Smart Elastomers for Use in Security Applications

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Abstract

Smart polymers are utilised for a variety of functions. This project aimed to produce a polymer which exhibits fluorescent emission in response to tensile stimuli. Previous fluorescence studies have shown this to be theoretically possible and fluorescence spectroscopy techniques can be used to establish the existence of such responses. A wide range of elastomers (styrene butadiene rubber, polyacrylates, polyurethane acrylates and polyurethanes) have been synthesised with aliphatic polyurethane elastomers being the most promising thus far.

Fluorescent labels (9-vinylanthracene, fluorescein and 1,5-dihydroxynaphthalene) have been successfully incorporated into elastomeric products as have heavy atom containing species (4-bromostyrene, 3-bromo-1,2-propane diol and 4-bromoresorcinol). A library of fluorescent and quenching prepolymers was built up which was then used in a wide range of combinations to produce elastomers containing both fluorophore and heavy atom containing species.

Quenching of the excited state was observed in solution for most fluorophore/heavy atom combinations. 4-Bromostyrene was shown to quench 9-vinylanthracene within solid cross-linked elastomers. 1,5-dihydroxynaphthalene was also successfully quenched within polymer sheets however the emission wavelength of 1,5-dihydroxynaphthalene is not visible to the naked eye. Fluorescein emits visible light but has not been successfully quenched within cross-linked elastomers, with the lifetimes actually increasing in some samples. This observation was attributed to delayed fluorescence resulting from triplet-triplet annihilation promoted by the intersystem crossing to the triplet state brought about by the heavy atom.

Generally speaking, the incorporation of fluorescent labels into solid elastomeric sheets had the effect of increasing the lifetime of the associated excited state. This is probably due to the polymer protecting the excited states from quenching due to atmospheric oxygen.

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Inovink
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EPSRC
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Research Council

Declaration

I herewith declare that I have produced this thesis without the prohibited assistance of third parties and without making use of aids other than those specified. All work contained herein is my own, except where accordingly referenced and acknowledged.

This thesis has been submitted to the University of Sheffield for the degree of Doctor of Philosophy, having not been submitted to any other institution for any other award.

The work for this thesis was conducted from September 2008 to December 2012 under the supervision of Stephen Rimmer and Linda Swanson at The University of Sheffield.

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Glossary

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AIBN	Azobisisobutyronitrile, page 47
BS	4-Bromostyrene, page 43
DSC	Differential Scanning Calorimetry, page 2
DVB	Divinylbenzene, page 50
EDTA	ethylenediaminetetraacetic acid, page 44
FT-IR	Fourier transform infrared spectroscopy, page 73
GFP	Green Fluorescent Protein, page 2
GPC	Gel Permeation Chromatography, page 47
HDI	Hexamethylene diisocyanate, page 71
HEA	Hydroxyethyl acrylate, page 69
IPDI	Isophorone diisocyanate, page 71
MDI	4,4'-Methylene diphenyl diisocyanate, page 71
Mn	Number Average Molecular Weight, page 47
Mw	Weight Average Molecular Weight, page 47
ND	Not Discovered, page 32
NMR	Nuclear Magnetic Resonance, page 21
PET	polyethylene terephthalate, page 157
PTFE	polytetrafluoroethylene, page 114
SBR	Styrene Butadiene Rubber, page 4
SDS	Sodium Dodecyl Sulfate, page 21
TCSPC	Time-Correlated Single Photon Counting, page 33
THF	Tetrahydrofuran, page 33
TPO	Diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide, page 51
VA	9-Vinylanthracene, page 43

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Introduction

1.1 Smart Polymers

Stimuli sensitive polymers are also known as smart or environmentally sensitive polymers. The behaviour of such polymers was described Gil and Hudson as such:

> "[Smart polymers] undergo relatively large and abrupt, physical or chemical changes in response to small external changes in environmental conditions."[1]

Environmental changes can include electrical, magnetic, mechanical or other chemical or physical changes. The responses can include a change in shape, solubility or fluorescence.[2] There are many uses for these responsive materials, including sensors and displays. For most applications; polymer responses must be highly controlled. Biocompatible stimuli sensitive polymers are of particular interest to medical researchers. Some hydrogels can exhibit a swelling response to changes in pH or ionic strength.[3] This response can be used as a targeted drug delivery system, whereby the drug is released as the gel swells in response to environmental changes during passage through the body.[4]

Other stimuli sensitive polymers are also being investigated for their use as drug delivery systems. Including those where the rate of drug release is controlled by a stimuli sensitive polymer that responds to a physiological change. This could lead to self-regulated drug delivery systems for the long-term treatment of conditions such as diabetes. This would allow the therapeutic agent (e.g. Insulin) to be released in accordance with the body's need for it.[5]

Fluorescence can be used to give information about many polymeric properties. Miscibility of polymers can be found if one polymer contains a fluorophore and the other its quencher.

The interactions between phase-separated fluorophores and quenchers can also give valuable information about the structure of the polymer.[6]

Properties such as conformation[7], chain length[8, 9] and chain packing[10, 11] and solubility[12] can all be investigated by fluorescence. The response of fluorescent polymers to changes such as pH can be followed. Fluorescent species can also be used as detectors for a variety of other species, such as metal cations[13] and the chemical vapours emanating from unexploded landmines[14]. More recently, single molecule fluorescence methods have been used to probe nanoscale polymer structure and dynamics.[11]

1.1.1 Tension

Tension, like both vibration and pressure, is a mechanical stimulus. Tension is a force, measured in Newtons, acting through material that is subject to forces at either end moving in opposite directions. Tension is usually measured by specialist equipment such as extensometers (tensometers), but can also be measured by optical (particularly useful for the measurement of larger deformations) and other methods.[15] This is usually done at equilibrium, i.e. when there is no net force on the material in question. Stress-strain curves can be plotted, and these give useful information on the polymer properties such as the peak stress and where tensile instability begins.[16] Various different tensile experiments are used such as the bulge test to give information on the stress-strain response under different stresses e.g. shear[17] or planar tension.[15]

1.1.2 Responses to Tension

Hofstraat et al[18] used charge-transfer fluorescence probes to investigate physical changes in polymers. Previously, polymerization kinetics and solvent effects were the main changes investigated by this technique. However this experiment shows the charge-transfer fluorescence probe reporting a strong response to the physical changes. These changes in intensity and wavelength were corresponded to data from bulk characterization methods like differential scanning calorimetry (DSC) and can be used at very low concentrations.[18]

1.1.3 Green Fluorescent Protein

There are few known polymers that change colour in response to a mechanical stimulus. Green fluorescent protein (GFP) is a natural product that is quenched by molecular distortion. GFP was first discovered in the jelly fish *Aequorea victoria*, and has since found widespread use as a marker for genetic expression in microbiology and biotechnology.

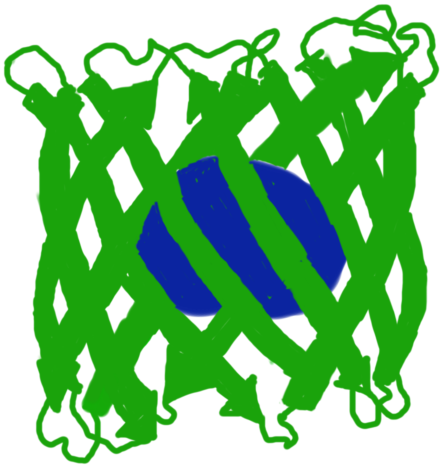


Figure 1.1: Green Fluorescent Protein - Showing the β-barrel structure (green) and the tripeptide chromophore Ser-dehydroTyr-Gly (blue) contained inside it.

The crystal structure of GFP was solved in 1996 by Yang et al[19] and found to comprise mainly of a unique β-barrel structure with some α-helical content and a tripeptide chromophore contained within the β-barrel (see Fig. 1.1) Work on green fluorescent protein has studied its spectral changes with application of an external force. Fluorescence quenching occurs when compression (thought to distort β-barrel structures) or tension (molecules can be pulled by NH_2 reactive probe) is applied; i.e. the fluorescence is quenched by the disruption of the molecular structure in close proximity to the chromophore.[20] It is thought that the β-barrel structure protects the chromophore from quenching by molecular oxygen and the disruption of the β-barrel therefore results in the quenching of the fluorescence.

1.1.4 Applications for Smart Polymers

The wide variety of responsive polymers available means that there are almost limitless potential applications for smart polymers. Smart polymers are utilised in security,[21] drug delivery,[5] cell culture,[22] chemical sensors[23] and a vast range of other functions. Smart polymers are becoming ubiquitous as understanding of their triggers increases. New smart polymers are constantly being developed with different stimuli and more controlled responses.

1.2 Elastomers

Elastomers are polymers which return to their original shape following a deformation. Most elastomers can be considered as very viscous elastic liquids and as such require crosslinking to show true elastic behaviour.[24] This can be achieved in a variety of ways including treatment with sulfur compounds, hydroxides, and radiation.[25, 26, 27, 28] However all of these additives have other effects on the properties of the elastomer being treated. The properties of elastomers can further be altered by other additives such as carbon black.[29] In this way, elastic polymers can be modified to have desirable properties such as durability, heat resistance and colour. A brief introduction to the specific elastomeric species used in this project will be provided at the start of the relevant chapters.

