parameter of the hyperbranched polymer is a key step in its application. If one or two co-monomers are needed, the change in the degree of branching of these polymers is not significant (for polymers with low molecular weight). However, if this number is elevated, the more linear unit growth occurs, and then less branched hyperbranched polymers are obtained. As the degree of branching plays a fundamental role in the structure of hyperbranched polymers, the structure of this polymer might be affected. This might leads the polymer to lose some dendritic properties and acquire more linear polymer properties.

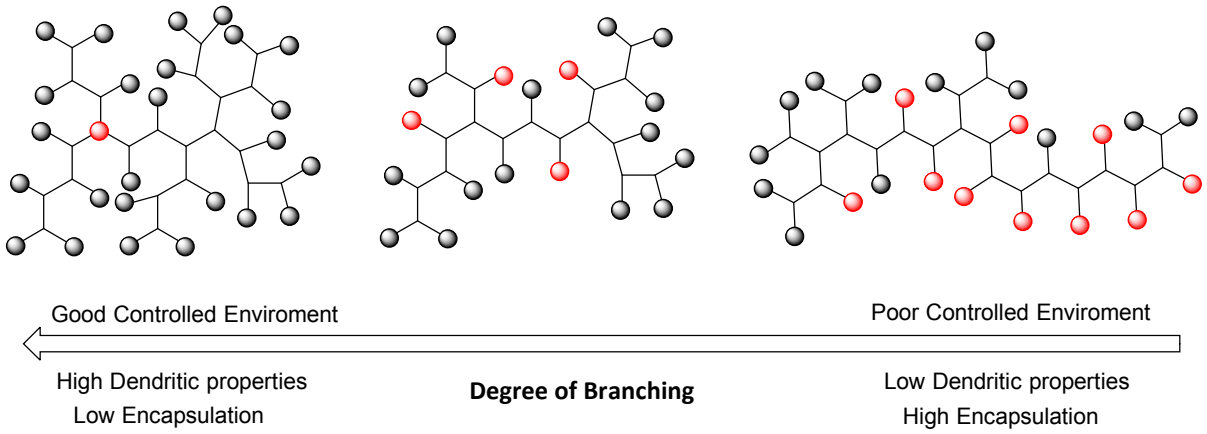


Figure.2.5. Schematic representation of the effect of the degree of branching on the structure of hyperbranched polymer.

2.2 Approch and considerations:

Nowadays, the average topological architecture of hyperbranched polymers could easily be determined by measuring the degree of branching (DB).[84,85] The higher the degree of branching, the more dendritic like the polymers, providing a greater number of end groups that will affect the physical properties.[85] For example, solubility could be controlled and viscosity decreased by a higher concentration of end groups caused by a higher degree of branching.[85,86] The degree of branching is an important property of hyperbanched polymers;

therefore, to copolymerise the hyperbranched polymer in order to obtain a high interior functionalised hyperbranched polymer, an examination of the structure of hyperbranched co-polymers is necessary. As stated previously, a hyperbranched polymer with a degree of branching of 50% is capable of replacing dendrimers in many applications because of its dendritic structure. Therefore, this study will be focused on the co-polymerisation of a hyperbranched polymer derived from an AB_2 monomer. The degree of branching of the resulting hyperbranched co-polymer will be varied under 50% upon the molar ratio of the co-monomer. Therefore, at some point the resulting hyperbranched co-polymer will lose its dendritic properties. For this reason, the effect of the degree of branching on the structure of a hyperbranched co-polymer will be part of this research. This study will explore the effect of the degree of branching on the bulk properties and the internal environment of hyperbranched polymers.

2.3 Bulk properties:

For the bulk properties, the effect of the degree of branching on viscosity will be examined. In general, branching causes a compact structure that result in a decrease in chain entanglement, leading to a decrease in viscosity. However, hyperbranched polymers possess lower viscosity than linear polymers at specific molecular weights. Therefore, any changing in viscosity due to decreasing the degree of branching proves that the molecule is more linear like. To carry out such a study, hyperbranched co-polymers with different degrees of branching and identical molecular weight should be synthesised. The obtained result will reveal any impact on the system.

2.4 Internal environment:

For the internal microenvironment, a binding study will be carried out to determine if there is any impact of the degree of branching. This study will be conducted by using varied degree of branching cored functionalised hyperbanched polymers. This research investigation will be modelled on that of the Twyman group previously mentioned in this chapter. To ensure the validity of our results, the study will be carried out using two different molecular weights, one above and one below the dense packing. The association constant will be measured by the determination of the binding of three differently sized

ligands to varied degree of branching porphyrin cored hyperbranched co-polymers by the UV/Vis titrations.

One of the possible outcomes is shown below in **Figure 2.6.** This shows that there is no effect on the degree of branching on the bulk properties or the internal environment (for both molecular weights). As confirmation of this, these polymers are still steric and possess the dendritic properties. Therefore, there is no limitation on co-polymerisation in this type of polymer and they could be used as a catalyst in a high loaded system.

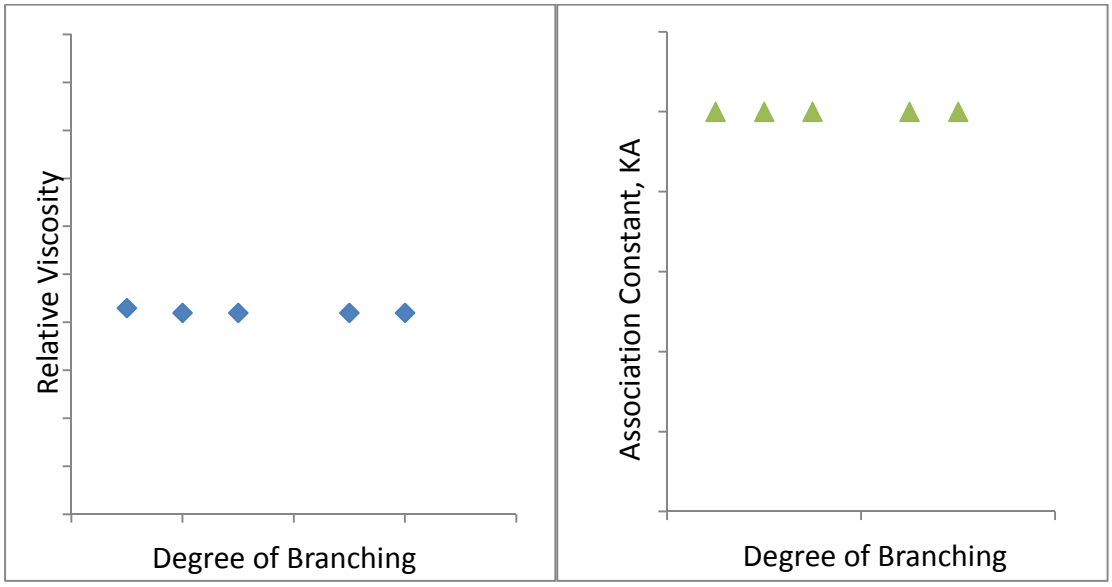


Figure.2.6. A) Figure to show the predicted effect of the degree of branching on viscosity, if no effect (left). B) Figure to show the effect of the degree of branching on the internal environment, if no effect (right).

Another possibility is shown below in **Figure 2.7.** This shows that the viscosity increases as the degree of branching decreases, proving that the polymer becomes more linear like. In terms of the internal environment, if the association constant changes, increased due to the steric effect or decreased due to the electronic effect, with a decreased degree of branching for both molecular weight polymers, this indicates that there will be less steric around the core and the system will be more open. In this case, the co-polymerisation of hyperbranched polymers derived from AB_2 monomers will be unfavourable. Therefore, further investigation to increase the degree of branching is required.

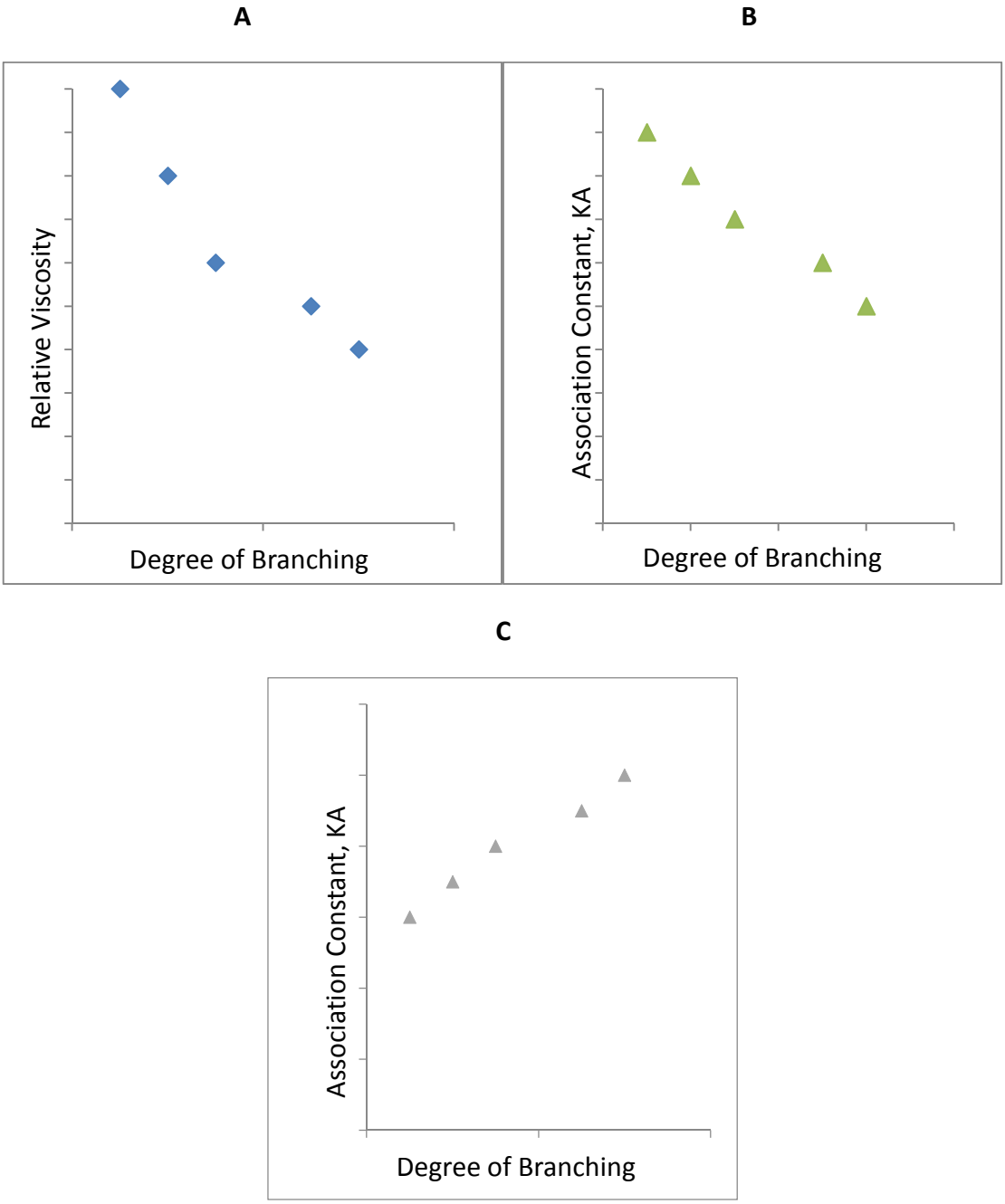


Figure.2.7. A) Figure to show the predicted effect of the degree of branching on viscosity, if there is an effect (left). B) Figure to show the predicted effect of the degree of branching on the internal environment (high molecular weight polymers), if there is an effect (right). C) Figure to show the predicted effect of the degree of branching on the internal environment (low molecular weight polymers), if there is an effect (below).

As the relationship between branching and viscosity has been widely addressed in the literature,[9,22]an attempt to develop a hyperbranched polymer system with a degree of branching higher than 50% will be made. Despite the fact that many methods to increase the degree of branching of hyperbranched polymers derived from AB_2 monomers have been reported in the literature, there are some limitations associated with using them due to

monomer type and polymerisation conditions.[58-62,87,88] However, many reports indicate that hyperbanched polymers derived from AB_3 monomers could provide hyperbranched polymers with a degree of branching on the average of 62%.[89] Therefore, by co-polymerisation those polymers, the degree of branching will be reduced to 50%, which leads to them possessing a dendritic like structure.

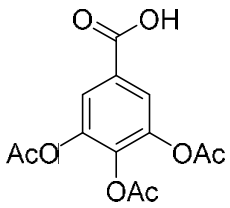


Figure.2.8. Schematic representation of the structure of AB_3 monomer.

The other possible method is post synthetic modification. In this method, the co-polymerisation of hyperbranched polymers is indirect due to using a functional group. The advantage of using this method is that the reaction conditions and the degree of branching can be controlled. In the case of reaction conditions, the modification of the functional group could be carried out at room temperature rather than in aggressive conditions, such as at an elevated temperature. In the case of controlling the degree of branching, the hyperbranched polymer will be co-polymerised with di-functional monomers. Then, the catalyst will be attached to the system via those functional groups. In this method, the loading of functionality could increase with a minimum decrease in the degree of branching. For example, the incorporation of four catalytic sites into hyperbranched polymers could be obtained by the direct co-polymerisation of four co-monomers. However, the same number of incorporated catalytic sites could be obtained by the indirect co-polymerisation via post synthetic modification method. This could be easily carried out by the co-polymerisation of two di-functional co-monomers see **Figure 2.9.** In the last chapter, the use of the highly interior functionalised hyperbranched system as a catalyst will be examined.

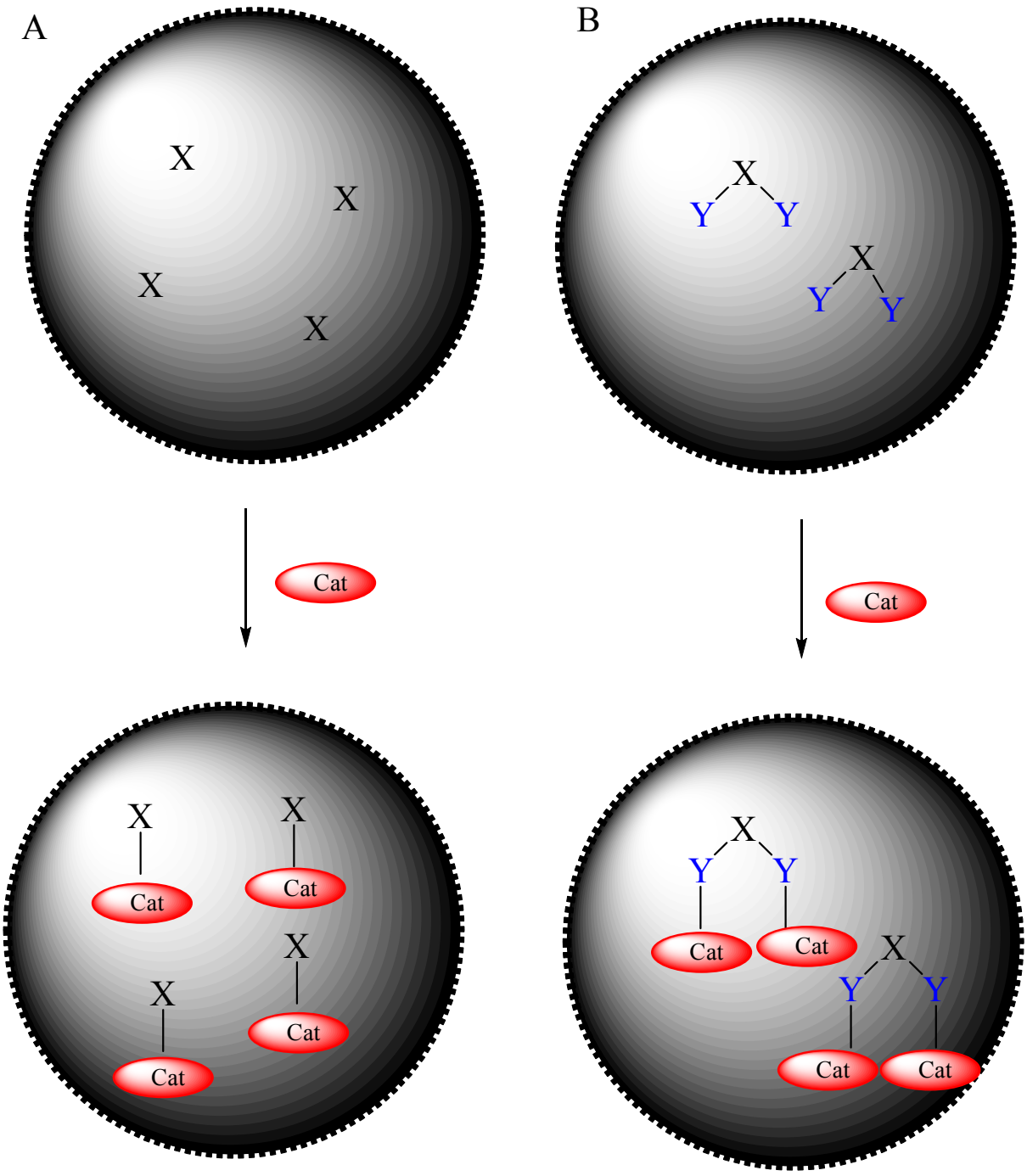


Figure.2.9. Schematic representation of A) Direct co-polymerisation of catalyst groups. B) Indirect co-polymerisation of catalyst groups via post synthetic modification method.

Chapter Three

The effect of the degree of branching on the bulk properties and the microenvironment of hyperbranched polymers

Chapter Three - The effect of the degree of branching on the bulk properties and the microenvironment of hyperbranched polymers

As previously mentioned in chapter two, the first stage of this project is to investigate the effect of the degree of branching on the bulk properties and internal environment of hyperbranched polymers. The aim of this investigation is to ascertain the maximum loading of functionality to a hyperbranched polymer without there being any effect on the dendritic properties of the polymer. Therefore, a hyperbranched polymer derived from the AB_2 monomer with a degree of branching of 50% was required for this study. A system fulfilling these requirements was developed synthetically by Turner, Hult and Voit.[90] The hyperbranched polyaryl ester was chosen as a model system. This polymer was synthesised from the AB_2 3,5-diacetoxybenzoic acid monomer. The reaction is reversible, and the equilibrium can generate a high molecular weight polymer through the removal of acetic acid.

3.1 The effect of the degree of branching on the bulk properties of hyperbranched polymers:

In terms of bulk properties, viscosity will be the subject of the following investigation. The viscosity of polymers is related to their molecular weight and degree of branching.[91-95] Polymers with branching units have a compact structure that gives them less viscosity than linear polymers. The increased branching leads to a more compact structure that has a direct effect on the viscosity. Regarding molecular weight, it is indicated that the viscosity of branching polymers is proportional to their molecular weight.[31] However, the increased viscosity that hyperbranched polymers possess is less than the increased viscosity of linear polymers at identical molecular weights.[31] Therefore, in order to carry out the investigation outlined above and provide a valid result for the ongoing research, a series of hyperbranched polymers with different degrees of branching and identical molecular weight must be synthesised. The degree of branching can be varied by altering the molar ratio of the co-monomer. Isopropylbenzoic acid was chosen as a co-monomer for a number of reasons, including it being available commercially, similar in structure to the main monomer, applicable to the polymerisation conditions, detectible by NMR (not overlapping with the main monomer peaks after polymerisation) and does not allow further branching.

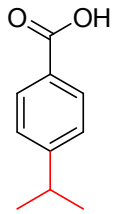


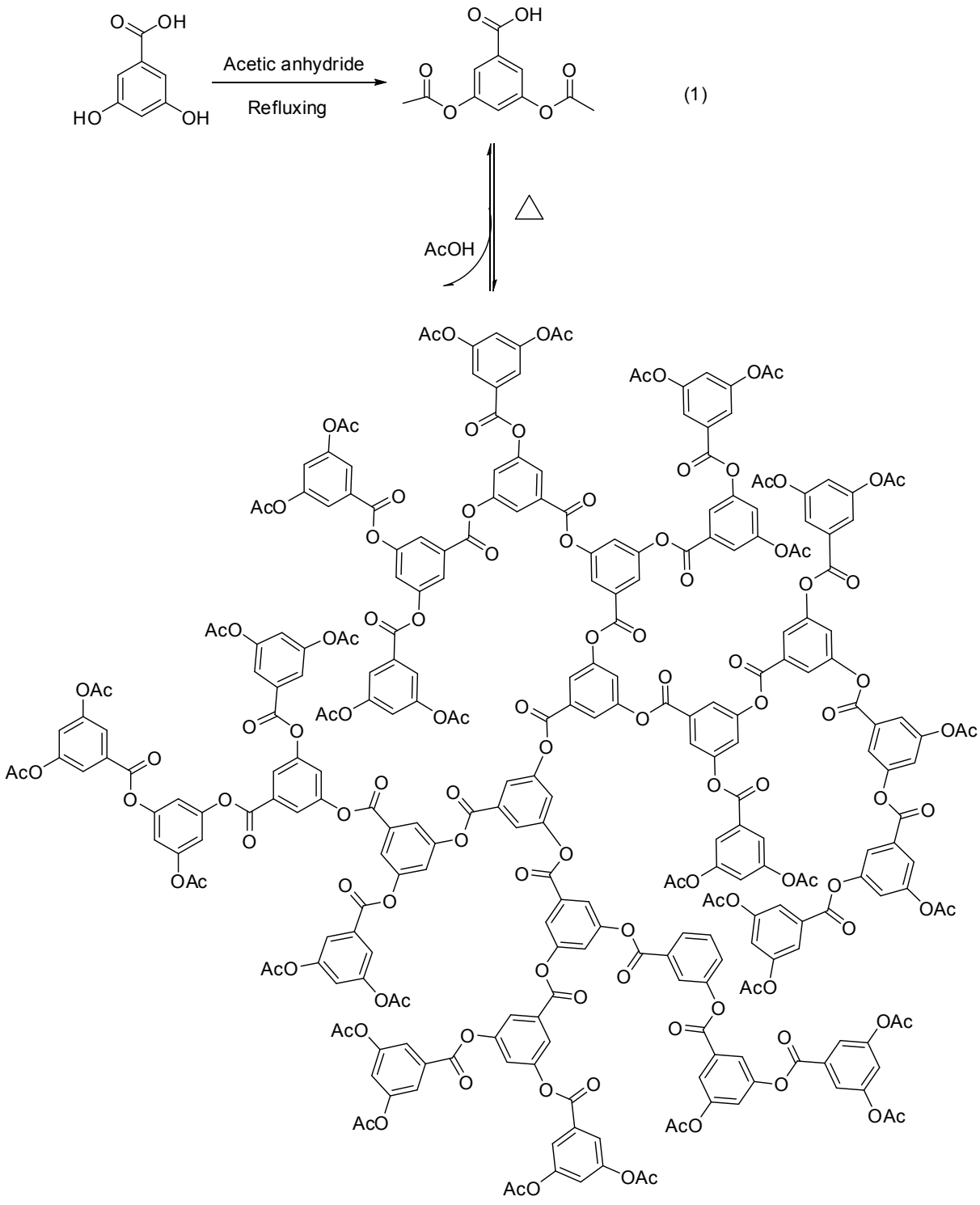
Figure.3.1. The structure of 4-isoprpaylbenzoic acid.

3.1.1 Synthesis of 3, 5-diacetoxybenzoic acid:

The monomer was synthesised via a single step reaction adapted from a methodology outlined by Turner et al.[90] 3, 5-diacetoxybenzoic acid was synthesised from the reaction of 3,5-dihydroxybenzoic acid with acetic anhydride. The monomer was refluxed with two equivalents of acetic anhydride for six hours, which resulted in a yellow solution. Then, the acetic anhydride was removed by vacuum using a distillation kit to avoid the risk of self-polymerisation at a high temperature. The purification process was simple to carry out. To start with, the yellow solution was dissolved in hot chloroform. It was then filtered, followed by precipitation in petroleum ether. This purification step was repeated twice to ensure a pure monomer was obtained. The product was filtered by vacuum filtration and then dried thoroughly. The monomer was characterised by ^{1}H NMR and IR. The ^{1}H NMR data indicated a broad singlet at 10.00 ppm from the proton of carboxylic acid. A doublet was observed at 7.80 ppm, corresponding to the aromatic *o*rtho protons. A triplet peak at 7.25 ppm was observed, corresponding to the para aromatic protons. Finally, a single peak was observed at 2.35 ppm, corresponding to the newly methyl protons of the acetoxy groups. IR data was in agreement with the published data. Additional support from mass spectrometry proved that the monomer was synthesised successfully in agreement with the published data. The reaction was prepared on a large scale to obtain the monomer in a yield of 36%. The next step was to prepare a hyperbranched polymer from the obtained monomer.

3.1.2 Polymerisation of 3, 5-diacetoxybenzoic acid:

Initially, the polymerisation was carried out in the absence of a co-monomer to achieve the maximum degree of branching possible. The polymerisation was carried out using a double stage procedure, involving two different temperatures.[90] Care was taken to ensure the reaction was performed in the absence of air. The reaction system was degassed and then flushed with nitrogen. The reaction was carried out in the solution phase using diphenyl ether as a solvent. The first stage of the polymerisation was started when the reaction was heated to 225 ^{0}C for 45 minutes. In this stage, the monomer was fully dissolved in the solvent and the initiation process of the polymerisation commenced. During this period, the oligomer product was formed. The temperature was then lowered to 180 ^{0}C, and the reaction was placed under a vacuum for four hours. As the reaction is reversible, the purpose of this final stage was to enable the polymer to achieve a high molecular weight by the removal of the acetic acid by-product. Finally, once the reaction time was completed, the purification process was carried out by dissolving the crude polymer in hot THF, followed by precipitation in a large excess of a cold methanol. The product was filtered and washed thoroughly with methanol and then dried. A variety of analytical techniques were used to confirm the success of the polymerisation procedure. From analysis of the molecular weight from the GPC, it was apparent that a polymer with a molecular weight of 14800 Da and a PDI of 2.3 was obtained. In the case of IR, the disappearance of the carboxylic acid group peak at 1690 cm^{-1} was indicated. The ^{1}H NMR spectrum also indicated that polymerisation had occurred. Two broad doublets peaks were observed at 8.10-7.80 ppm from two protons of *m*eta position in the monomer unit. These two protons of *m*eta position were equivalent before the polymerisation. As a result of the polymerisation, their equivalence ceased due to the number of different environments. The possible locations of the *m*eta protons are in the branched unit, the linear unit and the terminal unit. The terminal H_m protons are likely to be found at the periphery, but H_m may also be found anywhere in the dendritic structure that includes linear or dendritic units; therefore, many possible environments exist, resulting in two very broad doublets, as shown in **Figure.3.2**.



Scheme.3.1. Synthesis of 3, 5-diacetoxybenzoic acid (1) and sequence reaction to prepare hyperbranched poly (3, 5-diacetoxybenzoic acid) (2).

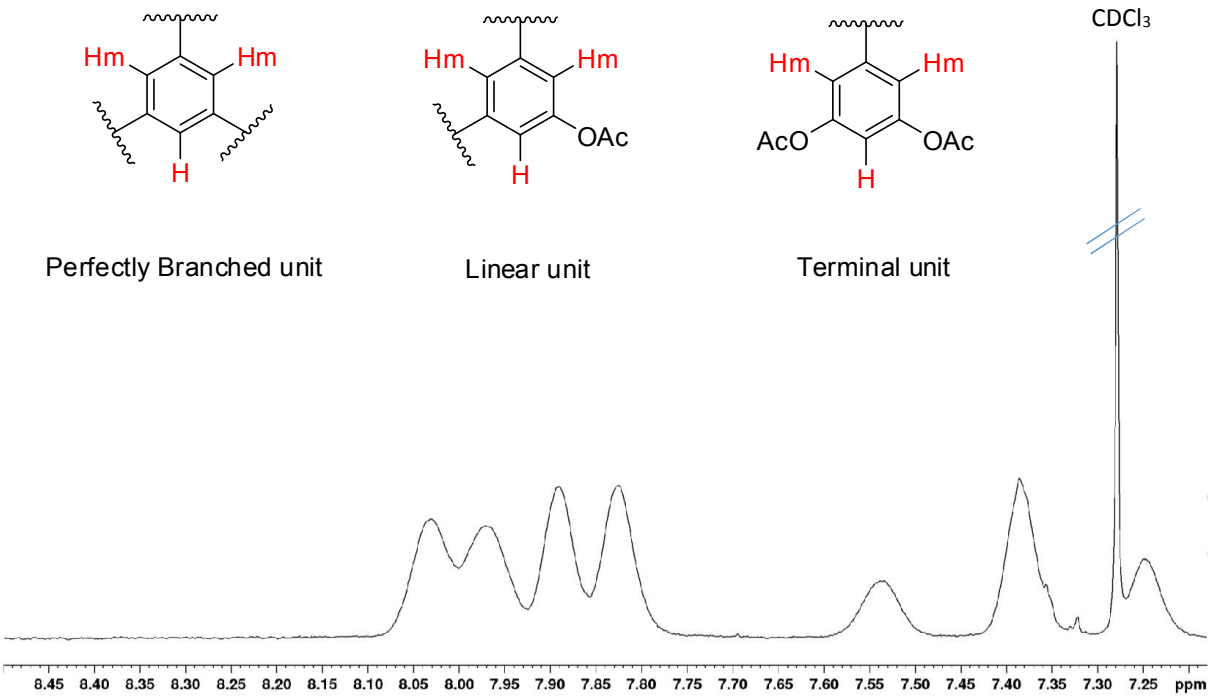


Figure.3.2. Polymerisation resonances and unit types in the ^{1}H NMR spectrum of the hyperbranched polymer system.

Three well defined singlets appeared at 7.60-7.20 ppm, corresponding to the proton in the para position of the monomer unit. In the case of the monomer, this para proton resides in a symmetrical environment between the two acetoxy groups, resulting in a single peak. However, when the polymerisation occurs, this becomes three well defined singlets, observed at 7.50 ppm, 7.40 ppm and 7.25 ppm, as a result of the three different environments, for the linear, branching and dendritic units shown below. Finally, a singlet peak observed at 2.30 ppm corresponded to three protons of the acetoxy group.

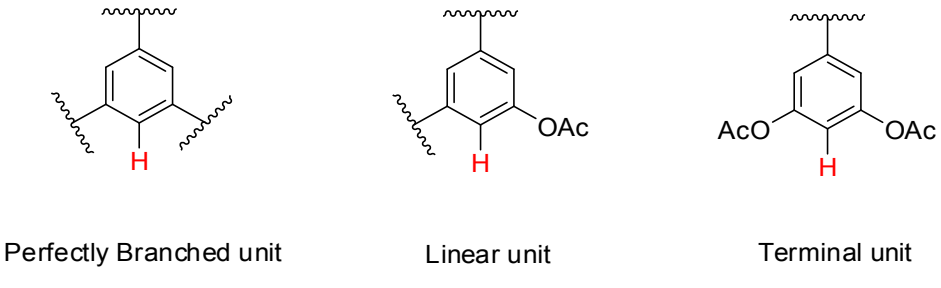


Figure.3.3.Architectural units in a dendritic structure.

As it was mentioned in the first chapter, ^{1}H NMR is a reliable technique widely used to determine the degree of branching. This is due to the possibility for such technique to detect the environment of the para proton in the three different units.

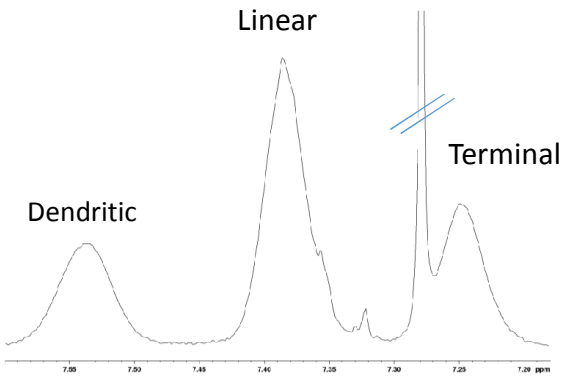


Figure.3.4. ^{1}H NMR resonance of the dendritic unit.

Therefore, the degree of branching can be easily calculated by detecting the integrations of the three well defined singlets and using the one of the equations explained in chapter one. Theoretically, hyperbranched polymers that are derived from the AB_2 monomer have a degree of branching of 50%. This is because the number of terminal units is controlled by the dendritic growth of the polymer. Linear growth involves the consumption of a terminal unit and the addition of a new one, resulting in no increase in the terminal unit. Dendritic growth converts a linear unit into a dendritic unit after the addition of a new terminal unit. Therefore, the number of terminal units is greater than the number of dendritic units. However, the quantity of these two units may be equal in the case of a higher degree of polymerisation. This indicates that the peaks at 7.50 ppm and 7.25 ppm are approximately equal and, therefore, correspond to the dendritic and terminal units. Thus, the peak at 7.40 corresponds to the linear units. Comparing the two remaining peaks, the peak at 7.25 ppm is slightly higher than the peak at 7.50 ppm, suggesting that the peak at 7.25 ppm corresponds to the terminal units, whereas the peak at 7.50 ppm corresponds to the dendritic units. This can also make an agreement for the shifts due to electronic withdrawing groups. Using the integration of these peaks in the previous equation, the degree of branching of the resulting polymer was calculated to be 49% . As a result, the

calculated degree of branching is close to the theoretical assumption, indicating that the peaks have been assigned correctly to their structural units.

3.1.3 Co-polymerisation of 3, 5-diacetoxybenzoic acid with isopropyl benzoic acid:

A series of hyperbranched co-polymers with different degrees of branching were prepared by condensation polymerisation of 3, 5-diacetoxybenzoic acid and different molar ratios of isopropylbenzoic acid (co-monomer). The monomer and co-monomer mixtures were heated in the presence of an equal weight of solvent. The solvent that was used in the polymerisations was diphenyl ether. The polymerisations were carried out using the procedure mentioned previously.[90] After a period of time, the temperature was lowered and the reaction was placed under low pressure to remove the excess acetic acid. The crude polymers were purified by dissolving them in hot THF, followed by precipitation in cold methanol to remove any unreacted materials. Finally, the products were filtered and dried by vacuum filtrations. ^{1}H NMR indicated that the co-polymerisation was carried out successfully by the presence of an additional isopropyl peak at 3.oo ppm, corresponding to one proton. In addition, a single peak at 1.30 ppm, corresponding to six protons, and another single peak at 8.20 ppm, corresponding to two protons was also observed.

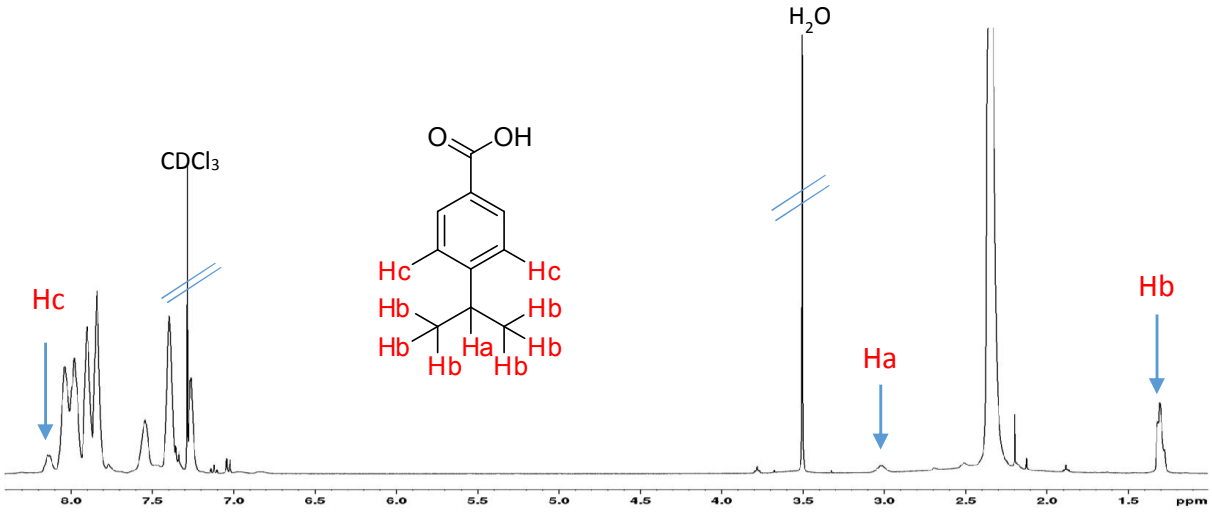
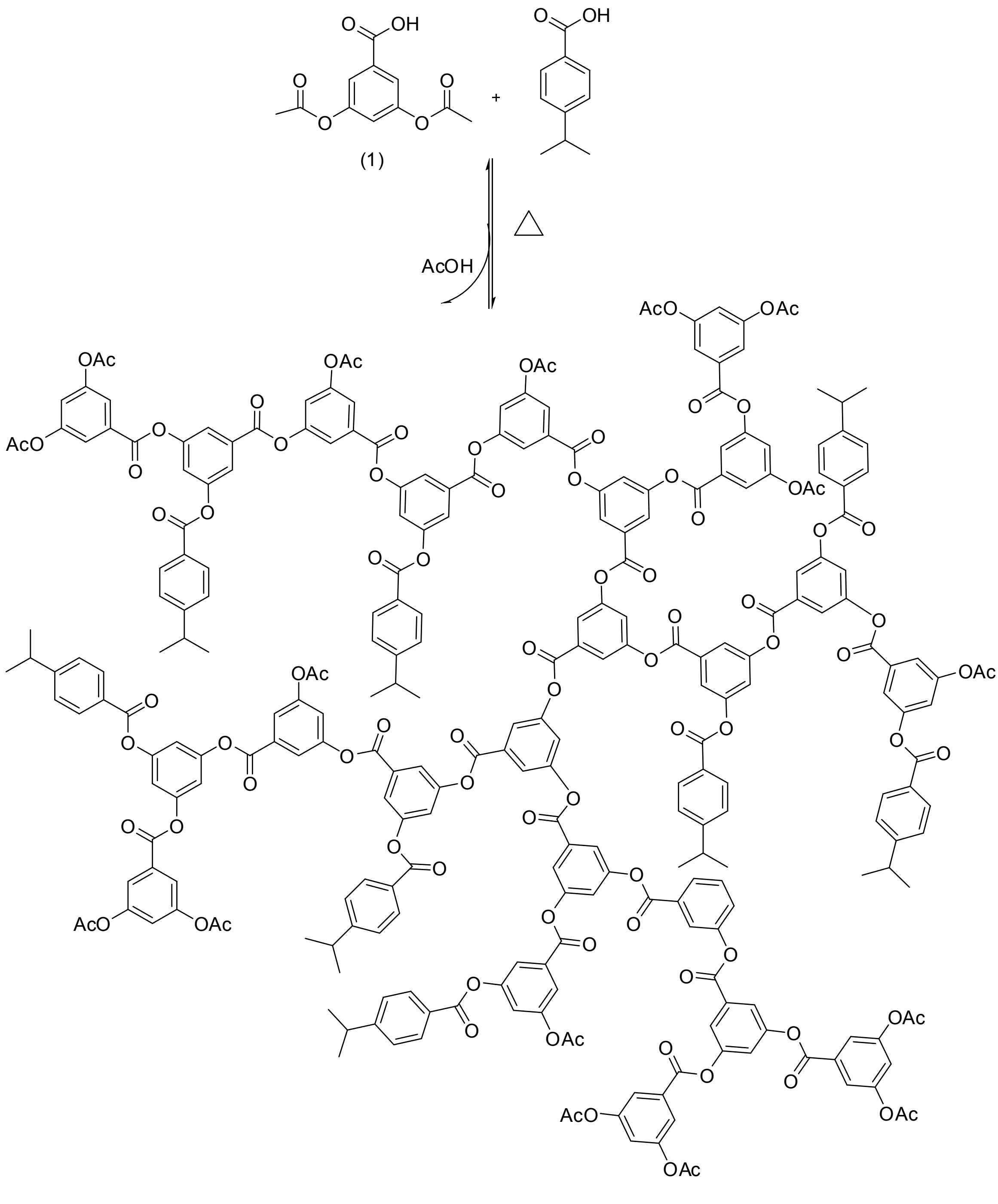


Figure.3.5. Figure to show ^{1}H NMR of hyperbranched co-polymer (3) prepared from 3, 5-diacetoxy benzoic acid and 4-isopropaylbenzoic acid.



(3)

Scheme.3.2. Synthesis hyprebanched co-polymer prepared from 3, 5-diacetoxybenzoic acid and 4-isoprpaylbenzoic acid (3).

GPC shows that polymers with different molecular weights ranging from 13000 to 18000 Da and polydispersities ranging from 2.5 to 7.5 were obtained, as can be seen in the table below.

Polymer ID	Co-monomer's Ratio	Mn	PDI	DB by Fréchet's equation	DB by Fery's equation
2	0	14800	2.3	49%	49%
3A	5%	13300	2.5	46%	47%
3B	10%	14600	4.2	42%	43%
3C	20%	16100	7.1	40%	41%
3D	30%	18000	7.5	37%	39%

Table.3.1. Represents the result of series of hyperbranched co-polymers using 4-isopropayl-benzoic acid.

The table shows that as the molar mass of the co-monomer increases the degree of branching decreases. This is expected and occurs because the addition of the co-monomer reduces the number of dendritic units and increases the number of linear units. The degree of branching described in **Table.3.1** was based on a calculation obtained from ^{1}H NMR. However, the accuracy associated with using the ^{1}H NMR technique to calculate the degree of branching of hyperbranched co-polymers is low. This is because the technique is unable to distinguish between the different environments of the protons in the aromatic region of the AB_2 monomer and the co-monomer (overlapping between signals occurred), as in shown **Figure.3.6.** This is due to the presence of a large number of units with a similar environment; therefore, the possibility of error occurrence is considered to be high.

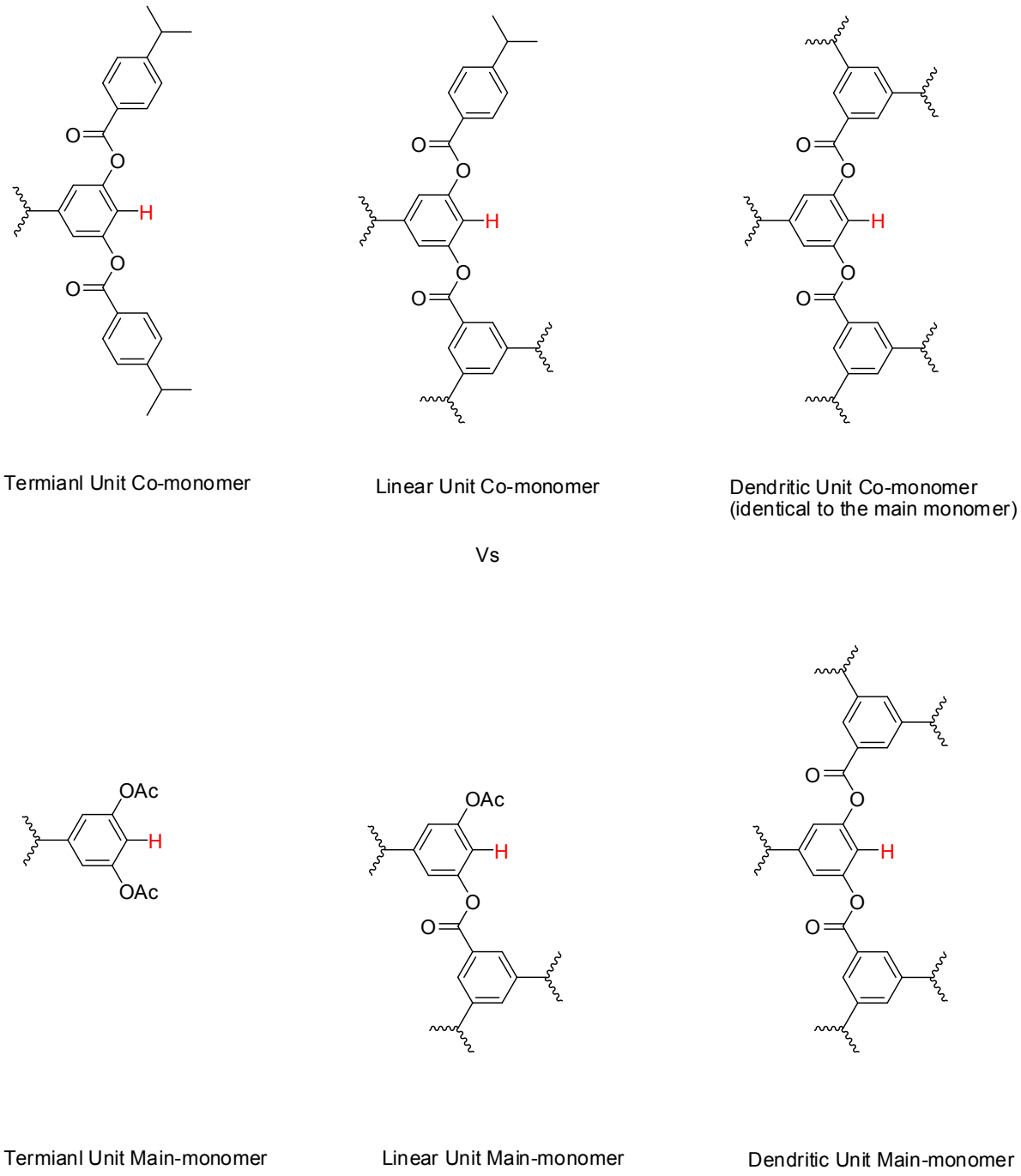


Figure.3.6. Figure to show different units in hyperbanched co-polymer with aromatic side chain (that are in identical environments and shifts).

In order to overcome this problem, it is preferable to use a new calculation or method to support the degree of branching estimated by ^{1}H NMR. As the degree of branching is directly affected by the level of incorporation of co-monomers, it is possible to estimate the degree of branching by measuring the level of incorporation of the co-monomers. This can easily be determined by ^{1}H NMR. Theoretically, the co-monomer can be incorporated into

the hyperbranched polymer in two possible ways. The first possibility is that the co-monomer is incorporated inside the hyperbranched polymers, which will affect the degree of branching. The second possibility is that the co-monomer is incorporated on the outside the hyperbranched polymers. However, there is an equal probability of these two possibility to be occurred. As either possibility is effected by the level of incorporation with equally probability, the degree of branching can be estimated as following.

$$DB = DB_0 - (\text{level of incorporation}/2) \qquad \textbf{Equation.3.2.}$$

Whereas, DB_0 is the degree of branching of the hyperbranched homo polymers. However, to ensure we have calculated the degree of branching with a minor margin for error, a comparison between the degrees of branching calculated by using ^{1}H NMR and the degree of branching obtained from the above equation based on theoretical calculations using the level of incorporation should be carried out.

Polymer ID	Calculated level of Incorporation by ^{1}H NMR	DB by ^{1}H NMR using Fréchet's equation	DB by ^{1}H NMR using Fery's equation	Estimated DB by Equation
2	0	49%	49%	49%
3A	5	46%	47%	47%
3B	10	45%	45%	44%
3C	22	40%	43%	38%
3D	37	37%	40%	31%

Table.3.2. Table represent the relation between level of incorporation and DB.

As can be seen, the two methods result in a different degree of branching. In the case of low incorporation of the co-monomer, the degree of branching is nearly the same whichever method is used. However, the difference between the two methods is more obvious in the case of a high level of incorporation. This is where the biggest error is expected (where we have the problem of peaks detection and contamination in the calculation by ^{1}H NMR).

Therefore, using the previously described equation to estimate the degree of branching is more efficient.

As the viscosity is directly affected by the molecular weight of the polymer, a series of hyperbranched co-polymers with different degrees of branching are necessary to possess a constant molecular weight in order to obtain a valid result. Those polymers could be obtained by the uses of a laboratory technique to fractionate all the obtained polymers. The bio-beads column technique was chosen to fractionate the polymers. After the fractionation of the polymers, GPC was used to measure the molecular weight (see **Table 2.3**).

An U-tube viscometer was used to measure the viscosity of each polymer. A constant concentrated solution was prepared using a suitable solvent, such as THF, for each polymer. The U-tube was held in a water bath set to a defined temperature. The tube was loaded with the chosen solvent (THF), and the temperature was allowed to equilibrate for 1 hour before measuring the viscosity of the solvent. After recording the viscosity of the solvent, the viscosity of the polymer was measured using the same technique. The measurement of the viscosity of all the polymers was repeated until a constant time was recorded. The average time was then calculated and recorded. This was necessary to ensure accuracy since there is a possibility of human error in the timing. Finally, the relative viscosities of each polymer were calculated simply by dividing the polymer viscosity by the solvent viscosity.

$$Relative\ viscosity = \frac{\text{polymer viscosity}}{\text{solvent viscosity}} \qquad \textbf{Equation.3.3.}$$

Polymer ID	M_n	PDI	DB	viscosity
2	14800	2.3	49%	0.950
3A	14200	2.5	47%	1.0
3B	15100	3.6	44%	1.10
3C	15200	6.4	38%	1.38
3D	15000	7.2	31%	1.65

Table.2.3. Table represent the viscosity data of series of hyperbranched co-polymers.