1.2.1 Methods of Elastomer Synthesis

1.2.1.1 Emulsion Polymerization

Emulsion polymerization is a method commonly used to make commercially required polymers, including styrene butadiene rubber (SBR.) Emulsion polymerisation requires the following;

- Monomers (e.g. styrene)
- Surfactant (e.g. Sodium dodecyl sulfate)
- Initiator (Usually radical producing; often a redox system)
- Heat transfer medium (e.g. water)

Both hot (41°C) and cold (5°C) processes are used to synthesise SBR.[30] Cold emulsion polymerization is favoured as a technique for rubber production as it gives relatively high molecular weight products over a relatively short time.[31, 32] The polymerization can either be a batch (all monomers added before initiator) or a continuous (monomers added over a time period either with or after initiator) reaction.[33] There are many other factors such as monomer composition and emulsifier concentration that affect the product[34] but temperature is the main influence.[35] It is important in radical initiated reactions to exclude oxygen from the reaction vessel, as it can compete with the monomers for the initiator.[36]

1.2.1.2 UV Polymerization

Ultraviolet light is part of the electromagnetic spectrum. It falls just outside the visible range with a wavelength of around 200 - 400 nm. UV polymerization usually requires a light-activated initiating species known as a photoinitiator, or a mix of photoinitiators. When the photoinitiation system is exposed to light of the correct wavelength and intensity, it will undergo a chemical reaction. Products of this reaction, often radical species, then proceed to initiate the polymerization reaction.[37, 38, 39] Fig. 1.2 gives an illustration of light-induced homolytic bond cleavage giving rise to two radicals from a photoinitiator.

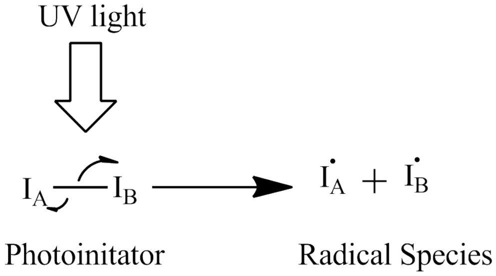


Figure 1.2: Photolytic Bond Cleavage - Illustrating the generic formation of radicals from an photoinitiator.

Many photoinitiators are catalytic and the polymerization will continue after the UV source has been removed. If the photoinitiator is not catalytic, it is essential that the UV light can penetrate through the whole sample during irradiation or the polymerization will be incomplete. It is also important to check the compatibility of the monomers with the photoinitiator as some combinations can lead to the formation of light-absorbing by-products.[40] Another concern is the presence of oxygen, which can lead to inhibition. Some UV polymerisations are resistant to the effects of oxygen but most are at least partially inhibited by it.[41] Fig. 1.3 shows the formation of peroxy radicals from molecular oxygen and a radical species. The peroxy radical formed is much less reactive than the initiator radical used to form it. Therefore the formation of these peroxy radicals leads to inhibition of the polymerisation reaction by slowing down the reaction propagation (Fig. 1.4) For this reason, photoinitiated polymerisations are often carried out under a nitrogen atmosphere. UV polymerization is usually a simple and consistent method for making polymers in a short time-frame.[42]

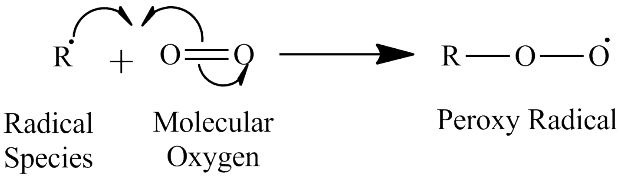


Figure 1.3: Inhibition by Oxygen - Illustrating the formation of a peroxy radical from a more reactive radical species

1.2.1.3 Radical Polymerization

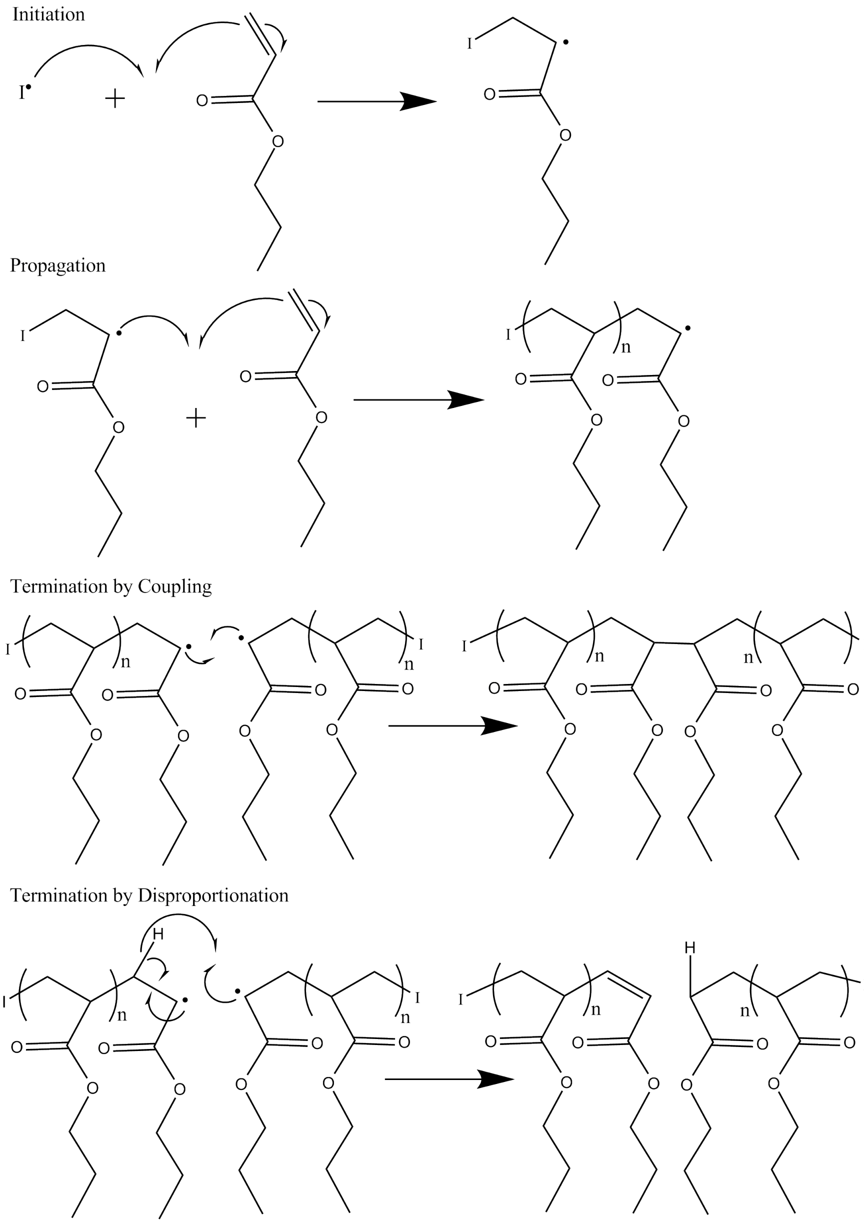


Figure 1.4: Overview of a Radical Polymerisation - Illustrating the initiation, propagation and termination steps.

Radical polymerisation, once initiated, continues via the propagation of the radical along the growing polymer chain (Fig. 1.4) with the addition of each monomer unit. The reaction ceases when there is no monomer remaining or is terminated when two active chains encounter each other. This termination can occur by coupling to form one longer chain, or by disproportionation which results in two slightly different chains (Fig. 1.4) The growing polymer chains can also be terminated by an encounter with a radical initiator molecule or certain contaminants or inhibitors. These inhibitors could be naturally present, such as molecular oxygen, or species which are deliberately added to mop up free radicals and short-stop the reaction. The quantity of radical initiator used corresponds to the chance of chain termination and therefore controls the molecular weight of the polymer formed. Radical polymerisations are termed ”living” if the reaction only stops when all the monomer is used up and not by any termination reactions. In the case of living radical polymerisation, the addition of more monomer will continue the polymerisation reaction.

1.3 Fluorescence

Fluorescence is a type of luminescence in which a photon is absorbed, followed by emission of another photon of lower energy and therefore longer wavelength (Fig. 1.5) this difference in wavelength is known as the Stokes shift. The energy difference is spent on molecular motion, or lost as kinetic or thermal energy.[43] The absorption step is the fastest in the process, occurring on a 10^{-15} s timescale, and this is usually followed by vibrational relaxation as shown in Fig. 1.5. Vibrational relaxation occurs over a slightly longer but still very short (10^{-13} s to 10^{-11} s) timescale and usually involves relaxation to the lowest possible vibrational level of the excited state. Therefore the Stokes shift is governed by the energy gap between the lowest vibrational level of the excited state and the vibrational level that the excited state occupied immediately following the absorption of the photon. It also follows that fluorescence usually occurs as a transition from the lowest possible vibrational level of the excited state to the ground state. The emission associated with fluorescence occurs over a 10^{-9} s to 10^{-7} s timescale, compared with another type of luminescence known as phosphorescence which occurs over a 10^{-4} s to 10^{1} s timescale. The excited state can be very different chemically to the ground state of the same species due to the difference in electronic configuration. In the ground state all electrons are spin paired; however this is not always the case in the excited state. In the excited state, if all electrons remain spin paired then it is referred to as a singlet state. If a set of electrons is spin unpaired then the state is termed a triplet state. Transitions from the ground to triplet state are spin forbidden and therefore extremely unlikely to occur, especially given the short timescale over which the absorption occurs. [43] Likewise; transitions from the triplet state to the ground state via fluorescence are also spin forbidden. The reversal of spin orientation that allows formation of a triplet excited state from a singlet excited state is called inter-system crossing.

It is important not to confuse fluorescence with either Rayleigh scattering or the Raman effect.[44] Rayleigh scattering is the scattering of light by molecules smaller than the wavelength of the light. The effect is responsible for the blue colour of the sky and large bodies of water, it is wavelength dependent and the molecules in the atmosphere scatter blue light most strongly. Rayleigh scattering can be differentiated from fluorescence because the wavelength of the photons involved remain unchanged during Rayleigh scattering unlike with fluorescence.

Raman Scattering or the Raman effect does cause the photons to change wavelength. However, unlike fluorescence, this change is not dependent on any energy difference or molecular transition i.e. it is not a resonant effect. This means that the Raman effect is not dependent on the wavelengths of the photons involved. Raman scattering also does not occur via an excited state and so can happen near instantly unlike fluorescence which occurs over a 10^{-9} s to 10^{-7} s timescale.[43] Both Raman and Rayleigh scattering can interfere with fluorescence spectroscopy but both are less favoured than fluorescence and it is easy to avoid the majority of Rayleigh scattering by not detecting photons at the same wavelength that the excitation source is emitting. Scattering effects are also why a machine ”prompt” is run before most fluorescence spectroscopy to establish a background profile for scattered light.

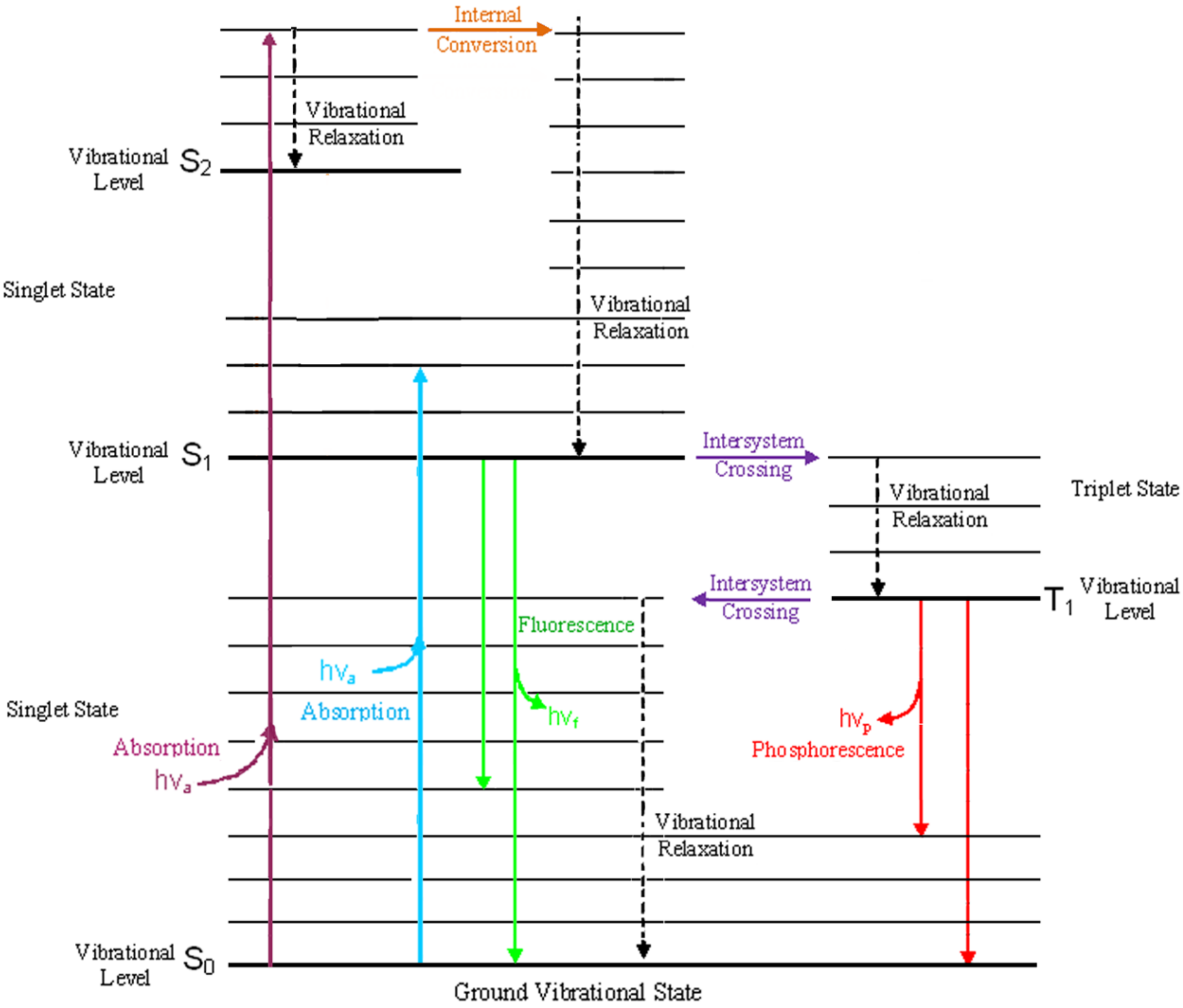


Figure 1.5: A Jablonski Diagram - Illustrating the vibrational energy levels and electronic states of a molecule and describes the transitions between them. These transitions can be radiative (involving the release of a photon) such as fluorescence and phosphorescence, or non-radiative such as inter-system crossing and internal conversion.

There are a wide variety of species that exhibit fluorescence and when used to add fluorescence to a polymer, cell, or other species they are termed fluorescent labels or tags. 9-Vinyl anthracene is a fairly common fluorescent species that absorbs light in the UV range and emits it in the visible spectrum as blue light. It can also be incorporated into polymerisation reactions as a fluorescent monomer.[45]

1.3.1 Fluorescence Spectroscopy

1.3.1.1 Excitation and Emission Spectra

Excitation and emission spectra are a type of steady state measurement. Steady state fluorescence data is recorded using a constant source of light paired with continuous detection of the photons emitted in response. The spectrophotometer used to record this data makes use of monochromators to ensure selective detection of photons with a set wavelength. To obtain the emission spectrum, the wavelength used to excite the sample is kept constant while the emission intensity is recorded across a series of wavelengths. In the same manner, the excitation spectrum is obtained by recording the emission intensity at a fixed wavelength while the sample is excited using a series of different wavelengths. The spectra obtained will display one or more peaks which correspond to favourable transitions between vibrational energy levels of both the ground and the excited states. Fig. 1.6 shows a schematic of these transitions with the distance between peaks corresponding to the energy gap between vibrational levels. As seen in Fig. 1.6 the excitation and emission spectra have a tendency to resemble each other but in reverse. This tendency is known as the mirror image rule[43] and occurs due to the gaps between vibrational energy levels being very similar in both the excited and the ground states, however there are many exceptions to this rule. Transitions between the ground state and the second excited state, chemical reactions involving the excited state, and the formation of charge-transfer complexes are a few things that can lead to deviation of the mirror image rule.

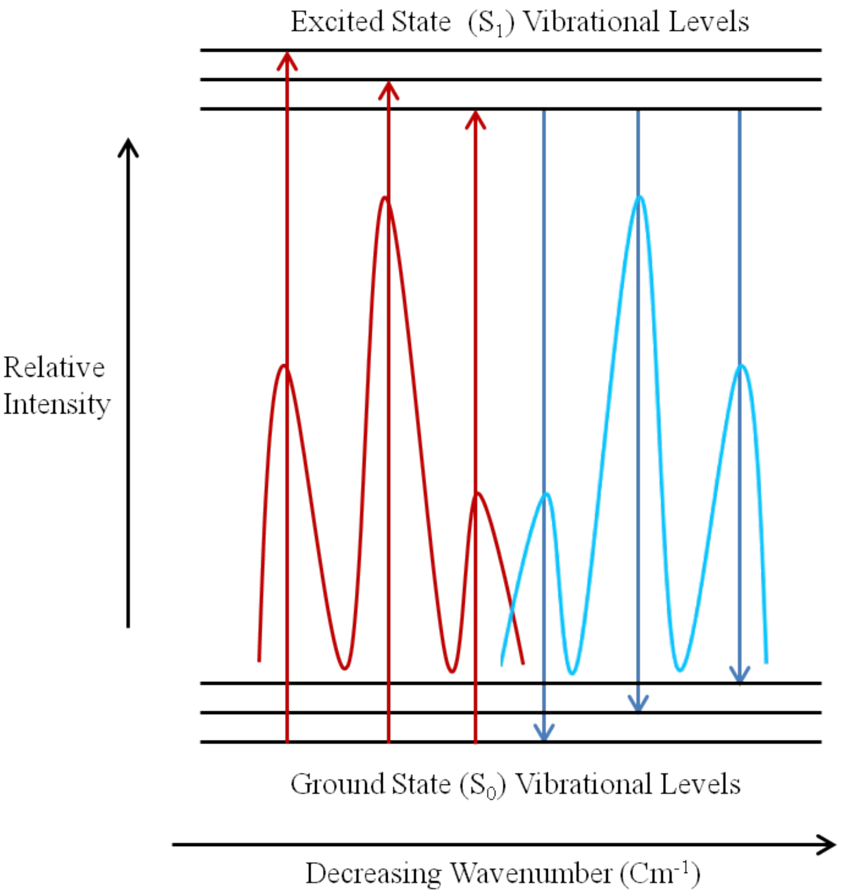


Figure 1.6: Schematic of Excitation and Emission Spectra - Illustrating the effects on the spectra of the vibrational energy levels of the ground and excited states. The excitation spectrum is shown in red and the emission spectrum is shown in blue

1.3.1.2 Fluorescence Lifetimes

A method for analysing energy transfer is to look at the excited state lifetimes of samples. This is a type of time-resolved measurement and uses pulses of light at a specific wavelength to excite the sample and then records the lifetime of the excited state created. This is the time taken between a pulse of electromagnetic radiation used to excite the fluorescent species and the detection of photons emitted in response. A series of such readings are be taken and the resultant data compiled into a histogram. This data distribution plot is then mathematically fitted to a model comprising of one or more exponential components. The number of exponential components used to fit the data depends on the label used and the environment it is in. Generally speaking, the more complicated the label system and its environment, the greater the number of exponentials required to give a good fit to the data.