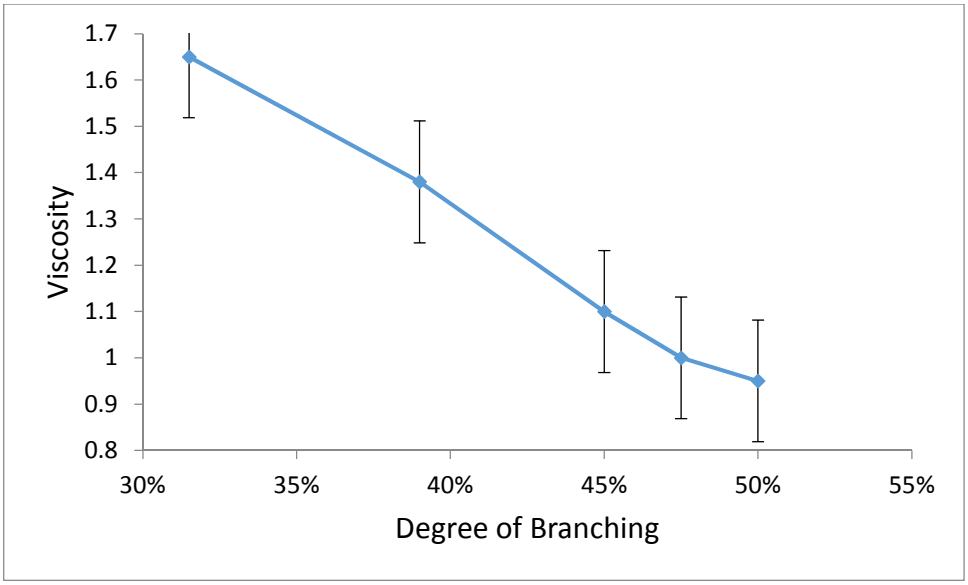


Figure.3.7. The relationship between the degree of branching and relative viscosity for hyperbranched polymers with varied PDI.

Figure.3.8. shows that as the degree of branching decreases the relative viscosity increases. However, there are two varying factors in this equation: the degree of branching and the polydispersity index. Although all polymers have a constant molecular weight, the polydispersity indexes (PDI) are varies. Therefore, in order to investigate the effect the degree of branching, constant PDI is required for valid results. However, it is worth mentioning that a published work indicated that some types of hyperbranched polymers possess a dendritic like behaviour in viscosity.[96] An examination to determine the effect of molecular weight on viscosity at a constant PDI for this type of polymer was carried out. Two hyperbranched homo-polymers with different molecular weights, constant polydispersity index and degree of branching were prepared. These polymers were synthesised using the general method of polymerisation described earlier in this chapter, paying attention to varying the time under low pressure. The obtained polymers possessed molecular weights of 8000 and 15000, and the polydispersity index was constant at 2.9. The viscosity of these polymers was unchanged. This indicates that the molecular weight does not play a major effect on dendritic structure in terms of bulk properties within the range of 8000 Da – 15000 Da.

Therefore, in the next step, the advantages of incorporating a core into a hyperbranched polymer to control the molecular weight distribution will be considered in order to prepare a series of hyperbranched polymers with different degrees of branching and polydispersity.

In most cases, core units are difficult to observe due to their relative minor contribution to the overall molecular structure. However, the molecule selected must be easily observed by ^{1}H NMR when incorporated into the hyperbranched polymer. Therefore, a simple structured core 4-nitrophenyl acetate was selected.

3.1.4 Synthesis of 4-nitrophenyl acetate cored hyperbranched co-polymers:

The synthesis was carried out using 4-nitrophenyl acetate as a core unit in a hyperbranched polymer system with the aim of controlling the molecular weight. The core/monomer (1:40) mixture was heated in the presence of diphenyl ether. The general polymerisation method described earlier in this chapter was used. The purification procedure includes dissolving the crud polymer in hot THF, followed by precipitation in icy methanol. It was possible to extract the unreacted 4-nitrophenyl acetate from the mixture by repeating the purification as it is dissolved in alcohol. The product was isolated by vacuum filtration and then dried. Conformation of the successful incorporation of the 4-nitrophenyl acetate core into the hyperbranched polymers was given by ^{1}H NMR. ^{1}H NMR shows a single peak observed at 8.35 that was in absent in the hyperbranched homo-polymer. This peak corresponds with aromatic β protons from 4-nitrophenyl ester.

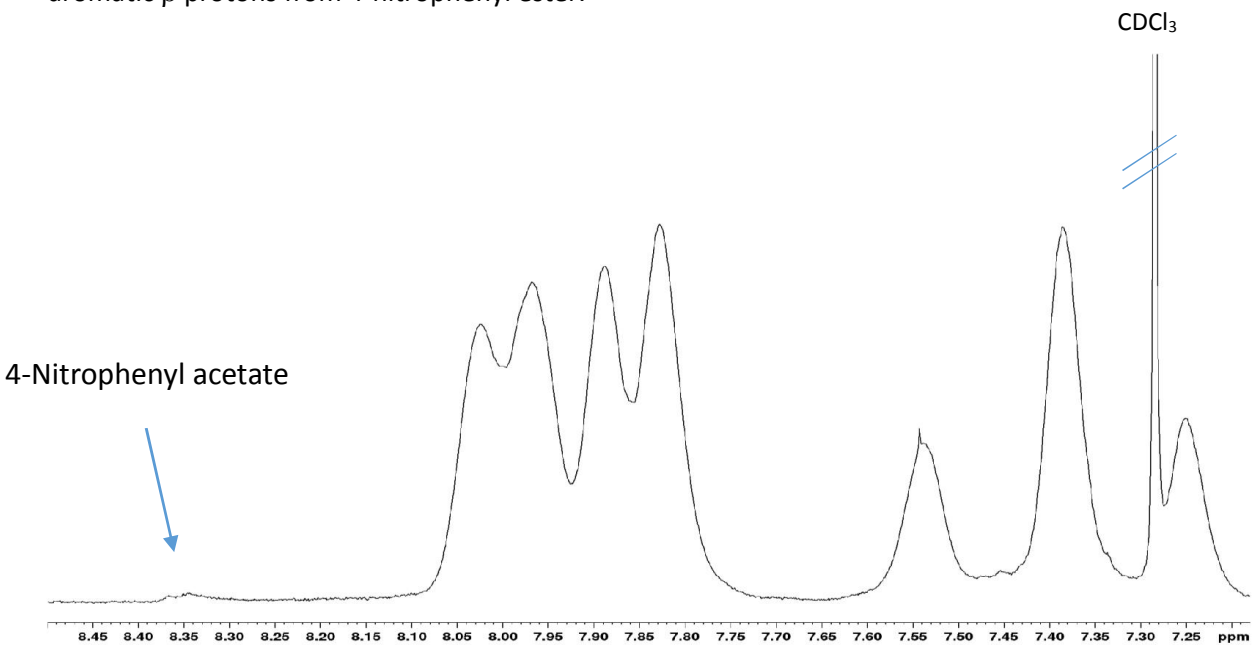
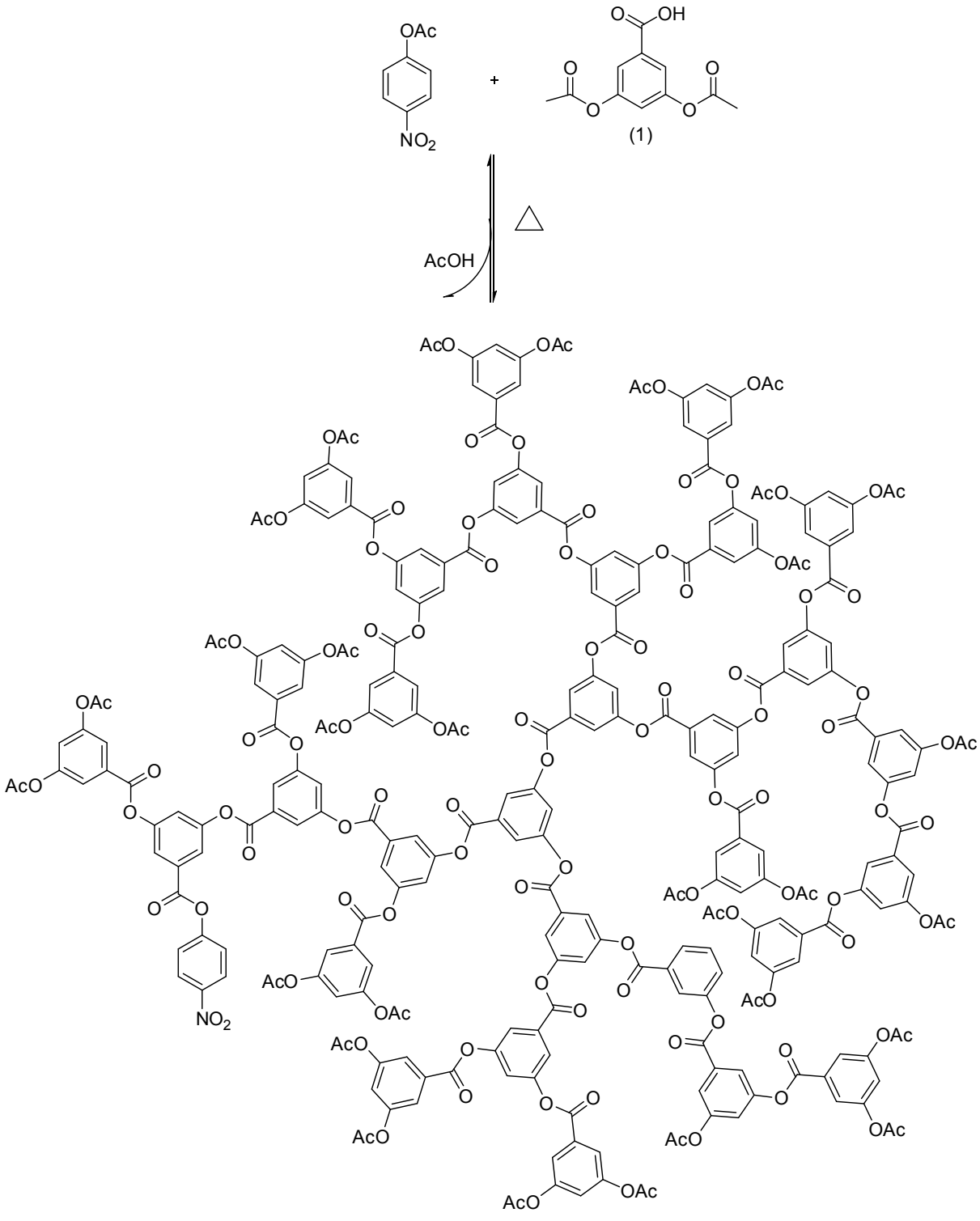


Figure.3.8. Figure to show ^{1}H NMR spectrum for the incorporation of 4-nitrophenyl acetate as a core in hyperbranched poly (3, 5-diacetoxybenzoic acid).



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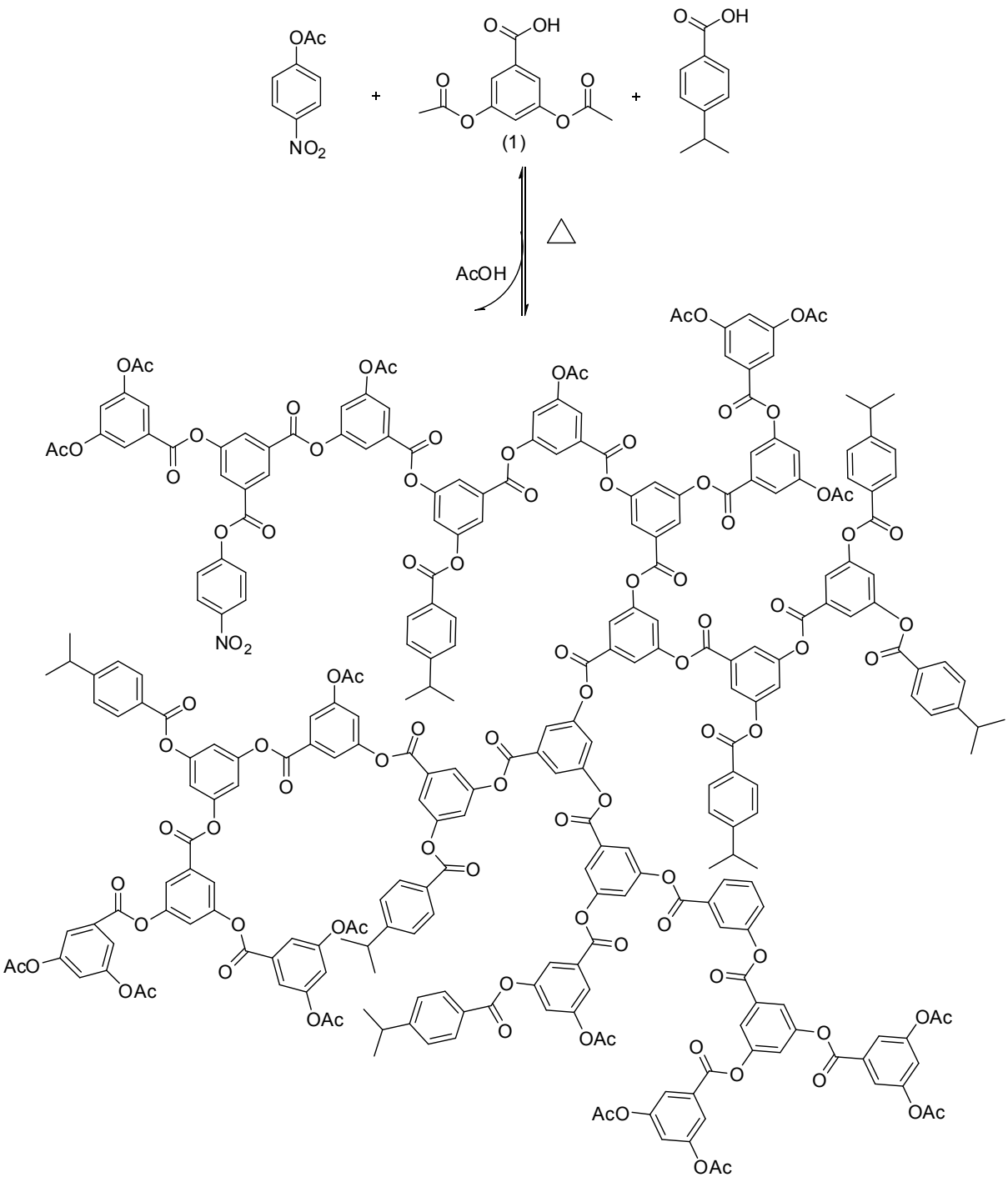
Scheme.3.3. Synthesis of 4-nitrophenyl acetate cored hyperbranched poly (3, 5-diacetoxybenzoic acid) (4).

Following confirmation of the incorporation of 4-nitrophenyl acetate as a core into hyperbranched homo-polymers, hyperbranched co-polymers with different molar ratios of co-monomers were synthesised in the presence of the core. The total ratio of the monomers and co-monomers was constant with the core being 1:40, as shown below in **Table 3.4.** ^{1}H NMR confirmed the presence of isopropyl groups peaks and the aromatic protons of 4-nitrophenyl ester in each polymer.

Sample No	Mn	PDI	DB	Ratio of Core:AB_2:Co-monomer	Level of incorporation
4	7200	3	48%	1:40	0%
5A	9800	3.9	45%	1:38:2	6%
5B	8900	3.8	40%	1:36:4	16%
5C	13900	4.2	37%	1:33:7	26%
5D	9200	3.9	25%	1:30:10	47%
5E	14000	5	18%	1:29:11	60%

Table3.4. the data of cored HBCO-Ps with different DB at constant core to monomers ratio.

The table above shows the molecular weight and the polydispersity index for hyperbranched polymers with different degree of branching. However, in order to study the effect of the viscosity, some of the obtained polymers were fractionated by using a bio-beads column to ensure that all the polymers had a constant polydispersity, as described below. Finally, the relative viscosities were measured by using the U-tube viscometer, as in the previously described procedure (see **Table 3.5**).



(5)

Scheme.3.4. Synthesis of 4-nitrophenyl acetate cored hyperbranched co-polymer (5).

Sample No	Mn	PDI	DB	Relative Viscosity
4	9100	3.2	48%	1.102
5A	9800	3.9	45%	1.109
5B	8900	3.8	40%	1.105
5C	9500	4	37%	1.102
5D	9200	3.9	25%	1.300
5E	9400	4	18%	1.520

Table.3.5. Table represent the data of a series of cored hyperbranched co-polymers and their viscosity.

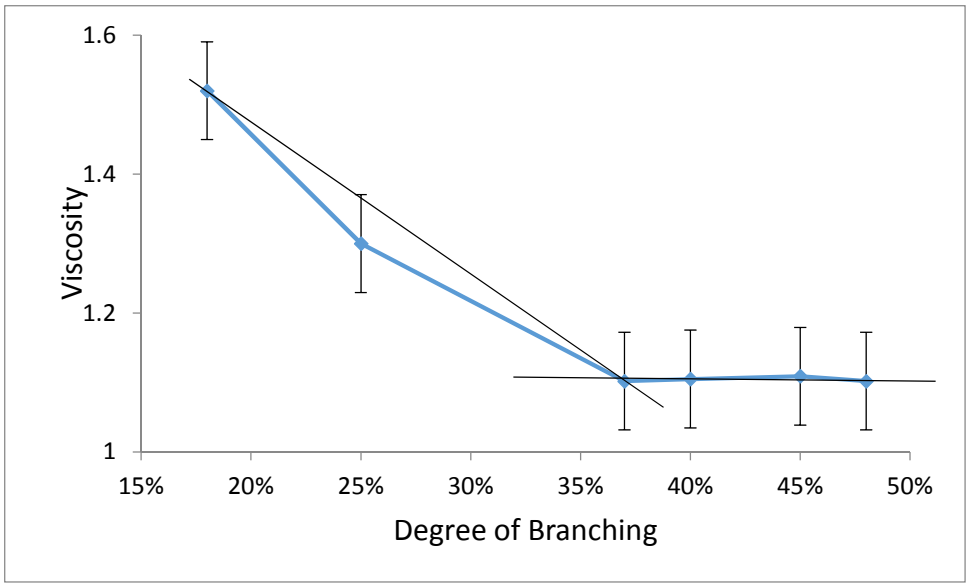


Figure.3.9. The relationship between the degree of branching and viscosity at constant PDI.

The graph above shows that the viscosity remains unchanged up to a degree of branching of 37%, which proves that hyperbranched polymers maintain their dendritic properties to this limit. Below 37%, there is a gradual increase in viscosity, which indicates that these types of hyperbranched polymers begin to lose their dendritic properties in term of bulk properties. As viscosity describes how the molecules interact with each other, the interaction of hyperbranched molecules is a minimum in a solution due to the globular structure caused by the presence of a high number of end groups on the surface. With the addition of a co-

monomer, there is an increase in the number of linear units as well as a decrease in the dendritic units. The increase in the number of linear units results in a decrease in the number of surface end groups. Therefore, at a specific limit, these polymers possess a more linear like structure rather than a globular structure and the interaction of these molecules increases in the solution.

This part of the study has focused on the bulk properties of hyperbranched polymers and how those polymers interact with each other in a solution. The next step is to study the effect of the degree of branching on the microenvironment of hyperbranched co-polymers. This is carried out by measuring the binding of varied size ligands to porphyrin cored hyperbranched polymers with a varied degree of branching.

3.2 The effect of the degree of branching on the microenvironment of hyperbranched polymers:

In nature, biological enzymes act as catalysts, allowing a chemical reaction to take place that would not in their absence.[5] This is due to their ability to optimise steric and electronic conditions for a specific reaction. The nature of the architecture of hyperbranched polymers caused by their globular structure provides them with the ability to be used as biological mimics, such as site isolation and controlling the microenvironment. However, work published by the Twyman group indicates that hyperbranched polymers are capable of being used for selectivity and controlled environments.[55] This work was explained in more detail in the previous chapter. In this part of the research, the same model system that was published previously is used to investigate the effect of the degree of branching on the microenvironment. The microenvironment of hyperbanched polymers could be examined by measuring the binding constant of a ligand to a porphyrin cored hyperbranched polymer.

Metal porphryins are capable of a binding interaction with a large number of electron donating species.[97] One well-characterized interaction is the binding of pyridine with zinc porphyrin.[98] Pyridine is able to coordinate to the metal centre of porphyrin using the lone pair on the nitrogen group.

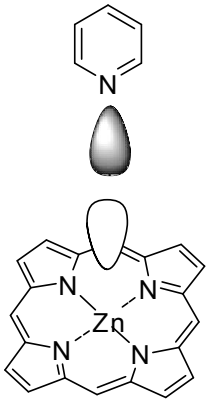


Figure.3.10. Figure to show the interaction between pyridine and the zinc functionalised porphyrin.

Two main factors must be considered when examining the binding interaction: electronic and steric factors. The HUMO-LUMO interaction is most favourable when the pyridyl is perpendicular to the plane of the porphyrin. When the steric factor occurs, it prevents the 90^0 interaction, the orbital overlap is less complete and the binding is weaker.

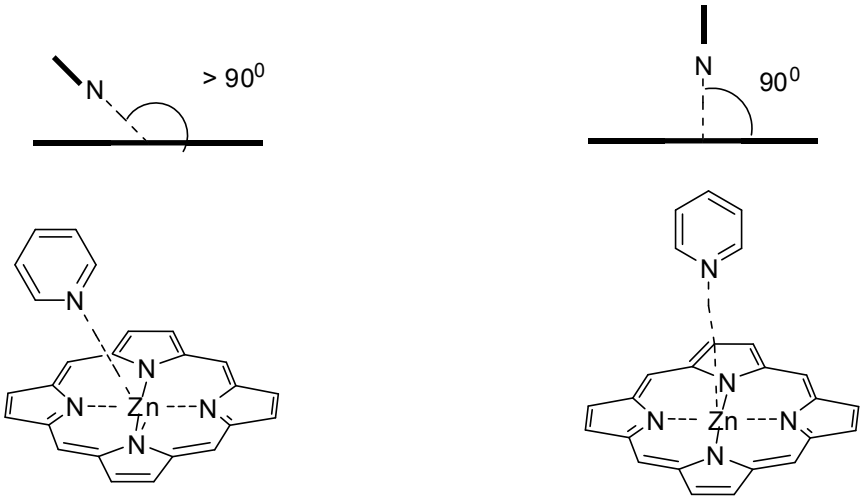
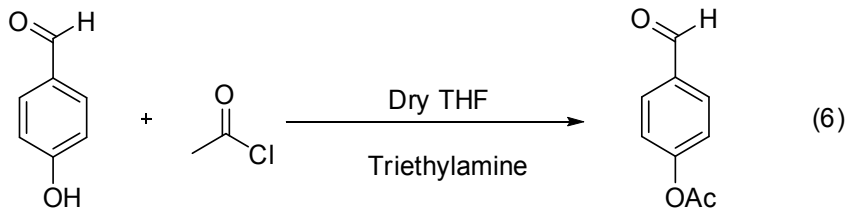


Figure.3.11. A schematic representation of the angular dependence for the binding of pyridine and the zinc functionalised porphyrin.

Therefore, if the degree of branching reduces the steric factor around the core, a change in the microenvironment of the hyperbanched polymer structure occurs. This leads to an increase in the value of the binding constant. This is due to an increase of overlapping the lone pair of the pyridyl nitrogen with the empty orbital of the zinc.

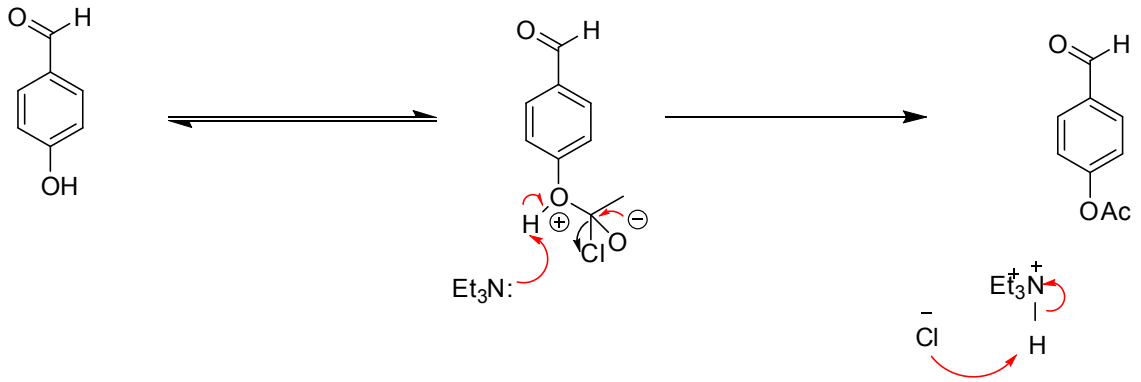
3.2.1 Synthesis of 4-acetoxybenzaldehyde:

Although 4-acetoxybenzaldehyde is commercially available, it is easily prepared in a good yield by the acetylation of 4-hydroxybenzaldhyde.



Scheme.3.5. Synthesis of 4-acetoxtbenzaldehyde (6).

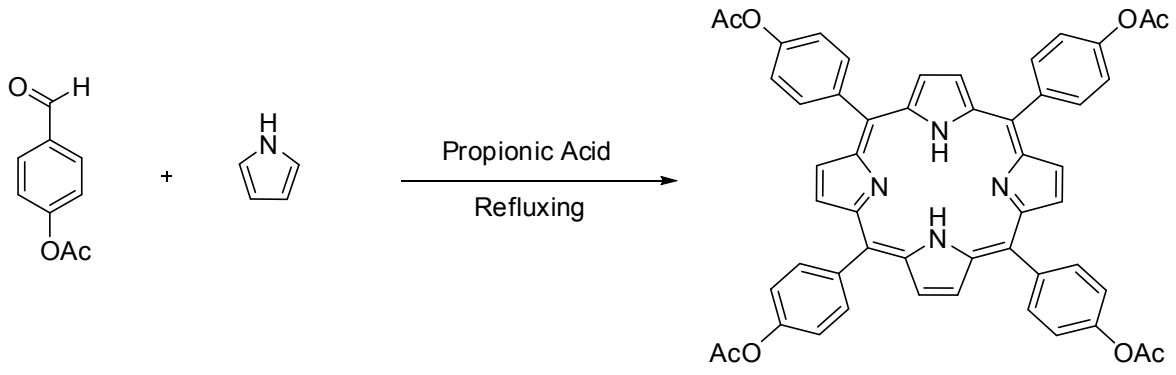
The acetylation reaction was carried out in dry tetrahydrofuran and acetyl chloride in the presence of triethyllamine, which acts as a catalyst at room temperature. The product was obtained in a good yield after thirty minutes. To ensure the purity of the product, it was washed with a saturated sodium hydrogen carbonate solution, followed by distilled water to remove any unwanted impurities. The mechanism of this reaction involves the deprotonation of phenolic hydrogen by triethyllamine. After the deprotonation takes place, a nucleophilic attack on the acetyl chloride occurs, forming a tetrahedral intermediate, which displaces the chloride to form the 4-acetoxybenzaldhyde and reactivate the triethyllamine catalyst. This mechanism allows a high purity product to be synthesised easily in a relatively good yield. Successful acetylation synthesis was confirmed by ^{1}H NMR and mass spectrometry. ^{1}H NMR showed a large singlet peak at 2.30 ppm, corresponding to new methyl protons of the acetoxy groups. Additional support from mass spectrometry indicated that the product was synthesised successfully.



Scheme3.6. Mechanism of the preparation of 4-acetoxtbenzaldehyde.

3.2.2 Synthesis of 4-acetoxyphenyl porphyrin:

Porphyrin was synthesised via a single step reaction adapted from a methodology originally outlined by Rothemund.[99,100] in the 1930s and developed later by Adler and Longo.[101,102] The reaction was performed with equivalent amounts of pyrrole and 4-acetoxybenzaldehyde. These reagents were refluxed in propionic acid for thirty minutes. A black slurry was obtained in the flask, consisting of a mixture of the product and other unwanted polypyrrolic structures. The product was easily isolated from the mixture reaction by vacuum filtration, followed by washing thoroughly with cold methanol. Finally, the obtained pure dark purple porphyrin was dried and analysed.



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Scheme3.7. Synthesis of tatraacetoxyphenyl porphyrin (7).

^{1}H NMR analysis of tetraacetoxy functionalised porphyrin showed a singlet peak at 8.92 ppm, corresponding to the pyrrolic hydrogens of the porphyrin ring. A doublet at 8.25 ppm and 7.52 ppm corresponding to the *o*rtho and *m*eta protons on the phenyl ring. A large peak was

observed at 2.60 ppm, corresponding to the methyl group of the acetocxy group. A further peak from the highly shielded inner protons was observed at -2.85 ppm. Mass spectrometry supported the success of the synthesis by showing a molecular ion peak of 847. UV/Vis spectrophotometry confirmed the literature by showing the intense absorption at 418 nm, corresponding to the Soret band and the presence of additional Q bands.

3.2.3 Synthesis of porphyrin cored hyperbranched polymer:

The polymerisation of 3, 5-diacetoxybenzoic acid in the presence of a TAPP core with a ratio of 1:20 was carried out using diphenyl ether as a solvent. The mixture was placed in a round bottom flask equipped with a distillation kit. The system was degassed and flushed with nitrogen. After degassing, the mixture was heated to 225 ^{0}C for 45 minutes. Then, the temperature was lowered to 180 ^{0}C and a vacuum was applied for 4 hours to remove the acetic acid. The crude polymer was purified by dissolving it in hot THF, followed by precipitation in cold methanol. Finally, the product was isolated by vacuum filtration and dried overnight. The presence of porphyrin was immediately observed due to the brown colour of the product.

The pale brown product was characterised by ^{1}H NMR, indicating that a hyperbranched polymer with a degree of branching of 48% had been successfully prepared. The incorporation of a TAPP core was confirmed by observing sharp and broad resonances at the chemical shift corresponding to a porphyrin. This suggested the presence of a mixture of free and incorporated porphyrin. A similar result was obtained from GPC, which shows a broad peak in the polymer and a sharp peak at the low molecular weight end. Therefore, a preparative size exclusion chromatography in the form of bio-beads was used to separate the free porphyrin from the polymer mixture, using DCM as an eluent. A further analysis by ^{1}H NMR and GPC indicated that the sharp peak corresponding to free porphyrin was no longer present in the GPC or in ^{1}H NMR. The molecular weight of the resulting polymer was 4000 Da, and the polydispersity index was 3. The UV spectrum showed 4 Q bands observed at 515, 553, 595, and 649 beside an intense Soret band at 418 nm characteristic of porphyrin.

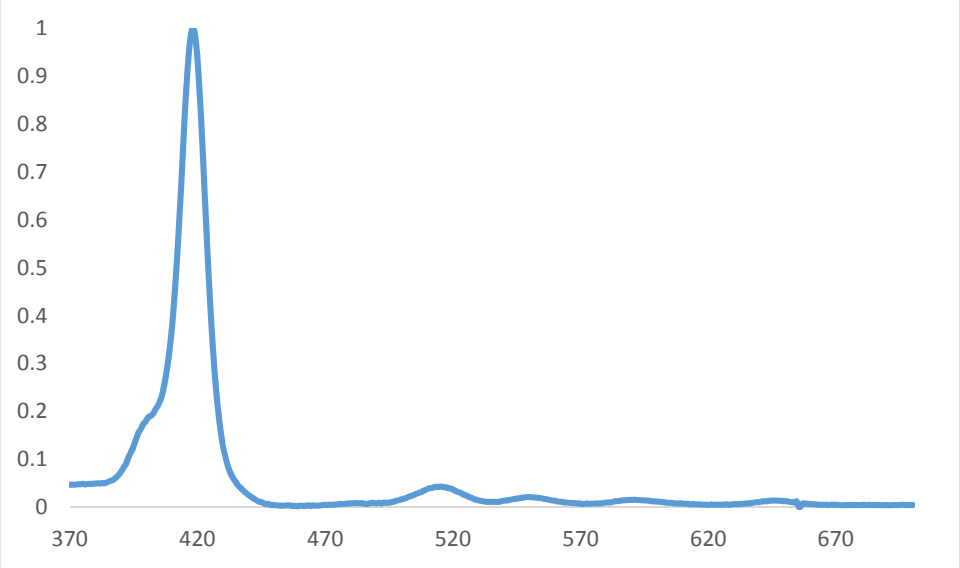
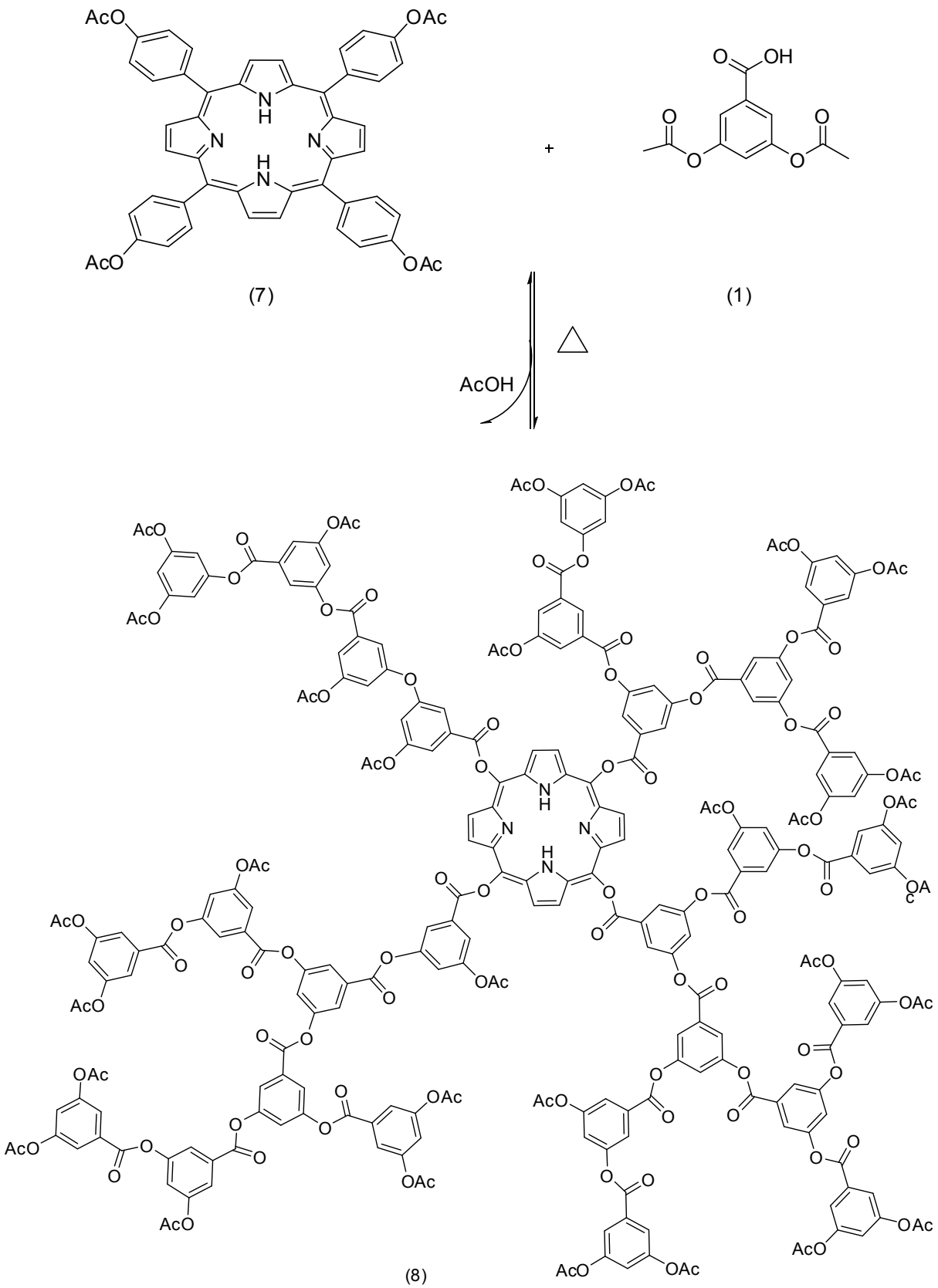


Figure.3.12. UV/Vis spectrometry data of TAPP cored hyperrbanched poly (3,5-diacetoxybenzoic acid).

After the conformation of the successful incorporation of a TAPP core into hyperbranched polymers, the preparation of TAPP cored hyperbranched polymers with various degrees of branching was carried out to examine the effect of the degree of branching on the microenvironment of hyperbranched polymers. In the addition of that, the effect of the degree of branching on the dense packing limit was examined.



Scheme.3.8. Synthesis of TAPP cored hyperbranched poly (3, 5-diacetoxybenzoic acid)(8).

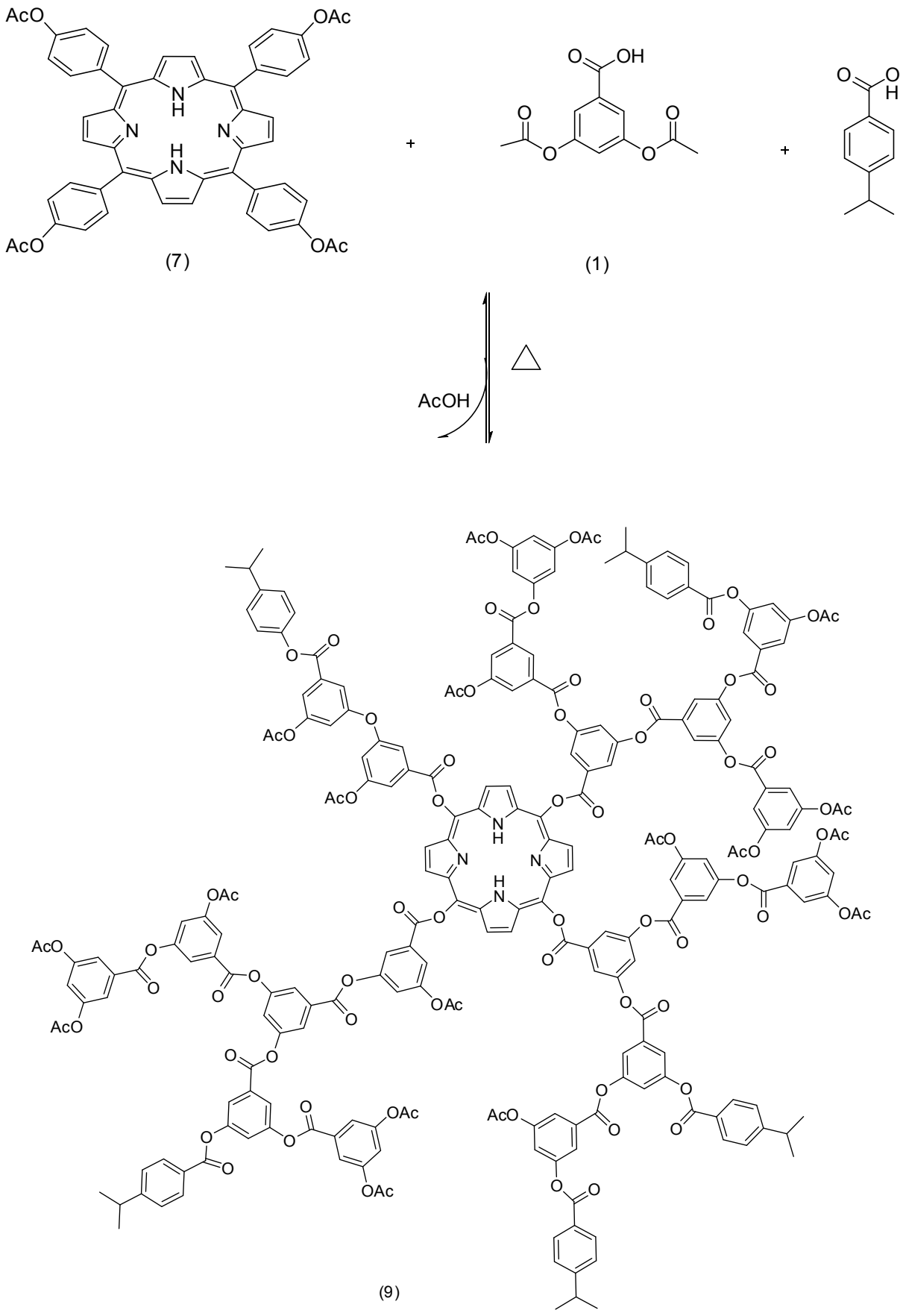
3.2.4 Synthesis of porphyrin cored hyperbranched co-polymers:

Polymerisation of 3, 5-diacetoxybenzoic acid with various molar ratios of 4-isopropylbenzoic acid in the presence of a constant ratio of 4-acetoxy tetraeaetocphenyl porphyrin to the total ratio of monomers and co-monomers was carried out using the general polymerisation methods explained earlier. After the purification process, all the obtained polymers were loaded onto a bio-beads column to remove unreacted TAPP. Finally, the obtained hyperbranched polymers were characterised by ^{1}H NMR, UV/Vis and GPC. ^{1}H NMR indicated the presence of TAPP peaks in the addition to 4-isopropyl peaks within the polymeric structure. UV/Vis indicated the successful incorporation of the TAPP core into a hyperbranched co-polymer system. GPC showed the polymerisations were successful, as seen in the table below.

Sample ID	Level of incorporation	DB	Mn	PDI
9A	6%	45%	5500	3.3
9B	12%	42%	5900	3.2
9C	22%	37%	4000	2.8
9D	52%	22%	4200	2.9

Table.3.6. Table represents the data of a series of hyperbranched polymers with different degree of branching below dense packing limit.

The table above represents the data of a series of hyperbanched polymers with various degrees of branching and a relatively constant polydispersity index (3.1±0.3). However, many attempts have been made to obtain a constant polydispersity index. Unfortunately, the obtained polymers possess the closest polydispersity index possible. The average molecular weight of the obtained polymers was below the dense packing limit; therefore, the obtained polymers were used for the ongoing study after metal insertion.

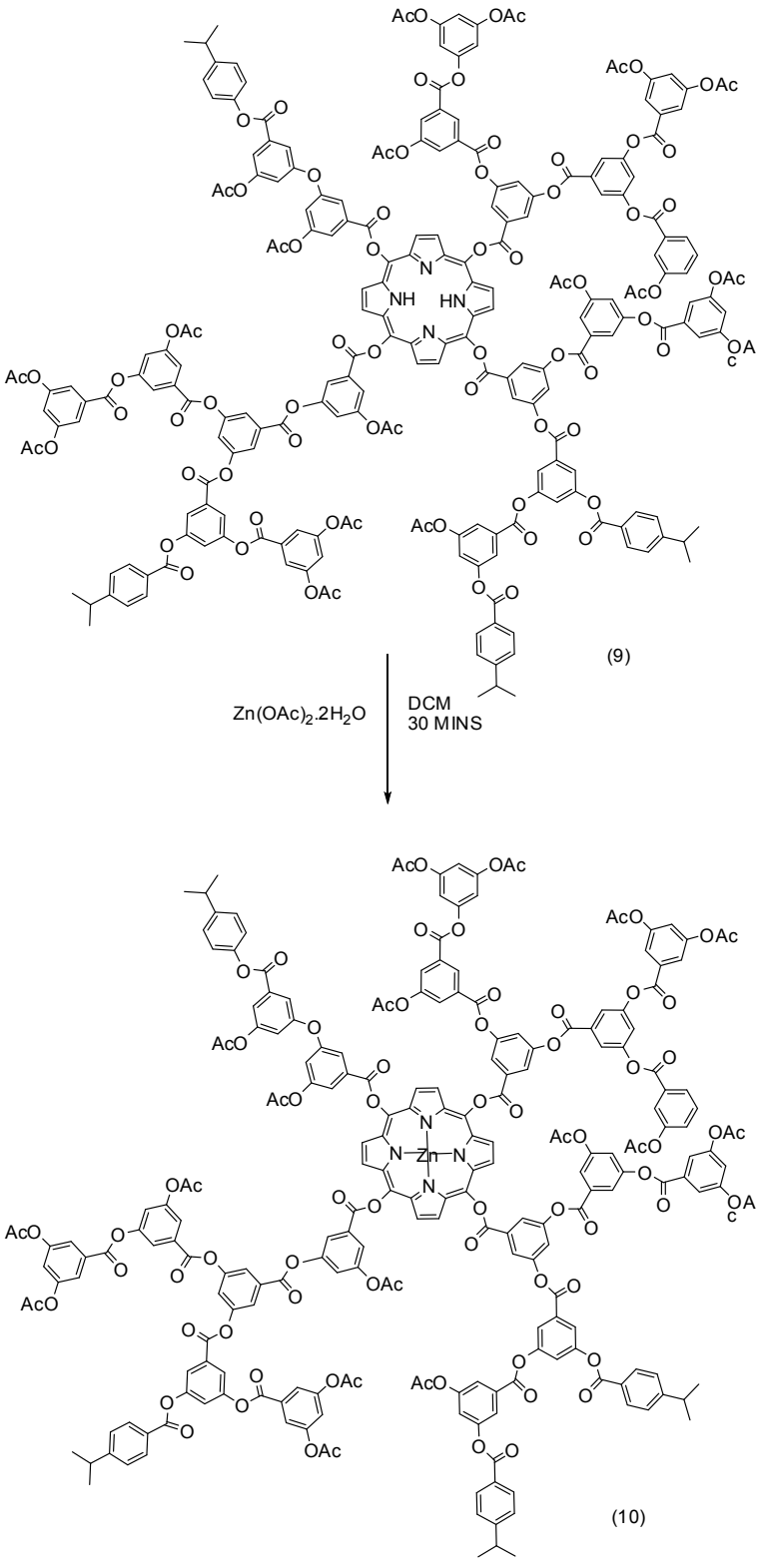


Scheme.3.9. Synthesis of TAPP cored hyperbranched copolymer (9).

3.2.5 Synthesis of zinc porphyrin cored hyperbranched co-polymers:

Metal inserted porphyrins are common in the literature.[103-110] However, zinc functionalised porphyrins were the area of interest as they have the properties required for a UV/Vis titration study.[97] After zinc insertion, the porphyrin loses two inner protons and the zinc bonds to each of the four inner nitrogen atoms, forming a four coordinate complex. The remaining coordination site allows the binding of a ligand. When the coordination between the zinc and the ligand takes place, the Soret band shifts around 10 nm from 418 to 428 nm.

Zinc porphrin cored hyperbranched poly (3, 5-diacetoxybenzoic acid) can be synthesised by reacting a porphyrin cored hyperbranched poly (3, 5-diacetoxybenzoic acid) with 10 equivalents of zinc acetate dehydrate in DCM. The solution is stirred at room temperature for 30 minutes. Unreacted zinc acetate is removed via filtration. The solvent is removed by rotary evaporation and then dissolved in THF and precipitated into cold methanol. The product is filtered and dried under reduced pressure. This method porphrin cored hyperbranched co-polymers. The yields ranged from 60% to 70%. ^{1}H NMR was used to confirm the successful insertion of zinc into the hyperbranched co-polymers. The highly shielded peak at around -2.85 ppm, corresponding to the inner protons, was no longer present after the metal insertion. Further confirmation was provided by UV/Vis spectrometry. There was a reduction in the number of Q bands from four in the starting material to two at 550 and 587 nm.



Scheme.3.10. Synthesis of zinc functionalised TAPP cored hyperbranched co-polymer (10).

3.2.6 Column separation:

In order to obtain polymers with a constant molecular weight and a polydispersity index above the dense packing limit, each polymer was fractionated into many different molecular weights. After zinc insertion, 300 mg of each hyperbranched co-polymer was loaded into preparative size exclusion chromatography. The separation was performed using a bio-bead column with DCM as an eluent. Each polymer was fractionated into four different molecular weights. After fractionation, each sample was dissolved in a minimum amount of THF and then precipitated into 10 ml of cold methanol. GPC was used to analysis the molecular weight of each sample. Four different samples with various degrees of branching, a relatively constant molecular weight above the dense packing limit and a constant polydispersity index were obtained, as can be seen in the table below.

Sample ID	DB	Mn	PDI
9A	45%	15300	3.3
9B	42%	15200	3.2
9C	37%	15400	3.4
9D	22%	14000	3.3

Table.3.7. Table represents the data of a series of hyperbranched polymers with different degree of branching below dense packing limit.

3.2.7 Binding study:

After polymer fractionations were characterised, the next step was to discover whether the degree of branching would affect the microenvironment of hyperbranched polymers. This was performed using UV/Vis titrations with several pyridyl ligands. The interaction between a pyridyl ligand and zinc porphyrin is concentration dependent. Therefore, it was necessary to use the appropriate concentration relation. The concentration must allow the interaction to take place within the absorption limits of the UV/Vis spectrometer. However, a previous study in our group showed that a concentration of 10^{-6} M corresponding to an absorbance

of 1.0, which is well within the limit of the UV/Vis spectrometer is an identical porphyrin concentration.

To carry out the titration study, a stock solution of 10^{-6} M zinc inserted hyperbranched polymer was prepared in DCM for each polymer. As the absorption is proportional to the concentration, the porphyrin concentration must remain constant throughout the titrations. Therefore, using DCM to prepare the pyridyl titre solution would lead to erroneous results because the porphyrin concentration would decrease throughout the titration. Hence, the stock zinc solution that was prepared previously was used to prepare the 10^{-2} M pyridyl titre solution.