The mathematic fit uses the following equation:

$$I_{(t)} = \sum_i \alpha_i exp(-t/\tau_i) \qquad \text{(Equation 1.1)}$$

Where $I_{(t)}$ is the lifetime of the excited state as a function of time (t) and α_i is the pre-exponential factor which corresponds to the amount of each component (τ_i) present. The value represented by i gives the number of exponential components used. I.e. for a single exponential fit, the equation will be used where $i = 1$. Statistical confidence in the mathematical fit is given by the χ^2 value; which is close to unity for a good fit, and the residuals; which should be randomly distributed around zero.

Where the decay of the excited state is not monoexponential, the average lifetime (τ) of all components can be calculated using the following equation:

$$\tau = \sum_i \alpha_i \tau_i^2 / \sum_i \alpha_i \tau_i \qquad \text{(Equation 1.2)}$$

The fluorescent lifetimes of samples give direct information on the degree of quenching. I.e. shorter lifetimes correspond to greater quenching. This in turn can give data on the structure of a polymer as the energy transfer involved in quenching is dependent on the distance between the fluorophore and its quencher.[43] It is important to note that the excited state lifetime is not dependent on the concentration of fluorophore as each point on the histogram corresponds to a single photon.

1.3.2 Excimers and Fluorescent Monomers

Excimers are dimeric molecules that are formed from two species (either different or the same) one or both of which are in an excited state.[46, 47] These molecules are very short-lived and can be suppressed by other species.[48] Excimer emission can be altered by various changes, including polymer species. Fluorescent monomers such as pyrene[49] and 9-Vinyl anthracene[7] can also be incorporated within the polymer. Naphthalimide derivatives are also used for their fluorescent properties, and their colour of emission can be altered by the substitution at the 4-position of the naphthalimide ring.[50]

1.3.3 Quenching of Fluorescence

Quenching can be used to describe a variety of processes and molecular interactions that result in the decrease of fluorescence intensity. Förster energy transfer can cause quenching over a relatively long range (∼100Å) compared with Stern-Volmer and heavy-atom quenching which occurs within contact distance (<20Å) Quenching of fluorescence directly corresponds to a shortening of the excited state lifetime. In solution, the rate of collision between fluorophore and quencher often controls the quenching. Therefore in solution, the quenching process is dependent on temperature and pressure.

1.3.3.1 Stern-Volmer Quenching

The Stern-Volmer relationship describes the kinetics of an intermolecular quenching process with the following equation:

$$\tau_0/\tau = 1 + k_q\tau_0[Q] \qquad \text{(Equation 1.3)}$$

Where τ_0 is the fluorescence intensity in the absence of quencher, τ is the fluorescence intensity in the presence of quencher, K_q is the quencher rate coefficient and $[Q]$ is the concentration of quencher.[43] In the case of Stern-Volmer quenching, a graph of τ_0/τ against [Q] will give a linear plot with an intercept of one. The gradient of such a plot can also be used to calculate k_q. This equation describes dynamic quenching which is quenching that is dependent on the rate of collision between fluorophore and quencher.

1.3.3.2 Heavy-Atom Quenching

Quenching can also occur when an electron flips spin, which promotes intersystem crossing; creating triplets at the expense of singlets as shown on the Jablonski diagram (Fig. 1.5) Emission from the triplet state is spin forbidden and so this can only occur very slowly. This means that although the triplets do not display fluorescence (release of a photon on a 10^{-9} s to 10^{-7} s timescale) they can display phosphorescence (release of a photon on a 10^{-4} s to 10^{1} s timescale) but this is usually quenched by oxygen in the environment[51] via energy transfer from the excited state to the oxygen. Because of this, the oxygen concentration and the oxygen saturation level in solutions is very important for this type of quenching.

Heavy atom quenching is also thought to work by increasing the incidence of intersystem crossing to the triplet state[52, 53, 54, 55] via spin-orbit (vibrational) coupling, although the exact mechanism is still unresolved. The heavy atom quencher used can affect the quenching rate (k_q) which can be under either diffusion or kinetic control. This variety in k_q has been tentatively attributed to the formation of an excimer complex (exciplex) although little evidence exists to support this theory.[56]

1.3.3.3 Förster Energy Transfer (FRET)

Förster or fluorescence energy transfer (also known as non-radiative energy transfer) is the mechanism by which energy is transferred from a donor chromophore (D) in the excited state to an acceptor chromophore (A) in the ground state. This is achieved through non-radiative dipole-dipole coupling and can only occur across a short distance (usually less than 100Å).[43]

As the rate of energy transfer from the donor to the acceptor is dependent on the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, FRET can be used to measure the distance between donor and acceptor pairs. This technique also allows for the monitoring of the degree of expansion and/or contraction of the elastomer. The Förster model for energy transfer shows that energy transfer is controlled by the Förster distance (R_0) which is the donor-acceptor distance at which the energy transfer efficiency is 50% The relationship is described as follows:

$$K_T(r) = 1/\tau_D(R_0/r)^6 \qquad \text{(Equation 1.4)}$$

Where $K_T(r)$ is the rate of energy transfer, $1/\tau_D$ is the donor decay rate and r is the distance between the donor and the acceptor.[57]

Förster energy transfer in excited state equilibria can result in cycles of excitation and emission that correspond to the ionisation of the excited state. [43] The tripeptide chromophore within GFP (Fig. 1.1) is known to exhibit a Förster cycle[58] (Fig. 1.7)

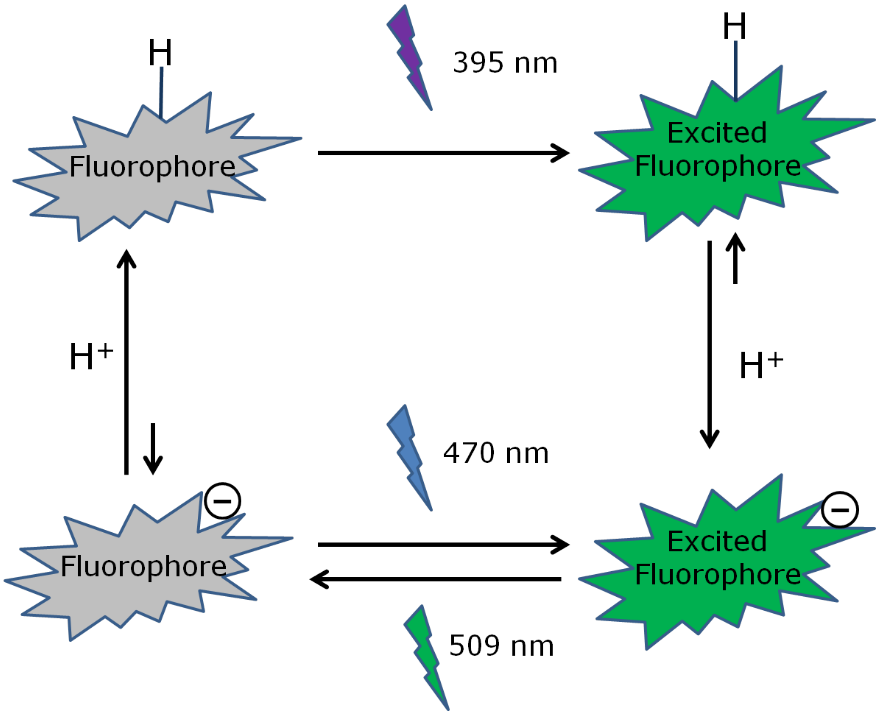


Figure 1.7: Overview of the Förster Cycle Within the GFP Chromophore - Showing ionisation and electronic state of the chromophore.

1.4 Security

1.4.1 Polymers for Security

Polymers have many uses in security applications, most notably in the validation of currency. Polypropylene has been used since 1988 as an added security feature on Australian banknotes and is now used at the substrate for banknotes around the world.[59] These polymer notes make use of a transparent polymer window that features an image as a security feature. On the Australian notes, this picture is of Captain James Cook and the Australian Coat of Arms and is only visible when viewed with a light source behind it. Polymer banknotes already comprise of several layers including opacification coatings, as well as being printed. This gives several opportunities to incorporate further security features, including fluorescent inks or coatings.

However there are few examples of previous work centred around the security applications of smart polymers exhibiting a specific fluorescent response to a mechanical stimulus. Researchers in Japan [60] claim to have created films from substituted polyacetylenes which change colour when stretched but the exact mechanism for this is still unknown. It is speculated that the colour change results from an alteration in the conjugated system of the main chain. Researchers from the University of Illinois[21] have designed a polymer that has a mechanophore embedded within the polymer chain. This system utilises spiropyran, a well-known photochromic dye used in colour-changing lenses. Ring opening reactions cause the spiropyran to change colour when exposed to light or a force.

1.4.2 Fluorescence in Security

The absorption of invisible UV light leading to re-emission of visible light has many applications in security. These include validation of currency and stamps, dye-packs, anti-theft devices and invisible inks or paints.

1.4.3 Surface Coatings

Surface coatings are thin coverings applied to a substrate such as paper or glass. These coatings can alter appearance, as well as other properties such as improved weathering and resistance to scratching or shattering.[61, 62] Stimuli-sensitive polymers can also be applied as coatings that can be used as chemical sensors.[63] Coatings can be applied to the surface of materials in a variety of ways e.g. brushed on, sprayed on or printed. K-bars allow coatings of different thicknesses and side-by-side application of more than one coating to allow easy comparison. A common printing technique for coating substrate is lithography where a smooth hydrophobic surface is used to apply the ink to the substrate. Photolithography uses light to transfer the printing pattern, and soft lithography uses replica moulding and self-assembly for the formation of μ- and n-structures. Intaglio printing utilises an engraved surface for ink application,[64] and letterpress is a technique using an embossed surface.

The major problem for the application of surface coatings is drop formation or reticulation of the coating formulation. Various wetting agents, surfactants and other additives can be used to ensure an even coat of the polymer ink.[65] UV coatings are those which can be applied as a liquid monomer mix containing a photoinitiator. This coating can then be cured after application to the substrate by exposure to UV light.

1.5 Aims and Objectives

1.5.1 Aims

The overall aim of this thesis is to work towards the development of a novel elastomer which exhibits a specific fluorescent response to a mechanical stimulus. Such a material would have many uses, particularly in security applications. A visible response to mechanical stimulus would allow visualisation of stress and add novel security feature to products required validation e.g. banknotes. A material of this type would allow a banknote (or other product to be validated) to be placed under a UV light and when pressure is placed on it (e.g. the note is bent) there would be an obvious increase in the fluorescence emission observed. Many places involved with the validation of currency already own a fluorescent light for the verification of existing security features so this would also involve minimal expenses for the end users of the security features. Very little work has been done to develop products of this nature. Previous research focussed mainly on either biological applications or on non-reversible, one-use colour changes.[21, 60] Therefore the aim for this project will be to try to develop a material that provides proof of principle for the concept rather than the development of a finished product.

The quenching of fluorescence by heavy atoms is governed by the proximity of the quencher to the fluorophore. This, in turn, is affected by the stretching and elongating of the polymer chains. Therefore the strategy employed by this project is the synthesis of novel elastomeric materials containing both fluorophores and heavy-atom quenchers as part of the polymer chain. This strategy should lead to a system where the application of tension causes an increase in the average distance between quencher and fluorophore which reduces the chance of quenching occurring. These elastomers can then be spectroscopically observed both in a relaxed state and when tension is applied to them to determine any difference in the lifetime of the excited state which corresponds to a change in the level of quenching.

1.5.2 Objectives

1. To build a library of elastomeric species containing fluorescent labels, heavy atom quenchers and a combination of the two.
2. To undertake fluorescence analysis of these elastomers and evaluate the quenching of fluorescence.
3. The overall objective of this project is to provide proof of principle for the ability to produce elastomers which exhibit a specific fluorescent response to a mechanical stimulus by incorporating both fluorophores and quenchers within a polymer chain.

2

The Synthesis of Styrene-Butadiene Elastomers

2.1 Introduction

Styrene-butadiene rubber (also known as SBR, GRS and Buna-s) is a random copolymer of styrene and butadiene. The emulsion polymerisation of styrene-butadiene rubber (SBR) has been utilised by industry since its development in the 1930's. It is favoured for use in industry due to its properties, including ease of processing and resistance to heat, wear and aging.[30] In industry, it is usually synthesised using a hot process under high pressure.[66] However this requires a high pressure reaction vessel. It is also possible to synthesise SBR using cold emulsion polymerisation, but again, in industry this is usually carried out in a pressurised reactor. Cold emulsion polymerisation usually results in a higher molecular weight product with a lower glass transition temperature (Tg) and greater elasticity than SBR formed using the hot process.

SBR can be used like natural rubber, but unlike natural rubber is not regular enough to crystallize on stretching, therefore it will need reinforcing for high tensile strength. The Tg of styrene is high, while the Tg of butadiene is very low. This allows the properties of SBR rubber to be altered in a predictable way by the adjustment of the monomer ratios. The properties of the rubber synthesised can be further modified by the incorporation of various additives. The ability to modify this well characterised elastic polymer made it a good candidate for the incorporation of fluorescent and quenching monomers. Also fluorescent and quenching monomers compatible with incorporation into this reaction are commercially available. The addition of these monomers may affect the properties of the resultant polymer, including its Tg and therefore elasticity. It is therefore important to be able to compensate by the further modification of product if necessary.

The aim of this work was initially to produce cold emulsion SBR in the laboratory at atmospheric pressure, rather than under increased pressure as common in industry. Once SBR had been successfully synthesised, fluorescent monomer would be introduced to the reaction mixture and fluorescent SBR synthesised. The next stage would be the incorporation of a heavy atom containing fluorescence quencher to the blend. The overall goal being the production of a highly elastic SBR containing both the fluorescent and quenching species as part of the main polymer chain. The heavy atom containing species must be incorporated in sufficient quantity for quenching of the fluorescence to be observed either by the human eye or via spectroscopy.

The intention was to utilise the well established recipes used in industry for the formation of cold-emulsion SBR. Fluorescent and quenching styrene analogues can then be added in place of equivalent styrene. This substitution of part of the styrene portion of the blend should help to reduce any deleterious effects of these modifications on the properties of the resultant rubber. This modified SBR will then be characterised and the method modified further as necessary to produce the desired properties.

Fluorescence spectroscopy will be used to measure the excited state lifetime of the fluorescent label (9-vinylanthracene) contained within the SBR. This can then be compared with the excited state lifetime of the label in SBR which also contains the fluorescence quencher (4-Bromostyrene.) Solution phase fluorescence spectra for the free 9-vinylanthracene are to be obtained as a reference. Solution spectra of the unbound 9-vinylanthracene in the presence of different concentrations of 4-bromostyrene can also be used to show the deactivation of the excited state by the heavy atom containing species.

2.2 Emulsion Polymerisation of Styrene-Butadiene Rubber

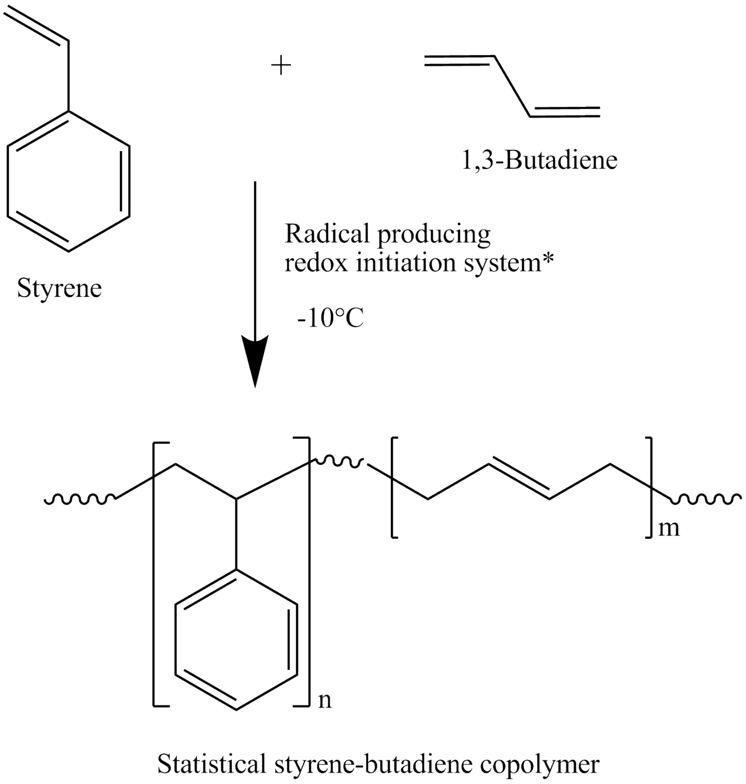


Figure 2.1: Synthesis of Styrene-Butadiene Rubber - An overview of the formation of SBR from Styrene and 1,3-Butadiene. *For details on the REDOX system please see Experimental section 6.1.2

2.2.1 Method One

Cold polymerised emulsion SBR is normally synthesised at 5°C under increased pressure. 1,3-butadiene exists as a gas at room temperature and pressure and has a boiling point of -4.5°C at atmospheric pressure. The standard industrial method for producing cold polymerised emulsion SBR uses temperatures above the boiling point of 1,3-butadiene but keeps the reaction mixture under increased pressure to maintain the presence of 1,3-butadiene within the emulsion and prevent it from escaping. As a pressurised reaction vessel was unavailable for this project, the intention was to synthesise cold polymerised emulsion SBR at atmospheric pressure. To prevent the 1,3-butadiene from escaping the reaction vessel as a gas and to keep it available in the emulsion for polymerisation, the temperature was lowered to -10°C, below the boiling point of 1,3-butadiene (-4.5°C).