When the binding occurs, the porphyrin Soret band shifts. In the case of zinc porphyrin, the shift is from 418 nm for unbound porphyrin to 428 nm for bound porphyrin. The presence of an isobestic point confirmed that the binding is taking place in identical environment.

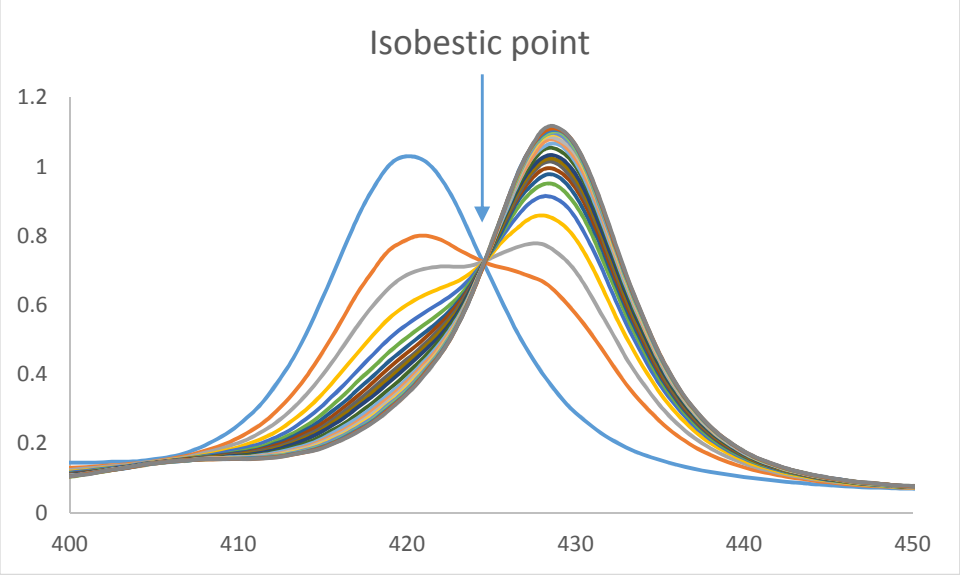


Figure3.13. Shifting of the Soret band from 418 nm to 428 nm.

Therefore, to obtain the binding constant, the change in absorbance at λ_{max} (y) was plotted against the moles of ligand added (x). Curve fitting software (Graphpad Prism) was used to analyse the binding data and obtain Kd for each polymer. The association constant (Ka) was easily calculated by taking the reciprocal of Kd.

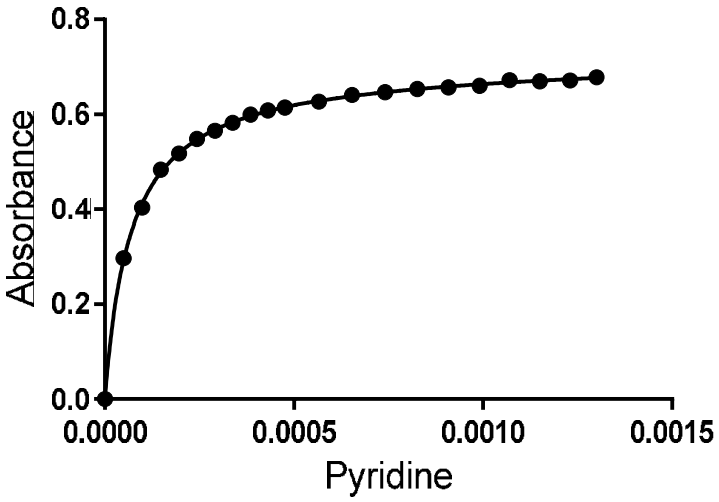


Figure.3.14. Absorbance vs the concentration of pyridine for hyperbranched co-polymer with degree of branching of 45% and Mn=15300.

It is worth mentioning that the calculation of the association constant of each polymer must be determined correctly with a minimum possible error. The titration was repeated several times for each polymer to minimise the errors. After performing the titration several times for each polymer, an average value for each point on the graph was calculated. If an obvious error occurred in any titration, it would be identified and excluded from the calculations.

The binding study was designed in two major stages. The first stage was to fix the ligand and vary the steric environment around the core by varying the degree of branching of the hyperbranched polymers. If the degree of branching affects the internal environment, the binding constant increases by decreasing the degree of branching. The second stage was to repeat the experiment with different sized ligands. This was to determine the effect of the degree of branching on the binding of different sized ligands. However, the study required three different sized ligands free of groups in the *o*rtho position. Therefore, pyridine, 3, 5-lutdine, and 3-phenyl pyridine were chosen carefully.

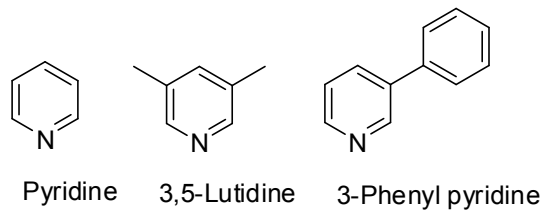


Figure.3.15. Pyridyl ligands for UV/Vis titration.

Steric and electronics play major roles in the interaction of ligands. Therefore, both should be considered for each ligand. The smallest ligand in this study, pyridine, was used as the control due to the lack of a side group, which indicates that steric and electronics will be unaffected. In the case of 3, 5-lutdine, the presence of two methyl groups leads to a steric and electronic effect. The donation from the two methyl groups increases the electronic factor; therefore, the interaction between 3, 5-lutdine and porphyrin should be stronger than the interaction between porphyrin and pyridine (based on electronic). Therefore, the association constant is expected to be greater than pyridine. 3-Phenyl pyridine contains a phenyl group, which is capable of conjugation with the pyridyl ring, and this encourages the electronic factor. However, the large size of the ligands might cause a reduction in the association constant. Therefore, it is predicted that the association constant is highest in 3, 5-lutdine, followed by 3-phenyl pyridine and pyridine.

The experimental work started with measuring the association constant of previously prepared zinc porphyrin cored low molecular weight hyperbranched polymers and ligands. Each ligands was bound to a series of hyperbranched polymers with a constant molecular weight, below dense packing, constant polydispersity and a different degree of branching. The results are shown in the figure below.

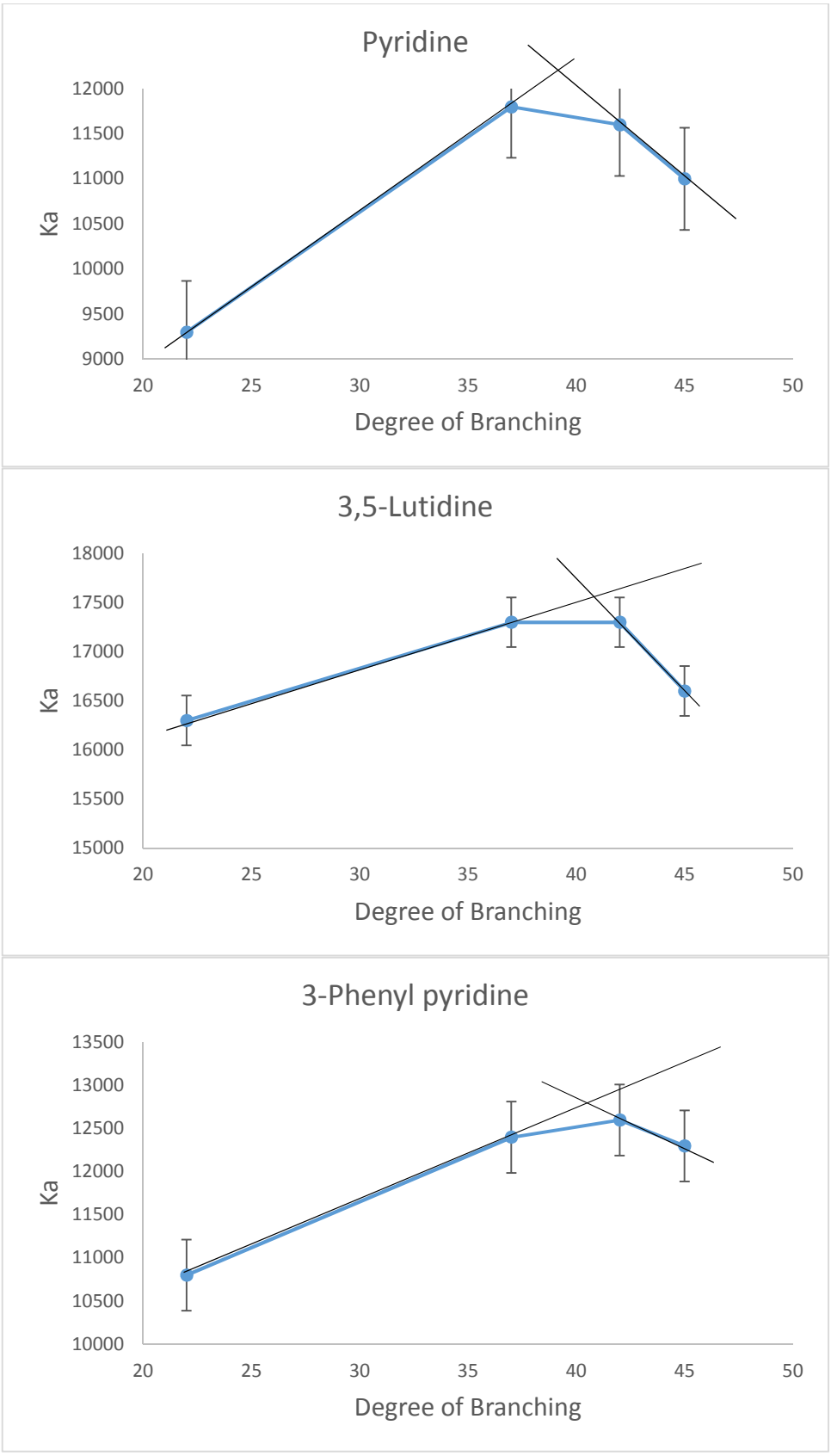


Figure.3.16. Binding data for pyridyl ligands with hyperbranched polymers below the dense packed limit (Mn=5000±1000).

As can be seen, the association constant of 3, 5-lutdine is higher than 3-phenyl pyridine and pyridine, as expected. This is due to the donation from the two methyl groups increases the electronic factor. The association constant of 3-phenyl pyridine and that of pyridine are close to each other. This is because of the relatively large size of 3-phenyl pyridine, which causes a weak interaction. However, it was expected that the association constant of 3-phenyl pyridine is higher than pyridine due to the conjugation with the pyridyl ring which enhance the electronic factor. In the case of the degree of branching, it was expected that the association constant of all the ligands would increase with the decreased degree of branching due to the decrease in the steric around the core. However, the obtained data shows there were a cut off observed at the degree of branching around 40%. Below the outlined cut off, the binding constant decreased with the decreased degree of branching. This is more obvious in the case of pyridine and 3-phenyl pyridine. The reason behind this decreased refers to the electronic factor. The decreased in the degree of branching causes a decreased in the electronic environment which effect negatively in the binding constant. Although the average value of each point in the graph was calculated several times to ensure the accuracy of data, the error parentage of using UV/Vis spectrometry which is 20% should be considered. Therefore, it could be included that this is change is negligible; however, those results are obtained from calculation the average of six experiments for each point.

In the case of hyperbranched polymers possessing a molecular weight above dense packing, the association constant is expected to be lower. This is because the increased molecular weight causes an increase in the steric around the core. However, dense packing limits depend on the degree of branching as well as the molecular weight. For more clarity, hyperbranched polymers with a degree of branching of 50% possess a dense packing structure at around 7000 Da -8000 Da. It is worthy to study the effect of the degree of branching above the dense packed limit. This is the reason for the selection of a molecular weight that was 100% higher than dense packed limit (Mn=15000 Da). The result are shown below in **Figure.3.18.**

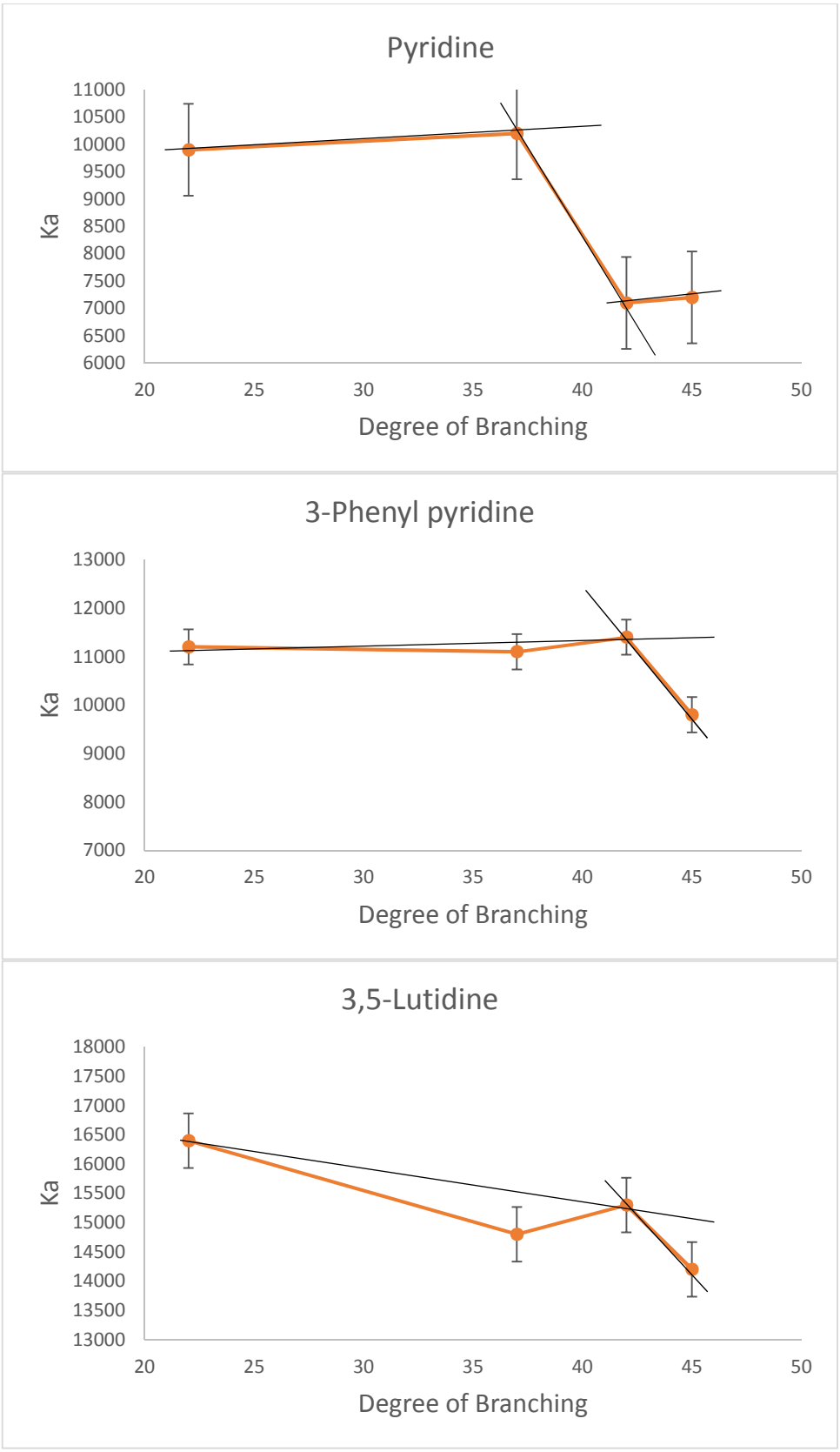


Figure.3.17. Binding data for pyridyl ligands with hyperbranched polymers above the dense packed limit (Mn=15000±1000).

The relation between the association constant of the pyridyl ligands and the degree of branching showed an obvious cut off at around 40% (as with low molecular weight polymer). Below the outlined cut offs, there was a significant increase in the association constant (observed in pyridine and 3, 5-lutdiene) due to the steric factor. As the degree of branching decreased, the steric around the binding sites decreased resulting a stronger binding occurrence. This indicated that indicated that steric effect overwhelm the electronic effect for hyperbanched polymers with molecular weight above dense packed limit.

On the case of the dense packing limit, it could be studied by comparing the association constant of each ligand in varies identical degree of branching in two different molecular weight below and above the dense packing limit. See **Figure 3.19.**

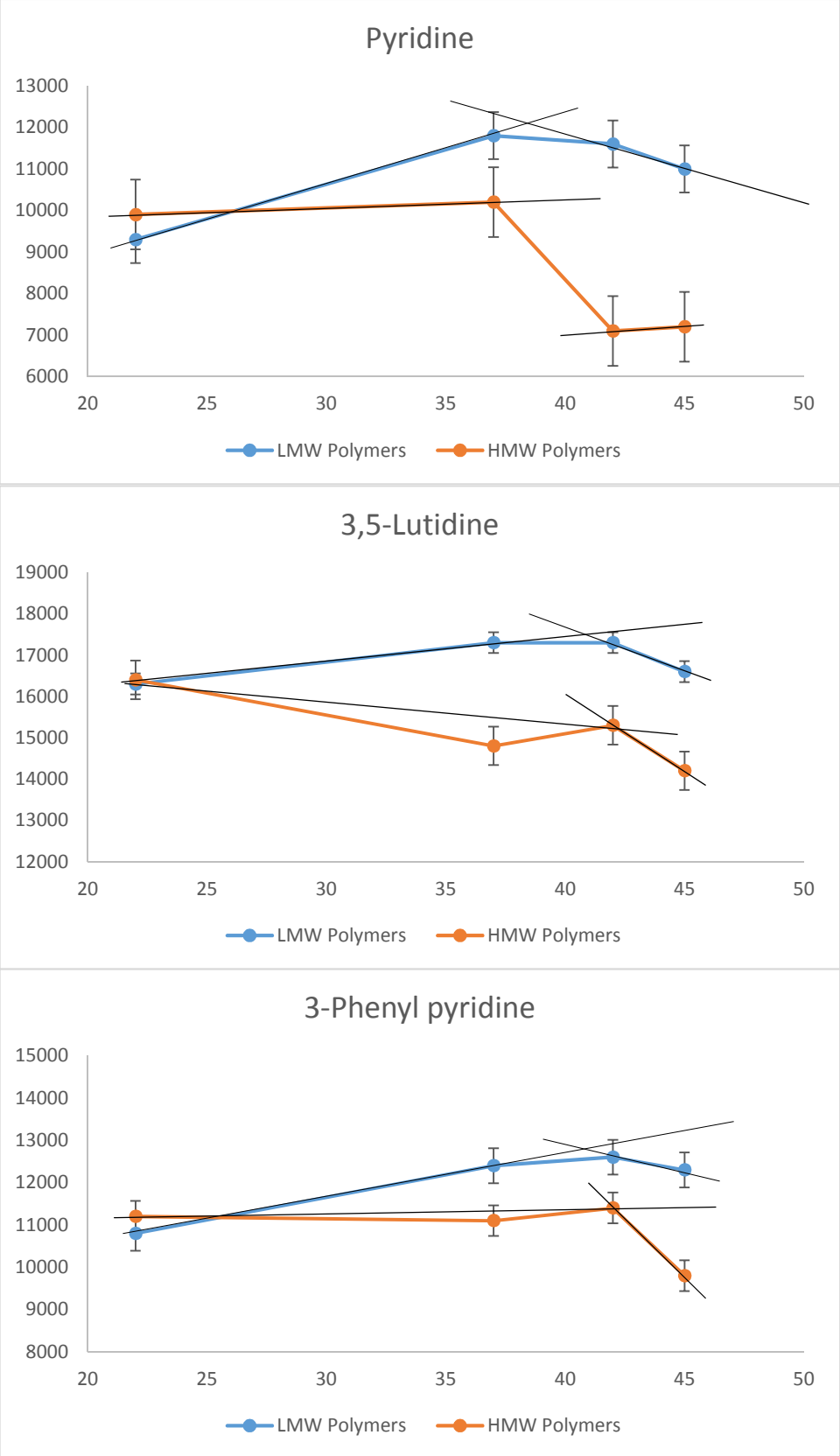


Figure.3.18. Binding data for pyridyl ligands (X=DB, Y=Ka) with two different molecular weight hyperbranched polymers (Mn=5000±1000, 15000±1000).

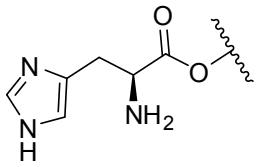
As it can be seen from figures above, there was a different value of binding constant of each ligand up to 37% whereas this difference disappeared at 22%. This indicates that degree of branching shifts the dense packing limit. Therefore, this indicate that hyperbanched polymers with low degree of branching (22%) possess a dense packed limit at molecular weight above 15000 Da. This is caused by the significant decreased in the steric around the binding sites. This is an approval for the importance linkage between the molecular weight and the degree of branching in terms of forming the dense packed limit of hyperbanched polymers.

The previous results revealed an interesting phenomenon worthy of further investigation. The viscosity study showed that the hyperbanched polymer systems keep their dendritic properties up to a degree of branching of 37%. The binding studies indicated that the binding constant is affected by molecular weight and the degree of branching. However, although molecular weight effects the binding constant, it does not seems to have much effect on the degree of branching as cut offs occur ≈ 40% for hyperbanched polymers below and above dense packing limits. In the last part of this study, the location of the co-monomers will be studied. Co-monomers could be in the interior of the hyperbranched polymers towards the core or the periphery. Therefore, it is worth carrying out a further examination to detect the location of the co-monomers the next step.

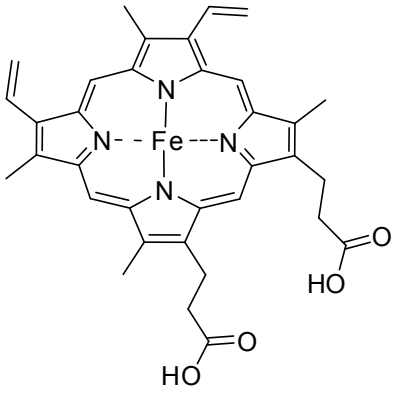
3.3 The location of co-monomers:

Metal ligands coordination is one of the most common non-covalent reactions in the biological world.[111-116] In nature, the haeme group in myoglobin is not covalently attached to the surrounding protein structure but is held non-covalently in the interior of the protein via coordination to a histidine group.[112] A synthetic model of this system was previously prepared by the Twyman group. Pyridine was used as an analogue to the imidazole ring of the histidine group. The work involved the preparation of pyridine cored hyperbanched polymers, and the binding of the pyridine to metal functionalised porphyrin was studied. In this part of my project, the previously outlined idea was used to investigate the location of co-monomers within the polymeric structure. The study involved the preparation of a similar model to the one used in the previous study of the co-polymerisation of 3, 5-

diacetoxy benzoic acid and isonicotinic acid as well as when studying the binding between pyridine interior functionalised hyperbanched co-polymers.



Histidine



Haeme

Figure3.19. The structural units of myoglobin.

The strategy used to determine the location of the co-monomer is to compare the association constant of the interaction of pyridine to zinc functionalised TAPP in two different experiments, paying attention to the steric factor. In the first experiment, pyridine was incorporated in the Interior of the hyperbanched polymer system and the interaction with Zn-TAPP was examined. In the second experiment, a control titration was conducted using 4-acetoxypyridine. As explained previously, this interaction is most favourable when the pyridyl is perpendicular to the plane of the porphyrin. When the steric occurs, it prevents the 90^0 interaction, the orbital overlap is less complete and the binding is weaker. Therefore, if the pyridine is located towards the periphery, the association constants will be close to each other in both experiments. However, the difference between the two association constants increases when the co-monomer is located towards the core.

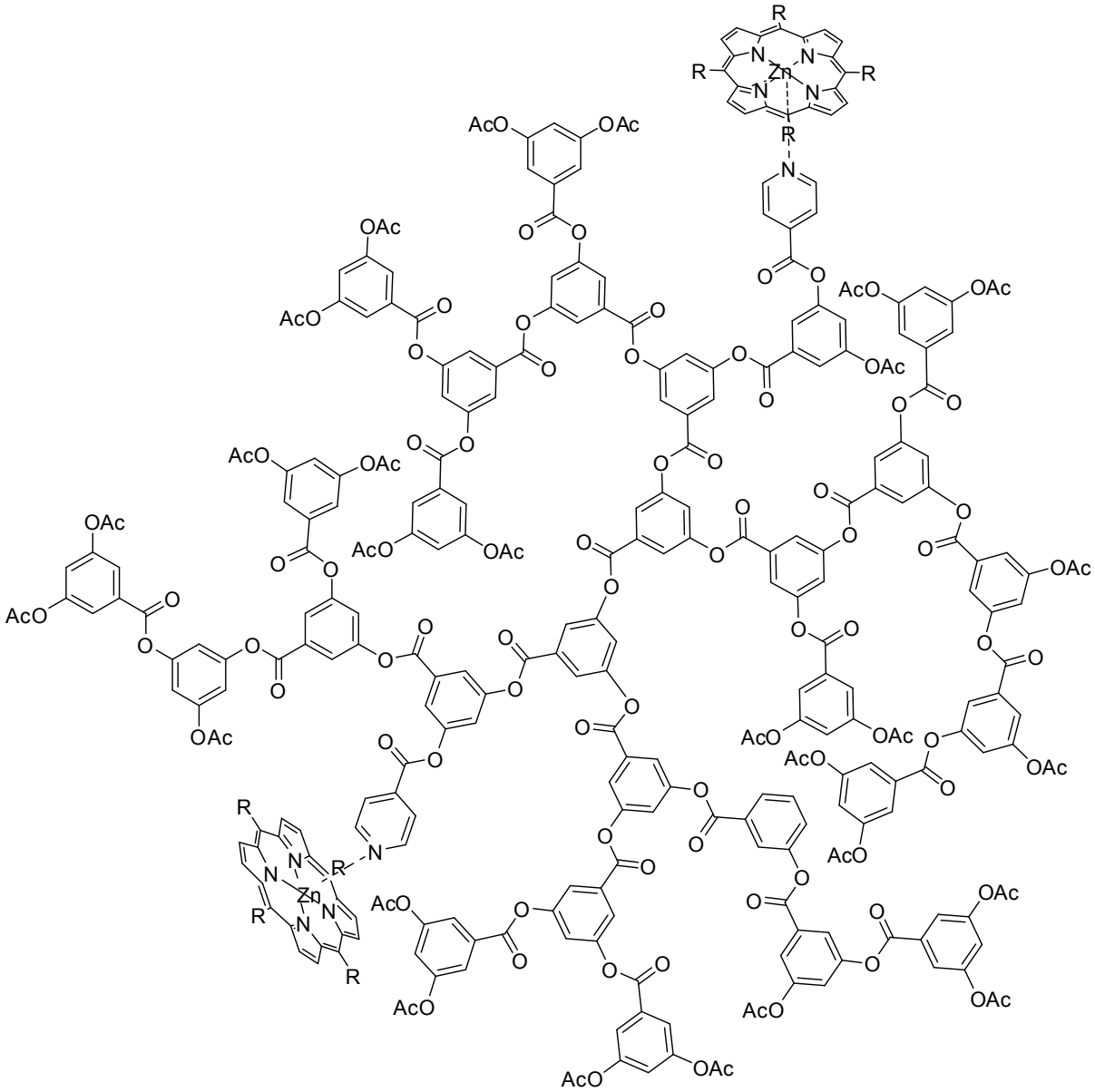
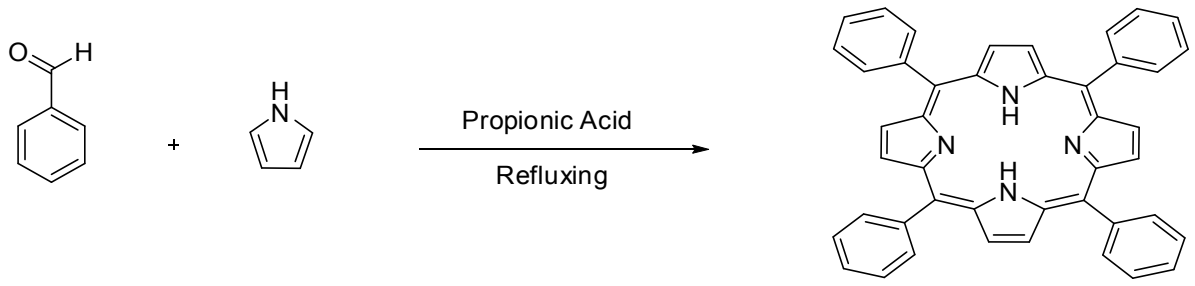


Figure.3.20. Figure to show the interaction of zinc functionalised TAPP to pyridine incorporated hyperbranched copolymers.

3.3.1 Synthesis of zinc functionalised tetraphenylporphyrin:

The first step was to prepare tetraphenylporphyrin. The reaction was performed in propionic acid with an equivalent number of moles of benzaldehyde and pyrrole. After half an hour of refluxing, the mixture was left to cool down at room temperature. The reaction mixture was filtered and washed with cold methanol, followed by warm distilled water. The washing step was repeated, and the product was dried overnight under high vacuum.



(11)

Scheme.3.11. Synthesis of TAPP (11).

The resulting product was confirmed by ^{1}H NMR and UV/Vis spectrophotometry. The analysis of ^{1}H NMR showed a singlet peak at 8.95 ppm, corresponding to the pyrrolic hydrogens of the porphyrin ring. A doublet at 8.30 ppm and 7.80 ppm corresponded to *o*rtho and *m*eta protons on the phenyl ring. A peak from the highly shielded inner protons was observed at -2.85 ppm. UV/Vis spectrophotometry indicated agreement with the literature by showing the intense absorption at 418 nm, corresponding with the Soret band and the presence of four additional Q bands observed at 518, 560, 590, and 648 nm.

The resulting product was functionalised by zinc. The process of functionalisation was similar to that of the TAPP cored HBP using zinc acetate dihydrate at room temperature. After dissolving the tetraphenylporphyrin in DCM, the reaction was carried out for thirty minutes. The unreacted zinc acetate was removed by filtration. Then, the solvent was removed by rotary evaporation. Finally, the product was filtered and dried under reduced pressure. Confirmation of the successful insertion of zinc into tetraphenylporphyrin was obtained from ^{1}H NMR and UV/Vis spectrophotometry. ^{1}H NMR indicated that the highly shielded inner protons that were observed at -2.85 ppm were no longer present. The UV/Vis spectrophotometry showed a reduction in the number of Q bands from four to two.

3.3.2 The co-polymerisation of 3, 5-diacetoxybenzoic acid and isonicotinic acid:

The co-polymerisation was carried out using the general polymerisation method that was described previously. Based on the previous results, the ratio of the isonicotinic acid was limited to 20% in this polymerisation. After the purification of the polymer, it was dried and characterized.

^{1}H NMR showed that a characteristic polymer peaks at 8.20-7.20 ppm, corresponding to the aromatic protons. A second single peak was observed at 2.35 ppm, corresponding to the acetoxy terminal group. In addition, a broad peak was observed at 8.85 ppm, corresponding to the alpha protons to the nitrogen in the pyridyl ester group. In the case of beta protons, they were under the polymer peak observed at 8.10-7.95. ^{1}H NMR indicated that the level of incorporation of co-monomers was 14%. Therefore, the degree of branching was 41%. GPC showed that a polymer with a molecular weight of 9700 Da was obtained.

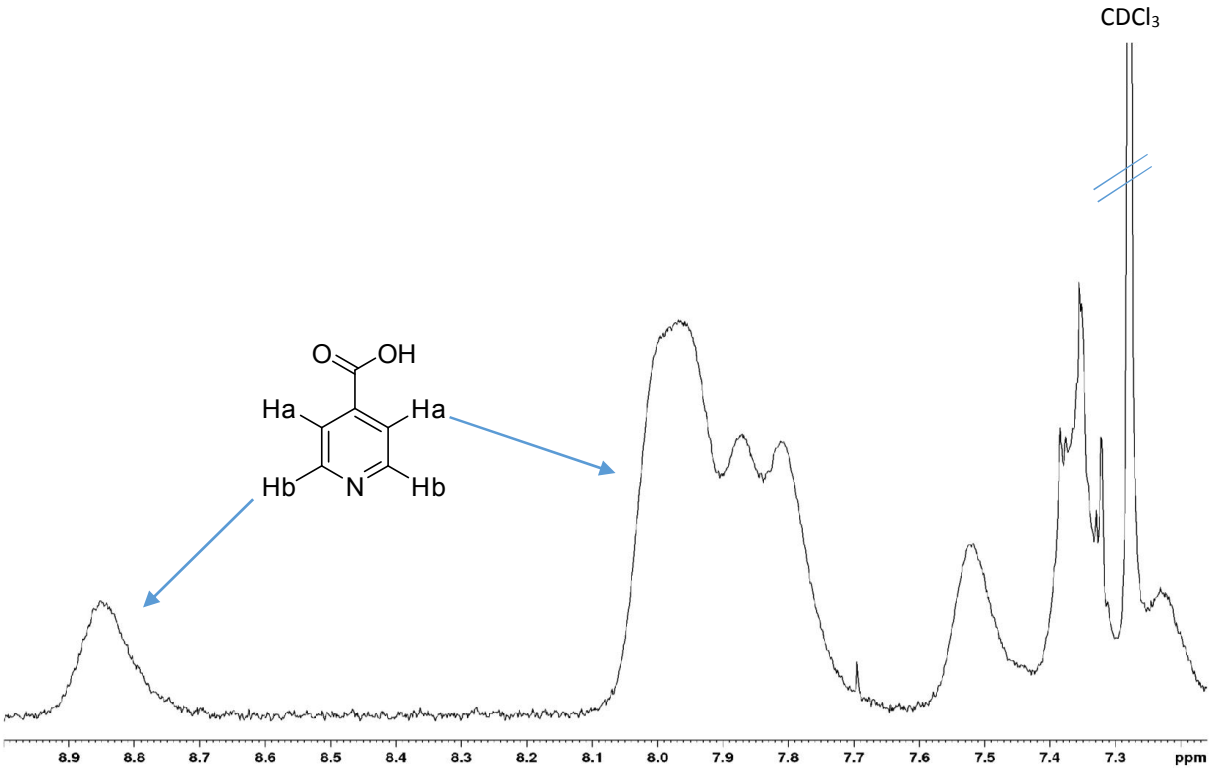
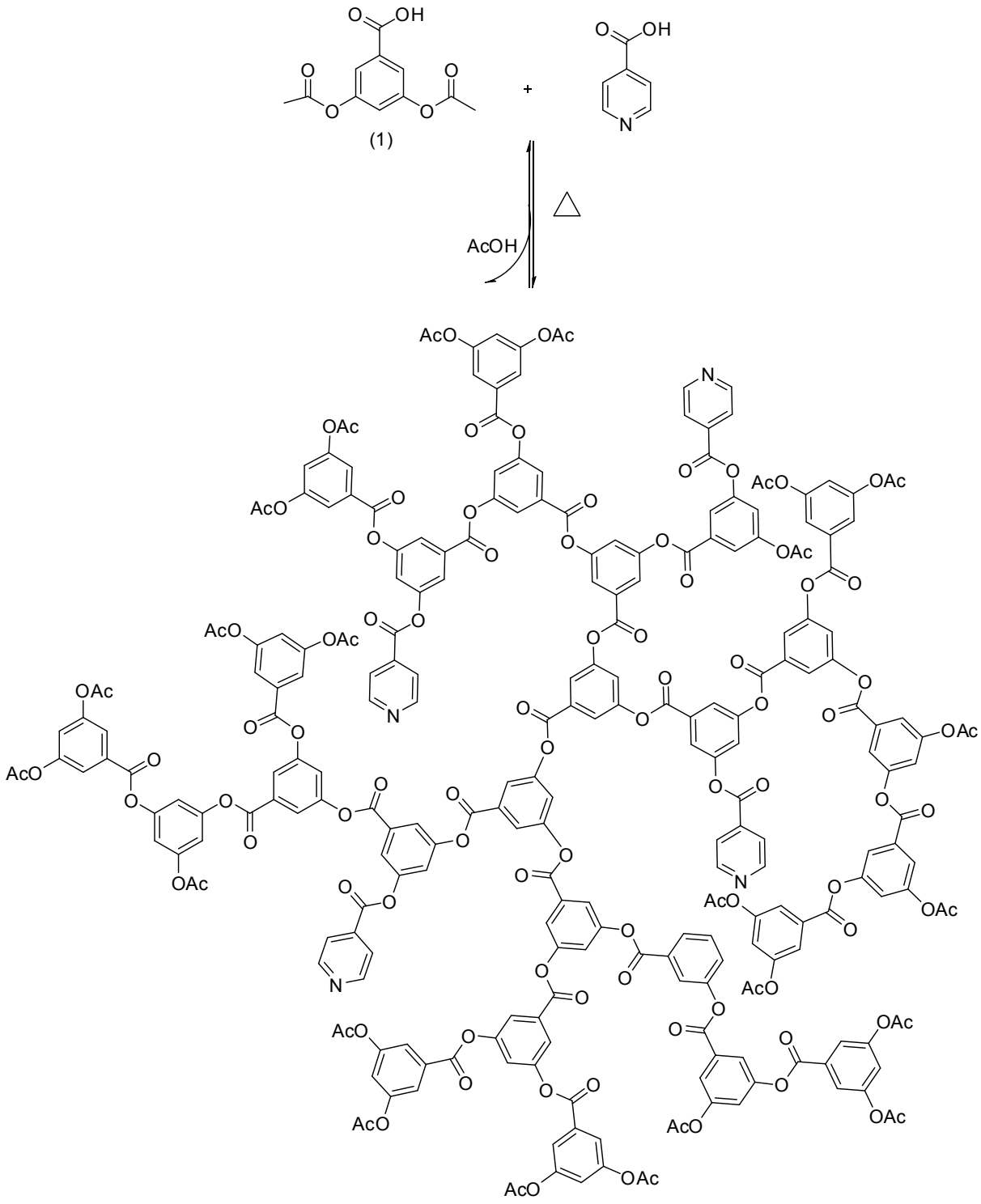


Figure.3.21. ^{1}H NMR spectrum of pyridine incorporated hyperbranched co-polymer (13).



Scheme.3.12. Synthesis of pyridine incorporated hyperbranched co-polymers.

3.3.3 Binding study:

Two binding experiments were carried out using UV/Vis spectrometry to explore the location of the co-monomer. A stock solution of 10^{-6} M of zinc functionalised tetraphenylporphyrin was prepared in DCM. This was used to prepare two different 10^{-2} M pyridyl titre solutions. In the first experiment, a solution was made of pyridine incorporated hyperbranched polymers using the stock solution that was prepared previously. A binding constant (Ka) of 3100 M^{-1} was calculated for the polymer/porphyrin interaction. In the second experiment, a solution was made of 4-acetoxypyridine using the same stock solution that was prepared previously. A binding constant (Ka) of 8300 M^{-1} was calculated for this experiment. The difference in the value of the association constant in those two experiments indicates that the pyridine is more likely to be located in the interior towards the core rather than the periphery. This can easily be explained; the slight reduction in the value of the association constant in the polymer is caused by the steric around pyridine. However, the presence of the isobestic point confirms that the binding takes place in identical environment.

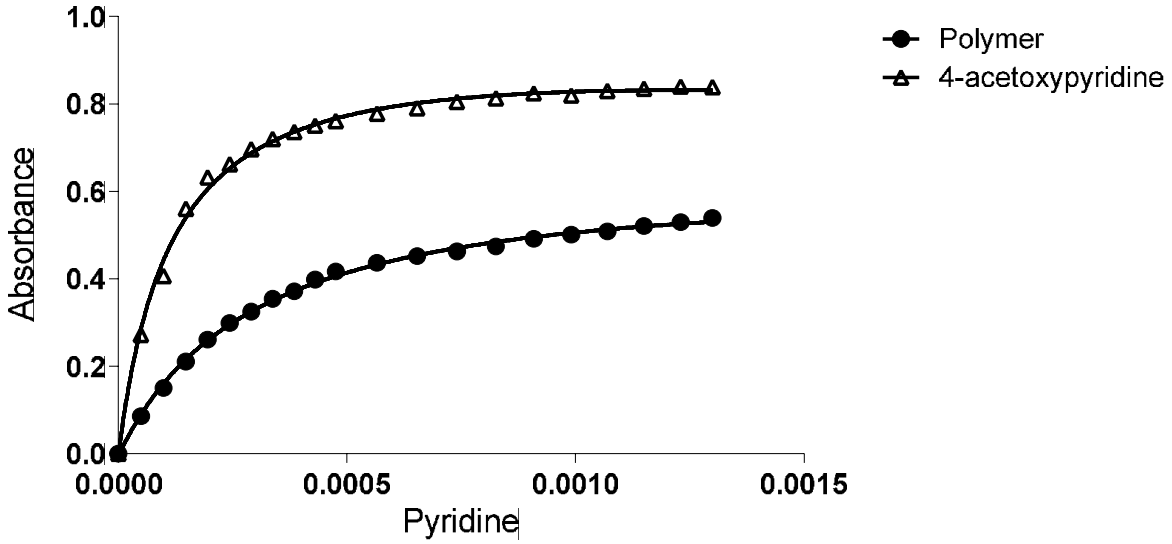


Figure.3.22. Binding curves of the two experiments.

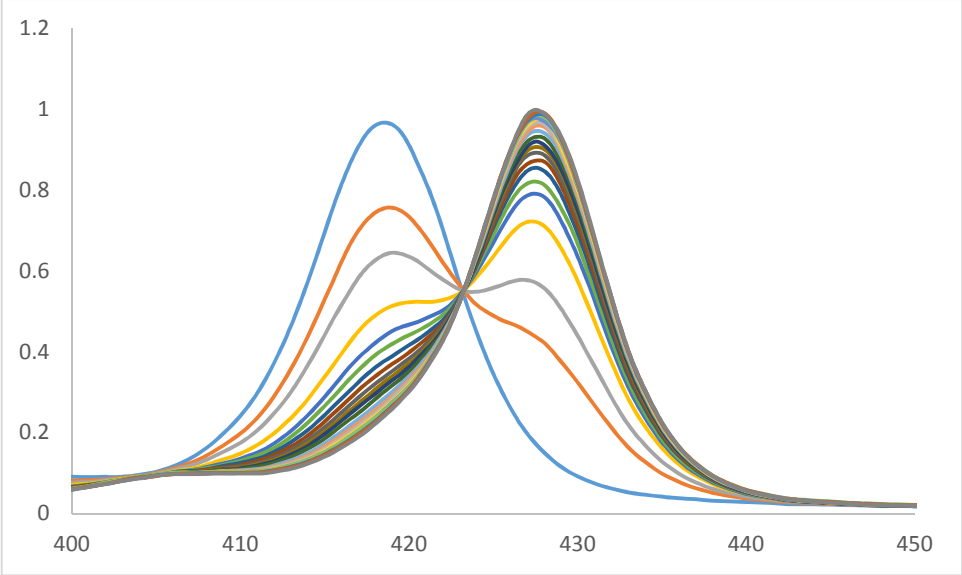


Figure.3.23. UV/Vis titration of 4-acetoxypyridine with TAPP.

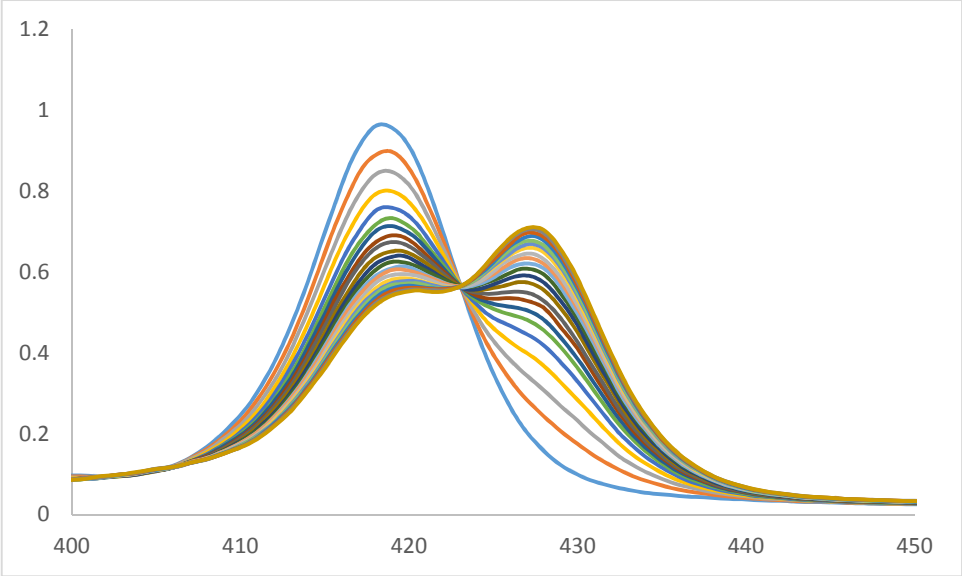


Figure.3.24. UV/Vis titration of pyridine incorporated hyperrbanched co-polymer with TAPP.

3.4 Conclusion:

The data presented in this chapter indicates the effect of co-polymerisation of the interior of hyperbranched polymers on their dendritic properties. The effect of the degree of branching on the bulk properties and internal microenvironment of hyperbranched polymers was investigated. The study included the synthesis of a series of hyperbranched polymers with different degrees of branching to examine the effect of the degree of branching on the bulk properties, in terms of viscosity, and on the microenvironment, in term of binding, of those types of polymers.

For the bulk properties, the study was designed to cover many parameters that could affect the viscosity of hyperbranched polymers, such as the polydispersity index and molecular weight. In terms of the polydispersity index, a series of hyperbranched polymers with various degrees of branching, ranging from 49% to 31%, a position on the polydispersity index between 2.3 and 7.2 and a relatively constant molecular weight of 15000 Da were prepared. As the degree of branching decreased, the viscosity increased, as did the position on the polydispersity index. In terms of molecular weight, the viscosity remained unchanged for hyperbranched polymers with a molecule weight of between 8000 Da and 15000 Da, various degrees of branching and a relatively constant position on the polydispersity index of 2.9. As a result of this, 4-nitrophenyl acetate was used as a core in order to control the polydispersity index, which has a major effect on the viscosity of hyperbranched polymers. Therefore, a series of cored hyperbranched polymers with a degree of branching ranging from 48% to 18% and a relatively constant molecular weight and position on the polydispersity index were prepared. The viscosity remained unchanged as the degree of branching decreased from 48% down to 37%. However, the viscosity increased as the degree of branching decreased from 37% down to 18%. This indicated that in terms of bulk properties, hyperbranched polymers retain their dendritic structure when the degree of branching is 37% or above. Therefore, regarding the advantages of the bulk properties of hyperbranched co-polymers, they could co-polymerise with a limited ratio of co-monomers without their bulk properties being affected.

For the microenvironment of hyperbranched polymers, the study was performed by studying the binding of pyridine ligands to zinc functionalised porphryin cored

hyperbranched polymers with different degrees of branching. This study was carried out on two different molecular weights, 15000 Da and 5000 Da, below and above the dense packing limit. For hyperbranched polymers with a molecular weight below the dense packing limit, the association constant decreased as the degree of branching decreased. This was due to the electronic effect. However, in the case of hyperbranched polymers with a molecular weight above the dense packing limit, the association constant increased as the degree of branching decreased, indicating that the steric around the core had decreased and the steric effect had overwhelmed the electronic effect. This indicates that the internal environment is affected by the degree of branching. The study also indicated that the dense packing limit is directly affected by the degree of branching and it shifts in the polymers with a low degree of branching.

In the last part of this chapter, the location of co-monomers in the interior of hyperbranched polymers was studied. This was carried out by comparing the association constants of binding pyridine incorporated hyperbranched polymers to porphyrin to control the experiment. The results indicated that the co-monomers were in identical environment and located in the interior, but towards the periphery of hyperbranched polymers. From the results of the previously discussed studies it can be concluded that hyperbranched polymers derived from AB_2 monomers with interior functionality could be used for biological applications with limited loading. Therefore, in order to increase the degree of branching, hyperbranched polymers derived from AB_3 monomer will be studied in the next chapter.

Future development of this work may include utilizing aliphatic hyperbranched polymers rather than aromatic polymers, and it is worthwhile comparing these in order to identify the minimum degree of branching that could be used to maintain the dendritic properties of those polymers.

Chapter Four

Hyperbranched polymer based on AB_3 monomer

Chapter Four - Hyperbranched polymer based on AB_3 monomer

4.1 Introduction:

The effect of co-polymerisation on the interior phase of hyperbranched polymers is clearly demonstrated in the research detailed in chapter three. The study was conducted on a model of a hyperbranched polymer based on the AB_2 monomer with a degree of branching of 50%. In order to maintain the structural features of this type of hyperbranched polymer, the maximum loading of functionality was limited to 20%. When the loading was increased above this limit, the hyperbranched polymers started to lose their dendritic features. Thus, the involvement of a hyperbranched polymer system with a higher degree of branching in the ongoing project is beneficial. The aim of this investigation is to achieve a higher loading of functionality than that of the hyperbranched polymers described in the previous chapter whilst maintaining the features of the dendritic structure (for example DB above 50%). Despite the fact that various methodologies to increase the degree of branching are described in the literature, many of these have limitations. For example, polymerisation methodologies and conditions.[58-62,87,88] However, it has been reported that the degree of branching is widely dependent on the type of monomer.[117] In theory, the polymerisation of an AB_2 monomer provides hyperbranched polymers with a degree of branching around 50%. This is because the presence of one reactive group from one type (A) and two reactive groups from another type (B_2) allow the polymer to grow in two directions, producing a highly branched polymer with a degree of branching of 50% without any crosslinking. Therefore, increasing the number of reactive groups (B) to more than two will cause the polymer to grow in more directions, providing a hyperbranched polymer with a degree of branching above 60%.[89]

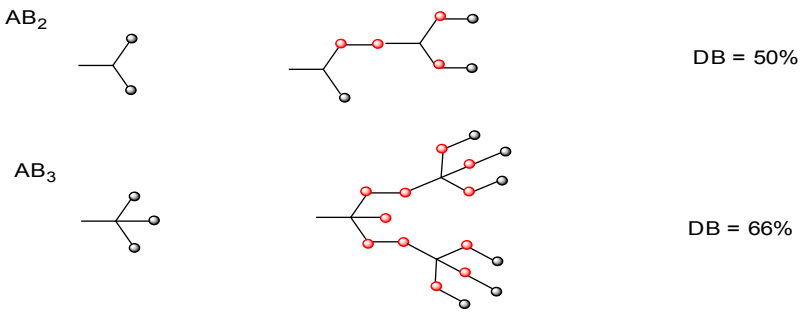
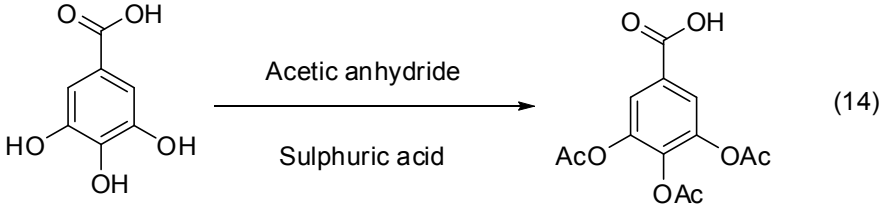


Figure.4.1. The proposed DB of polymers derived fromAB_2 and AB_3 monomers.

Chu and co-workers reported the polymerisation of AB_2, AB_3 and AB_4 monomers containing similar subunits to form hyperbranched poly (ether ketone) s. The degree of branching of a polymer obtained from an AB_4 monomer was 71%, whereas polymerisation of an AB_2 monomer yielded a polymer with a degree of branching of 49%.[87] Other work was carried out by Kakimoto and co-workers, who reported the synthesis of hyperbranched polyamides from AB_2 and AB_4 monomers. The degree of branching of a polymer obtained from an AB_4 monomer was 72%, whereas polymerisation of an AB_2 monomer yielded a degree of branching of 32%.[88] Recently, Li and co-workers prepared a series of hyperbranched co-polymers based on an AB_3 monomer with a different degree of branching ranging from 57% to 68%. The degree of branching was calculated from ^{13}C NMR.[89] Other research demonstrated that the same type of monomer leads to hyperbranched polymers with a degree of branching of 75%.[118] In this chapter, hyperbranched polymer based on an AB_3 monomer was polymerised to achieve high degree of branching around 66%, then an attempt was carried out to co-polymerise the system with co-monomer. As a consequence of the co-polymerisation of such a system, the degree of branching would decreased from around 66% to 40%, which is within the limit of the dendritic structure proposed in the previous chapter.

4.2 Synthetic Procedure:

The first step in achieving the co-polymerisation of a hyperbranched polymer based on an AB_3 monomer was to select the precise type of monomer and then to prepare the hyperbranched homo-polymer. The monomer selected was acetyl-protected gallic acid. This monomer possesses a similar structure to the AB_2 monomer that was studied in depth in the third chapter. The method used to synthesise acetyl-protected gallic acid was adapted from Kricheldorf et al.[119-121] as seen in **Scheme 4.1.**



(14)

Scheme.4.1. Synthesis of 3, 4, 5-triacetoxybenzoic acid (14).

The monomer 3,4,5-triacetoxybenzoic acid, was synthesised from 3,4,5-trihydroxybenzoic acid with acetic anhydride.[122] The monomer was dissolved in three equivalents of acetic anhydride, which resulted in a yellow solution. A drop of sulphuric acid was added to this solution as a catalyst. The temperature was raised to 70 ^{0}C for 15 minutes, and the reaction was then left to cool down to room temperature. Following this, water was added to precipitate out the product and remove the excess acetic anhydride. After three hours, the product was filtered off and washed in water several times. Finally, the monomer was dried and characterised. ^{1}H NMR showed a singlet at 7.80 ppm for two protons in the aromatic ring and a singlet peak at 2.30 ppm from the new methyl hydrogens of the acetoxy groups. In addition, a broad peak was observed at 12 ppm, corresponding to one proton in the carboxylic group. IR showed peaks at 1786 and 1689 cm^{-1}. It should be noted that the product was dissolved in chloroform but that the starting material is not soluble in chloroform.

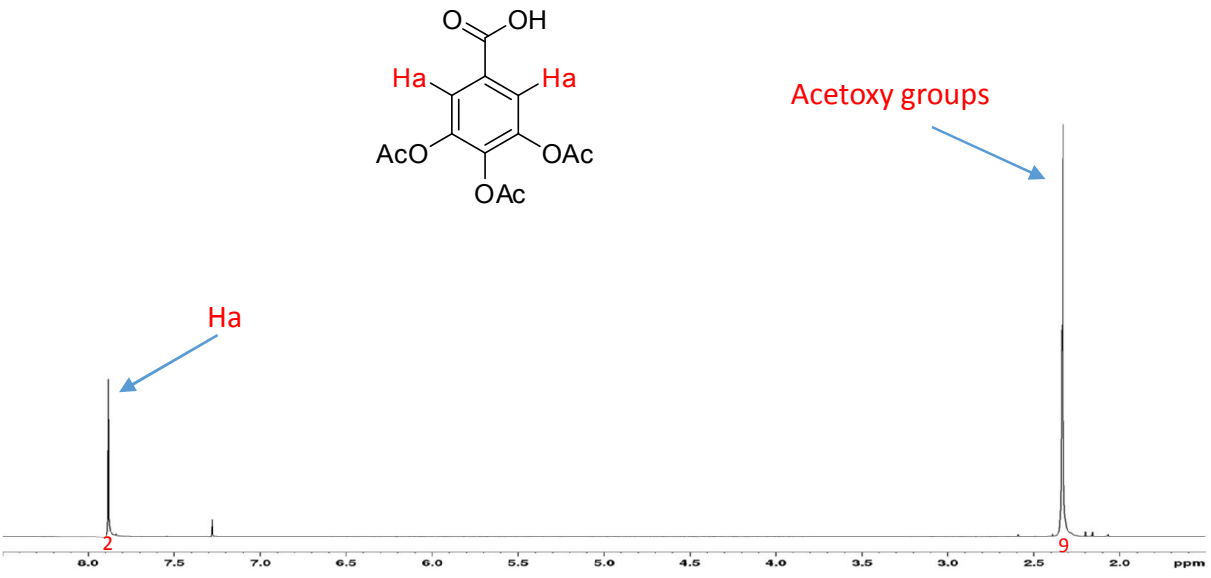
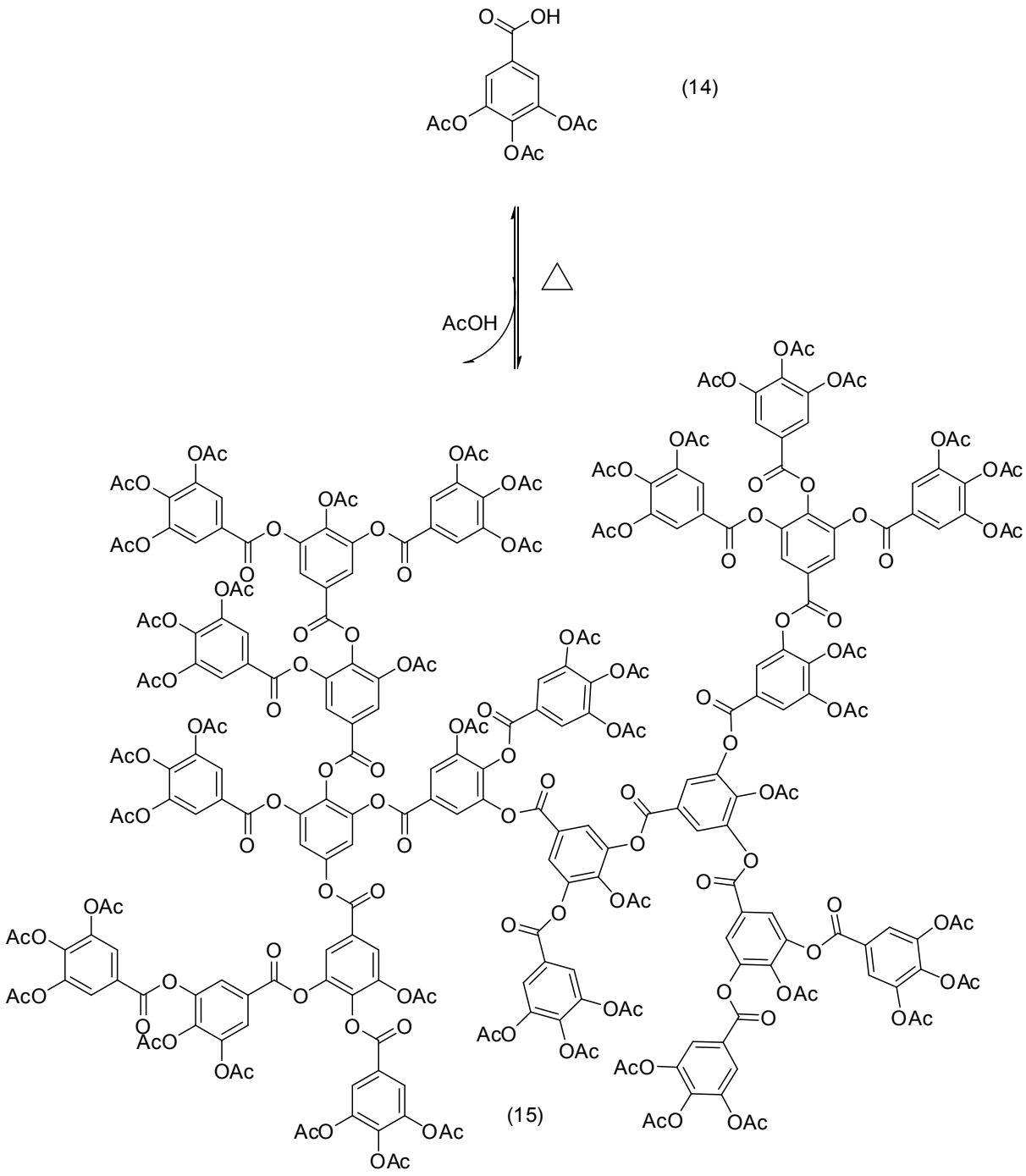


Figure.4.2. ^{1}H NMR spectrum of 3, 4, 5-triacetoxybenzoic acid.

Many attempts were made to create the appropriate conditions for polymerisation of 3, 4, 5-triacetoxy benzoic acid. These attempts included using various catalysts, such as magnesium oxide and toluenesulfonic acid monohydrate. However, gelation occurred at each attempt despite adding different amounts of each catalyst. Finally, polymerisation was achieved via the general method of polymerisation by changing the time and temperature

of the reaction. Diphenyl ether was used as the solvent. Polymerisation began after the reaction was heated to 250 ^{0}C for three hours to form oligomers. Following this, the reaction temperature was lowered to 180 ^{0}C and the reaction was put under reduced pressure for 4 hours. Finally, the polymer was purified by dissolving it in hot THF then precipitating it into cold methanol.

GPC indicated that a polymer with a molecular weight of 3000 Da and a polydispersity of 3.3 was obtained. ^{1}H NMR showed a broad peak at 8.20 to 7.70 ppm, corresponding to two aromatic protons. Another singlet peak was observed at 2.35 ppm, corresponding to nine protons from the acetoxy group. However, calculation of the degree of branching using ^{1}H NMR was not possible, in contrast with the hyperbranched polymers derived from the AB_2 monomer.



Scheme.4.2. Synthesis of poly (3, 4, 5-triacetoxybenzoic acid) hyperbranched polymer (15).

The degree of branching of such a system could be estimated from ^{13}C NMR, which is a less reliable method due to a lower resolution and a big difference in the relaxation rates. Frey indicated that there are four different dendritic units within the structure of this type of hyperbranched polymer.[123] These different units are dendritic (D), semi-dendritic (sD), linear (L) and terminal (T) (see **Figure 4.3**). The spectra of ^{13}C NMR of the polymer and monomer is shown in **Figure.4.3**. In ^{13}C NMR of the monomer, C_e, the aromatic carbon next to carbonyl group, is observed at 121.9 ppm. After polymerisation occurs, Ce splits into four peaks, observed at 125.9, 124.6, 122.9 and 118.5, indicating that there are four different environments. According to the chemical environment, the peaks 125.9, 124.6, 122.9 and 118.5 are assigned to $^{D}C_e$, $^{sD}C_e$, $^{D}C_e$ and $^{T}C_e$, respectively. However, Fery demonstrated that the degree of branching of such a system could be calculated very simply by using the equation 4.1. ^{13}C NMR indicated that a hyperbranched polymer with a degree of branching of 44% was obtained.

$$\text{Degree of Branching} = \frac{2D+sD}{2/3(3D+2sD+L)} \qquad \textbf{Equation.4.1.}$$

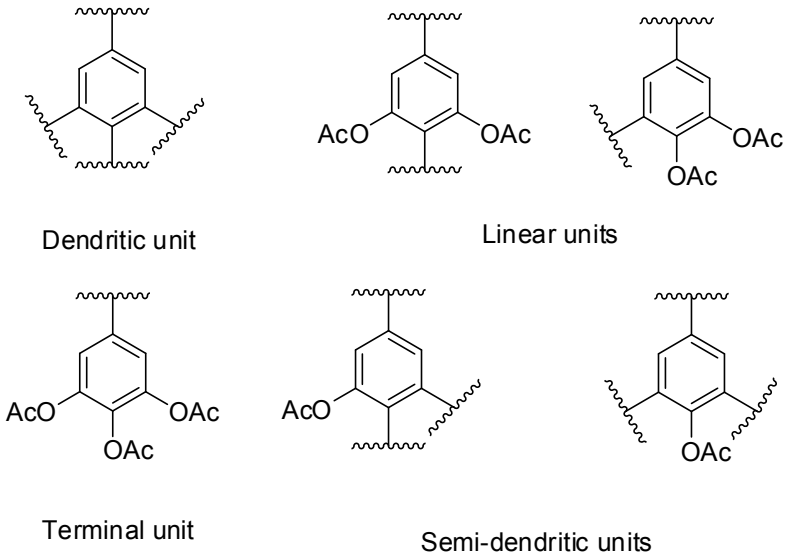


Figure.4.3. Architectural unites in within dendritic structure of AB_3 based polymer.

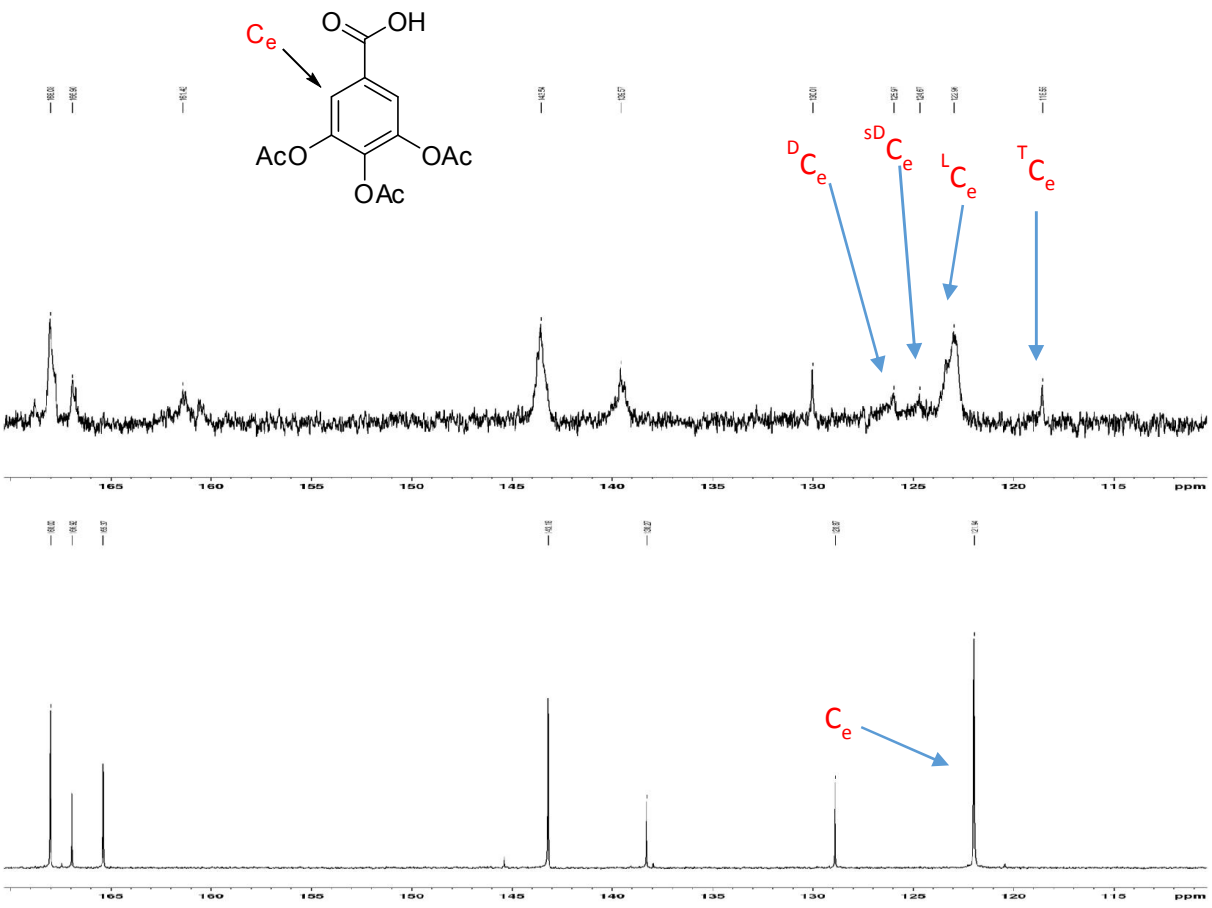


Figure.4.4. ^{13}C NMR spectrum of the monomer and polymer.

The **Figure.4.3.** illustrates the possible growth of the four dendritic units during polymerisation, which were considered for the calculation of the degree of branching. However, the principle of chemical reactivity should be considered as it plays a key role in the growth of these four dendritic units. Therefore, the possibility of the presence of a dendritic unit within the structure is very low due to steric interactions between the two bulky acetoxy groups (see **Figure 4.4**). As a result of this, the dendritic units within the structure of this type of hyperbranched polymer are similar to hyperbranched polymer based on an AB_2 monomer. Therefore, the degree of branching is 50% or less due to the high possibility of the presence of linear units within the structure.

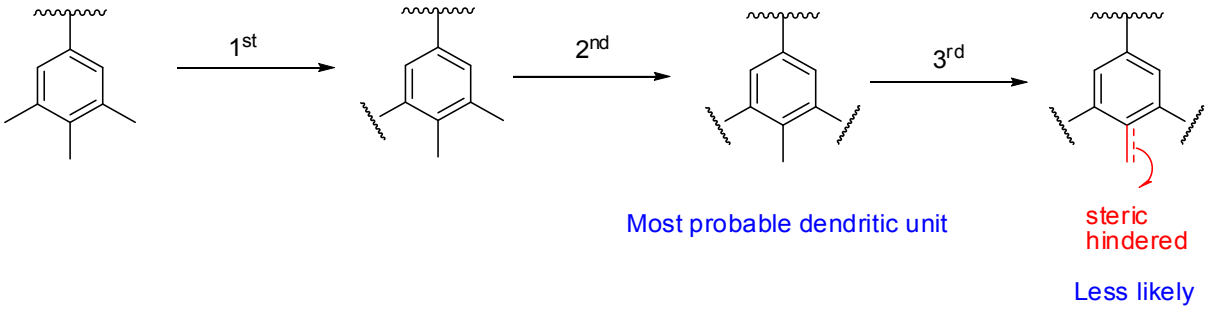


Figure.4.4. Polymerisation process of AB_3 monomer.

In order to increase the molecular weight, the reaction was repeated and attention was paid to complete the reaction by making the next stage of polymerisation longer. The maximum molecular weight was obtained for the resulting polymer when the reaction was placed under reduced pressure for six hours. The obtained hyperbranched polymer possessed a degree of branching of 44%, a molecular weight of 6000 Da and polydispersity of 2.5. A solubility issue occurred when the time was increased to over six hours. Unfortunately, further investigation into this type of polymer was not possible due to solubility issues when it was co-polymerised with co-monomers. Therefore, the work was directed at alternative methods of synthesising functional highly branched hyperbranched polymer.

4.3 Conclusion:

In this chapter, the aim was to develop a hyperbanched polymer system, based on AB_3 monomer, possessing degree of branching above 50%. The successful synthesis of monomer 3, 4, 5 tri-acetoxybenzoic acid and the appropriate polymerisation conditions for the polymerisation of this AB_3 monomer have been discussed. These conditions include the temperature, the presence of a catalyst, the reaction time and the time under the vacuum. The polymer was synthesised by condensation polymerisation in the absence of any catalyst. The obtained polymer possessed a lower molecular weight (3000 Da) than the molecular weight possessed by the polymers based on the AB_2 monomer caused by steric hindrance. The molecular weight increased slightly to a limited molecular weight (6000 Da) when the time of the reaction under reduced pressure was increased. It was not possible to calculate the degree of branching using ^{1}H NMR. Therefore, it was estimated using ^{13}C NMR. The degree of branching was 44%, which is less than the degree obtained by hyperbranched polymers based on the AB_2 monomer. This was a result of the steric hindrance that occurred during polymerisation. In conclusion, those polymers possess a dendritic structure similar to the polymers obtained by the polymerisation of the AB_2 monomer. Solubility issues were present at many stages of homo-polymerisation and after the co-polymerisation with the co-monomer. Therefore, future research should focus on the polymerisation of the AB_2 monomer as it is easier and more time effective. In the future, development of these polymers may include using aliphatic monomers rather than aromatics ones, which ought to minimise the occurrence of steric hindrance during polymerisation. In relation to measuring the degree of branching, co-polymerisation with a core may support the use of ^{1}H NMR instead of ^{13}C NMR.

Chapter Five

Post synthetic modification

Chapter Five - Post synthetic modification

5.1 Introduction:

Pervious chapters have indicated that hyperbanched polymers are able to maintain their dendritic properties after limited co-polymerisation with co-monomers in order to obtain highly functionalised interior. This finding adds to the importance of these polymers due to their potential use in a wide range of further biological applications, such as artificial blood and protein mimics.[54] However, the synthesis of hyperbranched co-polymers is typically conducted in aggressive conditions, such as at an elevated temperature and a reduced pressure.[124-133] As a result of this, the molecule of a co-monomer that is involved in the polymerisation process must possess robustness and low volatility in order to survive in the reaction conditions. As a consequence of this, the type of co-monomers that can be used in the polymerisation process is restricted due to them being volatilised or destroyed, and the possibility of identifying an alternative methodology is limited. These issues are obvious when it is necessary to functionalise the interior phase of hyperbanched polymer with a sensitive co-monomer molecule, where there is no possibility of this co-monomer surviving in the one pot polymerisation conditions. Therefore, logically, functionalisation must be performed after the polymerisation step. Thus, it is necessary to identify a general route based on post synthetic modification in order to provide an alternative methodology to the interior functionalisation of hyperbranched polymers using a sensitive co-monomer molecule. The literature contains several examples of work where post synthetic modification has been successfully applied to the core and peripheral functionalisation of hyperbranched polymers.[63,129,134-136]

The advantage of applying such a method hyperbranched polymers is that it allows the hyperbranched polymers to functionalise with assorted functional groups without changing the polymerisation procedure. This methodology was used to modify the core after polymerisation with many sensitive molecules. Twyman and co-workers employed post synthetic methodology to functionalise the focal point (core) of hyperbranched polyester.[63] The aim of this study was to synthesis amine cored hyperbranched polymers. The work was conducted by synthesising a 4-nitrophenyl cored poly (3, 5-diacetoxybenzoic acid) hyper-branched polymer using the general polymerisation method described earlier. Then, the

polymer was stirred with isobutyl amine for 4 hours at room temperature. ^{1}H NMR indicated that the amine had reacted with the polymer at the core.

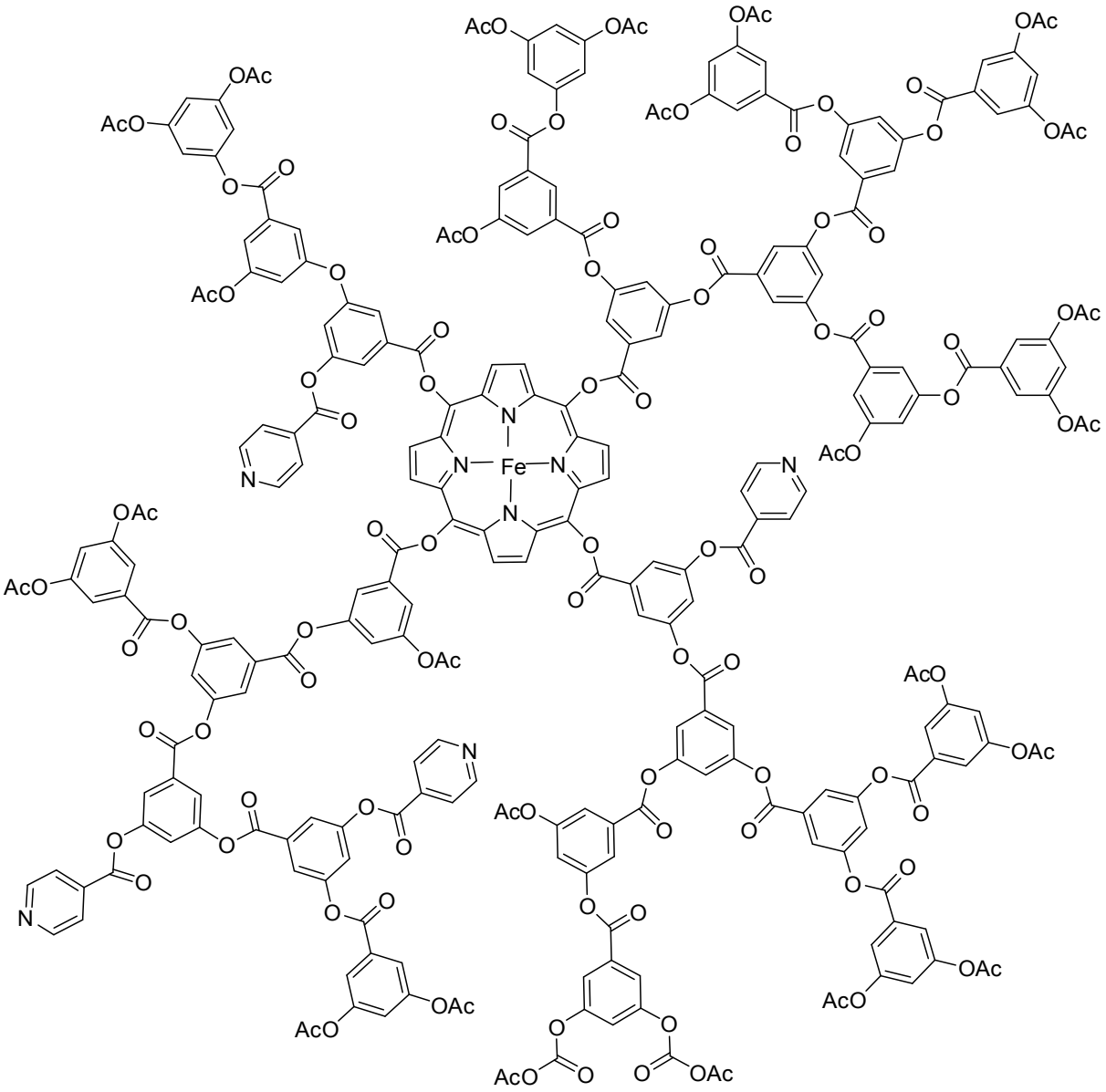


Figure.5.1. A synthetic model of artificial blood using hperbanched co-polymer functionalised with pyridine.

It is worthwhile mentioning that the chemical and physical properties of hyperbranched polymers can be controlled by modification of the terminal groups after the polymerisation. This type of modification could affect various factors, such as the glass transition temperature, solubility and the rheology of the final product.[129,135,137,138] Shu and Leu employed a post synthetic technique to functionalise the terminal groups of poly ether ketone hyperbanched polymers.[129] Different terminal groups were obtained for the same initial polymer by using a variety of different reactions, thus proving the flexibility and desirability of the post synthetic technique. Therefore, applying the post synthetic approach to the interior phase of hyperbanched polymers is a desirable action that requires further exploration.

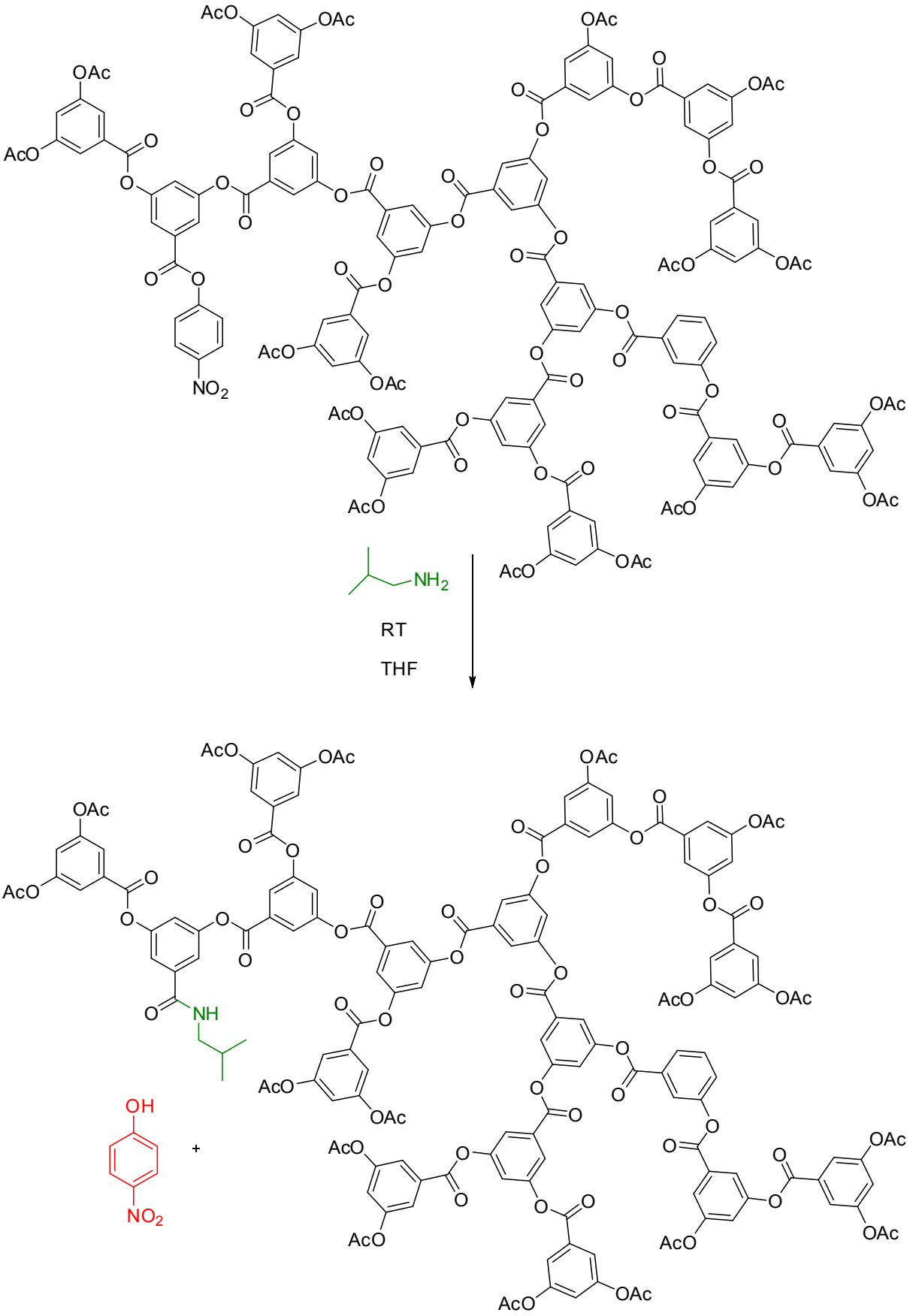


Figure.5.2. Post synthetic modification approach of the core of hyperbranched polymer.[63]

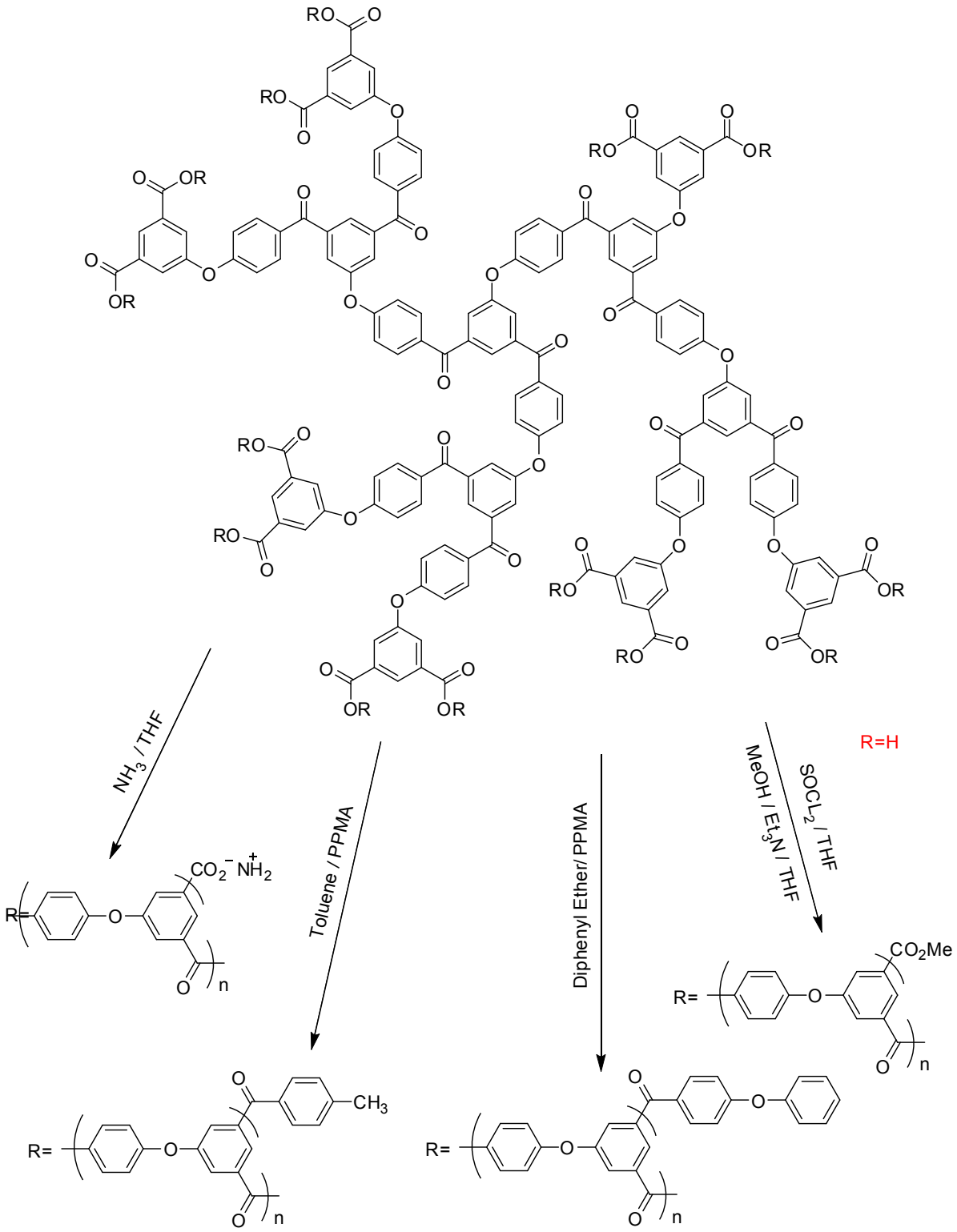


Figure.5.3. Post synthetic modification approach of the periphery of hyprbranched polymer.[129]

The aim of this chapter is to prepare hyperbranched polymers with internal functionality that can be modified with any desired co-monomer to be used in various applications, such as a catalyst and protein mimics. A possible outcome of applying the post synthetic approach to the internal phase of hyperbranched polymers is that the molecular weight of the hyperbanched co-polymer may increase if the reaction is performed at room temperature. Considering the reactivity of co-monomers, the co-polymerisation of an AB_2 monomer with some type of co-monomer, such as 4-methoxybenzoic and isonicotinic acid, limits the growth of the polymer, and thus obtained polymers will possess a relatively small molecular weight. As the functionalisation of the polymer is indirect (after the polymerisation), this issue could be overcome by synthesising hyperbranched polymers from an AB_2 monomer and a mono-functional co-monomer. Next, those functional groups would be modified after polymerisation with any desired molecule. In the case of the co-polymerisation of an AB_2 monomer with a di-functional co-monomer, the functionality could be increased and the degree of branching could decrease slightly. For example, theoretically, the co-polymerisation of an AB_2 monomer with a 20% molar ratio of a mono-monomer provides a hyperbanched polymer with 20% functionality and a 40% degree of branching. In order to obtain the same degree of functionality, the co-polymerisation of the same monomer should be performed with a 10% molar ratio of a di-functional co-monomer; the obtained polymers will possess the same degree of functionality and a 45% degree of branching. Therefore, the advantages of using a di-functional co-monomer instead of a mono-functional monomer in terms of the degree of branching were examined.

5.2 The strategy of the work:

The first stage of this study was to prepare hyperbanched polymers with functional groups by reacting an AB_2 monomer (3, 5 di- diacetoxybenzoic acid) with two different mono-functional co-monomers (AY_1). 4-hydroxybenzoic acid and 4-aminobenzoic acid were chosen as the co-monomers due to their commercial availability and their ability to survive in the polymerisation conditions. In order to reach the maximum functionality within the dendritic properties, the molar ratio of co-monomer was 20% to the main monomer, as described in the third chapter. Following confirmation of successful polymerisation, the AB_2 monomer was polymerised with the di-functional co-monomers (AY_2), 3, 5 di-hydroxybenzoic acid and

3, 5 di-amino benzoic acid. In the second stage of this study, those functional groups (Y) were reacted with any desired co-monomer, (Cat) for example, at room temperature. The study needed to be carefully thought through in terms of the overall cost, solvent compatibility and the general ease of the synthesis.

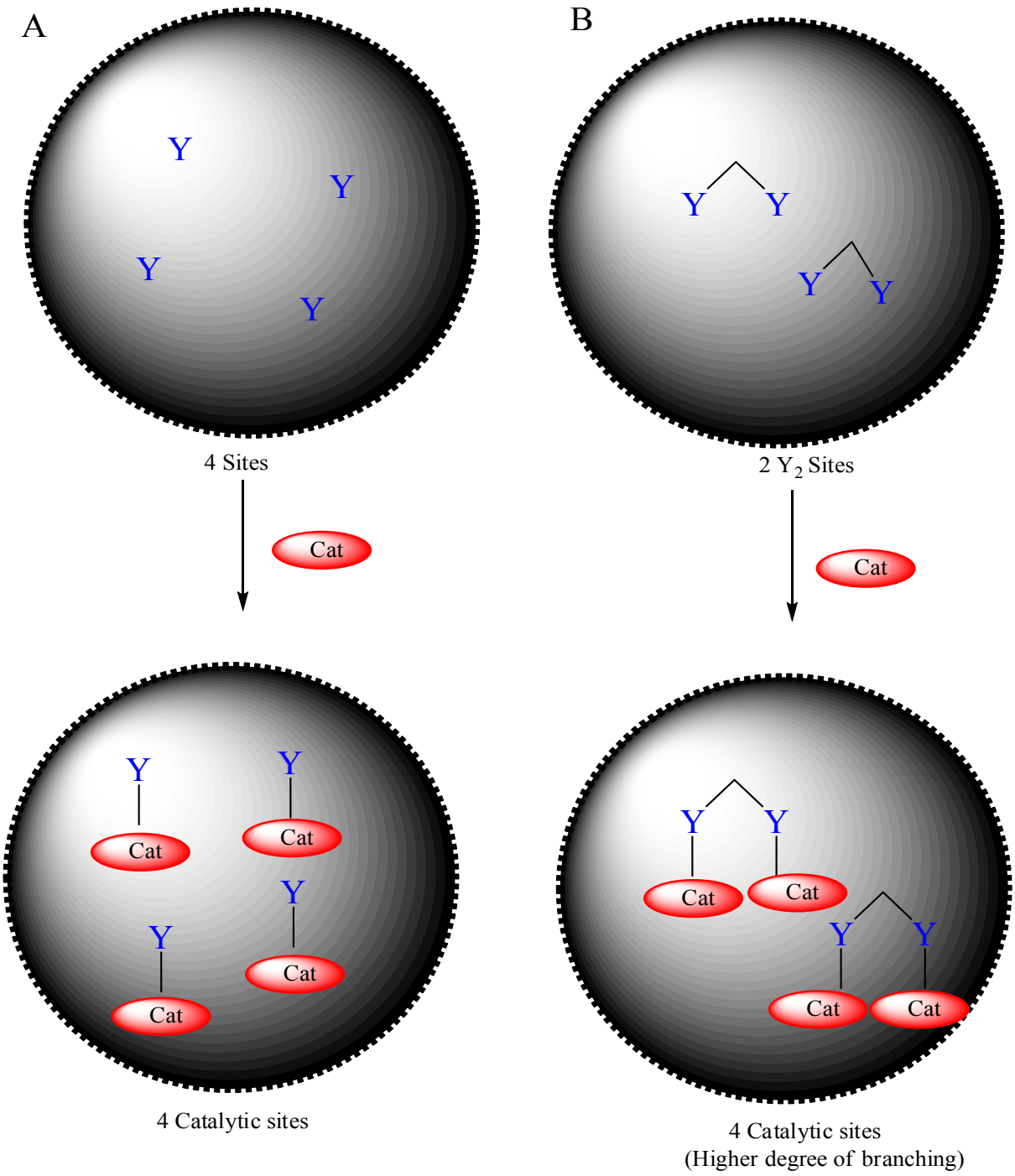
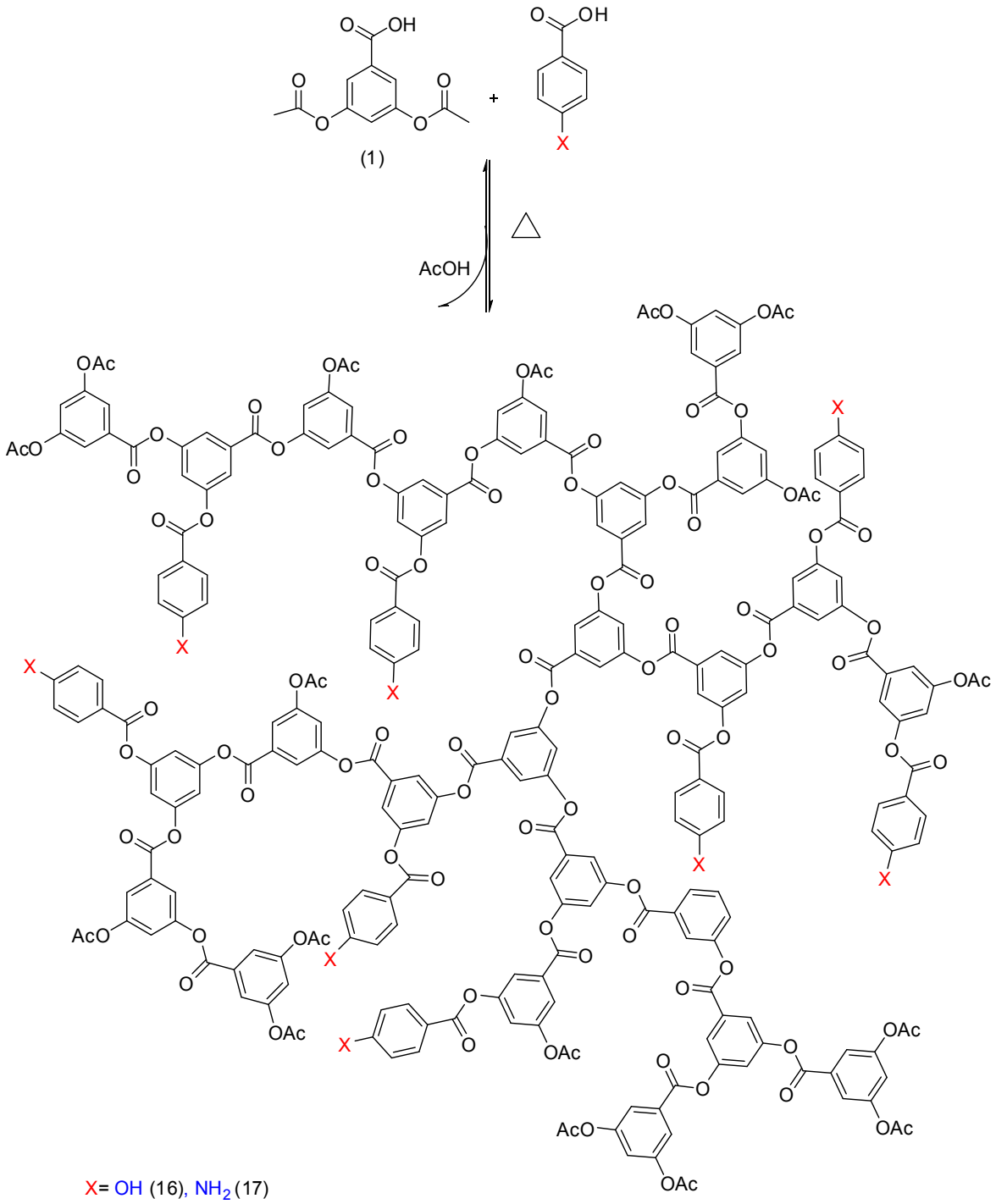


Figure.5.4. Schematic representation of post synthetic modification method: (A) using mono-functional co-monomer, (B) using di-functional co-monomer.

5.3 Synthesis of interior functional hyperbranched co-polymers:

The first step of the study was performed by preparing mono-functionalised hyperbranched co-polymers. Two different interior functionalised hyperbranched co-polymers were synthesised using the general polymerisation method described earlier in chapter three. The first was a hydroxyl functionalised hyperbranched co-polymer, which was obtained by the co-polymerisation of 3, 5-diacetoxybenzoic acid with 4-hdroxybenzoic acid. The second was an amine functionalised hyperbranched co-polymer which was obtained by the co-polymerisation of 3, 5-diacetoxybenzoic acid with 4-aminobenzoic acid. The molar ratio of both co-monomers corresponding to 5%, 10%, and 20% of the main monomer. The polymerisations were carried out in fixed conditions in the presence of equivalent masses of diphenyl ether. The purification of the crude polymers was performed after the removal of the solvent by dissolving the polymers in refluxed THF then by precipitation in icy methanol. Lastly, the final white product was filtered off and washed with methanol then dried under a vacuum. However, some polymers were difficult to purify due to solubility issues, as can be seen from the Table 5.1. The obtained polymers were analysed by ^{1}H NMR and GPC. It was noted that there is little possibility of ^{1}H NMR detecting the presence of functional groups due to the obfuscating of their protons by the polymer backbone. Therefore, to confirm the success of the synthesis of the hyperbanched polymers using ^{1}H NMR, simple calculations based on the integrations of ^{1}H NMR peaks were carried out. The calculations were made by recognising that the number of acetoxy groups of hyperbranched homo-polymers is equal to the number of aromatic protons. In this system of hyperbranched homo-polymers, there are three protons per aromatic repeat unit and three protons per acetate group, and therefore, the integration of the acetate peak is equal to the integration of the aromatic peaks. With the incorporation of the co-monomer into the system, these peaks are no longer equal due to the increase in the number of aromatic protons. This indicates that there will be a difference between the integration of aromatic protons and acetate groups. Therefore, the success of co-monomer incorporation will be demonstrated by subtracting the integration of the acetoxy peak from the integration of aromatic peaks. ^{1}H NMR indicated that hyperbranched co-polymers were prepared successfully when applying this method. It is worthwhile noting that the level of incorporation could be calculated by the previously explained technique.



Scheme.5.1. Synthesis of mono-functionalised poly (3, 5-diacetoxybenzoic acid) (16, 17).