The initial recipe (Experimental 6.1.2) adapted from standard industrial methods[67] used SDS (sodium dodecyl sulfate) as a surfactant and did not result in a homogeneous latex. The final latex was lumpy and had solid content of only $\sim 2\%$($\sim 13\%$ expected.) As the lumps were observed forming before the addition of monomers to the system, they were believed to be a result of the surfactant precipitating from solution at the lowered temperature.

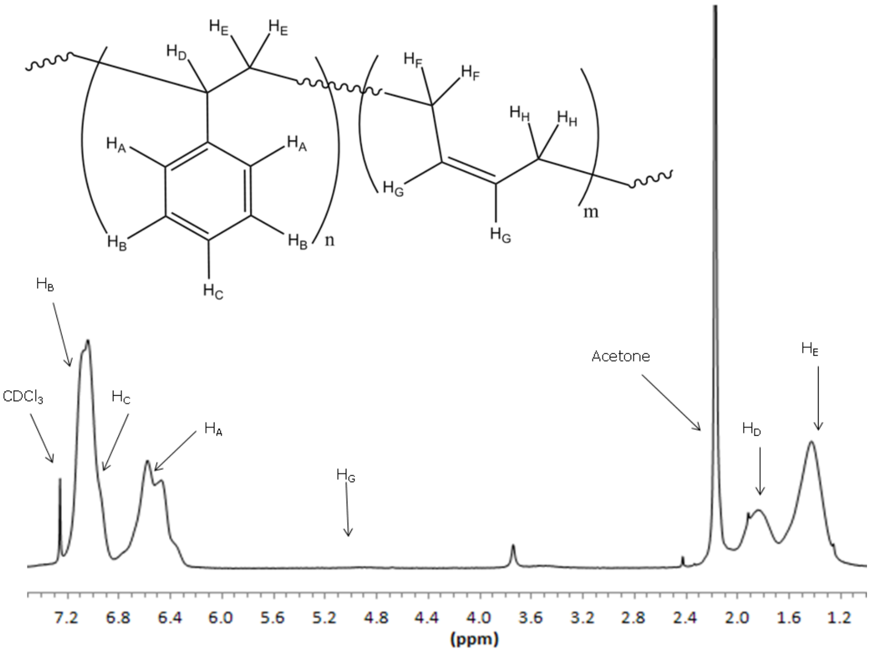


Figure 2.2: Assigned ^{1}HNMR Spectrum of SBR Synthesised Following Method One - Showing the presence of styrene but the absence of expected peaks for 1,3-butadiene at around 5.2 ppm

Once isolated from the latex, the product was found to be glassy and rigid. The ^{1}HNMR spectrum (Fig. 2.2) for this product did not display the expected peak for 1,3-butadiene, a doublet at around 5.2 ppm created by hydrogen atom attached to the carbon at either end of the double bond (labelled H_G on the ^{1}HNMR spectrum assignments.) This absence showed that the product either did not contain 1,3-butadiene or if it did, the levels were too low to be visible on the spectrum. A heavy presence of styrene was shown in the ^{1}HNMR spectrum. As the problems with the emulsion were attributed to the surfactant used, an alternate surfactant more suitable for lower temperatures was chosen for method two.

2.2.2 Method Two

1,4-Bis(2-ethylhexyl) sodium sulfosuccinate (Aerosol OT) was chosen as the surfactant for method two. The other change to the emulsion mixture was the addition of β-cyclodextrin as an aid to 1,3-butadiene solubility. Cyclodextrins have been previously shown to improve the aqueous solubility of butadienes.[68] β-Cyclodextrin forms a toroidal structure (Fig. 2.3) which is hydrophilic on the exterior and less hydrophilic in the interior. It is thought to form an inclusion complex with the 1,3-butadiene,[69] holding the 1,3-butadiene within the pore at the centre of the β-cyclodextrin until it encounters and reacts with the end of a growing polymer chain.

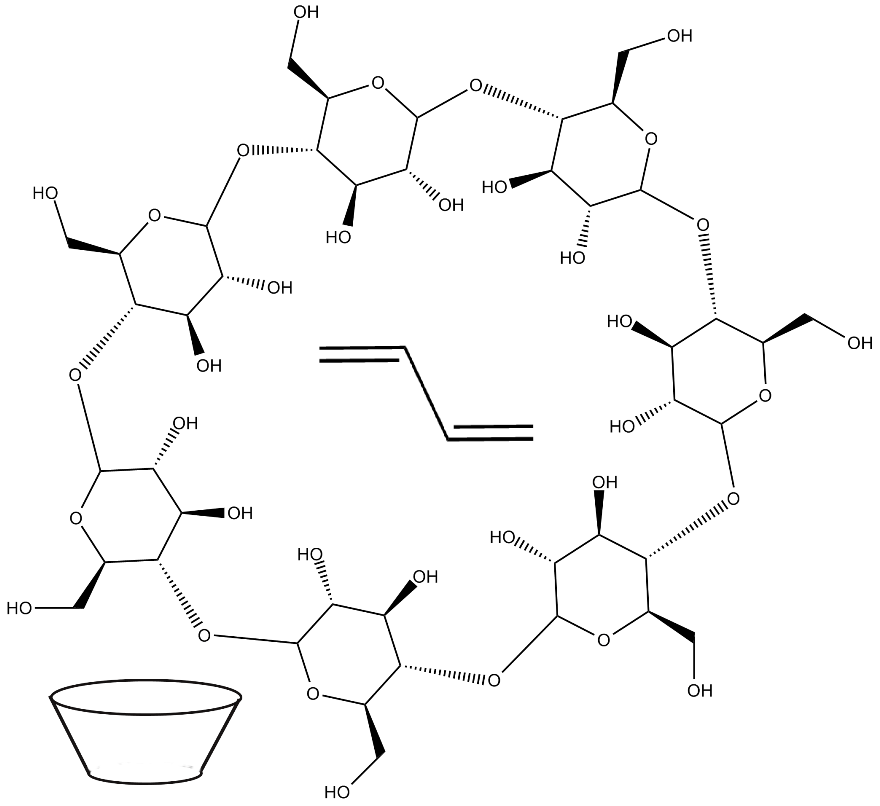


Figure 2.3: The Structure of β-Cyclodextrin - Also showing the toroidal shape of the molecule (bottom left)

The ^{1}HNMR data (Fig. 2.4) from the SBR product (after isolation from the latex) once again did not appear to show the presence of butadiene in the polymer chain. The ^{1}HNMR data (Fig. 2.2) from the product of method one and the ^{1}HNMR data (Fig. 2.4) from the product of method two are very similar. Both spectra showing the peaks around 6.2-7.2 ppm and 1.2-2.2 ppm that are typically associated with polystyrene and both spectra absent the doublet around 5.2 ppm associated with 1,3-butadiene.

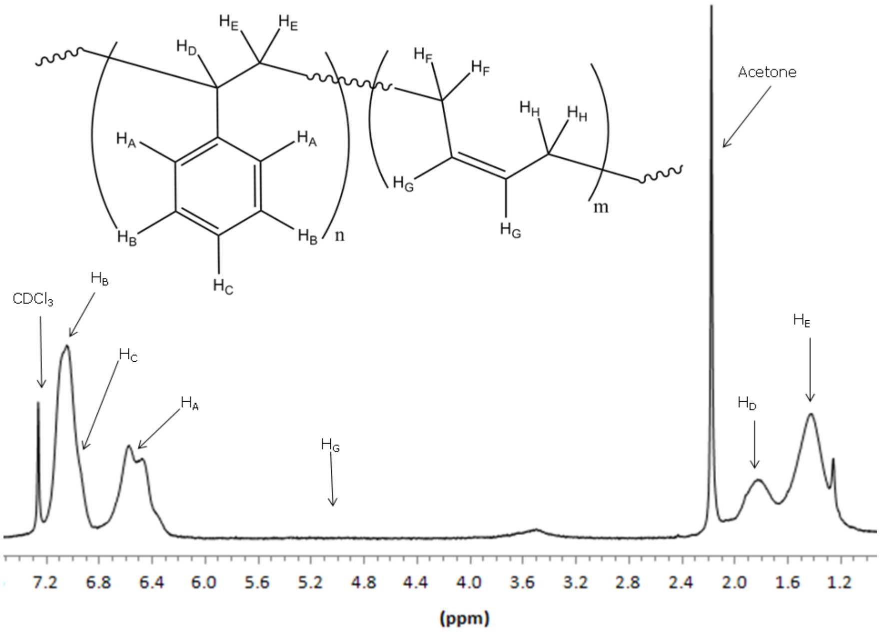


Figure 2.4: Assigned ^{1}HNMR Spectrum of SBR Synthesised Following Method Two - Again showing the presence of styrene but the absence of expected peak for 1,3-butadiene at around 5.2 ppm

The resultant latex from this method was found to have solid content of 3%. The expected solid (calculated from monomer) content of the product latex is 12.47% the expected butadiene content is 9.36% and styrene content is 3.12% this further indicates that the 1,3-butadiene is not copolymerising with the styrene but is being lost during the reaction. Once isolated from the latex, the product was again rigid with very little elasticity. All evidence points to the product of method two being polystyrene with little to no successful incorporation of 1,3-butadiene. A review of industrial methods for cold emulsion SBR synthesis showed that most methods were broadly similar but there were several different redox systems used for initiation. It was decided to repeat the synthesis using one of the alternate redox systems to see if changing the initiation system had any effect on the levels of 1,3-butadiene incorporated within the product.