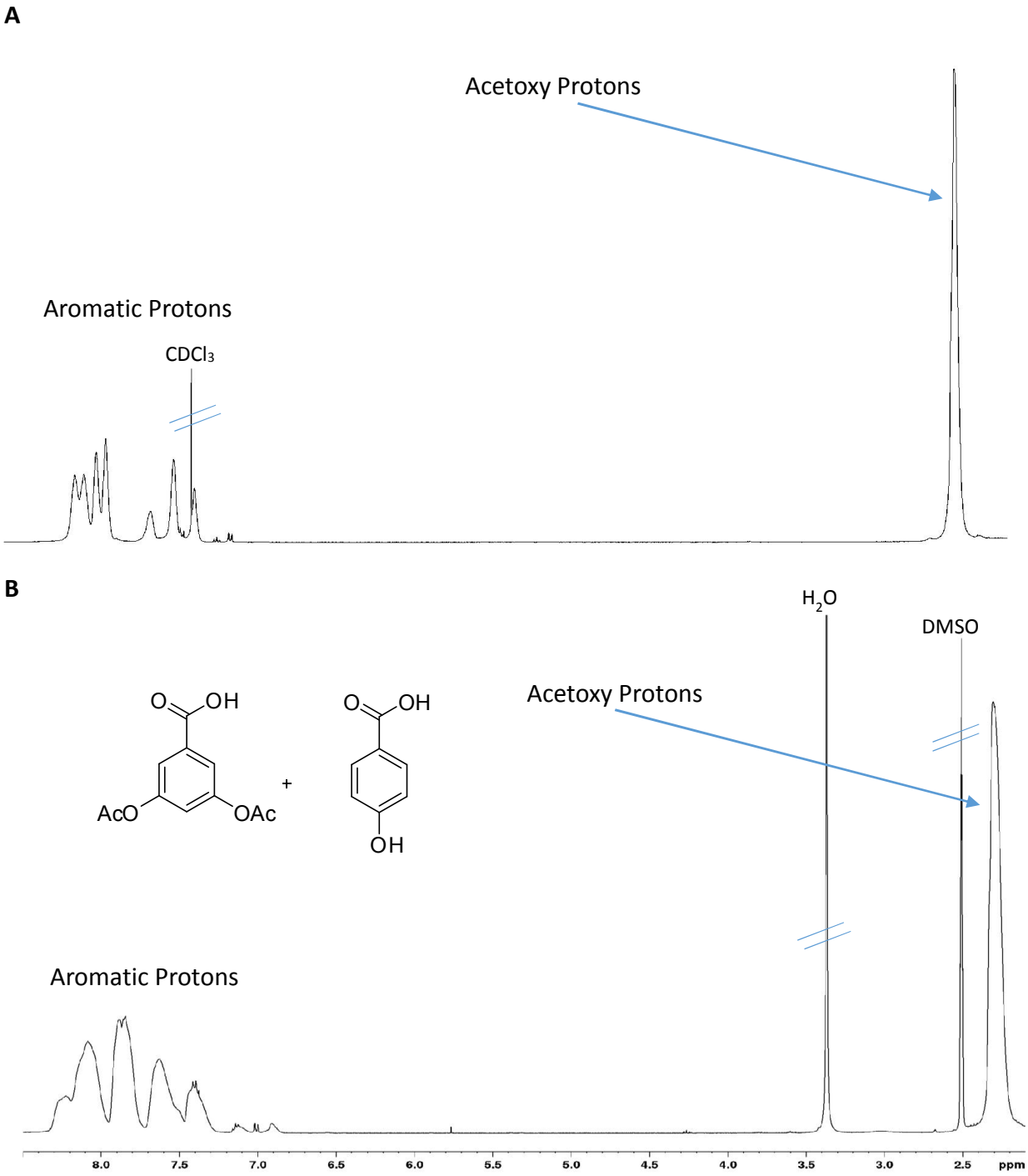


Figure.5.5. ^{1}H NMR spectrum of (A)-homo- hyperbanched poly (3, 5-diacetoxybenzoic acid) (2) in $CDCl_3$, (B) mono-hydroxyl functionalised poly (3, 5-diacetoxybenzoic acid) (16) in DMSO.

GPC provided further confirmation of successful co-polymerisation. GPC data shows that increasing the molar ratio of the co-monomers decreases the molecular weight of the polymer. This was more obvious when the polymerisations were carried out using 4-aminobenzoic acid as a co-monomer (see **Table5.1**).

Reaction	5%	10%	20%
AB2 + 4-hydroxybenzoic acid	17000	12900	9000
AB2 + 4-aminobenzoic acid	5500	4700	1700

Table.5.1. Represents the GPC data of series of two different mono-functionalised hyperbranched co-polymers (solubility issue in red).

For the highly amino functionalised hyperrbanched co-polymers (20% molar ratio of co-monomer), a solubility issue was faced during the purification process as a result of increasing the number of end functional groups of the polymers. This is because solubility is directly controlled by the nature of the end groups. Therefore, the polymer was excluded from the second step of the study. The table indicated that polymers that contain phenol groups possess a higher molecular weight than polymers with aniline groups. The difference between the molecular weights is due to phenol being more reactive with the acetoxy group than aniline. The conductivity of both the aniline and phenol groups depends on the efficiency of the para position of the functional groups, as seen below in **Figure 5.6**. The NH_2 group has higher conductivity than the OH group. As a result, the OH group at pare position will form a lower stable carbanion that has a greater ability to react with the acetoxy group to form the targeted co-polymer, whereas the NH_2 group limits the growth of the polymer.

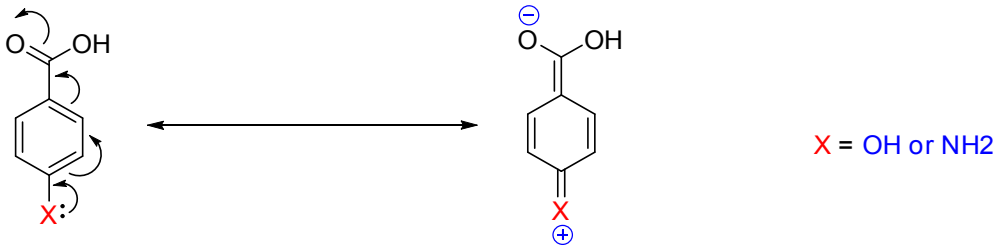
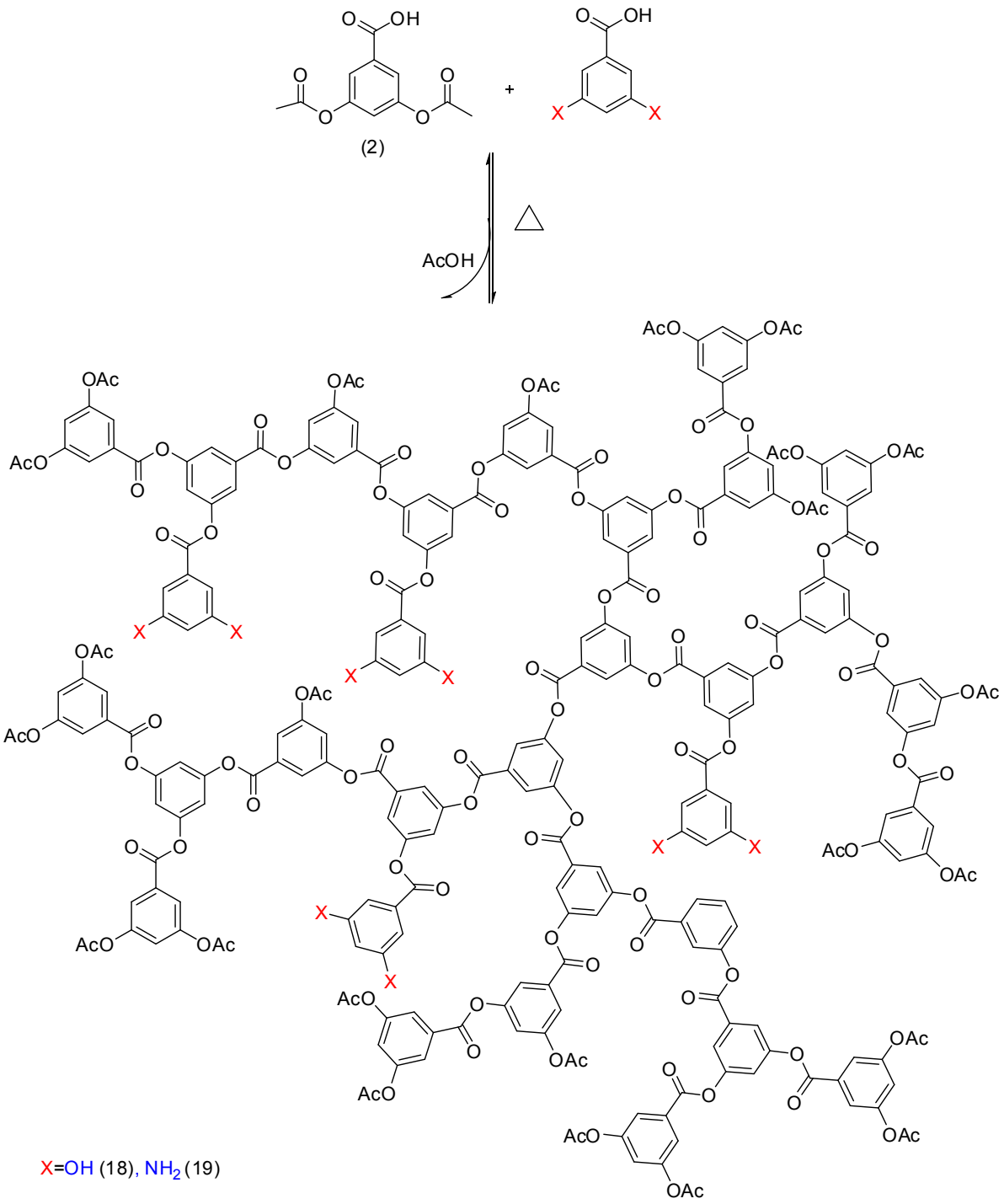


Figure.5.6. Conductivity of hydroxyl and amino functionalised co-monomers.

After the success of synthesising the mono-functional hyperbranched polymers, the decision was made to proceed to the next step of the study. Specifically the co-polymerisation of 3, 5-diacetoxybenzoic acid with two co-monomers possessing more than one functional group. However, to obtain an equal number of functional groups of similar functionality to the obtained polymers, the ratios of the co-monomers were decreased to half the size of the ratios used in the first step. The first co-polymerisation was conducted using 10% molar ratio of 3, 5 di-hydroxybenzoic acid to 3, 5 di-acetoxybenzoic acid, whereas the second co-polymerisation was carried out using 5% molar ratio of 3, 5-diaminobenzoic acid due to the solubility issue that faced previously. Both co-polymerisations were conducted in fixed conditions using the general polymerisation method described earlier. After the purification process, the characterisations of the obtained polymers were carried out using ^{1}H NMR and GPC. ^{1}H NMR indicated that the incorporation of selected co-monomers was carried out successfully by measuring the integration difference between the aromatic peaks and the acetoxy group's peak. GPC indicated that the polymers were synthesised successfully (see **Table 5.2**).



Scheme.5.2. Synthesis of di-functionalised poly (3, 5-diacetoxybenzoic acid)(18,19).

Reaction	Mn	PDI	Level of incorporation	DB
AB2 + 4-hydroxybenzoic acid (20%)	9000	3	10%	44%
AB2 + 4-aminobenzoic acid (10%)	4700	2.7	14%	42%
AB2 + 3,5-dihydroxybenzoic acid (10%)	5900	3	6%	46%
AB2 + 3,5-diaminobenzoic acid (5%)	5000	2.7	8%	45%

Table.5.2. ^{1}H NMR and GPC data of selected functionalised hyperbranched co-polymers for post synthetic methodology.

The modification of the functional groups was carried out by reacting each functionalised polymer (see **Table 5.2**.) with an acyl chloride compound. Acyl chloride is a good reactive acylation regent since the presence of chlorine enhances the reactivity of the carbonyl group because of its polar effect. Due to using the acyl chloride compounds, the modifications were obtained by the nucleophilic addition in which the nucleophilic reactants (OH, NH_2) bond to the electrophilic carbonyl carbon to create a tetrahedral intermediate, which undergoes elimination to produce the product **Figure.5.7**.

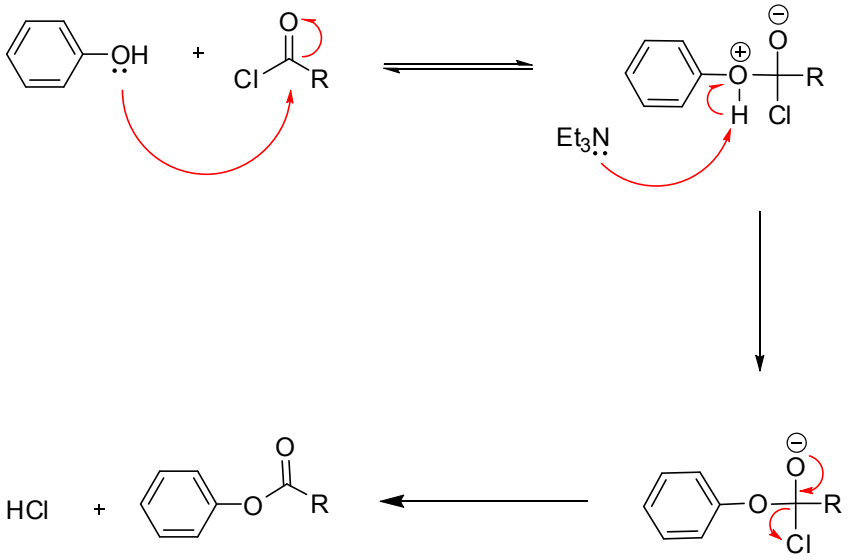


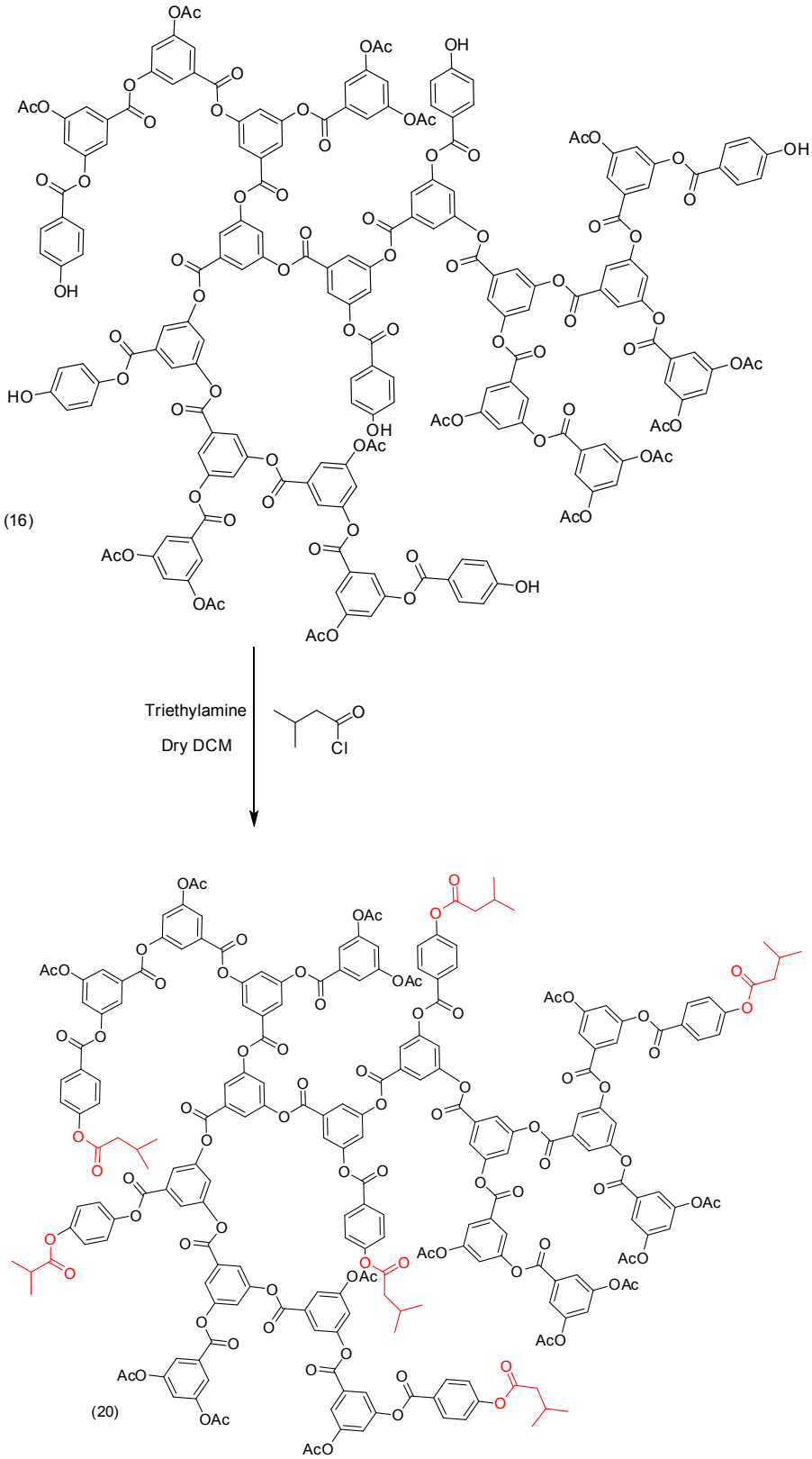
Figure.5.7. General mechanism of the alcohol with acyl chloride.

Those reactions were simply conducted by stirring both compounds overnight in a good solvent at room temperature. In these types of reactions, the presence of a base, such as pyridine or triethylamine, is usually required. The purification process included washing the obtained polymer with a base to remove the acid then with distilled water to remove the formed salt.

5.3.1 Reaction with Isovaleryl chloride:

Isovaleryl chloride was selected to test the viability of the previously prepared polymers for the post synthetic methodology. Isovaleryl chloride was chosen due to the intense doublt from the two methyl groups seen at around 1 ppm in its ^{1}H NMR spectrum. This peak could be easily observed in the ^{1}H NMR spectrum as it appeared in a region not occupied by the polymer peaks. The first examination was carried out using the mono functionalised hydroxyl hyperbanched poly (3, 5-diacetoxybenzoic acid). The polymer was stirred in dry DCM with an equivalents amount of isovaleryl chloride and triethylamine at room temperature for 24 hours to ensure the completion of the reaction. After that, purification was conducted by washing the polymer with saturated sodium hydrogen carbonate solution several times then with distilled water. Next, the layer of DCM was collected and the remaining traces of water were removed by stirring with magnesium sulphate. After the isolation of the magnesium sulphate, the DCM was removed by rotary evaporation, and the polymer was dissolved in THF then precipitated in cold methanol. Finally, the sediment polymer was isolated and collected as a powder. The fractionation technique was conducted using a bio-beads column to ensure the purity of the final polymer.

The obtained polymer was characterised by ^{1}H NMR and GPC. ^{1}H NMR indicated the appearance of a clear peak at 0.92 ppm corresponding to six protons from the newly added methyl groups (see **Figure 5.8**). The level of incorporation was calculated by measuring the integration of the new methyl peak and comparing it to the integration of the acetoxy group peak.



Scheme.5.3. Post synthetic reaction of mono-hydroxyl hyperbranched co-polymer with isovaleryl chloride.

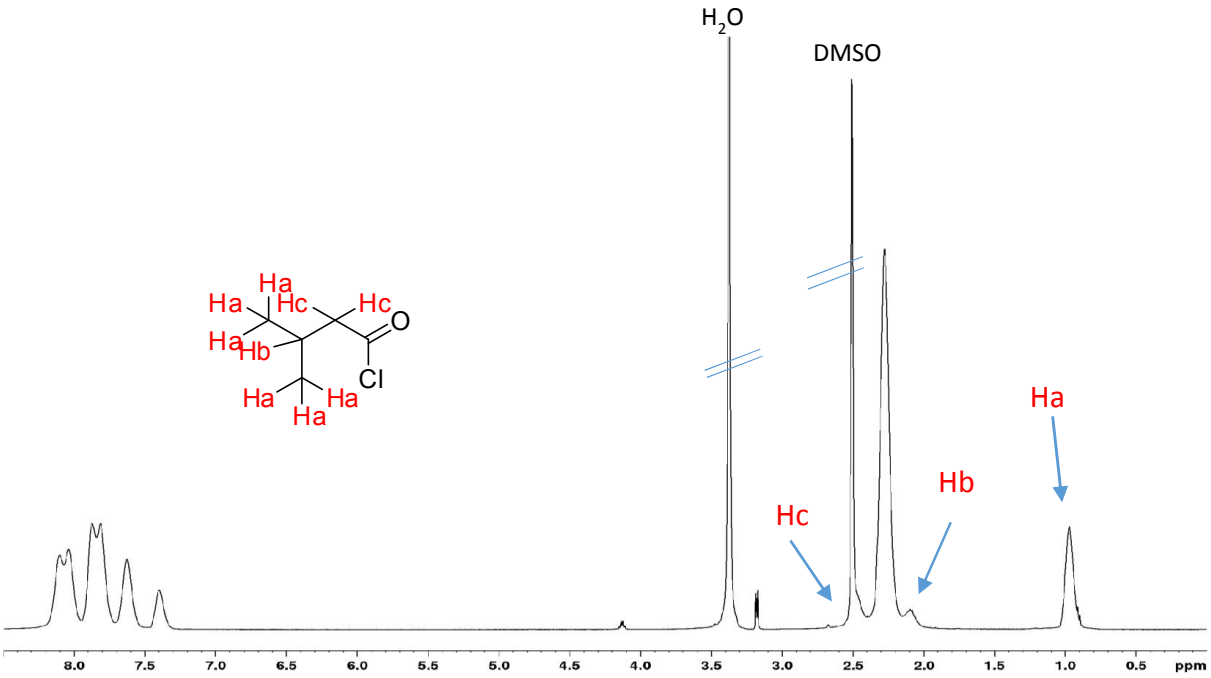


Figure.5.8. ^{1}H NMR spectrum of the resulted polymer of post synthetic reaction with mono-hydroxyl functionalised hyperbranched co-polymer with isovaleryl chloride in DMSO.

After confirmation of the success of the post synthetic method on hydroxyl functionalised hyperbanched co-polymers, the method was applied to previously prepared polymers that are outlined in **Table 5.3**. The ^{1}H NMR indicated that hyperbanched co-polymers were modified with isovaleryl chloride successfully. However, GPC indicated that those polymers possessed a higher molecular weight than expected. This increase in the molecular weight is due to the insensitive purification process were carried out after the polymerisation and the change in the hydrodynamic volume of the hyperbanched polymers. This is linked to the linear calibration of the GPC, which provides a smaller value than it should. After the modification of the functional group, the hydrodynamic volume will change, which leads to more accurate molecular weights. Comparing the outcomes of the modifications of the mono and di-functional group makes it clear that using di-functional hyperbanched co-polymers is more effective than those polymers with mono-functionality. For example, the mono and di functionality of the hydroxyl groups' hyperbanched polymers were selected for comparison because both polymers possess a good molecular weight before the modifications (above dense packing limit). The same amount of functionality was obtained, but the degree of branching was around 46% when using the di-functional co-monomer, whereas it was 43% when using the mono-functional co-monomer.

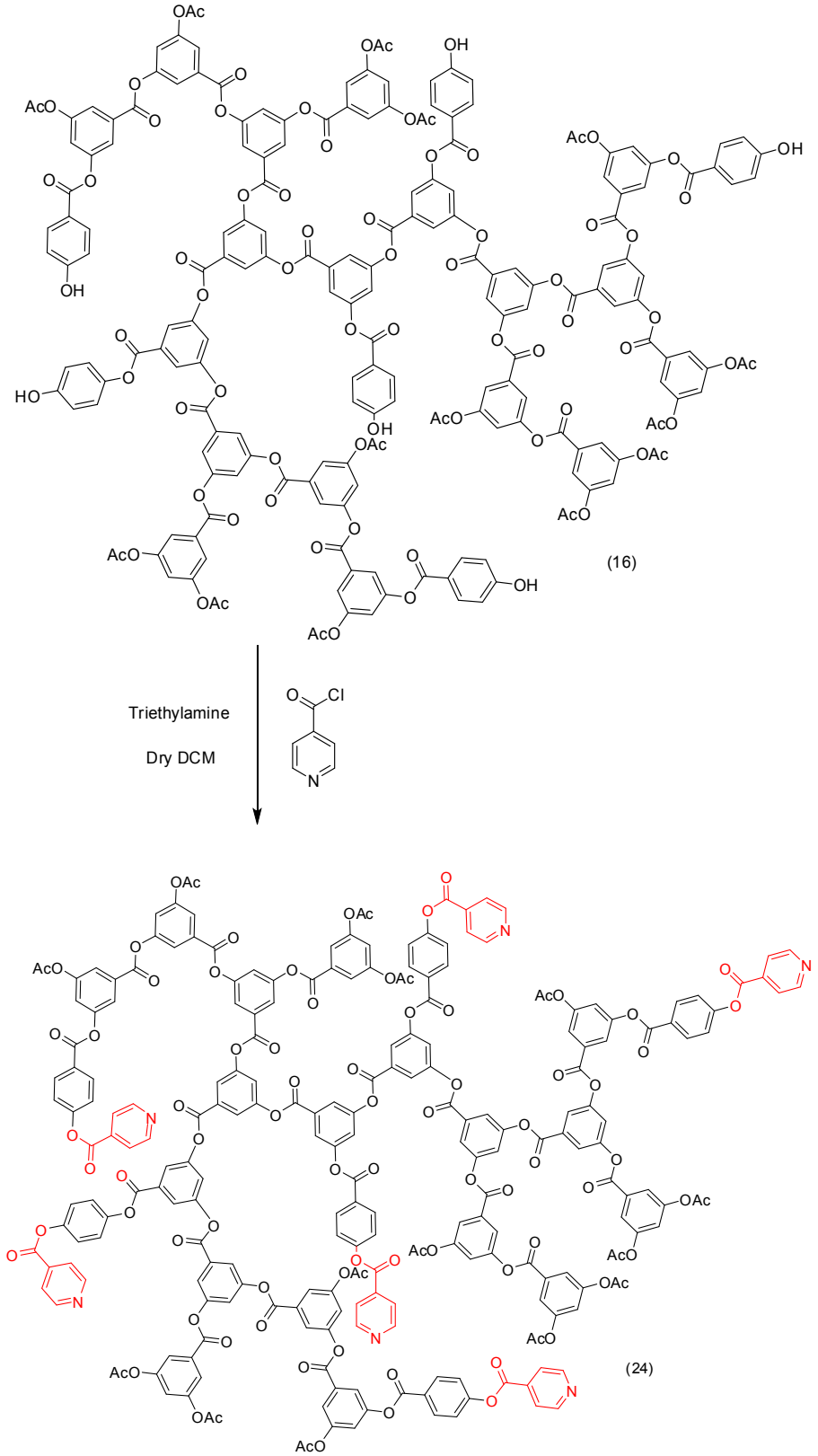
Starting polymers	Mn and PDI before modification	Mn and PDI after modification	Level of incoporation
AB_2+4-hydroxybenzoic acid	4000(3)	16000(2.2)	10%
AB_2+4-aminobenzoic acid	4700(2.7)	16000(2.5)	13%
AB_2+3,5-dihydroxybenzoic acid	5900(3)	14000(2.5)	10%
AB_2+3,5-diaminobenzoic acid	5000(2.7)	7000(1.8)	6%

Table.5.3. Represents the GPC data for post synthetic reaction with isovaleryl chloride.*Incorporation relative to the number of OH and NH_2 groups and further purification.

Comparing the mono with di-amino functionalised polymers showed that the former possess a higher level of incorporation even if they are both of a relatively similar molecular weight. This might be due to the solubility of the polymer. It was noted during the work that the di-amino functional co-polymer takes longer to solubilise in the solvent than the mono-amino functionalised co-polymer. However, the conversions were high for all co-polymers.

5.3.2 Reaction with Isonicotinoyl chloride:

The initial result using isovaleryl chloride encouraged us to use the post synthetic method to carry out an investigation that involved incorporation of various acyl chloride compounds. The first compound to be incorporated was pyridine. Pyridine is a catalyst widely used in many applications.[139, 140] A previous experiment indicated that the direct co-polymerisation of pyridine with 3,5diacetoxybenzoic acid leads to the production of a hyperbanched co-polymer possessing a molecular weight of around 8000 Da- 9000 Da and 42% degree of branching. Therefore, it is worthwhile comparing the methodology of both methods for the fixed co-monomer. Isonicotinic acid chloride was stirred with each functionalised co-polymer at room temperature overnight. After the purification process that included washing with acid then with distilled water, the obtained polymers were fractionated using a bio-beads column to remove the incorporated pyridine. Finally, the products were analysed by ^{1}H NMR and GPC.



Scheme.5.4. Post synthetic reaction of mono-hydroxyl hyperbranched co-polymer with isonicotinoyl chloride.

The successful incorporation of pyridine in all the obtained functionalised polymers was confirmed by ^{1}H NMR. A broad peak was observed at 8.85 ppm, corresponding to the alpha protons in the nitrogen of the pyridyl ester group. A second confirmation was obtained from the GPC, which indicated that the molecular weights of the polymers increased (see **Table 5.4**).

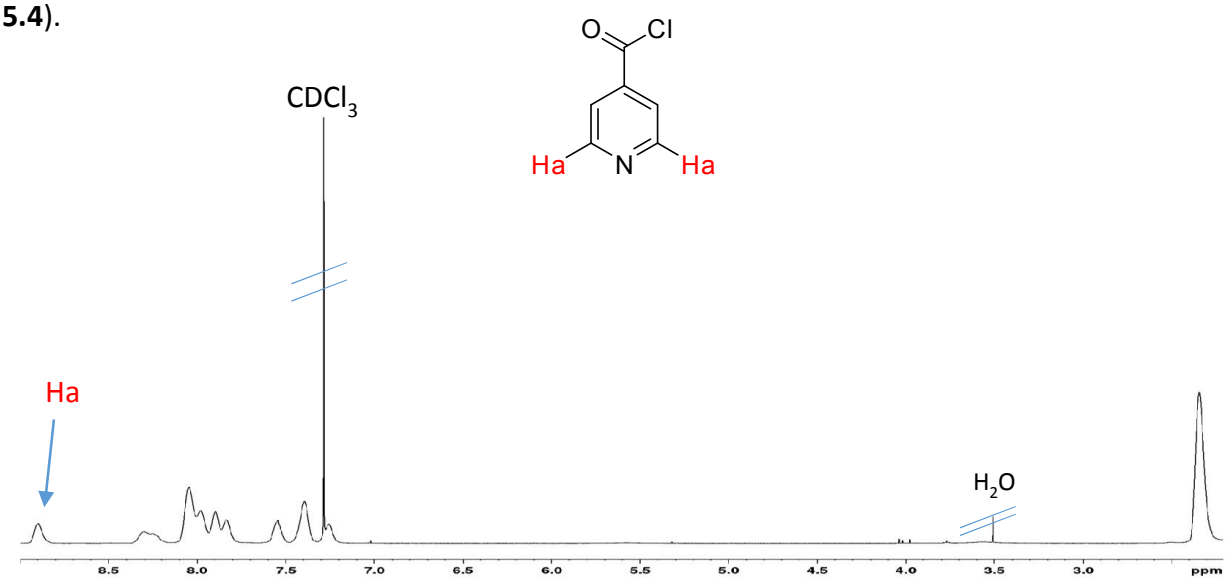


Figure.5.9. ^{1}H NMR spectrum of the resulted polymer of post synthetic reaction with mono-hydroxyl functionalised hyperbranched co-polymer with isonicotinoyl chloride (24) in $CDCl_3$.

Starting polymers	Mn and PDI before modification	Mn and PDI after modification	Level of incorporation
AB_2+4-hydroxybenzoic acid	4000(3)	15000(2.1)	10%
AB_2+4-aminobenzoic acid	4700(2.7)	14000(2.0)	13%
AB_2+3,5-dihydroxybenzoic acid	5900(3)	17000(2.6)	10%
AB_2+3,5-diaminobenzoic acid	5000(2.7)	7500(1.9)	5%

Table.5.4. Represents the GPC data for post synthetic reaction with isonicotinoyl chloride.

The data shows that the indirect co-polymerisation brought about a significant improvement in terms of the molecular weight and the degree of branching. Comparing the two co-polymerisation methods for the same co-monomer makes this clear. Due to conducting the co-polymerisation using 3,5 di-hydroxybenzoic acid, the obtained polymer possessed a molecular weight of 17000 Da and 10% loading of pyridine with a degree of

branching of 46%, which is much better than the values obtained using direct co-polymerisation.

5.3.3 Reaction with Palmitoyl chloride:

Controlling the solubility of polymers is one of the most important features of hyperbranched polymers. However, this feature could be simply obtained by the modification of the end groups with various compounds. For example, poly (3, 5 di-acetoxybenzoic acid) is soluble in polar solvents, such as THF, DCM, DMSO, $CHCL_3$ and DMF. However, by the modification of the end groups of hyperbranched co-polymers with a long chain compound allows them to be soluble in a solvent with low polarity such as toluene, ethyl acetate or even hexane. Therefore, it was interested to modify the obtained functional polymers with a long chain compounds to solubilise them low polar solvents.

Commercially available palmitoyl chloride was selected to be incorporated in the previously synthesised functionalised co-polymers. The general modification method was used, followed by the purification process described earlier. ^1H NMR indicated that the modification of the end groups with palmitoyl chloride was carried out successfully. A single peak was observed at 0.85 ppm, corresponding to three protons of the newly added methyl group. In addition, three peaks were observed at 2.60 ppm, 1.60 ppm and 1.20 ppm, corresponding to 28 protons in the methylene groups (see **Figure 5.10**)

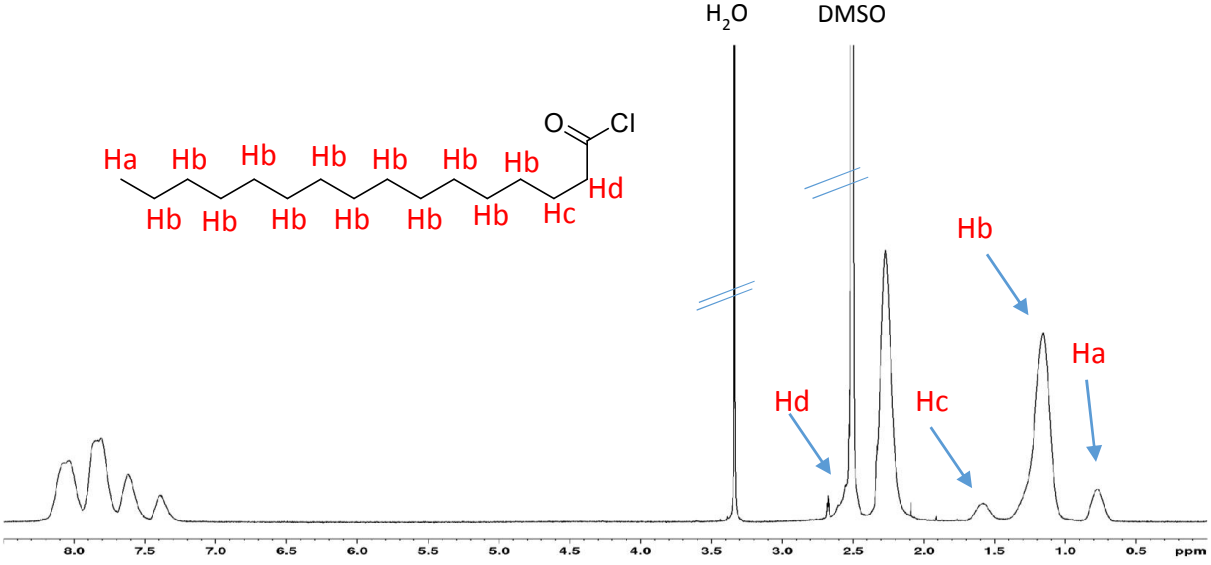


Figure.5.10. ^1H NMR spectrum of the resulted polymer of post synthetic reaction with mono-hydroxyl functionalised hyperbranched co-polymer with palmitoyl chloride (24) in DMSO.

Starting polymers	Mn and PDI before modification	Mn and PDI after modification	Level of incorporation
AB_2+4-hydroxybenzoic acid	4000(3)	18900(2.4)	10%
AB_2+4-aminobenzoic acid	4700(2.7)	18000(2.4)	12%
AB_2+3,5-dihydroxybenzoic acid	5900(3)	13000(2.6)	10%
AB_2+3,5-diaminobenzoic acid	5000(2.7)	7000(2.4)	6%

Table.5.5. Represents the GPC data for post synthetic reaction with palmitoyl chloride.

A second conformation was obtained from the GPC, which indicated an increase in the molecular weights (see **Table 5.5**). Solubility tests with low polar solvents, such as toluene, 1, 4-dioxane, ethyl acetate and hexane, were carried out to examine the solubility of the polymer before and after the modifications. All the examined hyperbranched co-polymers showed an improvement in their solubility in toluene, 1, 4-dioxane, and ethyl acetate, while they showed no improvement in hexane (see **Table 5.6**).

Polymer type	Toluene	1,4-Dioxane	Ethyl acetate	Hexane
Before Modification	--	--	--	--
After Modification	+++	+++	+++	+--

Table.5.6. Represents the solubility before and after the modification with palmitoyl chloride.

5.3.4 Reaction with carboxylic acids:

After successfully applying the post synthetic methodology to the co-polymerisation of the hydroxyl and amino functional hyperbranched co-polymers with acyl chlorides, the decision was made to conclude the co-polymerisations with carboxylic acid compounds due to the limited availability of acyl chloride compounds in form of some desirable co-monomers such as amino acids. Amino acids are widely used in biological and chemical applications. The direct co-polymerisation of amino acids with AB_2 monomer is impossible due to the sensitivity of these compounds to the aggressive conditions that used in the poly

condensation procedure. However, In order to carry out such a co-polymerisation (with functional hyperbranched co-polymers), the use of a coupling regent, such as DCC, was compulsory. DCC is a widely used coupling reagent in esterification reactions and peptide synthesis.[141] Therefore, reactions were carried out by dissolving 500 mg of each polymer in dry DMF at room temperature. Then, an equivalent amount of Boc-Ala-OH and DCC were added to the reaction mixtures. The reaction mixtures were then left at room temperature for 24 hours to ensure the completion of the reactions. Then, DCM was added to the mixtures. Next, the mixtures were washed many times with distilled water to remove the DMF. Then, a layer of DCM was collected and the remaining traces of water were removed by stirring with magnesium sulphate. After the isolation of the magnesium sulphate, the DCM was removed via rotary evaporation and the polymer was dissolved in THF and then precipitated in cold methanol. The sediment polymer was isolated and collected as a white powder. Finally, fractionation was conducted using a bio-beads column to ensure the purity of the final polymers. ^{1}H NMR indicated that the amino acid was successfully incorporated in the hyperbranched polymers with amino functionality by observing the single peak at 1.40 ppm, corresponding to twelve protons from the methyl and Boc groups. Additionally, a single peak was observed at 4.30, corresponding to the proton from the methane group (see **Figure 5.13** However, the incorporation of the same compound with the hydroxyl functional hyperbranched co-polymers was unsuccessful. The success of the incorporation using the amino functionalised hyperbranched polymers might be due to the presence of the lone pair of electrons on the nitrogen, which enhance the reactivity of the polymer. The presence of DCC enhances the formation of an amide bond between the carboxylic acid and the amine. The mechanism of the amide bond includes the deprotonation of the carboxylic acid of the amino acid by the nitrogen of the DCC to form carboxylate. Then, DCC undergoes a good electrophilic. Therefore, the carbon of the central bond was subjected to a nucleophilic attack by the carboxylate, moving the double bond to the nitrogen to leave the positive charge. After that, the carbon of carbonyl was subjected to a nucleophilic attack by the amine of the polymer to form a tetrahedral intermediate. Finally, the amide bond was formed after the proton transfer and expelling the leaving group. GPC data concurred with ^{1}H NMR data (see **Table 5.7**).

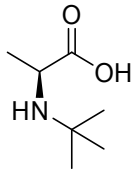
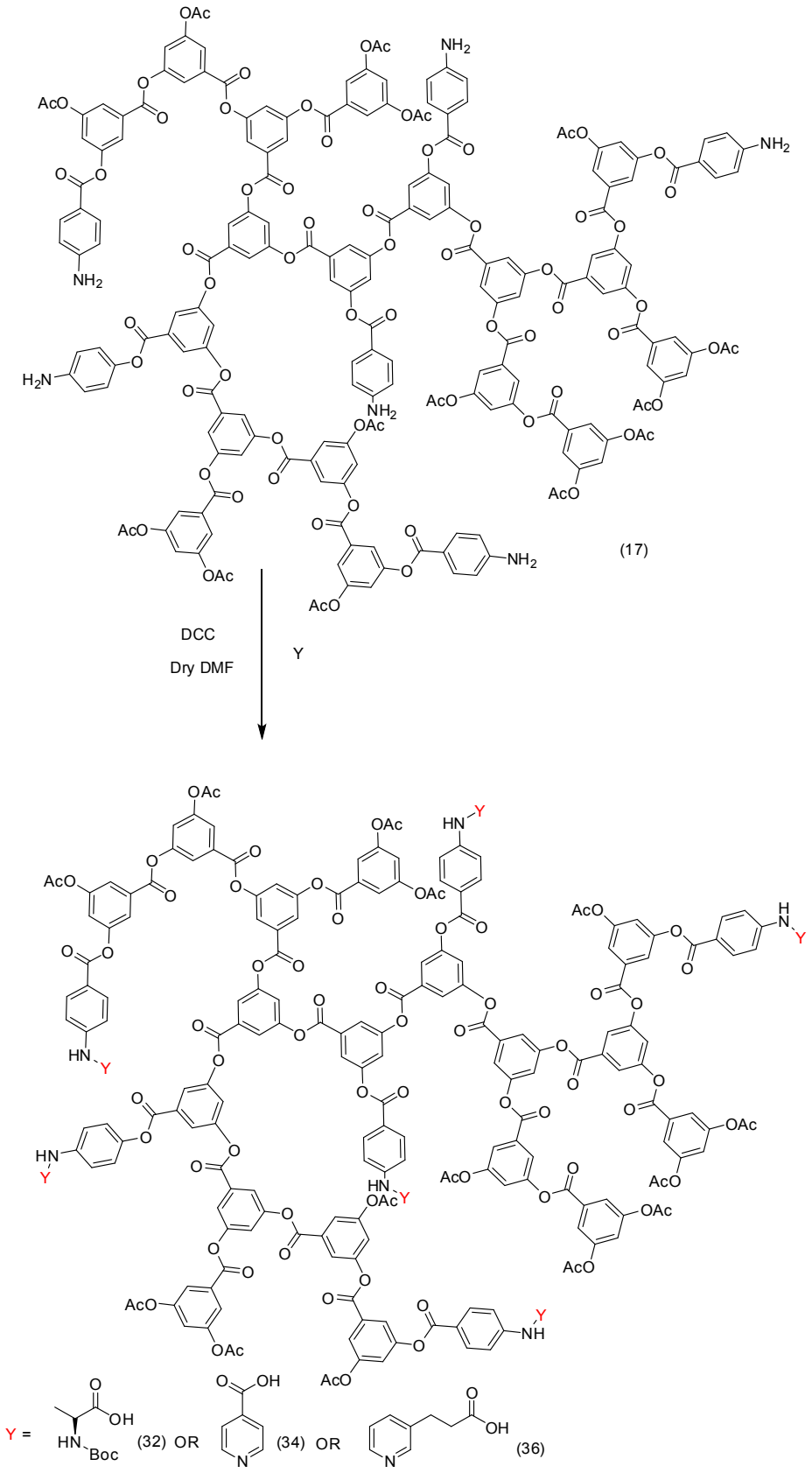


Figure.5.11. Structure of Boc-Ala-OH.

Therefore, due to this interesting finding, a decision was made to include various compounds to be incorporated in the amino functional hyperbranched co-polymers in fixed reaction conditions similar to Boc-Ala-OH. The second compound selected was isonicotinic acid. ^{1}H NMR indicated successful co-polymerisation with matching results to similar co-polymers that were prepared by the use of isonicotinic acid chloride. Finally, 3-pyridinepropionic acid was selected to undergo incorporation in amino functionalised hyperbranched co-polymers. ^{1}H NMR indicated the success of the co-polymerisation by observing two peaks at 8.50 ppm, corresponding to the alpha protons on the nitrogen of the pyridyl ester group (**Figure 5.14**) GPC also indicated the success of the incorporation (see **Table 5.7**).

Starting polymers	Boc-Ala-OH	Isonicotinic acid	3-Pyridinepropionic acid
AB_2+4-hydroxybenzoic acid	--	--	--
AB_2+4-aminobenzoic acid	15700 (3.1)	16600 (2.9)	13000 (2.7)
AB_2+3,5-dihydroxybenzoic acid	--	--	--
AB_2+3,5-diaminobenzoic acid	13300 (2.7)	14900 (2.1)	8000 (1.7)

Table.5.7. GPC data for post synthetic reaction of amino functionalised hyperbanched co-polymers with various compounds using DCC.



Scheme.5.5. Post synthetic reaction of mono-amino hyperbranched co-polymer with various compounds using DCC.

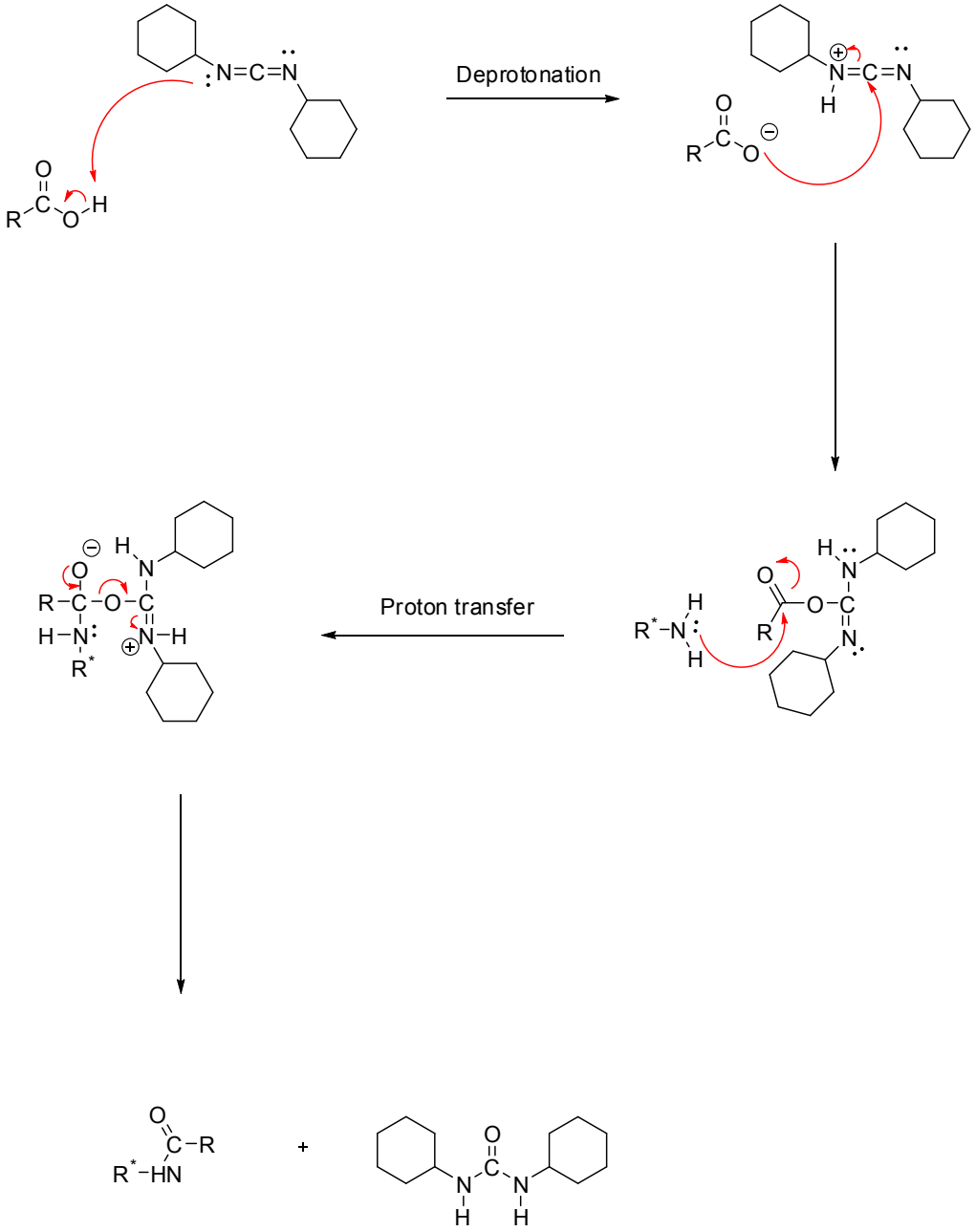


Figure.5.12. General Mechanism of forming amide bond.

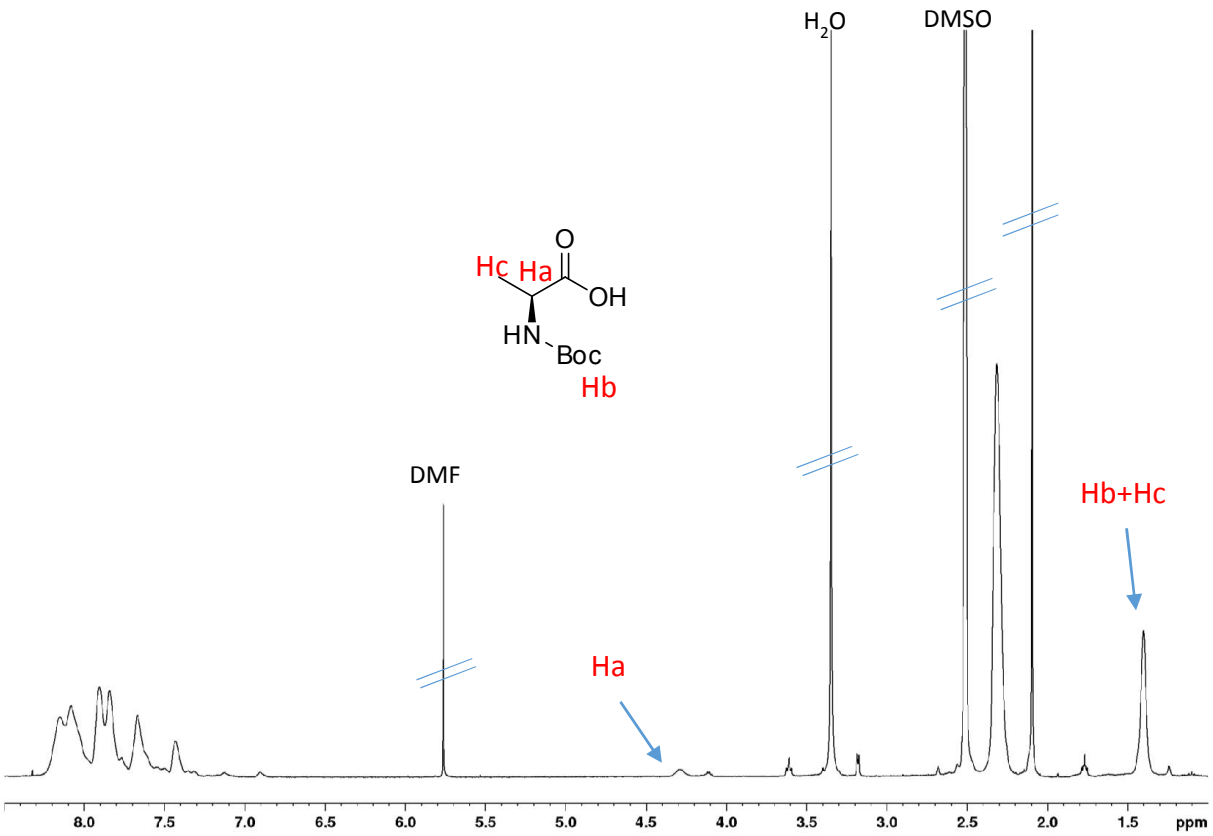


Figure.5.13. ^{1}H NMR spectrum of the resulted polymer of post synthetic reaction with mono-amino functionalised hyperbranched co-polymer with Boc-Ala-OH (23) in DMSO.

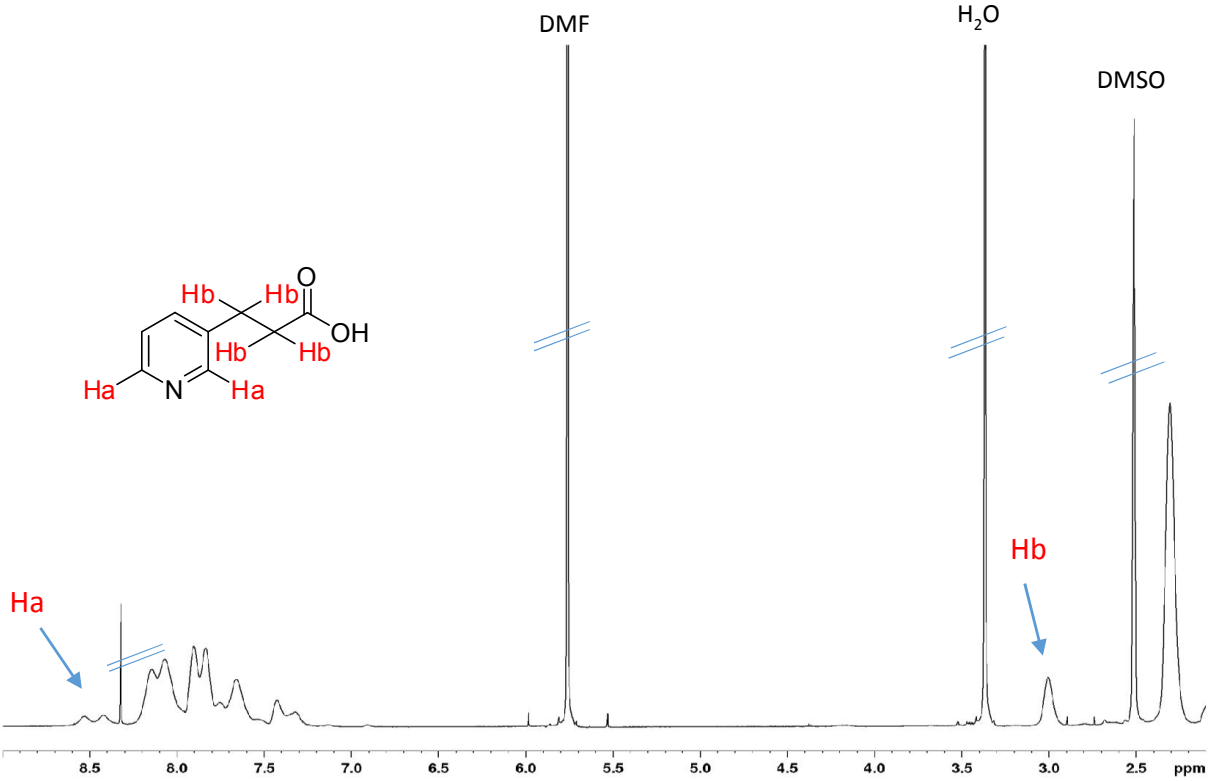


Figure.5.14. ^{1}H NMR spectrum of the resulted polymer of post synthetic reaction with mono-amino functionalised hyperbranched co-polymer with 3-Pyridinepropionic acid (36) in DMSO.

5.4 Conclusion:

The data presented in this chapter indicates that post synthetic methodology is a promising tool that can be used to create a wide range of functionalised hyperbranched polymers. The co-polymerisation of the AB_2 monomer with the hydroxyl functional co-monomer was successfully performed, and a maximum limit of incorporation was achieved, with a 20% molar ratio being obtained. The modification of hydroxy-functional co-polymers has various positive outcomes, including improving the molecular weight of the co-polymer obtained and making it possible to include a variety of sensitive functional unites (acyl chloride) in the process In the case of the modification of the di-functional hydroxyl co-polymer, the loadings were roughly equivalent to those of the co-polymers with mono-functionality, but the degree of branching was higher. The loading of amine functionalised co-polymers was half that of hydroxyl functionalised co-polymers due to the solubility issues that arose during the work. However, due to improvement in molecular weight and including several sensitive functional unites (acyl chloride) in the process, the results were similar to those obtained from hydroxyl functionalised hyperbanched polymers and were also promising. In addition, amino acids and other carboxylic acid compounds were successfully incorporated in amine functionalised hyperbranched polymers by using a coupling agent such as DCC. To conclude, post synthetic methodology is an advanced technique that can be used to increase the uses of hyperbranched co-polymers, improving their synthesis and physical properties.

Future development of this work may include increasing the level of incorporation and the molecular weight of amine functionalised hyperbranched co-polymers by the co-polymerisation of an AB_2 monomer with 4-(amino methyl) benzoic acid. Co-polymerisation with such a monomer will help to increase conductivity, and therefore, the molecular weight may also increase. For hydroxyl functionalised co-polymers, it is worth examining various coupling agents in order to include a carboxylic acids monomer in the co-polymerisation using post synthetic methodology.

Chapter Six

Functionalised hyperbranched co-polymer as a catalytic group

Chapter Six – Functionalised hyperbranched co-polymer as a catalytic group

6.1 Introduction:

The application of dendritic polymers as catalyst supports has received a great deal of attention, as they possess three dimensional branched globular structures. These macromolecular structures possess many specific properties in comparison with traditional catalyst support. Classically, the concept of a catalyst is associated with attempting to increase the rate of a particular reaction. However, catalysts may fulfil one (or more) of a large number of purposes. Catalysts may allow a reaction to take place in an environmentally friendly solvent, such as water, or help one to occur at a lower temperature or pressure. However, nowadays, catalysts may possess other important features, such as selectivity and recoverability.[142-144]There are two main classes of polymer supported catalysts, heterogeneous and homogenous.[145] Heterogeneous catalysts are not soluble in the reaction phase, whereas homogenous catalysts are soluble in the reaction phase.[146] Both types of catalysts have advantageous qualities that make them suitable for different applications.[147] In terms of catalytic activity, homogenous catalysts possess more catalytic activity than heterogeneous catalysts.[148] However, the main advantages of heterogeneous catalysts are ease of recovery and re-usability.[147] This is due to them being insoluble material in a solution based reaction, which allows easy removal from the reaction mixture simply by using filtration. This offers a simple purification process that increases the potential for re-usability. This property is also one of the main drawbacks associated with homogenous catalysts. Their solubility in the reaction mixture reduces the possibility of their precipitation in the reaction. Therefore, the purification process becomes more complicated than simple filtration. Thus, in order to benefit from the catalytic activity of a homogenous catalyst, it is necessary to find a synthetic method to separate and recover this type of catalyst from the reaction mixture. However, careful consideration should be given to this. There is a possibility of separation and recovery of the homogenous catalyst by distillation if the final product is volatile; otherwise more steps are needed. Polymer support catalysts were initially developed as a possible tool in homogenous catalyst separation and recovery.[149] Polymers have been used for catalyst support since the 1960s, with much work initially focusing on producing recoverable catalysts that can be used many times. [150] Due to

the potential benefits associated with recovery and re-usability of the catalyst in both economic and environmental fields, research work on polymer supported catalysts has occurred in both scientific and industrial laboratories. However, this interest in polymers increased following the emergence of dendritic polymers. Dendrimers as a soluble catalyst support have attracted much attention due to their ability to control the exact structure of the catalyst, including the number of catalytic units per molecule in addition to the location and environment in which they are located within the dendritic structure. Recovery is one of the most interesting features of dendrimers. The dendritic globular structure is very well suited to membrane filtration and other separation techniques, such as precipitation followed by simple filtration. Another important feature of dendrimers as a catalyst support is their ability to solubilise a hydrophobic catalyst within the dendritic structure and enhance the reactivity of the catalyst and control the microenvironment around the catalytic site. The location of the catalyst within the dendritic structure plays a key role in determining those features. Catalytic groups can be incorporated at the core or the surface of the dendrimer or encapsulated inside it. When catalytic groups are at the core of the dendrimer, the microenvironment around the catalyst will be different from that of a bulk solution. Since the construction of dendrimers varies, with different sizes and functional groups that have a different space structure and electronic effects, the steric and the electronic properties around the catalytic centre can also be controlled. This successful use of this feature of dendrimers has been reported in catalysts, shape selectivity, and recognition.[142-144, 151] When catalytic groups are attached to the periphery of the dendrimer, the loading capacity is high. Furthermore, the number of terminal catalytic groups can be controlled due to the nature of generation of the dendrimer. Catalytic ability can be improved through the cooperation of proximal units, and this is known as a positive dendritic effect. When catalytic groups are encapsulated inside the dendrimer, the specific space structure of the dendrimer makes it an effective porous stabilizer.[53,151]

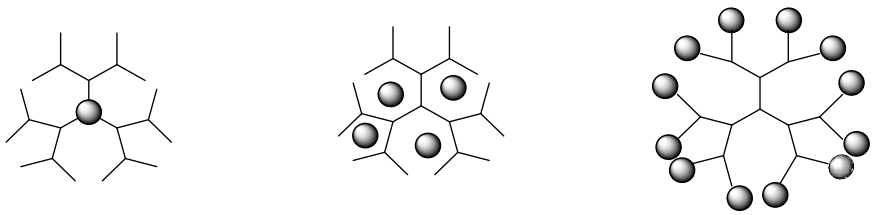


Figure.6.1. The possible locations of catalytic groups within the dendritic structure.

Alongside the extensive literature reporting on as a catalyst support, there has been much interest in the use of hyperbranched polymers. This is due to the time and cost problems associated with the synthesis and purification of dendrimers, which affect the commercial viability of large scale reactions, and recent developments in the synthesis of hyperbranched polymers and their properties. In addition to this, hyperbranched polymers may be suitable candidates for some applications due to their structural similarity to enzymes. This is because of their ability to encapsulate and protect as well as to control the reactant concentrations, which is useful for reactions that require a low substrate concentration or to prevent the product from reacting further with unwanted side reactions. However, a small number of reports in the literature discuss hyperbranched polymers as a catalyst support.[54,55] Most of those reports focus on core functionalised hyperbranched polymer catalyst support.[53] Pervious work by the Twyman group indicated that iron functionalised porphyrin cored hyperbranched polymers were an excellent catalyst for alkene epoxidation reactions.[55] This work was carried out using hyperbranched polymers as a catalyst for the epoxidation of 1-octene using iodosylbenzene as an oxygen donor. The site isolation property was studied by the fractionation of the previously mentioned hyperbranched polymers to three different molecular weights between 5000 Da and 16,000 Da corresponding to the second, third and fourth pseudo-generation dendrimers. In all experiments, the yield of the product was higher than that obtained using the porphyrin core molecule. In addition, the efficiency was increased as a result of increasing the molecular weight, proving a positive dendritic effect due to the electronic environment.

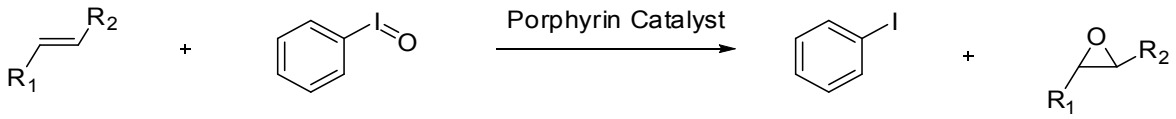


Figure.6.2. An alkene epoxidation reaction.

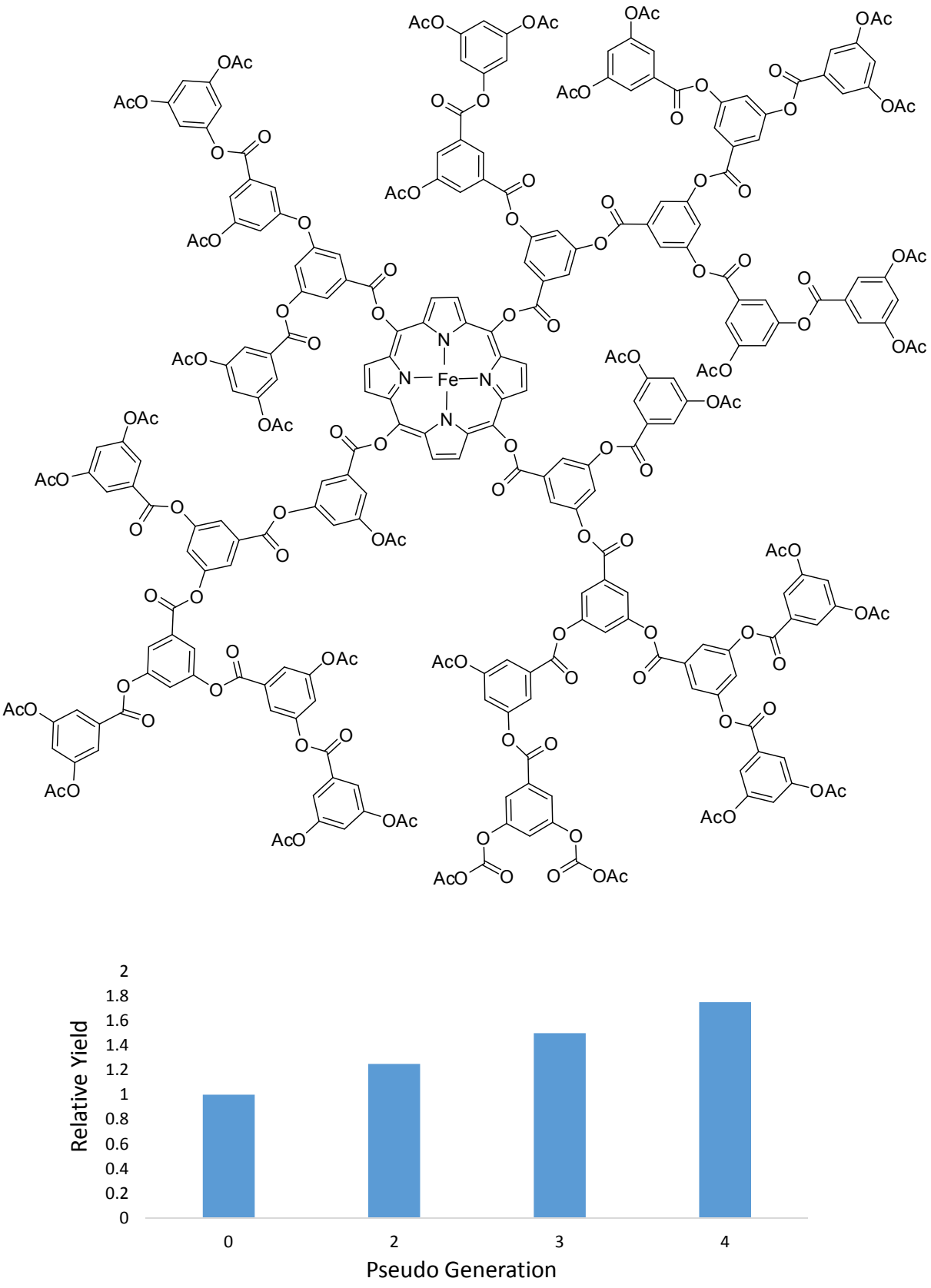


Figure.6.3. Schematic representation of iron functionalised TAPP cored hyperbranched polymer (above), representation of the yield of epoxidation reaction of 1-octene using the pseudo-generation hyperbanched polymer catalyst.[55]

Another example of utilizing hyperbranched polymers as a catalyst was described by the Tywman group.[152] Multi porphyrins containing hyperbranched poly (aryl ester) were successfully synthesised with the aim of binding two reactive species and catalysing a reaction between them. The hyperbranched system was tested using esterification between an alcohol and an activated ester. The reaction proceeded with a significant increase in the rate of reaction when using just 5mol % of the prepared polymer. This increase in the rate of the reaction was due to the increased local concentrations caused by the natural flexibility of the system as both regents bind in close proximity to each other, which allowed the product to be released and more starting material to bind.

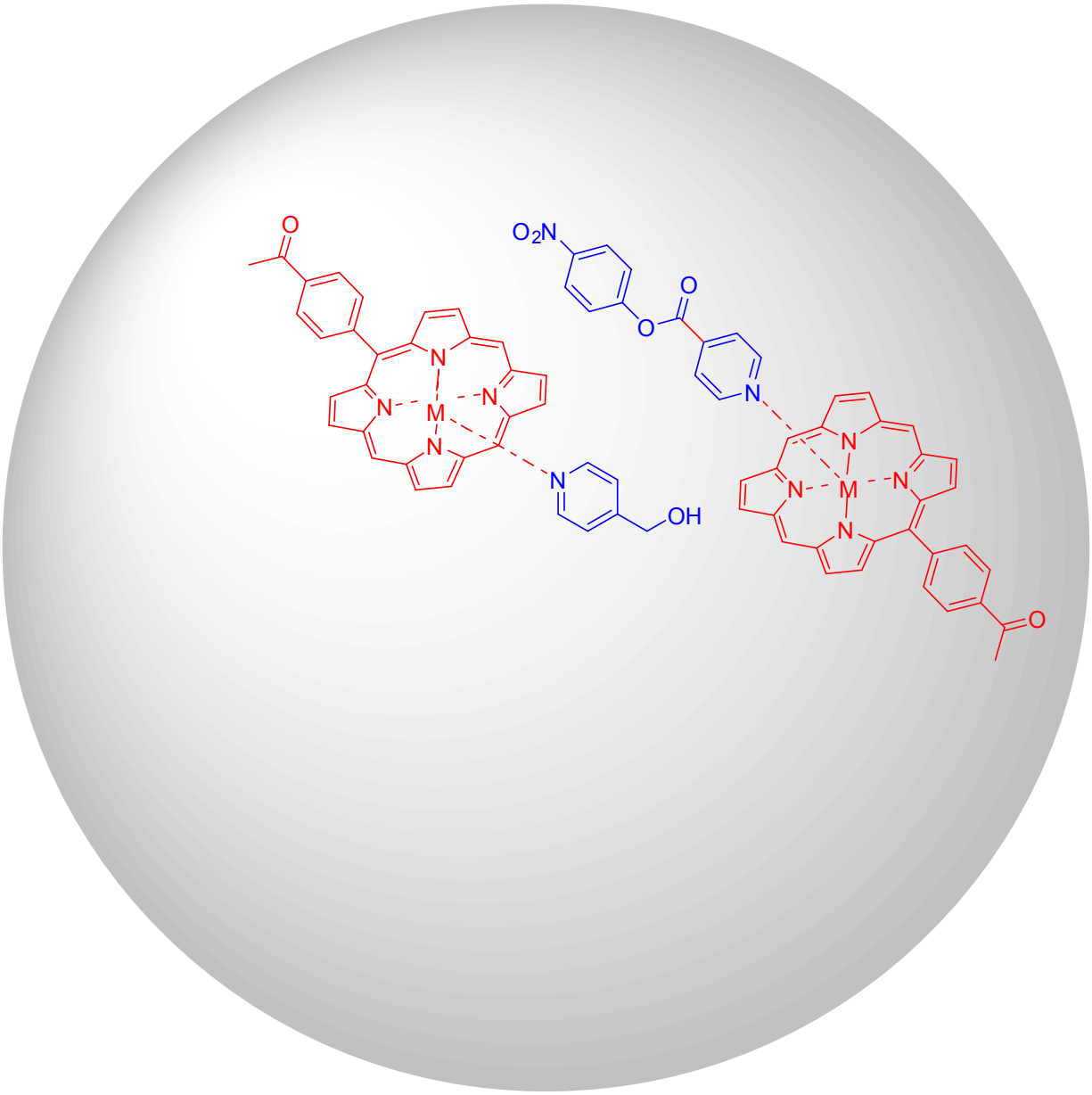


Figure.6.4. Schematic representation of the reaction of alcohol and activated ester inside hyperbranched polymers.[152]

As a result of much successful work that utilized catalytic core functionalized hyperbranched polymers, the benefits of using these systems for high loaded catalytic sites, which could be easily obtained via the synthesis of catalytic interior functionalised hyperbranched polymers, has become very clear. This could be achieved after the supported investigation into the ability of hyperbranched polymers to maintain their dendritic properties after limited co-polymerisation with co-monomers. High loaded catalytic support hyperbranched polymers attracted our interest because of their potential application as catalyst support.

The aim of this chapter is to examine highly loaded interior functionalised hyperbranched polymers as a catalyst support system. This will be carried out by the co-polymerisation of hyperbranched polymers with a 20% molar ratio catalytic co-monomer to obtain maximum loading of catalytic sites to maintain the dendritic properties of the dendritic system. However, the study will include many factors that could affect the ability of hyperbranched polymers to be used as catalyst support, such as the solvation effect and steric hindrance.

6.2 Soluble supported catalysis reaction:

A number of criteria had to be taken into consideration in the synthesis of a soluble catalyst support system. The first consideration was the type of monomer used to prepare the hyperbranched system. In order to meet the outlined project aims, the hyperbranched polymer must be derived from an AB_2 monomer. In addition, the polymer scaffold needs to be chemically and physically stable under the reaction conditions. Another consideration is the ease of functionalisation of the polymeric system during polymer synthesis. Bearing all the above in mind, a hyperbranched polyarylester was chosen for this research. Previous work with this polymer has shown that it is stable in aggressive, synthetic conditions and has good solubility in common solvents in addition to its ease of modification.

Pyridine was chosen as the catalyst to be incorporated within the hyperbranched polymer as it is widely used as a base catalyst in many chemical reactions.[139,140] The chemical properties of pyridine are affected by the lone pair of electrons on nitrogen, which cause the activity of pyridine. Therefore, in order to achieve the desired incorporation of the hyperbranched polymers, pyridine derivatives with a functional group (carboxylic acid) needed to be incorporated into the hyperbranched polymer structure. Two pyridine derivatives, known as nicotinic and isonicotinic acids, were commercially available at a reasonable cost so were suitable for use in the ongoing study. However, nicotinic acid was chosen to avoid the conjugation effect that may have been caused by isonicotinic acid.

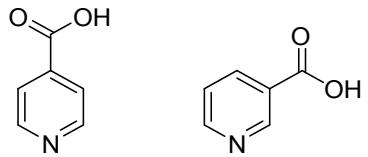


Figure.6.5. Scheme showing the derivatives of pyridine.

To examine the potential of highly loaded hyperbranched polymers as a catalyst support system, an appropriate reaction was selected.[153,154] The reaction selected involved pyridine forming an intermediate with an alkyne group, which can then react with aldehyde. The intermediate can then break down to release the pyridine catalyst and the product. This reaction was adapted from work carried out by Nair et al.[153,154]

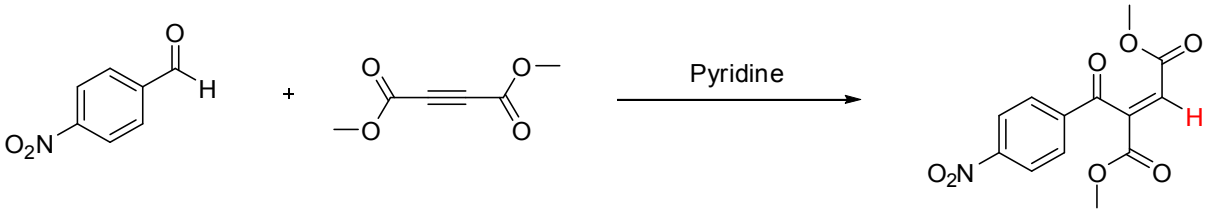


Figure.6.6. Synthesis of 2-(4-Nitro-benzoyl)-but-2-enedioic acid dimethyl ester.

However, there were a number of considerations when choosing this reaction. The first consideration was the involvement of pyridine as a catalyst in the reaction. In addition, the formation of a cyclic intermediate between pyridine and alkyne could enable us to investigate the possibility of using hyperbranched polymers as a catalytic support system. The success of involving a pyridine incorporated hyperbranched co-polymer in this reaction demonstrated the likelihood of obtaining similarly successful results when applying the same idea to a wide range of reactions and catalysts for various applications. The other consideration was the accuracy of monitoring the rate of the reaction. In order to examine the catalytic activity, the rate of reaction must be monitored accurately. The presence of the aldehyde peak would allow monitoring the rate of reaction and calculate the yield easily via ^{1}H NMR spectroscopy, as will be explained shortly. Two mechanisms for the outlined reaction were proposed and described by Nair et al.[153,154] In those two mechanisms, a pyridine catalysis was the starting material used to form the final desirable product. In both mechanisms, a pyridine catalyst will perform a nucleophilic attack on the alkyne followed by a nucleophilic attack of the intermediate on the aldehyde. The intermediate will then be broken down by proton transfer via either a cyclic or linear transition state process.

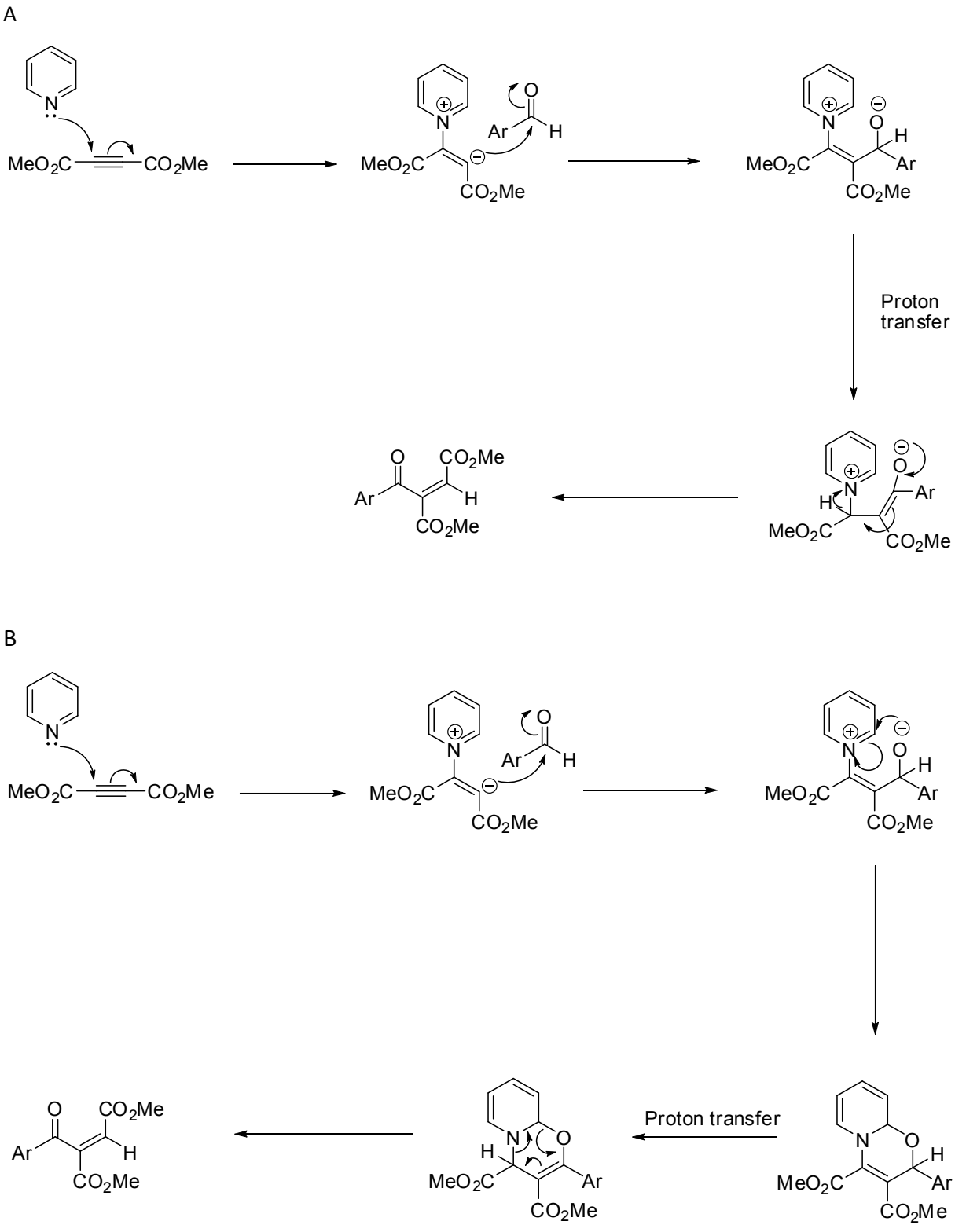


Figure.6.7. Two proposed reaction mechanisms for the catalysed reaction.[153,154]

6.2.1 Co-polymerisation of 3, 5-diacetoxybenzoic acid with nicotinic acid:

Initially, the co-polymerisation of 3, 5-diacetoxybenzoic acid with nicotinic acid was performed using the general polymerisation method discussed earlier. The ratio of the co-monomer was 20% molar ratio to the main monomer. The polymerisation was carried out in the absence of oxygen and in the presence of diphenyl ether as a solvent. After this, the purification process included dissolving in refluxed THF followed by precipitation in cold methanol. The polymer was then filtered and dried by vacuum. ^{1}H NMR showed that a characteristic polymer peaks at 8.10-7.15 ppm, corresponding to the aromatic protons. A second single peak was observed at 2.35 ppm, corresponding to the acetoxy terminal group. In addition, three peaks were observed at 9.45 ppm, 8.85 ppm and 8.50 ppm, corresponding to three protons in the pyridyl ester group. However, the forth proton of the pyridyl ester group overlapped with the peaks of the dendritic aromatic protons. ^{1}H NMR indicated that the level of incorporation of the co-monomers was 22%. Therefore, the degree of branching was estimated as 38%. GPC showed that a polymer with a molecular weight of 5000 Da with a PDI of 2.7 was obtained. It was noted that the molecular weight of the obtained polymer was below the dense packing. Therefore, it was decided to decrease the molar ratio of the nicotinic acid to 10% in order to increase the molecular weight. The co-polymerisation was repeated in similar conditions to the previous co-polymerisation. ^{1}H NMR indicated that the co-polymerisation was carried out successfully with the same result as the previously prepared polymer and a level of incorporation of 16%, which indicated that the degree of branching was 41%. GPC indicated that the polymer possessed a molecular weight of 14000 Da and a PDI of 3.2. After the successful incorporation of pyridine, the next step was to examine the prepared polymer as a catalyst support system.

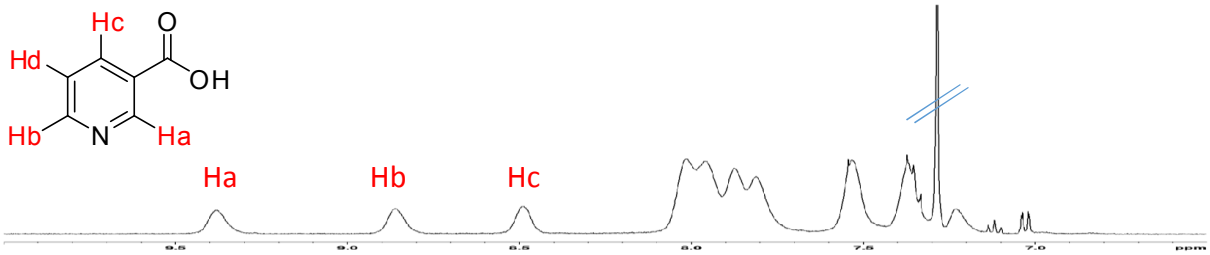
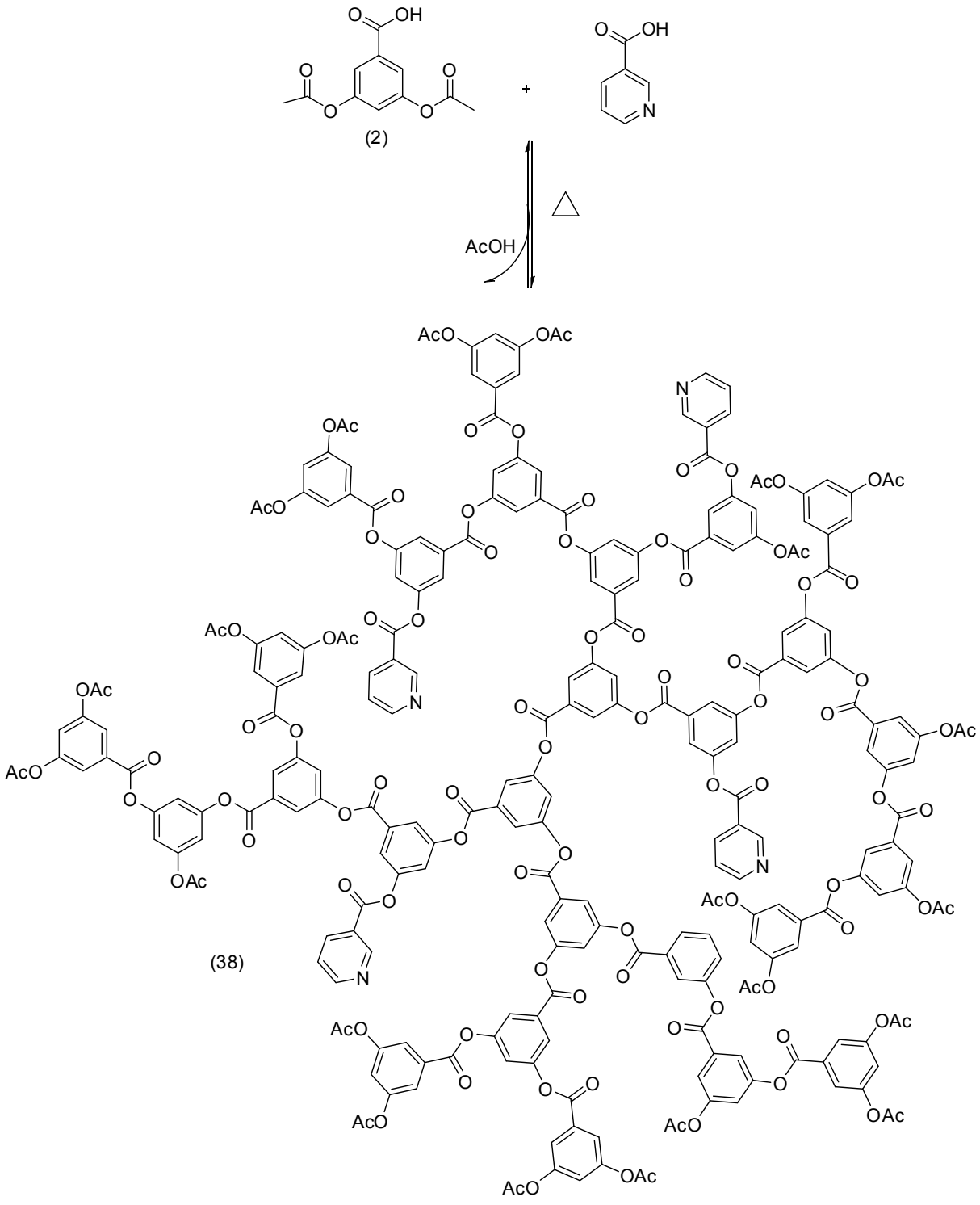
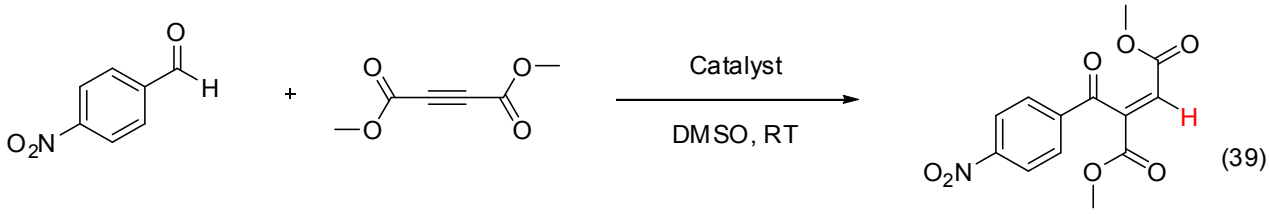


Figure.6.8. ^{1}H NMR spectrum of hyperbranched polymer prepared from 3,5-diacetoxy benzoic acid and nicotinic acid.



Scheme.6.1. Synthesis hyprebanched polymers prepared from 3,5-diacetoxybenzoic acid and nicotinic acid (38).

6.2.2 Reaction of an alkyne with an aromatic aldehyde in the presence of pyridine incorporated hyperbanched co-polymer:



Scheme.6.2. Synthesis of 2-(4-Nitro-benzoyl)-but-2-enedioic acid dimethyl ester (39).

A great deal of groundwork was done in relation to this reaction in order to establish the ideal conditions for its progression. Nair et al. suggested that the reaction could be completed in three hours. However, it was decided that allowing the reaction to stir for a week would give it a good chance to reach full completion. A variety of solvents were examined, but it was found that the reaction would only progress in DMSO, DMF, $CHCl_3$ and DME. However, it was decided to perform the reactions in deuterated solvents to avoid increasing the reaction rate caused by a rise in temperature during the removal of the solvent. Taking this into account, DMF and DME were excluded due to the limited availability of deuterated DMF and the poor solubility of hyperbranched polymers in DME. Therefore, DMSO was selected as a solvent at the starting point of this study.

To synthesise the desirable reaction product 2-(-4-nitro-benzoyl)-but-2-enedioic acid dimethyl ester, an equivalent molar ratio of 4-nitrobenzaldehyde was added to dimethylacetylene dicarboxylate (DMAD) in the presence of deuterated DMSO in a round bottom flask in a nitrogen atmosphere. The reaction was cooled to – 10 ^{0}C. Once the temperature was maintained, hyperbranched co-polymer was added such that total amount of pyridine equal to 20 % (as suggested by Nair et al.). This was calculated utilising the ^{1}H NMR spectra and GPC data. This calculation was carried out easily using the level of incorporation of the pyridine groups in the hyperbranched polymer from ^{1}H NMR and the molecular weight value from GPC. After the addition of the catalyst, it was noticed that the reaction mixture had turned a pinkish colour after the addition of the catalyst, which proved that the reaction had started to take place. The ice bath was removed and the mixture was allowed to return to room temperature. The reaction was left to stir for a week. During the

reaction period, the yield was monitored using ^{1}H NMR spectrometry. The completion of the reaction was achieved after a week, as confirmed by ^{1}H NMR.

^{1}H NMR showed two doublets at 8.40 ppm and 8.30 ppm, corresponding to the aromatic alpha protons in the starting material and product. A doublet was observed at 8.20 ppm, corresponding to the remaining aromatic protons of the starting material; however, the product peak overlapped with the polymeric peaks. A singlet from the alkene proton was observed at 7.11 ppm, and this was used to monitor the rate of the catalysis reaction. Another three singlets were observed between 3.50 ppm and 4.00 ppm, corresponding to the two methyl groups in both the starting material and the product. It was noted that the aromatic doublets of the product had shifted slightly up field and the singlet from the methyl group was split into two peaks. However, the presence of starting material peaks beside the product peaks in the ^{1}H NMR spectrum indicated that the reaction did not achieve 100% completion. Therefore, the yield was simply calculated by the most useful peaks in the aldehyde at 10.20 ppm and the new product peak at 7.15 ppm, which was 5%. The peak of the aldehyde was seen to decrease and the new product peak was seen to increase with time, indicating the decreasing molar concentration of aldehyde and the subsequent molar increase of the product.

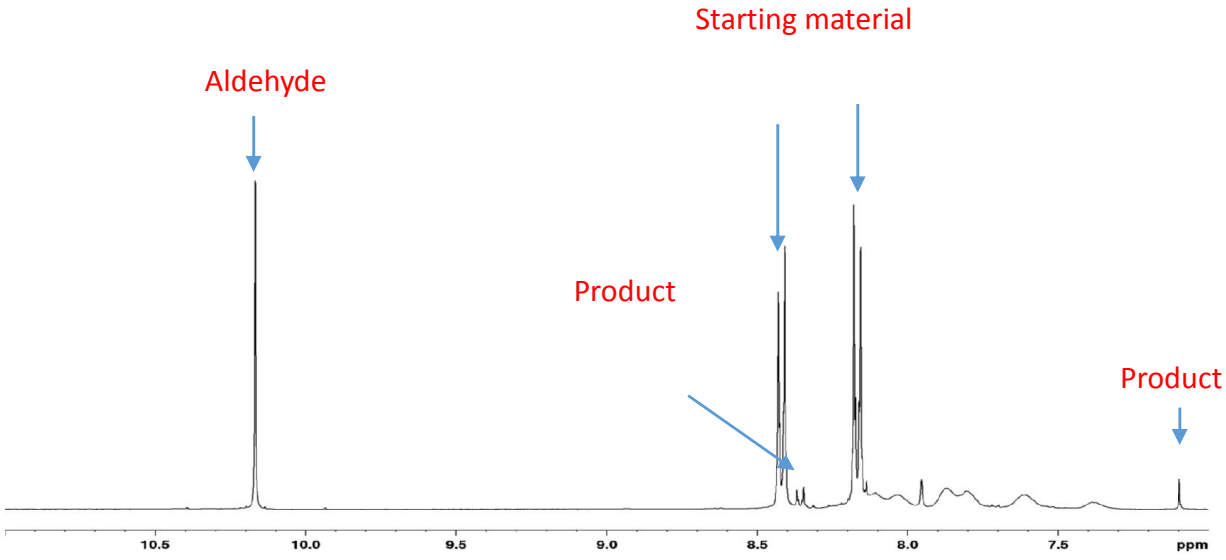


Figure.6.9. ^{1}H NMR spectrum of 2-(4-Nitro-benzoyl)-but-2-enedioic acid dimethyl ester (product) and starting material peaks.

Due to the low yield of the reaction carried out using a pyridine incorporated hyperbranched co-polymer, it was realised that nicotinic acid may not be the best pyridine derivative to be co-polymerised with the hyperbranched polymer. This might be due to the presence of a close electron withdrawing group (ester), which might affect the activity of the catalyst (reduces the nucleophilicity of the pyridine). Therefore, in order to examine the activity of this assigned catalyst, a control reaction was carried out using a pyridine with a substituted electron withdrawing ester group called methyl nicotinic.

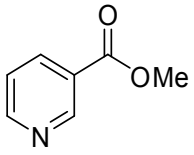


Figure.6.10. Scheme showing the structure of methyl nicotinic.

The reaction of an alkyne with an aromatic aldehyde was performed using methyl nicotinic as a catalyst. Analysis by ^{1}H NMR revealed that the reaction had progressed to 8% completion in three days, just slightly better than the polymer. This implies that factors other than electronic factors cause the slight reduction in catalytic activity shown by the polymer. It is likely that this factor is steric as pyridine on the polymer is somewhat hindered. Although the polymer catalyst appears to be a less efficient one, within the margin of error, the extent of the reaction completion exhibited by the polymer and methyl nicotinic are the same. However, to overcome the problem of the extremely low yield obtained due to the nature of the chosen pyridine derivative, it was proposed that instead of using a nicotinic acid, a monomer with a spacer between the ester link and the pyridine group could be used to eliminate the problem. This spacer would break the conjugation between the polymer backbone and the pyridine group, reducing the effect on the ester linkage when the pyridine unit acts a catalyst.

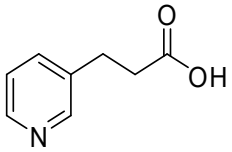


Figure.6.11. The structure of 3- pyridine-propionic acid.

6.2.3 Reaction of an alkyne with an aromatic aldehyde in the presence of picoline:

In order to examine the activity of the second selected co-monomer, it was necessary to conduct a controlled reaction using a similar pyridine derivative called picoline, which is a commercially available compound with similar functionality to the selected co-monomer. The reaction was performed in identical conditions to the previous reactions.

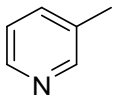


Figure.6.12. Scheme showing the structure of picoline.

The yield of the reaction was calculated by ^{1}H NMR, which indicated that the reaction was completed after three days. The spectrum indicated the appearance of a single peak at 7.11 ppm, which can be attributed to the new proton of the product, and a sharp decrease in the peak at 10.18 ppm, corresponding to the starting material. The reaction was completed after three days, with a yield of 90%, as can be seen in the figure below.