2.2.3 Method Three

Aerosol OT was kept as the surfactant for method three as it remained in solution at the reaction temperature and provided a stable emulsion (see Fig. 2.17) in method two. The initiation system was altered to another redox system commonly used in industry[70] (experimental 6.1.4) The β-Cyclodextrin was also kept as part of the emulsion mixture as a solubility aid for the 1,3-butadiene to give the best possible chance for incorporation.

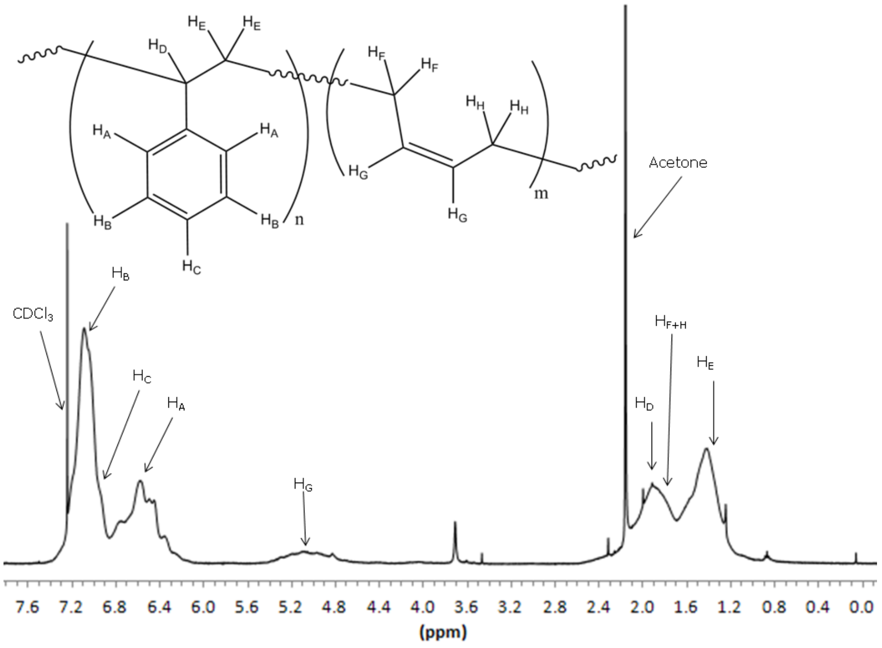


Figure 2.5: Assigned^{1}HNMR Spectrum of SBR Synthesised Following Method Three - Showing limited presence of 1,3-butadiene in the product at around 5.2 ppm

As seen in the ^{1}HNMR spectrum (Fig. 2.5) there is now a peak around 5.2 ppm unlike the spectra seen previously (Fig. 2.2 and 2.4). This indicates that 1,3-butadiene has been successfully included within the polymer chain. However the peak is broad and short and not the tall doublet expected from 1,3-butadiene. Integration of the ^{1}HNMR data shows that the 1,3-butadiene only comprises $\sim$ 16% of the isolated polymer. The monomer ratio of the emulsion mixture should give rise to a polymer comprising $\sim$ 75% 1,3-butadiene so the product still contains only a fifth of the 1,3-butadiene expected. The product Tg was also much higher than desired (actual Tg of $\sim 103°C$ compared with desired Tg of $\sim -50°C$) and the product glassy and inelastic.

2.2.4 Condensation of 1,3-Butadiene Prior to Polymerisation

As the problems with the synthesis were attributed to incorporation of the 1,3-butadiene monomer it was posited that the 1,3-butadiene was not entering the reaction mixture. The 1,3-butadiene was thought to be either forming a gaseous layer above the reaction mixture or escaping the reaction vessel altogether. Previous methods involved bubbling gaseous 1,3-butadiene through the emulsion which was cooled below the boiling point of 1,3-butadiene

($-4.5°C$). This would mean that the 1,3-butadiene would need to condense or react during the time taken to pass through the cooled reaction mixture in order to be incorporated within the product. As the reaction mixture could only be cooled to $\sim -10°C$ which is not far below the boiling point of 1,3-butadiene, it is possible that the 1,3-butadiene passes through the reaction mixture too quickly to be sufficiently cooled to prevent escape. The solution proposed was to cool the 1,3-butadiene gas below its boiling point and allow it to condense into a liquid prior to addition into the reaction mixture. To this end a bespoke condensing column was purchased and incorporated within the emulsion polymerisation rig between the syringe pump and the reaction vessel inlet (see experimental section Fig. 6.1) Syntheses utilising this condenser were performed using the third method described previously as this gave the most promising results and highest incorporation of 1,3-butadiene in the product (Tab. 2.1) of any of the methods described previously.

Method	Solid Content of Latex/%	Butadiene Content of Solid/%
1	~ 2	ND
2	~ 3	ND
3	~ 5	~ 16

Table 2.1: A Comparison Of Latex Solid Contents - Showing the Butadiene Content as Calculated from ^{1}HNMR Integrals

The use of a condenser for the 1,3-butadiene gas was successful with the liquid 1,3-butadiene visibly present within the condenser prior to addition into the reaction mixture. The product was rubbery with a much lower Tg (Tab. 2.5) although the Tg was still above room temperature. ^{1}HNMR data (Fig. 2.6) confirmed the presence of butadiene with a clear doublet seen around 5.2 ppm instead of the much smaller broad peak seen in the product synthesised without the condenser (Fig. 2.5).

The solid content measured for this product was around 10% and integration of the ^{1}HNMR Spectrum showed that butadiene comprises around 69% of the isolated solid. These figures are still lower than the expected values (12.5% and 75% respectively) but the butadiene content of the product has been greatly increased by the use of the condenser.

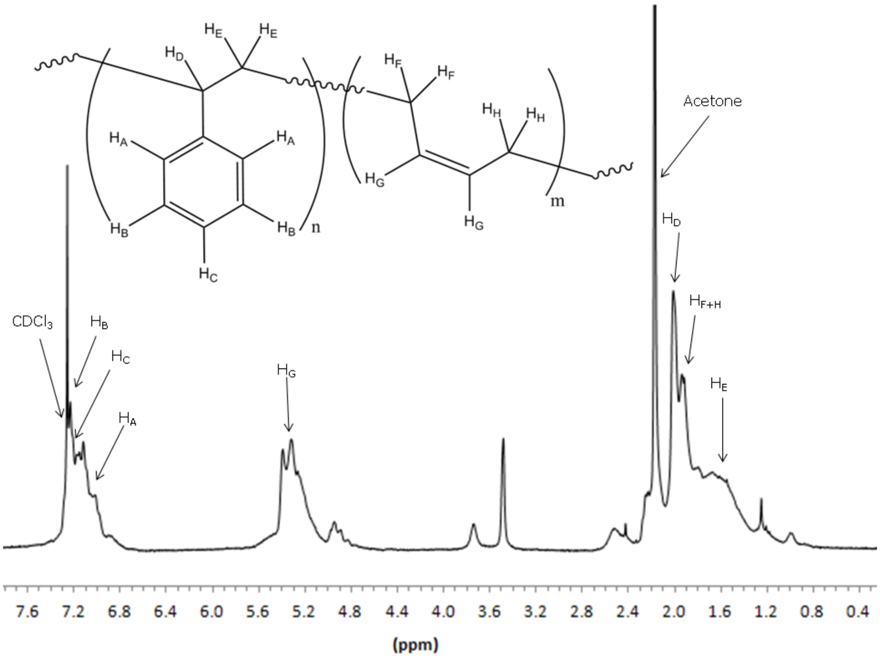


Figure 2.6: ^{1}HNMR Spectrum of SBR Synthesised With 1,3-Butadiene Condensed Prior to Addition - Showing the presence of 1,3-butadiene in the product by the doublet seen at around 5.2 ppm

As the product formed contained 1,3-butadiene, the decision was taken to proceed to the next step and introduce a fluorescent label to the reaction mixture. Although a Tg well below room temperature is required for the product to have rubbery properties, the SBR species produced can be modified to have a lower Tg following the successful incorporation of the fluorescent and quenching monomers. The ability to incorporate fluorophores and fluorescent quenchers within the polymer chain is vital for this project and should be assessed as a priority before any attempts are made to modify other properties. Addition of a fluorophore will also allow excited state lifetimes to be recorded for the products which is also very important for this project and any products must be suitable for analysis using a spectrophotometer.