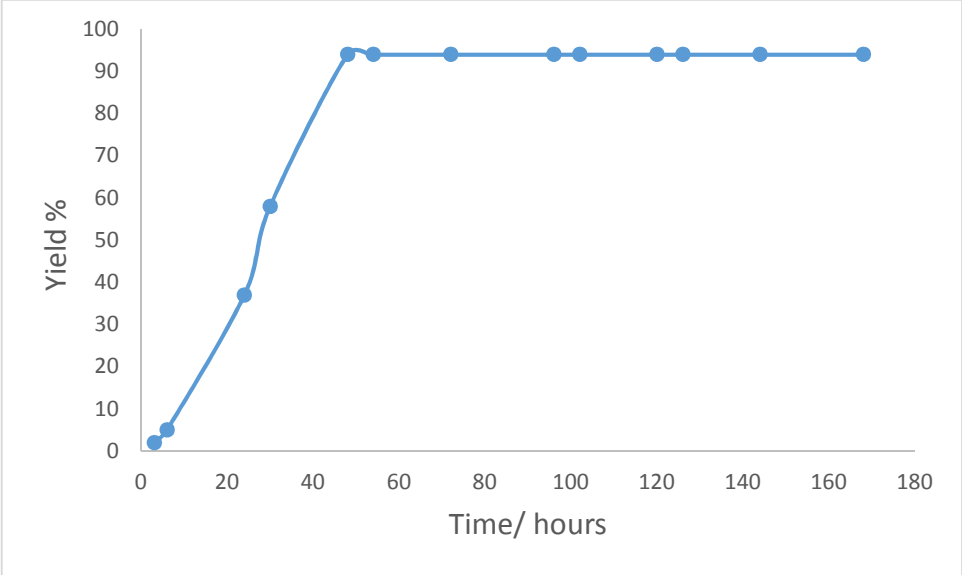


Figure.6.13. Reaction between DMAD and 4-nitrobenzaldhyde in the presence of picoline**.**

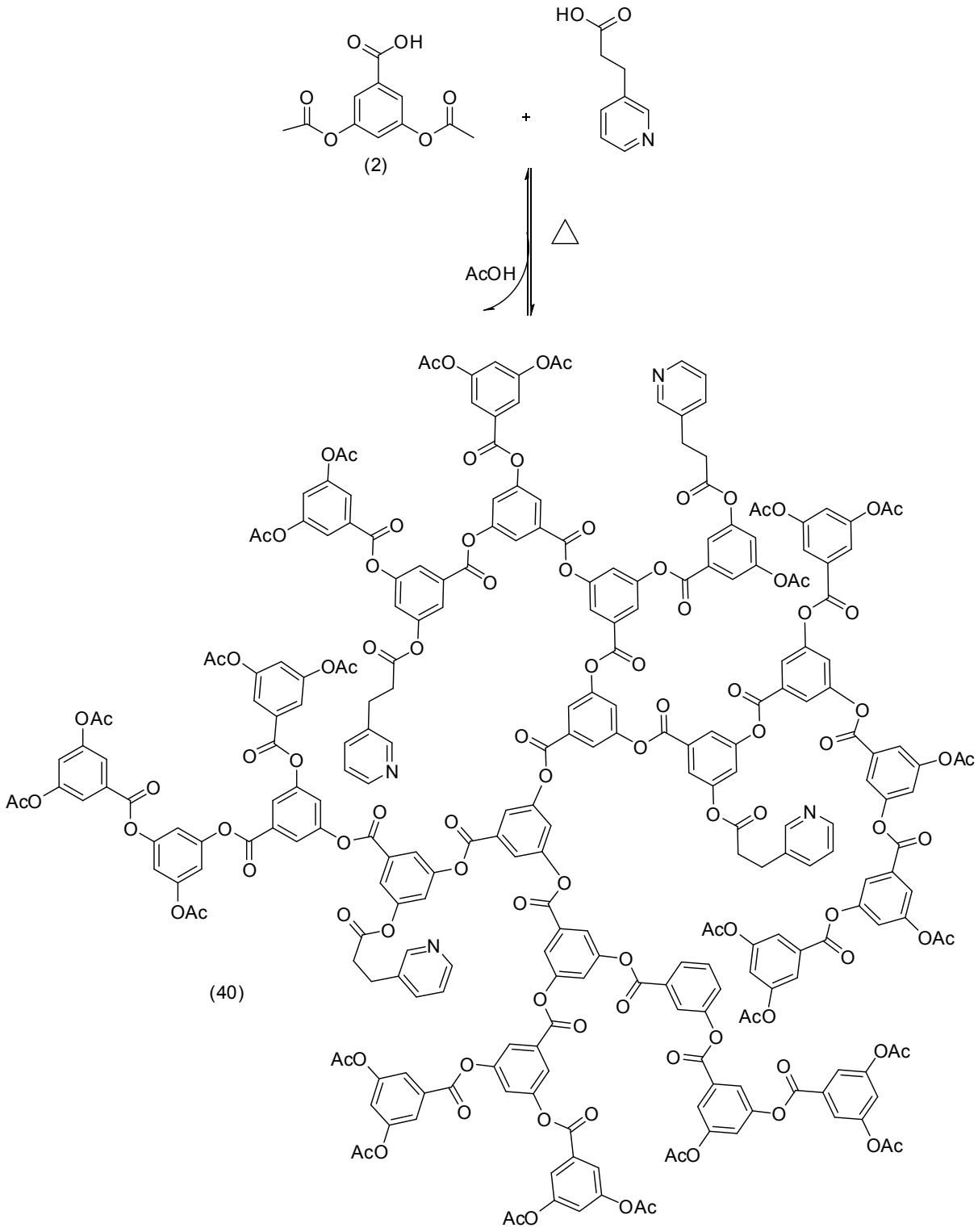
The high yield achieved using picoline supported the choice of 3-pyridinepropionic acid as the second co-monomer. The next step was the incorporation of pyridine within the hyperbranched polymer reaction 3, 5-diacetoxybenzoic acid with 3-pyridinepropionic acid.

6.2.4 Co-polymerisation of 3, 5-diacetoxybenzoic acid with 3-pyridine - propionic acid:

3, 5-Diacetoxybenzoic acid was co-polymerised with various molar ratios of the selected co-monomer 3-pyridinepropionic acid using the general polymerisation method described in this thesis. The selected molar ratios of 3-pyridinepropionic acid were 5%, 10% and 20%. The synthesised polymers showed all the characteristic peaks associated with hyperbranched poly (3, 5-diacetoxybenzoic acid). The incorporation of 3-pyridinepropionic acid was confirmed by a broad peak at 3.10 ppm, corresponding to four protons from the linkers CH_2, and two broad peaks at 8.50 ppm, corresponding to the protons on the carbon adjacent to the nitrogen. GPC indicated that polymers with various molecular weights and polydispersity indexes were obtained, as can be seen in the table below.

Sample ID	Starting conc. of co-monomer	Level of incorporation	DB	Mn	PDI	Number of pyridine
MAS 41	5%	10%	44%	10000	1.7	6
MAS 40	10%	20%	38%	4400	3.7	4
MAS 20	20%	25%	35%	2100	3	3

Table.6.1. GPC data for the series of hyperbranched co-polymers using different molar ratio of 3-pyridinepropionic acid.



Scheme.6.3. Synthesis hyprebanched polymers prepared from 3, 5-diacetoxybenzoic acid and 3-pyridinepropionic acid (40).

6.2.5 Reaction of an alkyne with an aromatic aldehyde in the presence of pyridine incorporated hyperbanched co-polymer (MAS 41):

In order to continue the investigation into the ability of hyperbranched polymers to act as a catalyst system support, the polymer identified MAS 41 was selected to catalyse the alkyne with aldehyde reaction due to its relatively high molecular weight, which is above the dense packing limit. The reaction method followed the same procedure as the previous reactions. The reaction was catalysed by a 20% molar ratio of pyridine, and this was calculated from ^{1}H NMR and the GPC data on the polymer. The reaction was left to stir for a week. During the reaction period, the yield was monitored by ^{1}H NMR spectrometry. The reaction was completed after a week, as confirmed by ^{1}H NMR.

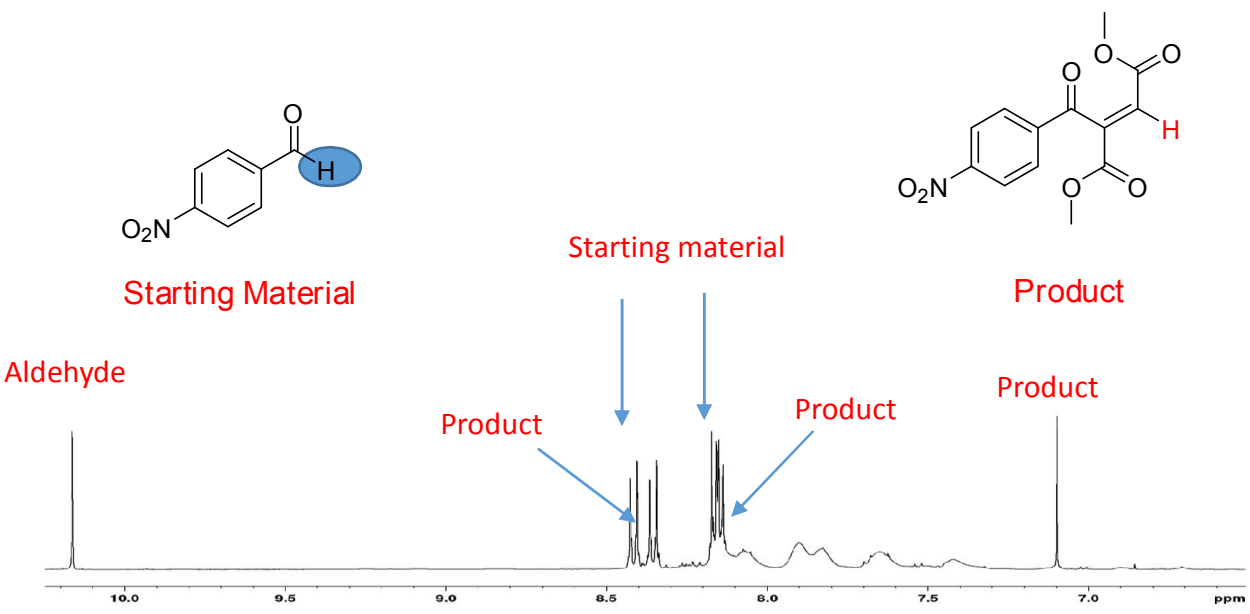


Figure.6.14. ^{1}H NMR spectrum of 2-(4-Nitro-benzoyl)-but-2-enedioic acid dimethyl ester (39) (product) and starting material peaks using pyridine incorporated hyperrbanched polymer (40).

After five days, the ^{1}H NMR spectrum indicated that the ratio between the product peak and the starting material peak was 1:0.5, which meant that the reaction had proceeded to 50% completion. This yield was constant up to the seventh day, which meant the reaction was terminated.

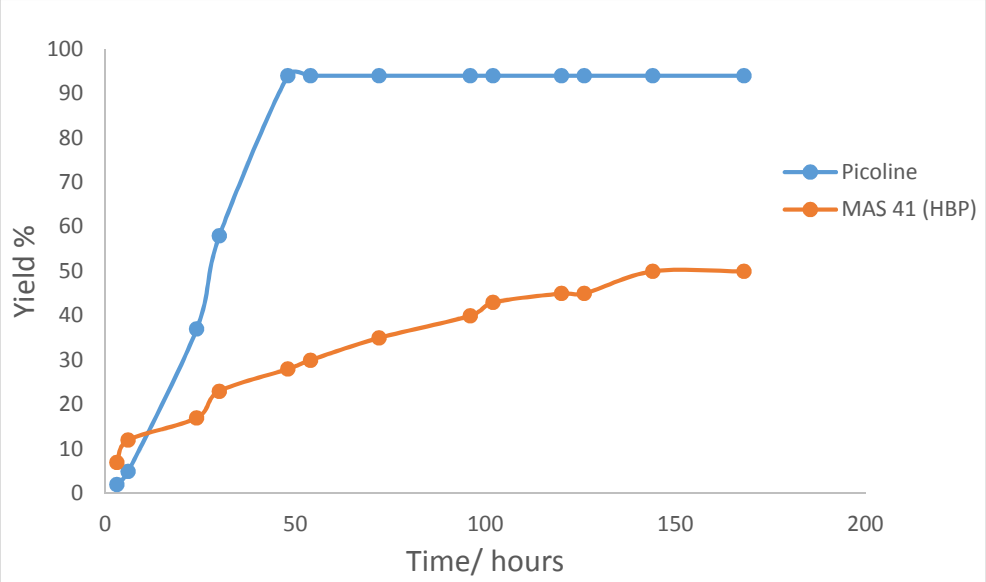


Figure.6.15. Reaction between DMAD and 4-nitrobenzaldhyde in the presence of picoline and pyridine incorporated hyperbanched polymer (40).

The hyperbranched polymers proved their ability to act as a catalytic system support, but their catalytic activity was not as good as the efficiency exhibited by the control reaction using pyridine. The reduction in the catalytic activity shown by the polymer was due to steric factor as pyridines were within the polymer structure.

In terms of recovery and re-usability, it was not possible to remove the DMSO solvent as the high temperature required will affect the final product. Therefore, the reaction was repeated using DMF as the solvent. After completion of the reaction, the polymer was successfully recovered from the reaction mixture with a good yield of 90%. This was simply achieved via the precipitation of the polymer in cold methanol. Subsequently, the polymer was filtered and washed with methanol. The recovered polymer was analysed by ^{1}H NMR and GPC. Analysis by GPC indicated that the polymer possesses the same molecular weight and PDI. ^{1}H NMR revealed that the polymer was recovered successfully. However, the spectrum indicated that the incorporation of pyridine was significantly reduced as there was a decrease in the ratio of incorporated pyridine to 33% (2 out of 6). This suggested that pyridine can be cleaved during the reaction or the purification. Due to the high level of impurities in the polymer and the decrease in pyridine groups, the decision was taken not to carry out a second reaction using the recovered polymer.

6.3 The effect of the Solvent:

Another factor affecting the reaction rate is solvent.[155] The reaction rate is directly affected by the solvent polarity. However, this effect is based on the nature of the reaction intermediate. If the reaction forms a charged intermediate, increasing the polarity of the solvent will increase the rate of the reaction by stabilizing the charge species and lowering the activation energy of the transition state. However, if the charge is neutralized during the reaction, increasing the polarity of the solvent will have less of an effect on the rate of the reaction.[155]

Hyperbranched polymers occupy a relatively large space in solution when compared with smaller molecules. They can be considered as a separate nanospace capable of dissolving small molecules within themselves (electronic effect). As the catalyst was placed within the dendritic structure of the hyperbranched polymer, any catalytic reaction also takes place within the polymer, which provide a different environment to the bulk solution. Therefore, changing the bulk solvent should not affect the environment inside hyperbranched polymers and, therefore, have no effect on the reaction rate. Thus, to examine the solvent dependency of hyperbranched polymers, an experiment comparing the alkyne and aldehyde reaction was carried out in two different solvents in identical conditions. Deuterated DMSO and $CHCl_3$ were selected as the reaction solvents. Those two solvents were selected due to their difference in polarity. The first phase of the experiment was called the controlled reactions phase. The aim of this phase was to perform the reaction in the two selected solvents using picoline as a catalyst. The second phase was the polymer reaction phase. This phase aimed to repeat both experiments using a pyridine incorporated hyperbanched co-polymer. In the controlled reactions phase, both reactions were completed in three days. However, the yield of the reaction performed in DMSO was 94%, whereas the yield using chloroform was 62%. This confirms the effect of the solvent on catalytic activity. The different yield of the two reactions was due to the intermediate being more stable in DMSO than in chloroform because of the high polarity of the DMSO. The positive charge of the intermediate is more stabilized in DMSO than in chloroform, leading to an improvement in the yield of the reaction performed in DMSO.

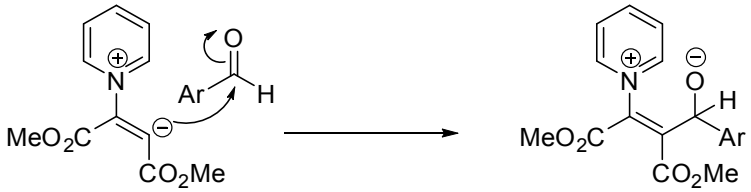


Figure.6.16. Scheme showing the substrate of the reaction.

In the polymer reaction phase, both experiments were completed within a week. However, the yield of the reaction that was performed in DMSO was 50%, whereas the yield when using chloroform was a mere 5%. This indicates that the reaction in chloroform is more than ten times more effective (decreased form 66% to 5%) when using picoline rather than a hyperbranched polymer as a catalyst. Alternatively, we can describe the result by stating that the polymer is effect (inhibit) the reaction in $CHCl_3$. In the case of using DMSO as a solvent, the reaction when using picoline is twice as effective when using the same polymer (decreased from 94% to 50%) (See **Figure 6.17**).

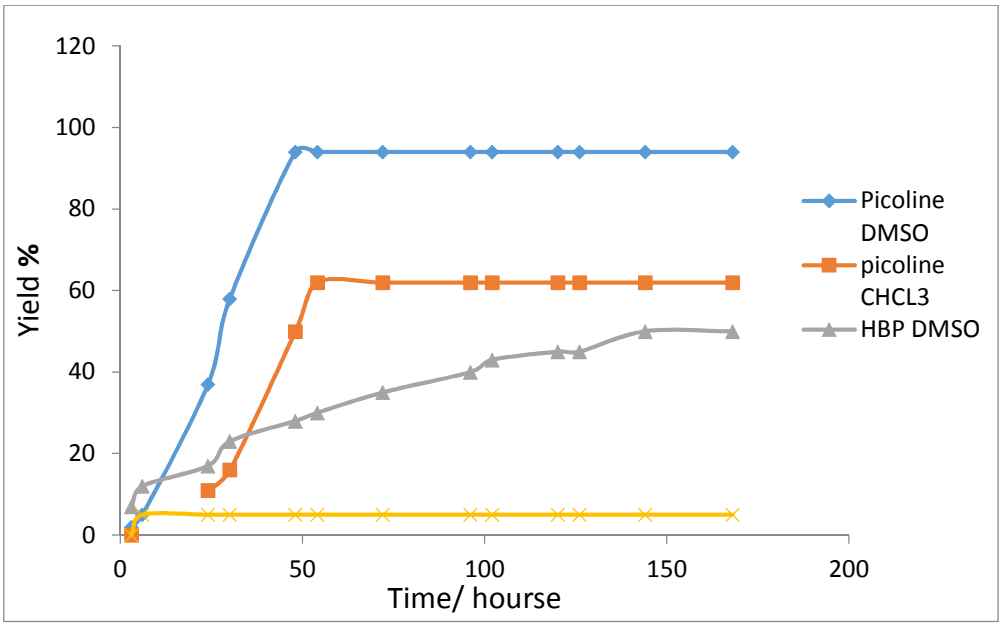


Figure.6.17. Reaction between DMAD and 4-nitrobenzaldhyde in the presence of picoline and pyridine incorporated hyperbanched polymer in DMSO and $CHCl_3$.

As a hyperbranched polymer possesses a different nanospace to the bulk solvent, the reaction rate catalysed by a hyperbranched polymer catalyst will be different to the reaction rate catalysed by picoline due to the presence of two different environments in the reaction media. If the environment of a hyperbranched polymer is a good solvent for the substrate, a

reaction will be observed. In contrast, if the environment of a hyperbranched polymer is a poor solvent for the substrate, the substrate will be excluded and the reaction inhibited. When using DMSO, the hyperbranched polymer offers a good solvation environment for the substrate, so the substrate can get inside the dendritic structure, promoting the occurrence of a reaction. When using chloroform, the substrate prefers to be solvated by the bulk solvent. Therefore, the polymeric structure creates a barrier between the substrate and the catalytic sites, affecting the reaction rate. The results of the solvent effect experiment indicate that the reaction rate is affected by the nature of the substrate and its effect on the environment of the hyperbranched polymers. However, this property could be used positively to control some types of reaction. For example, if many reactions need to take place in one pot containing a hyperbranched polymer and a solvent, they could be controlled so that they take place either inside the hyperbanched polymer or the bulk solvent.

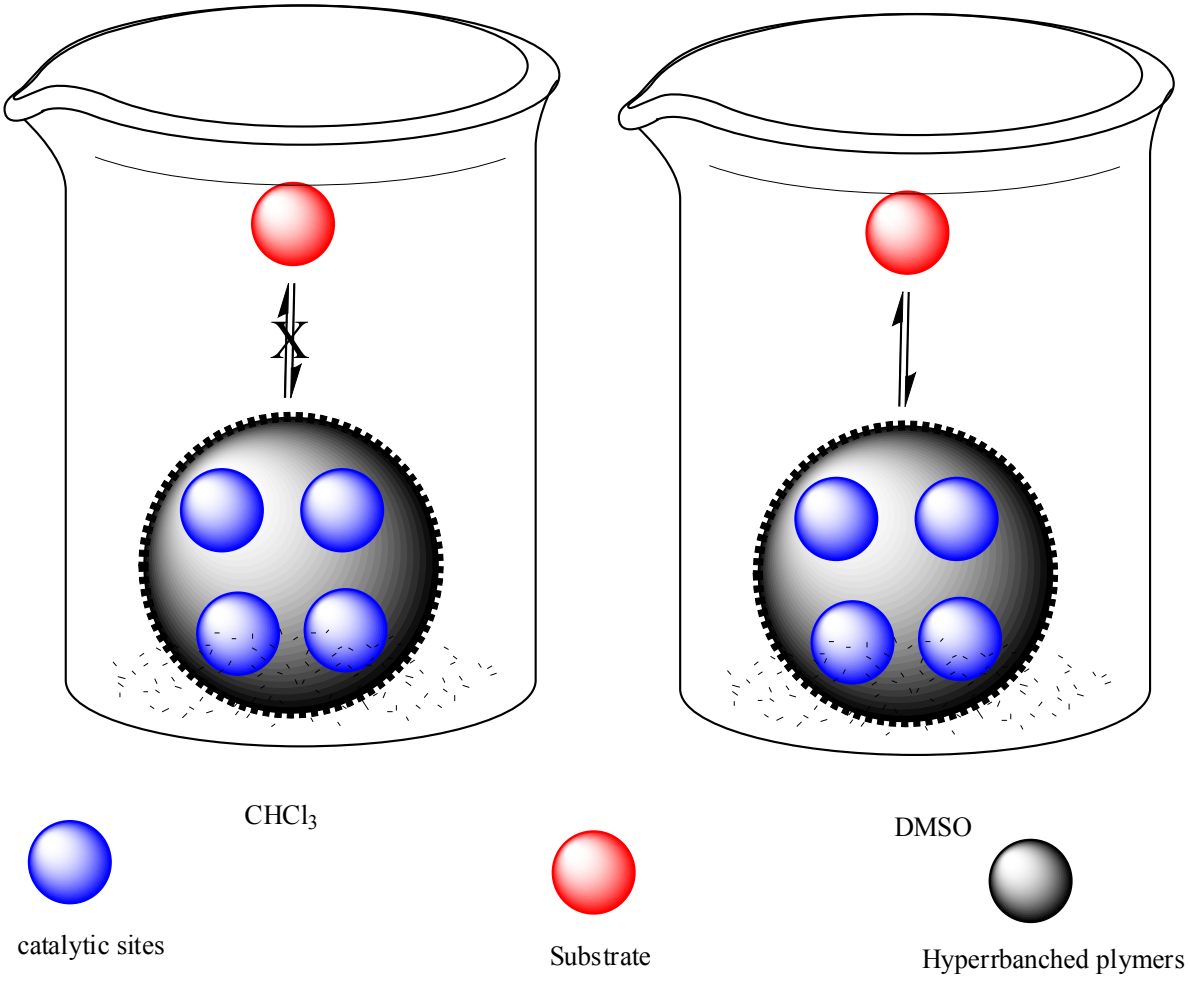


Figure.6.19. The effect of hyperbanched polymer structure on the rate of reaction.

6.4 Conclusion:

In this chapter, two different pyridine functionalised hyperbranched polymers were synthesised and their ability to act as a soluble catalyst system support was demonstrated. This was carried out via a test reaction of alkyne with aldehyde. Both polymers were synthesised by poly condensation and purified using a simple precipitation technique. The incorporation of pyridine was confirmed by ^{1}H NMR and GPC. The degree of branching of both polymers was above 40%, which is within the dendritic structure limit proposed in this thesis. Moreover, the molecular weights were above the dense packing limit. The first polymer used in this study was synthesised by the co-polymerisation of 3, 5-diacetoxybenzoic acid and nictionic acid. This polymer showed restricted ability as a catalytic support system due to the effect of the ester link on the pyridine unit as it decreases the nucleophilicity of the pyridine when acting as a catalyst. The second polymer was synthesised to overcome the problem caused by the ester link. A co-monomer with a space between the ester link and the pyridine units, 3-pyridinepropionic acid, was successfully co-polymerised with 3, 5-diacetoxybenzoic acid. This polymer showed good ability to act as a catalytic support system. Comparing it with the control experiment indicates that the steric and electronic environment around the pyridine groups caused by the nature of hyperbranched polymers reduces their ability to act as a catalyst. However, in terms of recovery, the test reaction of alkyne with aldehyde was carried out using DMF as a solvent. The polymer was recovered from the reaction mixture with a good yield via a simple precipitation. GPC indicated that the polymer maintained its high molecular weight. ^{1}H NMR indicated that the polymer still possessed its dendritic structure; however, there was a decrease in the level of pyridine incorporated. This suggested that some pyridine groups were cleaved due to the polymer undergoing hydrolysis during the reaction. However, the reusability of the polymer was not undertaken due to the high level of impurities in the recovered polymer and the pyridine cleaving issue. A solvent effect study proposed that reaction rate will be effected by nature of the substrate towards the environment of hyperbranched polymers. This study was performed using two deuterated solvents: DMSO and $CHCl_3$. In DMSO, the polymer possessed a good environment for the substrate, allowing the reaction to take place. In the case of $CHCl_3$, the substrate prefers the bulk solvent to the environment inside the hyperbanched polymer, which excluded the

substrate from the catalytic sites within the dendritic structure. This made it possible to control selectivity reactions.

Future development of this catalyst system could take two paths. In terms of recovery and reusability, the recovered polymers could undergo careful purification to be used as a catalyst a second time. However, the type of hyperbranched polymer may change from polyester to polyether to resolve the pyridine cleaving issue. Therefore, a pyridine incorporated hyperbranched polymer could act as a catalyst in many different reactions. In terms of yield improvement, increasing the loading of pyridine decreases the branching, which affects the steric around the catalytic sites, allowing them to work better in catalytic reactions. The next step may involve investigation into whether it is possible or not to co-polymerise other types of catalyst with the polymer and to examine their ability to act as a catalytic system. However, it is worth mentioning that the success of co-polymerisation varied co-monomers with 3, 5-diacetoxybenzoic acid in the previous chapters suggests that the potential for loading a variety of catalyst molecules is promising.

Chapter Seven

Experimental

Chapter Seven - Experimental

7.1 General Descriptions of Chemicals and Instrumentation

7.1.1 Solvents and Reagents

All chemicals and reagents were obtained from commercial suppliers, such as Sigma Aldrich and Fisher, and freshly used without any further purification unless otherwise stated. Dry solvents were obtained from the chemistry store. Biobeads SX-1 was purchased from Bio-Rad Co.

7.1.2 NMR Spectroscopy

Deuterated solvents supplied by Sigma Aldrich were used to prepare all NMR samples. A Bruker Avance at 400 MHz with 5mm probe was used to record ^{1}H and ^{12} C NMR for characterization. The NMR spectra were analysed using Topspin 3.0 NMR software.

7.1.3 Infra-Red Spectroscopy

Perkin Elmer Spectrum RX FT-IR System in the range of 700-4000cm^{-1} was used to record all Infra-Red samples.

7.1.4 Analytical Gel permeation Chromatography

GPC data was performed using a GPC at room temperature. Some samples were characterized by GPC with a polystyrene high molecular weight column setup consisting of 3x300mm PL gel 10um. Other samples were characterized by GPC with a polystyrene low molecular weight column setup consisting of 2x600mm PL gel 5um. THF GPC grade supplied by Fisher was used to dissolve and run all samples. Toluene was used as a flow marker before the sample was injected into the column via a 10 um filter.

7.1.5 Preparative Size Exclusion Chromatography

SX-1 beads were used to prepare the bio beads column. These beads were left overnight in DCM to swell before being loaded into a chromatography column. The column was washed thoroughly with DCM to remove any uncrossed linked beads. The sample was loaded into the column after dissolving it with a minimum amount of DCM. Fractionated samples were collected and analysed by GPC.

7.1.6 Mass Spectroscopy

Electrospray ionisation mass spectrometry (ESI) was used to analyse the sample. The instrument used was a Watersn LCT mass spectrometer.

7.1.7 Melting Point

Gallenkamp melting point apparatus.

7.1.8 Ultra Violet/Visible spectroscopy

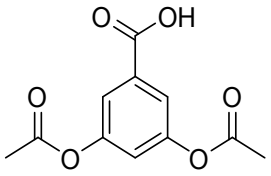
The absorbance was recorded using on a Specord s600 UV/Vis Spectrometer and analysed using its attached Software (WinASPECT).

7.1.9 UV/Vis Titrations

Solutions of zinc inserted porphyrins with a concentration of 10^{-6} M were prepared in dichloromethane; this corresponds to an absorbance of unity at λ_{max}. Solutions containing a large excess of pyridyl ligand units with a concentration of 10^{-2}M were then prepared using the porphyrin stock solution to ensure a constant concentration of porphyrin throughout the titration. 2 ml of the porphyrin solution was measured into a dried cuvette, and aliquots of ligand solution between 10 µl and 300 µl were added. UV/Vis wavelength scans were taken after each addition, monitoring the Soret band at 428nm. Solutions were freshly made and used immediately after preparation to ensure constant concentration.

7.2 Synthetic Procedure

7.2.1 The preparation of 3, 5-diacetoxybenzoic acid (1):



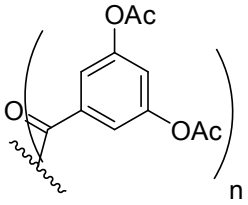
3, 5-dihydroxybenzioic acid (77.0 g, 0.50mol) was placed in 500mL round bottom flask with magnetic stirrer and 250mL of acetic anhydride. The mixture was heated to above 145 ^{0}C to reflux for 6 hours before the acetic acid was removed by using a vacuum. A viscous solution was obtained containing a small amount of insoluble materials. The compound was filtered hot after dissolving in 100mL refluxing chloroform. The liquid was added to 500mL petroleum ether and white solid precipitated. The mixture was left overnight then filtered and washed with petroleum ether.

Yield: 48.0g, 36%; ^{1}H NMR ($CDCl_3$,400MHz) δ 10.00 (br s, 1H, -COOH), 7.80 (d, J = 2 Hz, 2H, Ar *o*-CH), 7.25 (t, J = 2 Hz, 1H, Ar *p*-CH), 2.35 (s, 6H, -CH_3), ^{13}CNMR($CDCl_3$) δ_C 169.9, 168.8, 151.0, 131.4, 122.0, 121.1, 120.9, 21.0; IR Relevant peak: ν_{max}/cm^{-1} 3400-2400, 1769 (COOR), 1690 (COOH), 1604; MH^+ = 237 gmol^{-1}; MP 160-164°C.

General procedure for the polymerisation:

3, 5-diacetoxybenzoic acid (various amount) and diphenyl ether (various amount) were placed into a round bottom flask, which was degassed and flushed with nitrogen. The mixture was then heated to 225 ^{0}C. After 45 minutes (T1), the temperature was reduced to 180 ^{0}C and then the reaction was placed under reduced pressure for 4 hours (T2). The polymer mixture was dissolved in 50 mL of hot THF and precipitated in 600 mL of cold methanol. The resulting solid was filtered and washed with cold methanol.

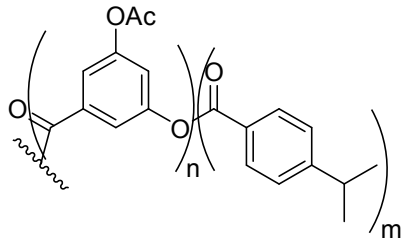
7.2.2 The polymerisation of 3, 5-diacetoxybenzoic acid (2):



The general procedure was followed where 3, 5-diacetoxybenzoic acid (3.98g, 0.02mol) and diphenyl ether (4.07g) were reacted together, yielding the polymer. (P1, T1= 45 min, T2= 1 hour), (P2, T1= 45 min, T2= 4hour), (P1, T1= 60 min, T2= 4 hour).

Yield: 2.5g, 63%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.10-7.80(br m_4, 2H, [Polymer] Ar *o*-CH), 7.60-7.20 (br m_3, 1H, [Polymer] Ar *p*-CH), 2.30 (s, 3H, [Polymer] -CH_3) ^{13}CNMR ($CDCl_3$) δ_C 168.7, 162.7, 151.1, 130.9, 130.7, 121.2, 120.9, 20.9, FTIR (cm^{-1}) 2923, 2159, 1748(COOR) 1280,1261 GPC (P1, M_n = 8100 Da PDI = 2.9), (P2, M_n = 14800 Da PDI = 2.3), (P3,M_n = 18300 Da PDI = 2.8).

7.2.3.1 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 4-isopropylbenzoic acid 5 % (3A):



The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.7g, 7.14mmol), 4-isopropylbenzoic acid (0.058g, 0.357mmol) and diphenyl ether (1.8g) were reacted together, yielding the polymer.

Yield: 1.3g, 76 %; ^{1}HNMR ($CDCl_3$, 400MHz) 8.25-8.15 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.60 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.15 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.40 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.30 (s, 6H, [Polymer] (C<u>H</u>$_3)_2$), ^{13}CNMR ($CDCl_3$) δ_C 168.6, 162.7, 151.3, 151.1, 130.9, 130.7, 126.8, 121.3, 120.9, 23.6, 21.0, GPC M_n = 13300 Da PDI = 2.5.

7.2.3.2 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 4-isopropylbenzoic acid 10 % (3B):

The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.7g, 7.14mmol), 4-isopropylbenzoic acid (0.117g, 0.714mmol) and diphenyl ether (1.8g) were reacted together, yielding the polymer.

Yield: 1.1g, 64%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.20-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.05-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.20 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.35 (s, 6H, [Polymer] (C<u>H</u>$_3)_2$), ^{13}CNMR($CDCl_3$) δ_C 168.6, 162.7, 151.3, 151.1, 131.1, 130.9, 130.7, 130.5, 126.8, 121.3, 120.9, 34.3, 23.6, 21.0, GPC M_n = 14600 Da PDI = 4.2.

7.2.3.3 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 4-isopropylbenzoic acid 20 % (3C):

The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.7g, 7.14mmol), 4-isopropylbenzoic acid (0.234g, 1.42mmol) and diphenyl ether (1.9g) were reacted together, yielding the polymer.

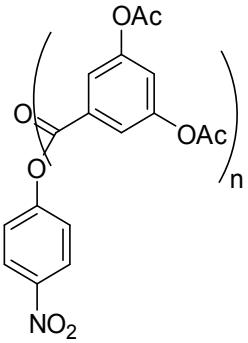
Yield: 1.1g, 64%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.20-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.10 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.25 (s, 6H, [Polymer] (C<u>H</u>$_3)_2$), ^{13}CNMR($CDCl_3$) δ_C 168.6, 162.7, 151.2, 130.9, 130.5, 126.8, 126.2, 120.8, 34.3, 23.6, 20.9, GPC M_n = 16100 Da PDI = 7.1.

7.2.3.4 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 4-isopropylbenzoic acid 30 % (3D):

The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.7g, 7.14mmol), 4-isopropylbenzoic acid (0.351g, 2.14mmol) and diphenyl ether (2.0g) were reacted together, yielding the polymer.

Yield: 1.2g, 70%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.25-8.15 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.15 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.25 (s, 6H, [Polymer] (C<u>H</u>$_3)_2$),), ^{13}CNMR($CDCl_3$) δ_C 168.5, 162.7, 151.2, 130.9, 130.5, 126.8, 126.3, 121.2, 120.8, 34.3, 23.6, 20.9, GPC M_n = 18000 Da PDI = 7.0.

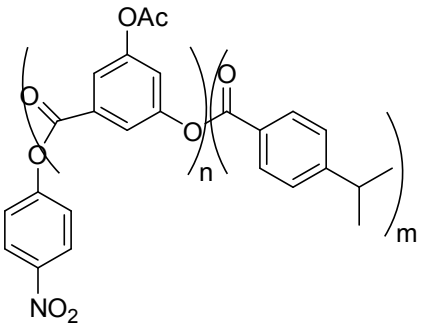
7.2.4 Polymerisation of 3, 5-diacetoxybenzoic acid and 4-nitrophenyl acetate core (4):



The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 4-nitrophenyl acetate (0.028g, 0.157mmol) and diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 0.9g, 53%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.35 (br d, 2H, [PNP] Ar *m*-C<u>H</u>), 8.05-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.20 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 2.25 (s, 3H, [Polymer] -C<u>H</u>$_3$) ^{13}CNMR ($CDCl_3$) δ_C 186.7, 162.7, 151.1, 130.9, 130.7, 121.3, 120.9, 21.00, GPC M_n = 7200 Da PDI = 3.

7.2.5.1 Co-polymerisation of 3, 5-diacetoxybenzoic acid, 4-nitrophenyl acetate and 4-isopropylbenzoic acid 5 % (5A):



The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 4-nitrophenyl acetate (0.028g, 0.157mmol) and 4-isopropylbenzoic acid (0.052g, 0.315mmol), diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 1.3g, 76%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.32 (br d, 2H, [PNP] Ar *m*-C<u>H</u>), 8.15-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.10 (br m_3, 1H, [Polymer]

Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u> $(CH_3)_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.30 (s, 6H, [Polymer] $(C\underline{H}_3)_2$), ^{13}CNMR (DMSO) δC $_{169.2}$, 151.5, 130.5, 121.3, 119.0, 34.0, 23.7, 21.1, GPC M_n = 9800 Da PDI = 3.9.

7.2.5.2 Co-polymerisation of 3, 5-diacetoxybenzoic acid, 4-nitrophenyl acetate and 4-isopropylbenzoic acid 10 % (5B):

The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 4-nitrophenyl acetate (0.28g, 0.157mmol) and 4-isopropylbenzoic acid (0.104g, 0.63mmol), diphenyl ether (1.7g) were reacted together, yielding the polymer.

Yield: 1.0g, 58%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.32 (br d, 2H, [PNP] Ar *m*-C<u>H</u>),8.15-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.10 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.30 (s, 6H, [Polymer] $(C\underline{H}_3)_2$), ^{13}CNMR (DMSO) δ_C 168.7, 162.7, 151.1, 130.9, 130.5, 129.7, 126.8, 123.2, 121.3, 120.9,118.8, 34.3, 23.6, 21.2, GPC M_n = 8900 Da PDI = 3.8.

7.2.5.3 Co-polymerisation of 3, 5-diacetoxybenzoic acid, 4-nitrophenyl acetate and 4-isopropylbenzoic acid 20 % (5C):

The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 4-nitrophenyl acetate (0.028g, 0.157mmol) and 4-isopropylbenzoic acid (206g, 1.26mmol), diphenyl ether (1.8g) were reacted together, yielding the polymer.

Yield: 1.2g, 70%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.32 (br d, 2H, [PNP] Ar *m*-C<u>H</u>),8.15-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.10 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.30 (s, 6H, [Polymer] $(C\underline{H}_3)_2$), ^{13}CNMR (DMSO) δ_C 168.7, 162.7, 155.7, 151.1, 130.9, 130.53, 126.8, 126.2, 121.3, 120.9, 34.3, 23.6, 21.0, GPC M_n = 13900 Da PDI = 4.2

7.2.5.4 Co-polymerisation of 3, 5-diacetoxybenzoic acid, 4-nitrophenyl acetate and 4-isopropylbenzoic acid 30 % (5D):

The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 4-nitrophenyl acetate (0.028g, 0.157mmol) and 4-isopropylbenzoic acid (0.314g, 1.89mmol), diphenyl ether (1.9 g) were reacted together, yielding the polymer.

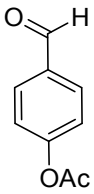
Yield: 1.2g, 70%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.32 (br d, 2H, [PNP] Ar *m*-C<u>H</u>),8.15-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.10 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>$(CH_3)_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.30 (s, 6H, [Polymer] $(C\underline{H}_3)_2$) ^{13}CNMR (DMSO) δ_C 168.7, 164.5, 162.7, 155.7, 151.1, 130.9, 130.5, 126.8, 126.2, 121.3, 120.9, 34.3, 23.6, 21.0, GPC M_n = 9200 Da PDI = 3.4.

7.2.5.5 Co-polymerisation of 3, 5-diacetoxybenzoic acid, 4-nitrophenyl acetate and 4-isopropylbenzoic acid 40 % (5E):

The general procedure was followed where 3,5-diacetoxybenzoic acid (1.5g, 6.3mmol), 4-nitrophenyl acetate (0.028g, 0.157mmol) and 4-isopropylbenzoic acid (0.413g, 2.52mmol), diphenyl ether (2.0g) were reacted together, yielding the polymer.

Yield: 1.1g, 64%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.32 (br d, 2H, [PNP] Ar *m*-C<u>H</u>),8.15-8.10 (br s, 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.70 (br m_4, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.10 (br m_3, 1H, [Polymer] Ar *p*-C<u>H</u>), 3.00 (s, 1H, [Polymer] C<u>H</u>(CH_3)$_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.30 (s, 6H, [Polymer] (C<u>H</u>$_3$)$_2$) , ^{13}CNMR (DMSO) δ_C 168.7, 164.5, 162.7, 155.7, 151.6, 151.1, 130.9, 130.5, 126.8, 126.2, 121.5, 121.3, 120.9, 34.3, 23.6, 31.02, GPC M_n = 14000 Da PDI = 4.

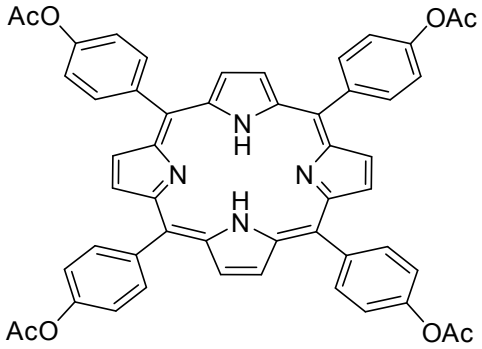
7.2.6 The preparation of 4-acetoxybenzaldehyde (6):



In a round bottom flask that fixed with refluxing condenser (20.0g, 163mmol) of 4-hydroxybenzaldehyde, (30mL, 215mmol) of triethylamine and (800mL) of anhydrous THF were placed. The mixture was stirred under nitrogen for 10 minutes and then (30mL, 420mmol) of acetyl chloride was added as drop wise via syringe, stirring was then continued under nitrogen at 25 ^{0}C for half hours at room temperature. The reaction mixture was filtered and the white solid was washed with THF and the disposed of. THF was removed via rotary evaporation. (100mL) of dichloromethane was used to dissolve the brown oil and washed with saturated sodium hydrogen carbonate solution (200mL) followed by distilled water (200mL). The washing step was repeated and the layer of DCM was collected. Then, the remaining traces of water in the solution was removed by adding magnesium sulphate and filtrated off. The product as brown oil was collected by removing the solvent via rotary evaporation.

Yield: 17.5g, 65%; ^{1}H NMR ($CDCl_3$, 400MHz): δ 9.95 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H, Ar-H), 7.25 (d, J = 8.5 Hz, 2H, Ar-H), 2.30 (s, 3H); ^{13}CNMR ($CDCl_3$, 400MHz): δ 190.9, 168.6, 155.3, 133.9, 131.1, 122.3, 21.0; MH^+= 163 $gmol^{-1}$.

7.2.7 5, 10, 15, 20-tetrakis (3, 5-diacetoxyphenyl)-21H, 23H-porphyrin, TAPP (7):

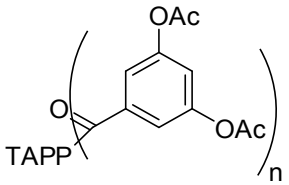


In a round bottom flask (15.0g, 91.46mmol) of 4-acetoxybenzaldehyde and (6.14mL, 91.4mmol) of freshly distilled pyrrole were added to (200mL) of refluxing propionic acid. The reaction was refluxed for a half hour and then the mixture was left to cool down at

room temperature. The reaction mixture was filtered and washed with (10mL) of cold methanol followed by (10mL) of warm distilled water. The washing step was repeated and the product was dried under high vacuum overnight and collected.

Yield: 5.0g, 26%; ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.92 (s, 8H, pyrrolic β-H) 8.25 (d, J = 8.5 Hz, 8H, phenylic *o*-CH). 7.52 (d, J = 8.5 Hz, 8H, phenylic *m*-CH), 2.60 (s, 12H, CH_3), -2.85 (s, 2H, NH); ^{13}C NMR ($CDCl_3$): δ 169.6, 150.6, 139.5, 135.3, 119.9, 119.2, 21.4; UV Absorbance: λ_{max}= 418 nm (CH_2Cl_2); MH^+= 847 $gmol^{-1}$.

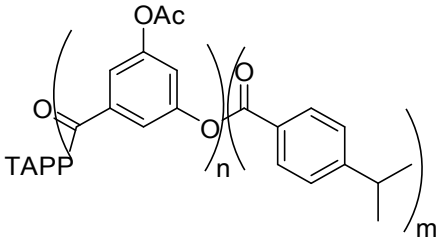
7.2.8 Polymerisation of 3, 5-diacetoxybenzoic acid and TAPP core (8):



The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 5, 10, 15, 20-tetrakis(3, 5-diacetoxyphenyl)-21H, 23H-porphyrin (0.135g, 0.157mmol), and diphenyl ether (1.6g) were reacted together, yielding the polymer. The polymer was loaded into bio-beads column to remove the unreacted TAPP.

Yield: 1.0g, 66% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.90 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 2.30 (br s, 3H, [Polymer] CH_3) -2.85 (s, 2H, NH); ^{13}C NMR δ 168.8, 162.7, 151.1, 130.8, 121.2, 120.9, 20.9: UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 553, 595,649 GPC M_n = 4000 Da PDI = 3.

7.2.8.1 Co-polymerisation of 3, 5-diacetoxybenzoic acid, TAPP and 4-isopropylbenzoic acid 5 % (9A):



The general procedure was followed where 3,5-diacetoxybenzoic acid (1.5g, 6.3mmol), 5, 10, 15, 20-tetrakis (3, 5-diacetoxyphenyl)-21H, 23H-porphyrin (0.135g, 0.157mmol), 4-isopropylbenzoic acid (0.052g, 0.315mmol), and diphenyl ether (1.6g) were reacted together, yielding the polymer. The polymer was loaded into bio-beads column to remove the unreacted TAPP.

Yield: 0.9g, 60% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), -2.90 (s, 2H, NH); ^{13}C NMR δ 168.7, 162.7, 151.1, 130.9, 130.7, 130.5, 126.8, 121.3, 120.9, 34.3,

23.6, 21.0: UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 549, 592, 648, GPC M_n = 5500 Da PDI = 3.3.

7.2.8.2 Co-polymerisation of 3, 5-diacetoxybenzoic acid, TAPP and 4-isopropylbenzoic acid 10 % (9B):

The general procedure was followed where 3,5-diacetoxybenzoic acid (1.5g, 6.3mmol), 5, 10, 15, 20-tetrakis (3, 5-diacetoxyphenyl)-21H, 23H-porphyrin (0.135g, 0.157mmol), 4-isopropylbenzoic acid (0.104g, 0.63mmol) and diphenyl ether (1.7g) were reacted together, yielding the polymer. The polymer was loaded into bio-beads column to remove the unreacted TAPP.

Yield: 1.0g, 66% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), -2.90 (s, 2H, NH); ^{13}C NMR δ 168.7, 162.7, 151.1, 130.9, 130.7, 130.5, 126.8, 121.3, 120.9, 34.3, 23.6, 21.0, UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 549, 592, 648, GPC M_n = 5900 Da PDI = 3.2.

7.2.8.3 Co-polymerisation of 3, 5-diacetoxybenzoic acid, TAPP and 4-isopropylbenzoic acid 20 % (9C):

The general procedure was followed where 3,5-diacetoxybenzoic acid (1.5g, 6.3mmol), 5, 10, 15, 20-tetrakis (3, 5-diacetoxyphenyl)-21H, 23H-porphyrin (0.135g, 0.157mmol), 4-isopropylbenzoic acid (206mg, 1.26mmol) and diphenyl ether (1.8g) were reacted together, yielding the polymer. The polymer was loaded into bio-beads column to remove the unreacted TAPP.

Yield: 1.0g, 66% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), -2.90 (s, 2H, NH); ^{13}C NMR δ 168.7, 164.5, 162.7, 155.7, 151.5, 151.1, 130.9, 130.5, 126.8, 126.2, 121.3, 120.9, 34.3, 23.6, 21.0,UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 549, 592, 648, GPC M_n = 4000 Da PDI = 2.8.

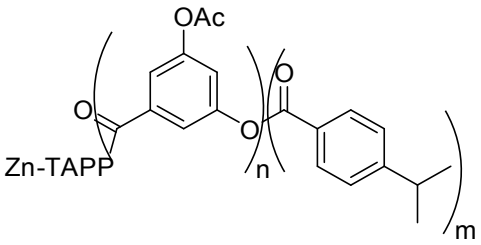
7.2.8.4 Co-polymerisation of 3, 5-diacetoxybenzoic acid, TAPP and 4-isopropylbenzoic acid 30 % (9D):

The general procedure was followed where 3,5-diacetoxybenzoic acid (1.5g, 6.3mmol), 5, 10, 15, 20-tetrakis (3, 5-diacetoxyphenyl)-21H, 23H-porphyrin (0.135g, 0.157mmol), 4-isopropylbenzoic acid (0.314g, 1.89mmol) and diphenyl ether (1.9g) were reacted together, yielding the polymer. The polymer was loaded into bio-beads column to remove the unreacted TAPP.

Yield: 0.8g, 53% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), -2.90

(s, 2H, NH); ^{13}C NMR δ 168.7, 164.5, 162.7, 155.7, 151.6, 151.1, 130.9, 130.7, 130.5, 126.8 , 126.2, 121.5, 121.3, 120.9, 34.3, 23.6, 21.0,UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 549, 592, 648, GPC M_n = 4200 Da PDI = 2.9.

7.2.9 Zinc insertion into TAPP-cored hyperbranched co-polymers (10):



TAPP cored hyperbrancd polymer (500mg) and Zn (OAc) $_2$•H_2O (685mg, 0.75mmol) were dissolved in dichloromethane (100mL). The solution was then stirred at room temperature for 30 minutes. Unreacted zinc acetate was removed via filtration. The solvent was removed by rotary evaporation and then dissolved in THF and precipitated into cold methanol. The product was filtered and dried under reduced pressure.

Yield: 300mg, 60%; ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.60 (8H, br d, [TAPP] phenylic *o*-CH), 8.20 (d, 8H, [TAPP] phenylic *m*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 548.

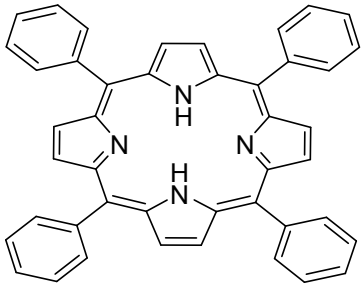
5% isopropylbenzoic acid: Yield: 270mg, 54% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 548.

10% isopropylbenzoic acid: Yield: 270mg, 54% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 548.

20% isopropylbenzoic acid: Yield: 290mg, 58% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 548.

30% isopropylbenzoic acid: Yield: 230mg, 46% ^{1}H NMR ($CDCl_3$, 400MHz), δ 8.89 (br s, 8H, [TAPP] pyrrolic-β-H), 8.20 (8H, br d, [TAPP] phenylic *o*-CH), 8.10 (br s, 2H, [Polymer] Ar *m*-CH), 8.10-7.80 (br d, 2H, [Polymer] Ar *p*-CH), 7.65 (d, 8H, [TAPP] phenylic *m*-CH), 7.60-7.30 (br d, 1H, [Polymer] Ar *o*-CH), 3.00 (s, 1H, [Polymer] $CH(CH_3)_2$), 2.30 (br s, 3H, [Polymer] CH_3), 1.30 (s, 6H, [Polymer] $(CH_3)_2$), UV Absorbance (CH_2Cl_2) λ_{max}= 419, 515, 548.

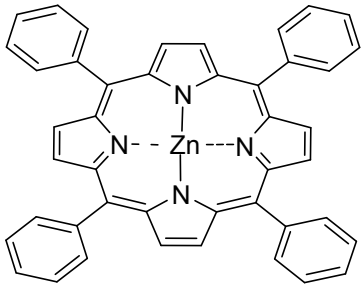
7.2.10 The preparation of tetraphenylporphyrin (11):



In a round bottom flask (14.50g, 91.46mmol) of benzaldehyde and (6.0mL, 91.4mmol) of freshly distilled pyrrole were added to (200mL) of refluxing propionic acid. The reaction was refluxed for a half hour and then the mixture was left to cool down at room temperature. The reaction mixture was filtered and washed with (10mL) of cold Methanol followed by (10mL) of warm distilled water. The washing step was repeated and the product was dried under high vacuum overnight and collected.

Yield: 4.5g, 32%; ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.95 (s, 8H, pyrrolic β-H), 8.30 (dd, J = 2, 7.5 Hz 8H, phenylic *o*-CH), 7.80 (m, 12H, Phenylic m-CH, Phenylic p-CH), -2.85 (s, 2H, NH); ^{13}C NMR ($CDCl_3$): δ 142.19, 134.58, 127.73, 126.70, 120.16; UV Absorbance: λ_{max}= 418, 518, 560, 590, 648 (CH_2Cl_2); MH^+= 613 $gmol^{-1}$.

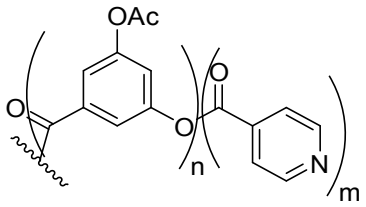
7.2.11 Zinc insertion to tetraphenylporphyrin (12):



1.0g of tetraphenylporphyrin and Zn $(OAc)_2 \bullet H_2O$ (685mg, 0.75mmol) were dissolved in dichloromethane (100mL). The solution was then stirred at room temperature for 30 minutes. Unreacted zinc acetate was removed via filtration. The solvent was removed by rotary evaporation. The product was filtered and dried under reduced pressure.

Yield: 650mg, 65% ($CDCl_3$, 400MHz), δ 8.91 (br s, 8H, [TAPP] pyrrolic-β-H), 8.25 (dd, J = 2, 7.5 Hz 8H, phenylic *o*-CH),), 7.85 (m, 12H, Phenylic m-CH, Phenylic p-CH), ^{13}C NMR ($CDCl_3$): δ 150.2, 142.8, 134.4, 132.0, 127.5, 126.5, 121.1, UV Absorbance (CH_2Cl_2) λ_{max}= 420, 528, 550, MH^+= 675 $gmol^{-1}$.

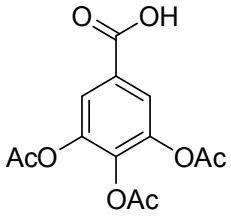
7.2.12 Co-polymerisation of 3, 5-diacetoxybenzoic acid and isonicotinic acid (13):



20%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), isonicotinic acid (0.155g, 1.26mmol) and diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 1.1g, 73%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.85 (br m, 2H, [Polymer] Py-Ar-C<u>H</u>), 8.20 -7.70 (br m, 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.15 (br m, 1H, [Polymer] Ar *p*-C<u>H</u>), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$), ^{13}CNMR ($CDCl_3$) δ_C 168.8, 163.4, 162.7, 158.5, 151.4, 151.0, 130.6, 130.4, 129.9, 123.3, 121.8, 121.3, 120.9, 118.5, 114.0, 21.0, 20.7, GPC M_n = 9700 Da PDI = 2.9.

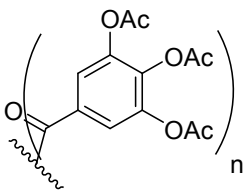
7.2.13 Preparation of 3, 4, 5-triacetoxybenzoic acid (14):



In a 250mL round-bottom flask, with a magnetic stirrer, were combined gallic acid (5.0g, 29mmol) and acetic anhydride (17mL, 176mmol, excess).The slurry was stirred as a catalytic amount of sulfuric acid (32µl) was added. The temperature rose rapidly from 21 to 75.for about 5 min, and the slurry became a clear yellow solution. The mixture was stirred and allowed to cool to room temperature over 20 min. 100mL of water was added to the flask to remove any excess acetic anhydride. After further stirring for 2.5 h, a white crystalline product was isolated by filtration and further washed with three times of 20mL water. The acetyl-protected gallic acid product was dried in a stream of air for 10 min and then vacuum-dried overnight.

Yield: 8.0g, 92% ^{1}H NMR (DMSO, 400MHz) 7.80 (d, 2H, Ar*o*-C<u>H</u>), 2.30 (s, 9H, -C<u>H</u>$_3$), ^{13}CNMR (DMSO) δ_C 168.0, 166.9, 165.3, 143.1, 138.2, 128.8, 121.9, 20.9, 20.3, 19.7 IR Relevant peak: ν_{max}/cm^{-1} 3400-2400, 1768 (COOR), 1689 (COOH), 1592; MH^+ = 295 gmol^{-1}; MP 166 °C.

7.2.14 Polymerisation of 3, 4, 5-triacetoxybenzoic acid (15):

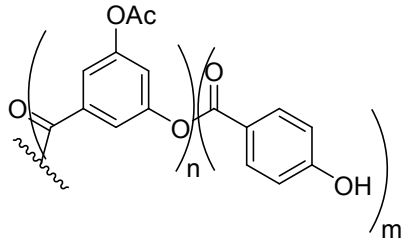


3,4,5-triacetoxybenzoic acid (2.0g, 0.060mol) and diphenyl ether (2.0g) were placed into a round bottom flask, which was degassed and flushed with nitrogen. The mixture was then heated to 225 ^{0}C. After 3 hours the temperature was reduced to 180 ^{0}C and the reaction was placed under reduced pressure for (V_1=4, V_2=6) hours. The polymer mixture was

dissolved in hot THF and precipitated in 500ml of methanol. The resulting solid was filtered and washed with cold methanol.

Yield: 1.3g, 65%; ^{1}HNMR (DMSO, 400MHz) 8.20-7.70(br m, 2H, [Polymer] Ar *o*-C<u>H</u>),2.35 (s, 3H,[Polymer]-C<u>H</u>$_3$),^{13}CNMR(DMSO) δ_C 168.0, 166.9, 161.4, 143.5, 139.5, 130.0, 125.9, 124.6, 122.9, 118.5, 20.3, 19.8, GPC(V_1,M_n = 3000 Da PDI = 2.4) (V_2,M_n = 6000 Da PDI = 2.5).

7.2.15 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 4-hydroxybenzoic acid (16):



5%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (2.0g, 8.4mmol), 4-hydroxybenzoic acid (0.057g, 0.420mmol) and diphenyl ether (2.05g) were reacted together, yielding the polymer.

Yield: 1.1g, 55%; ^{1}HNMR (DMSO, 400MHz) 9.50 (br s, 1H, [Polymer] -O<u>H</u>), 8.35-7.25 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> and, Ar *p*-C<u>H</u>), 7.15 -6.85 (br m, 2H, [Polymer] Ar *m*-C<u>H</u>-C-OH), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$),^{13}CNMR (DMSO) δ_C 168.8, 163.5, 162.7, 151.0, 131.6, 130.6, 122.5, 121.9, 121.3, 120.9, 114.8, 20.7, GPC M_n = 17000 Da PDI = 3.6.

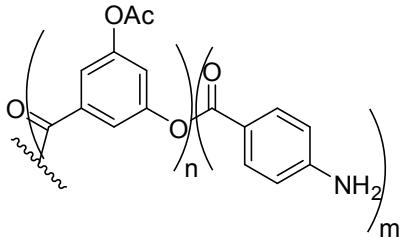
10%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (2.0g, 8.4mmol), 4-hydroxybenzoic acid (0.117g, 0.84mmol) and diphenyl ether (12.0g) were reacted together, yielding the polymer.

Yield: 1.2g, 60%; ^{1}HNMR (DMSO, 400MHz) 9.50 (br s, 1H, [Polymer] -O<u>H</u>), 8.35-7.25 (br m$_4$, 3H, [Polymer] Ar *o*-C<u>H</u>),and, Ar *p*-C<u>H</u>), 7.15-6.85 (br m, 2H, [Polymer] Ar *m*-C<u>H</u>-C-OH), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$),^{13}CNMR (DMSO) δ_C 168.8, 163.4, 162.7, 158.6, 156.6, 154.9, 151.0, 131.6, 130.6, 130.5, 129.9, 123.3, 122.5, 121.8, 121.3, 120.9, 118.5, 114.8, 114.0, 20.7, GPC M_n = 12900 Da PDI = 2.4.

20%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (10.0g, 42mmol), 4-hydroxybenzoic acid (1.16g, 8.40mmol) and diphenyl ether (12.0g) were reacted together, yielding the polymer.

Yield: 6.9g, 70%; ^{1}HNMR (DMSO, 400MHz) 9.50 (br s, 1H, [Polymer] -O<u>H</u>), 8.35-7.25 (br m$_4$, 3H, [Polymer] Ar *o*-C<u>H</u>),and, Ar *p*-C<u>H</u>), 7.20-6.80 (br m$_2$, 2H, [Polymer] Ar *m*-C<u>H</u>-C-OH), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$),^{13}CNMR (DMSO) δ_C 168.9, 163.4, 162.7, 154.9, 151.0, 131.6, 130.6, 122.5, 121.9, 121.3, 120.9, 120.4, 114.0, 20.74, GPC M_n = 9300 Da PDI = 3.1

7.2.16 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 4-aminobenzoic acid (17):



5%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (2.0g, 8.40mmol), 4-aminobenzoic acid (0.057g, 0.420mmol) and diphenyl ether (2.10g) were reacted together, yielding the polymer.

Yield: 1.3g, 65%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.20-7.15 (br m, 3H, [Polymer] Ar *o*-CH, and Ar *p*-CH), 7.10-6.80 (br m, 2H, [Polymer] Ar *m*-CH-C-NH), 2.30 (s, 3H, [Polymer] -CH_3),^{13}CNMR (DMSO) δ_C 168.9, 163.7, 163.4, 162.7, 158.6, 151.0, 144.5, 131.2, 130.6, 121.9, 121.3, 120.9, 118.3,114.8, 114.0, 20.7, GPC M_n = 5500 Da PDI = 2.9.

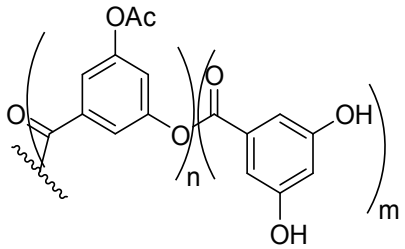
10%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (10.0g, 42mmol), 4-aminobenzoic acid (0.707g, 4.20mmol) and diphenyl ether (11.0g) were reacted together, yielding the polymer.

Yield: 6.5g, 65%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.20-7.15 (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.10-6.80 (br m, 2H, [Polymer] Ar *m*-CH-C-NH), 2.30 (s, 3H, [Polymer] -CH_3),^{13}CNMR (DMSO) δ_C 168.9, 163.7, 163.4, 162.7, 158.6, 151.0, 144.5, 131.2, 130.6, 121.8, 121.3, 120.9, 118.5, 118.3, 114.8, 114.0, 20.7, GPC M_n = 4700 Da PDI = 2.7.

20%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (10.0g, 42mmol), 4-aminobenzoic acid (1.30g, 8.40mmol) and diphenyl ether (11.0g) were reacted together, yielding the polymer.

Yield: 6.5g, 65%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.20-7.15 (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.10-6.80 (br m, 2H, [Polymer] Ar *m*-CH-C-NH), 2.30 (s, 3H, [Polymer] -CH_3),^{13}CNMR (DMSO) δ_C 168.9, 163.7, 151.5, 151.0, 130.6, 130.0, 123.3, 121.8, 121.3, 120.9, 118.5, 114.0, 20.7, GPC M_n = 1700 Da PDI = 2.0.

7.2.17 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 3, 5-dihydroxybenzoic acid (18):

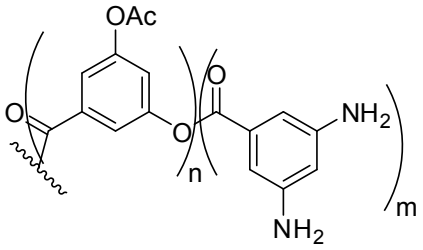


The general procedure was followed where 3, 5-diacetoxy benzoic acid (10g, 42mmol), 3, 5-dihydroxybenzoic acid (0.650g, 4.20mmol) and diphenyl ether (11.0g) were reacted together, yielding the polymer.

Yield: 6.0g, 60%; ^{1}HNMR (DMSO, 400MHz) 9.50 (br s, 1H, [Polymer] -OH), 8.20-7.15 (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.10-6.80 (br m, 1H, [Polymer] *p*-CH of co-monomer),

2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$),^{13}CNMR (DMSO) δ_C 168.9, 163.4, 162.7, 158.6, 158.5, 156.6, 151.4, 151.0, 130.6, 130.5, 130.1, 129.9, 123.3, 121.8, 121.3, 120.9, 118.5, 114.8, 114.0, 106.9, 20.7, GPC M_n = 5900 Da PDI = 3.

7.2.18 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 3, 5-diaminobenzoic acid (19):



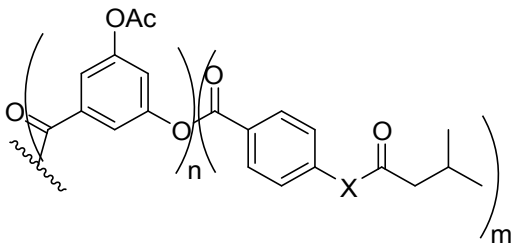
The general procedure was followed where 3, 5-diacetoxy benzoic acid (10g, 42mmol), 3, 5-diaminobenzoic acid (0.319g, 2.10mmol) and diphenyl ether (11g) were reacted together, yielding the polymer.

Yield: 5.50g, 55%; ^{1}HNMR (DMSO, 400MHz) 10.30 (br s, 1H, [Polymer] - N<u>H</u>), 8.20-7.15 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 7.10-6.70 (br m, 2H, [Polymer] Ar *o*-C<u>H</u>-C-NH$_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$),^{13}CNMR (DMSO) δ_C 168.9, 163.6, 163.4, 162.7, 158.5, 151.4, 151.0, 140.0, 130.6, 130.5, 121.8, 121.3, 120.2, 114.9, 114.0, 108.5, 105.1, 20.7, GPC M_n = 5000 Da PDI = 2.7.

7.2.19 General producer of the modification of hyperbranched co-polymers:

500mg of each mono or di-functional hyperbranched co-polymers was placed separately in a 100mL round bottom flask with a bar of stirrer under nitrogen. About 50mL of dry DCM was added to dissolve these polymers. A fixed amount of (18µl, 1.3x10^{-4}mol) of Et_3N was add and then followed by slow addition of (1.3x10^{-4}mol) of various compounds. The mixture was left overnight (24 hours) under room temperature. The obtained polymer was washed with saturated sodium hydrogen carbonate solution (70mL) followed by distilled water (70mL). The washing step was repeated and the layer of DCM was collected. Then, the remaining traces of water in the solution was removed by adding magnesium sulphate and filtrated off. Finally, DCM was removed by the rotary evaporation and the polymer dissolved in THF and precipitated in cold methanol then left in the fridge. By filtration and drying under reduced pressure, the sediment polymer was collected as powder. The polymer was loaded into bio-beads column to remove the unreacted materials.

7.2.19.1 Modification of mono-functionalised hyperbranched co-polymers with isovaleryl chloride (20, 21):

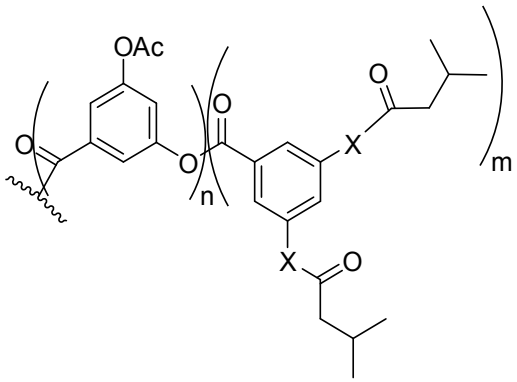


Isovaleryl chloride (16µl, 1.3x10^{-4}mol).

X=OH: Yield = 320mg, 64%, ^{1}HNMR (DMSO, 400MHz) 8.25-7.30 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.40 (br s, 2H[Polymer] C<u>H</u>$_2$-CH-CH$_3$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 2.10 (m, 1H,[Polymer] CH$_2$-C<u>H</u>-CH$_3$), 1.00 (d, 3H, [Polymer] CH$_2$-CH-C<u>H</u>$_3$), ^{13}CNMR ($CDCl_3$) δ_C 168.7, 162.7, 151.2, 151.1, 131.9, 130.9, 122.0, 121.3, 120.9, 25.7, 22.4, 21.0, GPC M_n = 16000 Da PDI = 2.2.

X=NH: Yield = 300mg, 60%, ^{1}HNMR ($CHCl_3$, 400MHz) 8.30-7.55 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.40 (br s, 2H[Polymer] C<u>H</u>$_2$-CH-CH$_3$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 2.15 (m, 1H,[Polymer] CH$_2$-C<u>H</u>-CH$_3$), 1.00 (d, 3H, [Polymer] CH$_2$-CH-C<u>H</u>$_3$), ^{13}CNMR (DMSO) δ_C 169.3, 163.2, 151.5, 131.1, 122.3, 121.8, 121.3, 22.5, 21.2, GPC M_n =16000 Da PDI = 2.5.

7.2.19.2. Modification of di-functionalised hyperbranched co-polymers with isovaleryl chloride (22, 23):

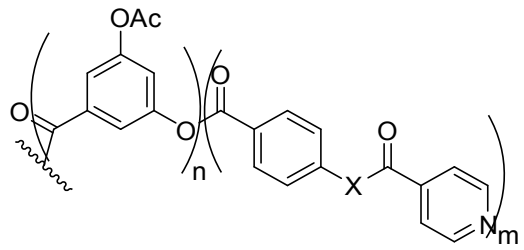


Isovaleryl chloride (16µl, 1.3x10^{-4}mol).

X=OH: Yield = 200mg, 40%, ^{1}HNMR (DMSO, 400MHz) 8.30-7.25 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.30 (br s, 2H[Polymer] C<u>H</u>$_2$-CH-CH$_3$), 2.20 (s, 3H, [Polymer] -C<u>H</u>$_3$), 2.00 (m, 1H,[Polymer] CH$_2$-C<u>H</u>-CH$_3$), 1.00 (d, 3H, [Polymer] CH$_2$-CH-C<u>H</u>$_3$) , ^{13}CNMR (DMSO) δ_C 169.3, 163.2, 151.5, 131.1, 122.3, 121.8, 121.5, 42.6, 25.5, 22.4, 21.1, GPC M_n = 14000 Da PDI = 2.5.

X=NH: Yield = 300mg, 60%, ^{1}HNMR (DMSO, 400MHz) 8.30-7.20 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.40 (br s, 2H[Polymer] C<u>H</u>$_2$-CH-CH$_3$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 2.15 (m, 1H,[Polymer] CH$_2$-C<u>H</u>-CH$_3$), 1.00 (d, 3H, [Polymer] CH$_2$-CH-C<u>H</u>$_3$), ^{13}CNMR (DMSO) δ_C 169.3, 163.2, 151.5, 131.5, 131.1, 122.3, 121.8, 121.3, 120.3, 42.6, 25.5, 22.5, 21.2, GPC M_n =7000 Da PDI = 1.8.

7.2.19.3 Modification of mono-functionalised hyperbranched co-polymers with isonicotinic acid chloride (24, 25):

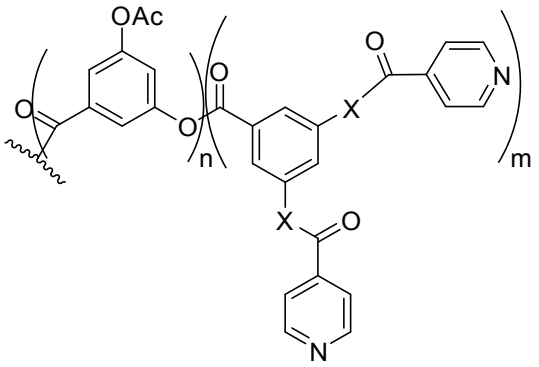


Isonicotinic acid chloride (23mg, 1.3x10^{-4}mol).

X=OH: Yield = 180mg, 36%, ^{1}HNMR ($CDCl_3$, 400MHz) 8.85 (br s , 2H, [Polymer] Py-Ar-C<u>H</u>), 8.45-8.20 (br m , 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.15 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.35 (s, 3H, [Polymer]-C<u>H</u>$_3$),^{13}CNMR($CDCl_3$) δ_C 168.7, 162.7, 151.1, 131.9, 130.9, 123.4, 122.0, 121.3, 120.9, 21.0, GPC M_n = 15000 Da PDI = 2.1.

X=NH: Yield = 240mg, 48%, ^{1}HNMR ($CDCl_3$, 400MHz) 8.70 (br s , 2H, [Polymer] Py-Ar-C<u>H</u>), 8.40-8.20 (br m , 2H, [Polymer] Ar *m*-C<u>H</u>), 8.15-7.10 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), ^{13}CNMR (DMSO) δ_C 168.7, 162.7, 151.1, 130.9, 121.3, 120.9, 21.0, GPC M_n = 14000 Da PDI = 2.0.

7.2.19.4 Modification of di-functionalised hyperbranched co-polymers with isonicotinic acid chloride (26, 27):

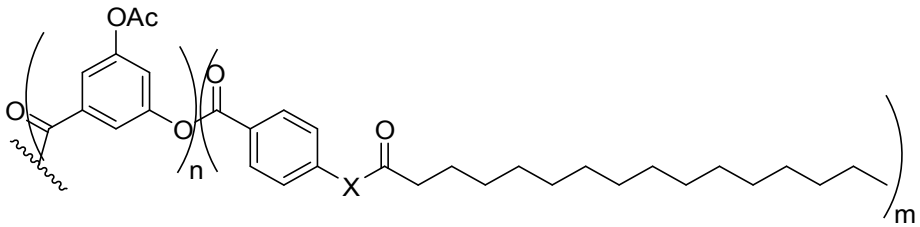


Isonicotinic acid chloride (23mg, 1.3x10^{-4}mol).

X=OH: Yield = 300mg, 60%, ^{1}HNMR ($CDCl_3$, 400MHz) 8.75 (br s , 2H, [Polymer] Py-Ar-C<u>H</u>), 8.40-8.20 (br m , 2H, [Polymer] Ar *m*-C<u>H</u>), 8.10-7.20 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$), ^{13}CNMR (DMSO) δ_C 168.8, 166.2, 162.6, 151.0, 150.5, 122.7, 121.8, 121.3, 120.8, 118.5, 20.6, GPC M_n = 17000 Da PDI = 2.6.

X=NH: Yield = 340mg, 68%, ^{1}HNMR ($CDCl_3$, 400MHz) 8.75 (br s , 2H, [Polymer] Py-Ar-C<u>H</u>), 8.40-8.20 (br m , 2H, [Polymer] Ar *m*-C<u>H</u>), 8.15-7.15 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.35 (s, 3H, [Polymer] -C<u>H</u>$_3$) ^{13}CNMR (DMSO) δ_C 168.7, 162.7, 151.4, 150.8, 124.8, 121.3, 120.8, 20.9 , GPC M_n = 7500 Da PDI = 1.9.

7.2.19.5 Modification of mono-functionalised hyperbranched co-polymers with palmitoyl chloride (28, 29):



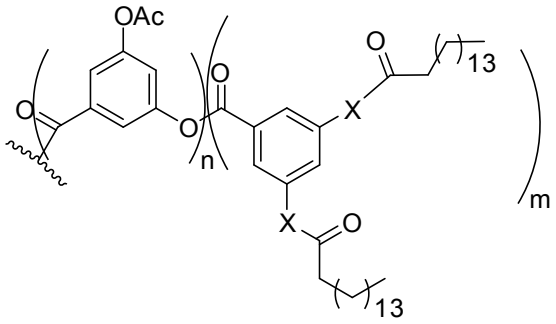
Palmitoyl chloride (40µl, 1.3x10^{-4}mol).

X=OH: Yield = 220mg, 44%, ^{1}HNMR (DMSO, 400MHz) 8.20-7.30 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.60 (br s, 2H[Polymer] CO-C<u>H</u>$_2$-CH$_2$), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.60 (br s, 2H,[Polymer] CO-CH$_2$-C<u>H</u>$_2$-CH$_2$), 1.20 (m, 2H, [Polymer] CO-CH$_2$-CH$_2$-C<u>H</u>$_2$-CH$_2$), 0.90 (br s,

3H,[Polymer] CH_2-C<u>H</u>$_3$, ^{13}CNMR (DMSO) δ_C 168.6, 161.5, 151.3, 150.8, 131.1, 124.8, 121.6, 120.7, 34.0, 29.5, 20.8, 14.1, GPC M_n = 18900 Da PDI = 2.4.

X=NH: Yield = 180mg, 36%, ^{1}HNMR (DMSO, 400MHz) 8.25-7.20 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.50 (br s, 2H[Polymer] CO-C<u>H</u>$_2$-CH_2), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.60 (br s, 2H,[Polymer] CO-CH_2-C<u>H</u>$_2$-CH_2), 1.20 (m, 2H, [Polymer] CO-CH_2-CH_2-C<u>H</u>$_2$-CH_2), 0.90 (br s, 3H,[Polymer] CH_2-C<u>H</u>$_3$)), ^{13}CNMR (DMSO) δ_C 168.6, 161.5, 151.3, 150.8, 131.1, 124.8, 121.6, 120.7, 34.1, 29.5, 20.9, 14.0, GPC M_n =18000 Da PDI = 2.4.

7.2.19.6 Modification of di-functionalised hyperbranched co-polymers with palmitoyl chloride (30, 31):



Palmitoyl chloride (40µl, 1.3x10^{-4}mol).

X=OH: Yield = 290mg, 58%, ^{1}HNMR (DMSO, 400MHz) 8.20-7.10 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.60 (br s, 2H[Polymer] CO-C<u>H</u>$_2$-CH_2), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.60 (br s, 2H,[Polymer] CO-CH_2-C<u>H</u>$_2$-CH_2), 1.20 (m, 2H, [Polymer] CO-CH_2-CH_2-C<u>H</u>$_2$-CH_2), 0.90 (br s, 3H,[Polymer] CH_2-C<u>H</u>$_3$),),^{13}CNMR (DMSO) δ_C 168.8, 162.8, 150.9, 124.8, 121.9, 120.9, 34.0, 29.5, 20.9, 14.0, GPC M_n = 13000 Da PDI = 2.6.

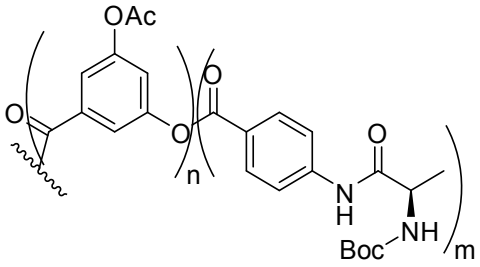
X=NH: Yield = 310mg, 62%, ^{1}HNMR (DMSO, 400MHz) 8.25-7.20 (br m, 3H, [Polymer] Ar *o*-C<u>H</u> , and Ar *p*-C<u>H</u>), 2.50 (br s, 2H[Polymer] CO-C<u>H</u>$_2$-CH_2), 2.30 (s, 3H, [Polymer] -C<u>H</u>$_3$), 1.60 (br s, 2H,[Polymer] CO-CH_2-C<u>H</u>$_2$-CH_2), 1.20 (m, 2H, [Polymer] CO-CH_2-CH_2-C<u>H</u>$_2$-CH_2), 0.90 (br s, 3H,[Polymer] CH_2-C<u>H</u>$_3$), ^{13}CNMR (DMSO) δ_C 168.9, 163.3, 151.9, 124.7, 121.8, 121.7, 120.9, 34.2, 31.1, 21.0, 14.0, GPC M_n =7000 Da PDI = 2.4.

7.2.20 General producer of the modification of amino-functionalised hyperbranched co-polymers:

500mg of each mono or di-amino functionalized hyperbranched co-polymers was placed separately in a 100mL round bottom flask with a bar of stirrer under nitrogen. About 50mL of dry DMF was added to dissolve these polymers. A fixed amount of (3.7g, 1.3x10^{-4}mol) of DCC was add and then followed by slow addition of (1.3x10^{-4}mol) of various compounds. The mixture was left overnight (24 hours) under room temperature. Then, DCM was added to the mixture and washed thoroughly with water to remove the DMF. Then, the layer of DCM was collected and the remaining traces of water in the solution was removed by adding magnesium sulphate and filtrated off. Finally, DCM was removed by the rotary evaporation and the polymer dissolved in THF and precipitated in cold methanol then left in the fridge. By filtration and drying under reduced pressure, the sediment polymer was

collected as powder. The polymer was loaded into bio-beads column to remove the unreacted materials.

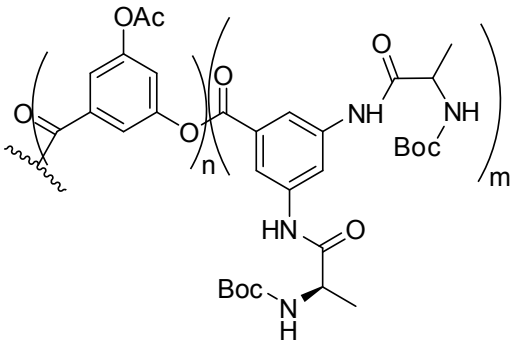
7.2.20.1 Modification of amino functionalised hyperbranched co-polymers with amino acid (Boc-Ala-OH) using DCC (32):



Boc-Ala-OH (25mg, $1.3x10^{-4}$mol).

Yield: 300mg, 60%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.30-7.35(br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.15-6.80 (br m_2, 2H, [Polymer] Ar *o*-CH-C-NH), 4.30 (br, s, 1H, CO-CH-NH), 2.30 (s, 3H, [Polymer] -CH_3), 1.40 (s, 12H, Boc,CH_3CH), ^{13}CNMR (DMSO) δ_C 169.3, 163.2, 151.5, 131.1, 122.4, 121.8, 121.4, 79.4, 79.1, 55.3, 31.1, 28.5, 21.2, GPC M_n = 15700 Da PDI = 3.1.

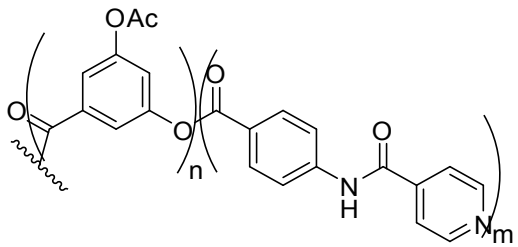
7.2.20.2 Modification of di-amino functionalised hyperbranched co-polymers with amino acid (Boc-Ala-OH) using DCC (33):



Boc-Ala-OH (25mg, $1.3x10^{-4}$mol).

Yield: 330mg, 66%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.20-7. (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.10-6.80 (br m_2, 2H, [Polymer] Ar *o*-CH-C-NH), 4.30 (br, s, 1H, CO-CH-NH) 2.30 (s, 3H, [Polymer] -CH_3), 1.40 (s, 12H, Boc,CH_3CH), ^{13}CNMR (DMSO) δ_C 172.2, 169.4, 163.2, 155.9, 151.6, 131.3, 131.2, 122.4, 121.9, 121.4, 79.0, 55.3, 28.5, 21.2, 16.9,GPC Mn = 13300 Da PDI = 2.7.

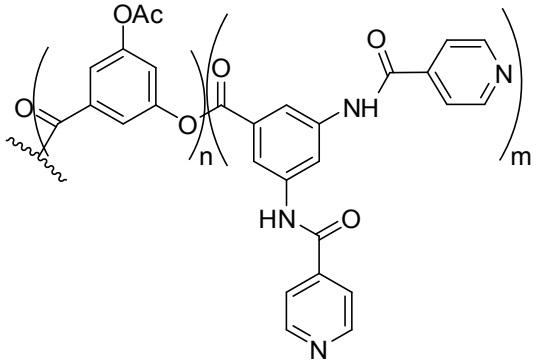
7.2.20.3 Modification of amino functionalised hyperbranched co-polymers with isonicotinic acid using DCC (34):



Isonicotinic acid (16mg, 1.3x10^{-4}mol).

Yield: 250mg, 50%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.85 (br s , 2H, [Polymer] Py-Ar-CH), 8.20-7.15 (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 2.35 (s, 3H, [Polymer] -CH$_3$), ^{13}CNMR (DMSO) δ_C 168.8, 162.7, 151.0, 150.8, 124.8, 121.8, 121.3, 120.8, 20.7, GPC M_n = 16600 Da PDI = 2.9.

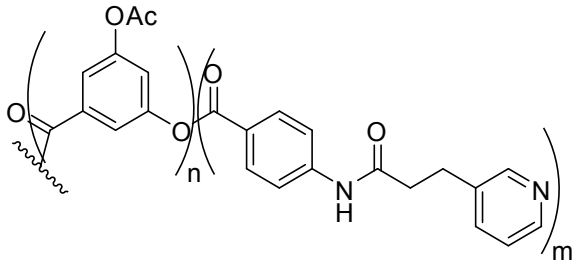
7.2.20.4 Modification of di-amino functionalised hyperbranched co-polymers with isonicotinic acid using DCC (35):



Isonicotinic acid (16mg, 1.3x10^{-4}mol).

Yield: 320mg, 64%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.85 (br s, 2H, [Polymer] Py-Ar-CH), 8.20-7. 15 (br m, 3H, [Polymer] Ar *o*-CH, and Ar *p*-CH), 2.35 (s, 3H, [Polymer] -CH$_3$), ^{13}CNMR (DMSO) δ_C 168.8, 162.7, 151.4, 151.0, 150.8, 139.1, 124.8, 120.8, 20.9, 20.7, GPC M_n = 14900 Da PDI = 2.1.

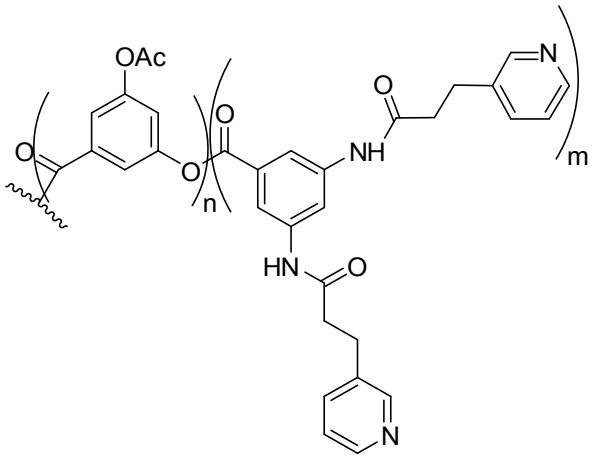
7.2.20.5 Modification of amino functionalised hyperbranched co-polymers with 3-pyridinepropionic acid using DCC (36):



3-Pyridinepropionic acid (20mg, 1.3x10^{-4}mol).

Yield: 390 mg, 78%; ^{1}HNMR (DMSO, 400MHz) 10.50 (br s, 1H, [Polymer] -NH), 8.55 (s , 1H, [Polymer] 4-Py-Ar-CH-N), 8.40 (s ,1H, [Polymer] 2-Py-Ar-CH-N),), 8.20-7.20 (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.10-6.80 (br m , 2H, [Polymer] Py-Ar-CH), 3.10 (s, 4H, [Polymer] CH_2CH_2CONH), 2.35 (s, 3H, [Polymer] -CH$_3$), ^{13}CNMR (DMSO) δ_C 169.3, 163.2, 151.5, 131.1, 131.0, 122.3, 121.8, 121.4, 27.5, 21.2, GPC M_n = 13000 Da PDI = 2.7.

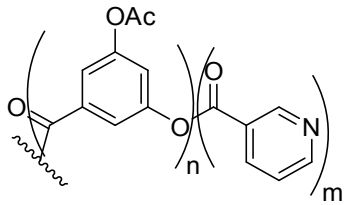
7.2.20.6 Modification of di-amino functionalised hyperbranched co-polymers with 3-pyridinepropionic acid using DCC (37):



3-Pyridinepropionic acid (20mg, $1.3x10^{-4}$mol).

Yield: 290mg, 58%; ^{1}HNMR (DMSO, 400MHz) 10.30 (br s, 1H, [Polymer] -NH), 8.58 (s , 1H, [Polymer] 4-Py-Ar-CH-N), 8.44(s , 1H, [Polymer] 2-Py-Ar-CH-N),8.10-7.15 (br m, 3H, [Polymer] Ar *o*-CH , and Ar *p*-CH), 7.10-6.80 (br m , 2H, [Polymer] Py-Ar-CH), 3.10 (s, 4H, [Polymer] CH_2CH_2CONH), 2.35 (s, 3H, [Polymer] -CH_3) ^{13}CNMR (DMSO) δ_C 169.4, 163.3, 151.6, 131.2, 122.3, 121.4, 121.9, 121.4, 27.7, 21.2, GPC M_n = 8000 Da PDI = 1.7.

7.2.21 Co-polymerisation of 3, 5-diacetoxybenzoic acid and nicotinic acid (38):



10%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), nicotinic acid (0.077g, 0.630mmol) and diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 1.0g, 66%; ^{1}HNMR ($CDCl_3$, 400MHz) 9.40 (s, 1H, [Polymer] Py-Ar-CH), 8.85 (s, 1H, [Polymer] Py-Ar-CH), 8.50 (s, 1H, [Polymer] Py-Ar-CH), 8.10-7.70 (br m, 2H, [Polymer] Ar *o*-CH), 7.60-7.15 (br m, 1H, [Polymer] Ar *p*-CH), 2.25 (s, 3H, [Polymer] -CH_3), ^{13}C NMR (DMSO): δ 168.8, 162.7, 151.0, 137.5, 130.6, 130.4, 121.8, 121.3, 120.9, 20.7, GPCM_n= 14000 Da PDI = 3.2.

20%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), nicotinic acid (0.155 g, 1.26 mmol) and diphenyl ether (1.6 g) were reacted together, yielding the polymer.

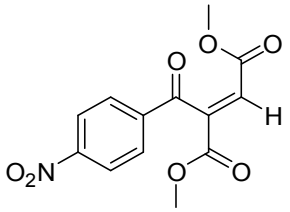
Yield: 0.8g, 53%; ^{1}HNMR ($CDCl_3$, 400MHz) 9.40 (s, 1H, [Polymer] Py-Ar-CH), 8.90 (s, 1H, [Polymer] Py-Ar-CH), 8.50 (s, 1H, [Polymer] Py-Ar-CH)), 8.20 -7.60 (br m, 2H, [Polymer] Ar *o*-CH), 7.60-7.15 (br m, 1H, [Polymer] Ar *p*-CH), 2.25 (s, 3H, [Polymer] -CH_3) , ^{13}C NMR (DMSO): δ 168.7, 162.7, 151.1, 130.9, 121.32, 120.9, 21.0, GPC M_n = 5000 Da PDI = 2.7.

7.2.22 Reaction of DMAD with 4-nitrobenzaldehyde catalyzed by nicotinic hyperbranched co-polymer (39A):

In a dry degassed round bottom flask DMAD (200mg, 1.407mmol) and 4-nitrobenzldehyde (212mg, 1.407mmol) were dissolved in deuterated DMSO under nitrogen. The reaction was cooled to – 10 ^{0}C. Once the temperature was maintained, nicotinic hyperbranched co-polymer (20%, 250mg) was added. The colourless reaction mixture was turned to pinkish colour after the addition of the catalyst. The ice bath was removed and the mixture allowed to return to room temperature. The reaction was left to stir for a week.

Yield: 5%; ^{1}H NMR (DMSO, 400MHz), δ 10.30 (s, 1H, COH) starting material, 8.40 (d, 2H, Ar-*m*-C<u>H</u>) product, 8.30 (d, 2H, Ar-*m*-C<u>H</u>) starting material, 8.20 (d, 2H, Ar-*o*-C<u>H</u>) product, 8.10 (d, 2H, Ar-*o*-C<u>H</u>) starting material, 7.15 (s, 1H, C=C<u>H</u>-COOR), 3.70 (s, 3H, COOC<u>H</u>$_3$).

7.2.23 Reaction of DMAD with 4-nitrobenzaldehyde catalyzed by methyl nicotinate (39B):



In a dry degassed round bottom flask DMAD (200mg, 1.407mmol) and 4-nitrobenzldehyde (212mg, 1.407mmol) were dissolved in deuterated DMSO under nitrogen. The reaction was cooled to – 10 ^{0}C. Once the temperature was maintained, methyl nicotinate (20%, 38mg) was added. The colourless reaction mixture was turned to pinkish colour after the addition of the catalyst. The ice bath was removed and the mixture allowed to return to room temperature. The reaction was left to stir for a week.

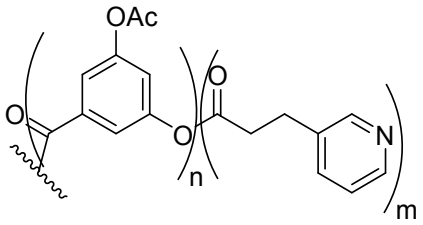
Yield: 8%; ^{1}H NMR (DMSO, 400MHz), δ 10.30 (s, 1H, COH) starting material, 8.40 (d, 2H, Ar-*m*-C<u>H</u>) product, 8.30 (d, 2H, Ar-*m*-C<u>H</u>) starting material, 8.20 (d, 2H, Ar-*o*-C<u>H</u>) product, 8.10 (d, 2H, Ar-*o*-C<u>H</u>) starting material, 7.15 (s, 1H, C=C<u>H</u>-COOR), 3.70 (s, 3H, COOC<u>H</u>$_3$).

7.2.24 Reaction of DMAD with 4-nitrobenzaldehyde catalyzed by picoline (39C):

In a dry degassed round bottom flask DMAD (200mg, 1.407mmol) and 4-nitrobenzldehyde (212mg, 1.407mmol) were dissolved in deuterated (A:DMSO)(B:$CHCL_3$) under nitrogen. The reaction was cooled to – 10 ^{0}C. Once the temperature was maintained, picoline (20%, 26mg) was added. The colourless reaction mixture was turned to pinkish colour after the addition of the catalyst. The ice bath was removed and the mixture allowed to return to room temperature. The reaction was left to stir for a week.

Yield: A DMSO= 94%; B $CHCL_3$=62% ^{1}H NMR (DMSO, 400MHz), δ 10.30 (s, 1H, COH) starting material, 8.40 (d, 2H, Ar-*m*-C<u>H</u>) product, 8.30 (d, 2H, Ar-*m*-C<u>H</u>) starting material, 8.20 (d, 2H, Ar-*o*-C<u>H</u>) product, 8.10 (d, 2H, Ar-*o*-C<u>H</u>) starting material, 7.15 (s, 1H, C=C<u>H</u>-COOR), 3.70 (s, 3H, COOC<u>H</u>$_3$).

7.2.25 Co-polymerisation of 3, 5-diacetoxybenzoic acid and 3-pyridinepropionic acid (40):



5%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 3-pyridinepropionic acid (0.047g, 0.315mmol) and diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 0.85g, 56%; ^{1}HNMR ($CDCl_3$, 400MHz) 8.56 (s , 1H, [Polymer] 4-Py-Ar-C<u>H</u>-N), 8.45(s , 1H, [Polymer] 2-Py-Ar-C<u>H</u>-N), 8.10-7.60 (br m , 2H, [Polymer] Ar *o*-C<u>H</u>),7.50-7.15 (br m , 1H, [Polymer] Ar *p*-C<u>H</u>), 7.10-6.80 (br m , 2H, [Polymer] Py-Ar-C<u>H</u>), 3.10 (s, 2H, [Polymer] CH_2C<u>H</u>COOR), 2.25 (s, 3H, [Polymer] -C<u>H_3</u>) ^{13}C NMR ($CDCl_3$): δ 168.9, 163.4, 162.7, 158.6, 151.5, 151.0, 149.6, 147.4, 130.6, 130.0, 123.3, 121.9, 121.4, 120.9, 118.5, 114.9, 114.0, 27.0, 20.7, GPC M_n = 10000 Da PDI = 1.7.

10%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 3-pyridinepropionic acid (0.095g, 0.630mmol) and diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 1g, 66%; ^{1}HNMR ($CDCl_3$, 400MHz)) 8.56 (s , 1H, [Polymer] 4-Py-Ar-C<u>H</u>-N), 8.45(s , 1H, [Polymer] 2-Py-Ar-C<u>H</u>-N),8.10-7.60 (br m , 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.15 (br m , 1H, [Polymer] Ar *p*-C<u>H</u>), 7.10-6.80 (br m , 2H, [Polymer] Py-Ar-C<u>H</u>), 3.10 (s, 2H, [Polymer] CH_2C<u>H</u>COOR), 2.25 (s, 3H, [Polymer] -C<u>H_3</u>), ^{13}C) ^{13}C NMR ($CDCl_3$): δ 168.6, 162.7, 151.1, 130.7, 121.2, 120.8, 20.9, GPC M_n = 4400 Da PDI = 3.7.

20%: The general procedure was followed where 3, 5-diacetoxybenzoic acid (1.5g, 6.3mmol), 3-pyridinepropionic acid (0.195g, 1.26mmol) and diphenyl ether (1.6g) were reacted together, yielding the polymer.

Yield: 0.82g, 54%; ^{1}HNMR ($CDCl_3$, 400MHz)) 8.54 (s , 1H, [Polymer] 4-Py-Ar-C<u>H</u>-N), 8.42(s , 1H, [Polymer] 2-Py-Ar-C<u>H</u>-N),8.10-7.60 (br m , 2H, [Polymer] Ar *o*-C<u>H</u>), 7.60-7.15 (br m , 1H, [Polymer] Ar *p*-C<u>H</u>), 7.10-6.80 (br m , 2H, [Polymer] Py-Ar-C<u>H</u>), 3.10 (s, 2H, [Polymer] CH_2C<u>H</u>COOR), 2.25 (s, 3H, [Polymer] -C<u>H_3</u>), ^{13}C NMR ($CDCl_3$): δ 168.8, 162.7, 151.1, 130.9, 121.3, 120.9, 21.0, GPC M_n = 2100 Da PDI = 3.

7.2.26 Reaction of DMAD with 4-nitrobenzaldehyde catalyzed by pyridinepropionic hyperbranched co-polymers (39D):

In a dry degassed round bottom flask DMAD (200mg, 1.407mmol) and 4-nitrobenzldehyde (212mg, 1.407mmol) were dissolved in deuterated (A:DMSO)(B:$CHCL_3$)(C:DMF) under nitrogen. The reaction was cooled to – 10 ^{0}C. Once the temperature was maintained, pyridinepropionic hyperbranched co-polymer (20%, 500mg) was added. The colourless reaction mixture was turned to pinkish colour after the addition of the catalyst. The ice bath was removed and the mixture allowed to return to room temperature. The reaction was left to stir for a week.

Yield: A DMSO= 50%; B $CHCL_3$= 5%; ^1H NMR (DMSO, 400MHz), δ 10.30 (s, 1H, COH) starting material, 8.40 (d, 2H, Ar-*m*-CH) product, 8.30 (d, 2H, Ar-*m*-CH) starting material, 8.20 (d, 2H, Ar-*o*-CH) product, 8.10 (d, 2H, Ar-*o*-CH) starting material, 7.15 (s, 1H, C=CH-COOR), 3.70 (s, 3H, $COOCH_3$), Recoverd polymer: DMF was used as solvent. Yield: 240 mg,80%; 8.56 (s , 1H, [Polymer] 4-Py-Ar-CH-N), 8.45(s , 1H, [Polymer] 2-Py-Ar-CH-N),8.10-7.60 (br m , 2H, [Polymer] Ar *o*-CH), 7.60-7.15 (br m , 1H, [Polymer] Ar *p*-CH), 7.10-6.80 (br m , 2H, [Polymer] Py-Ar-CH), 3.10 (m, 2H, [Polymer] CH_2CHCOOR), 2.25 (s, 3H, [Polymer] -CH_3), GPC M_n = 10500 Da PDI = 1.8.

Chapter Eight

References

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