2.3 Emulsion Polymerisation of Styrene-Butadiene Rubber Containing the Fluorescent Label 9-Vinylanthracene

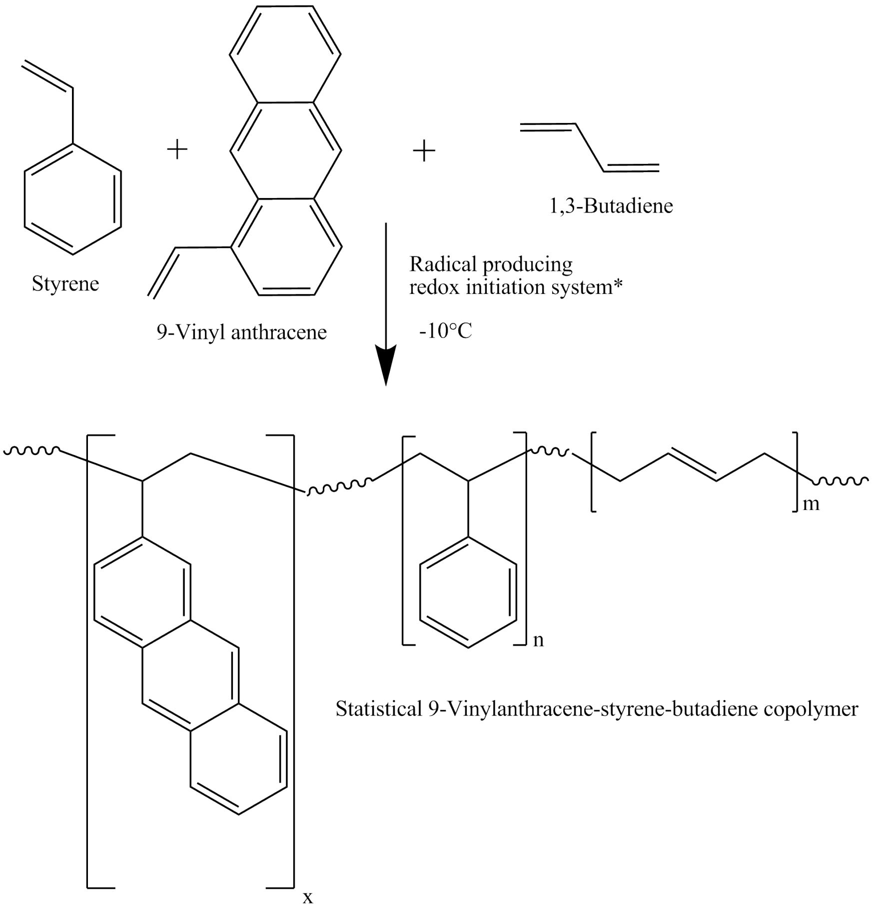


Figure 2.7: Synthesis of 9-Vinylanthracene Labelled Styrene-Butadiene Rubber - *For details on the REDOX system please see Experimental section 6.1.4

9-Vinylanthracene was chosen as the fluorescent label to be incorporated within the SBR. 9-Vinylanthracene was chosen due to its similarity in structure and properties with styrene. This similarity should allow for compatibility of the fluorescent label with the other monomers used allowing the 9-vinylanthracene to be incorporated as part of the polymer backbone successfully and without greatly altering the properties of the product. 9-Vinylanthracene is also commercially available and well characterised.[71] 9-Vinylanthracene has also seen previous use as a fluorescent label so its fluorescent properties are well known. [72] The synthesis was conducted as described in the previous method using the condenser for 1,3-butadiene but with 0.1 wt% 9-vinylanthracene replacing a (molar) equivalent of styrene. A colloidally stable latex (at $25°C$) as shown by ζ-potential values lower than -25 mV[73] (Fig.

2.17) was produced from the emulsion mixture containing 0.1 wt% 9-vinylanthracene in place of a molar equivalent of styrene.

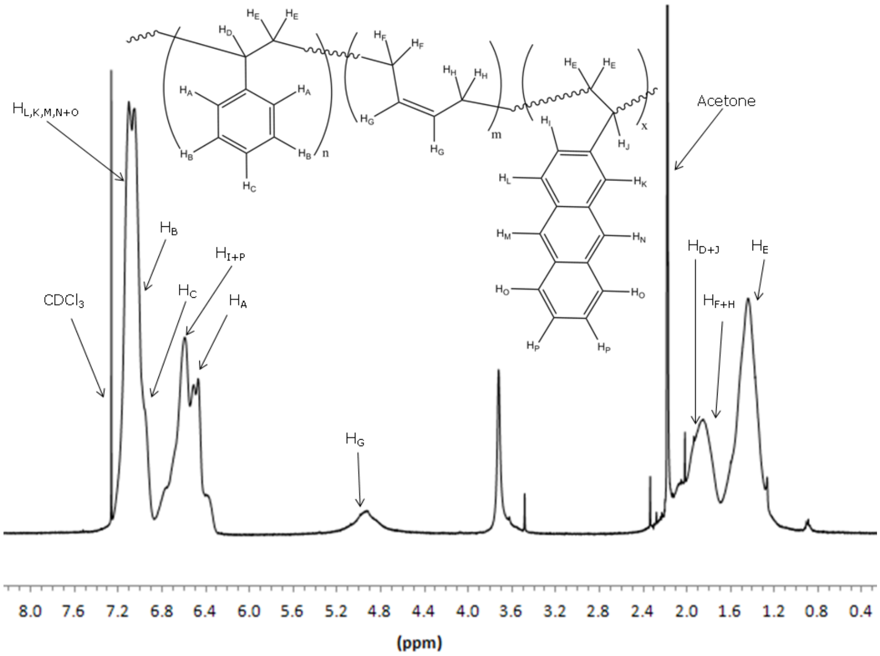


Figure 2.8: ^{1}HNMR Spectrum of SBR Containing the Fluorescent Label 9-Vinylanthracene - Showing the presence of 1,3-butadiene in the product by the peak seen at around 5.2 ppm

9-Vinylanthracene contains more hydrogen atoms in an aromatic environment than the styrene but gives the same number of aliphatic hydrogens on the polymer backbone. Integration of the peaks in the ^{1}HNMR spectrum (Fig. 2.8) shows in increase in the proportion of aromatic hydrogens compared with aliphatic hydrogens. This implies that the 9-vinylanthracene has been successfully incorporated within the polymer chain. Further evidence for this incorporation was the observation of fluorescent emission when the sample was viewed under UV (365 nm) light (Fig. 2.9) following isolation from the latex and washing with acetone.

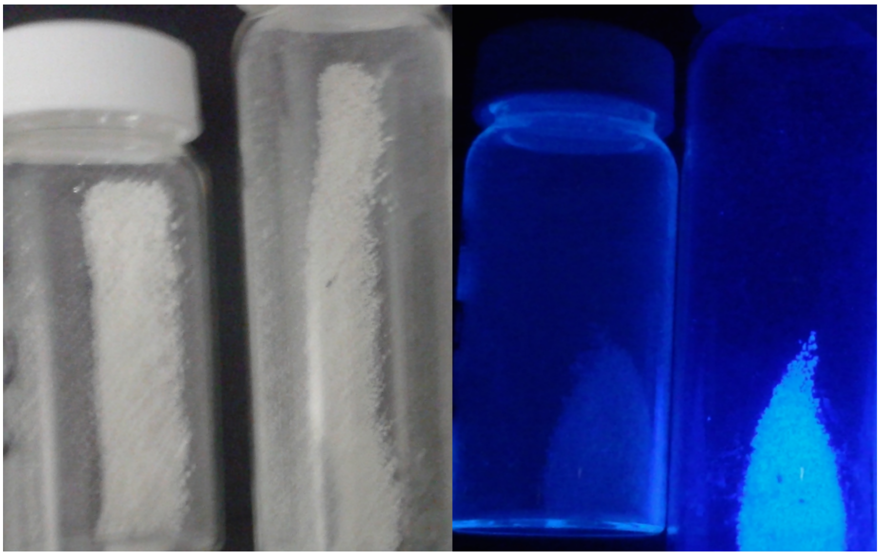


Figure 2.9: SBR (left) and 9-Vinylanthracene Containing SBR (right) Viewed Under Natural and UV (365 nm) Light - Showing the visible blue emission typical of anthracene species from the labelled SBR on the right. N.B. There is a slight blue colour to both sample tubes but this is due to the glass scattering the UV light.

The ^{1}HNMR spectrum (Fig. 2.8) still shows the presence of 1,3-butadiene in the product by the peak seen at around 5.2 ppm. However the peak is much smaller than seen in the ^{1}HNMR spectrum from the product not containing 9-vinylanthracene (Fig. 2.6) and the doublet appearance no longer as visible. This implies that the 1,3-butadiene is once again not being incorporated at the expected levels. However, as the previous product showed that it is possible to incorporate 1,3-butadiene at high levels (around 69% of the isolated solid) under atmospheric pressure in the laboratory, the decision was taken to once again proceed to the next step and introduce a fluorescent quencher to the reaction mixture. SBR containing both fluorophore and quencher is essential for the continuation of the project. If this can be successfully produced, then further work can be undertaken to increase 1,3-butadiene levels and/or otherwise adjust the properties of the modified SBRs to be more suitable for the end application.

2.4 Emulsion Polymerisation of Styrene-Butadiene Rubber Containing the Fluorescent Label 9-Vinylanthracene and the Heavy-Atom Quencher 4-Bromostyrene.

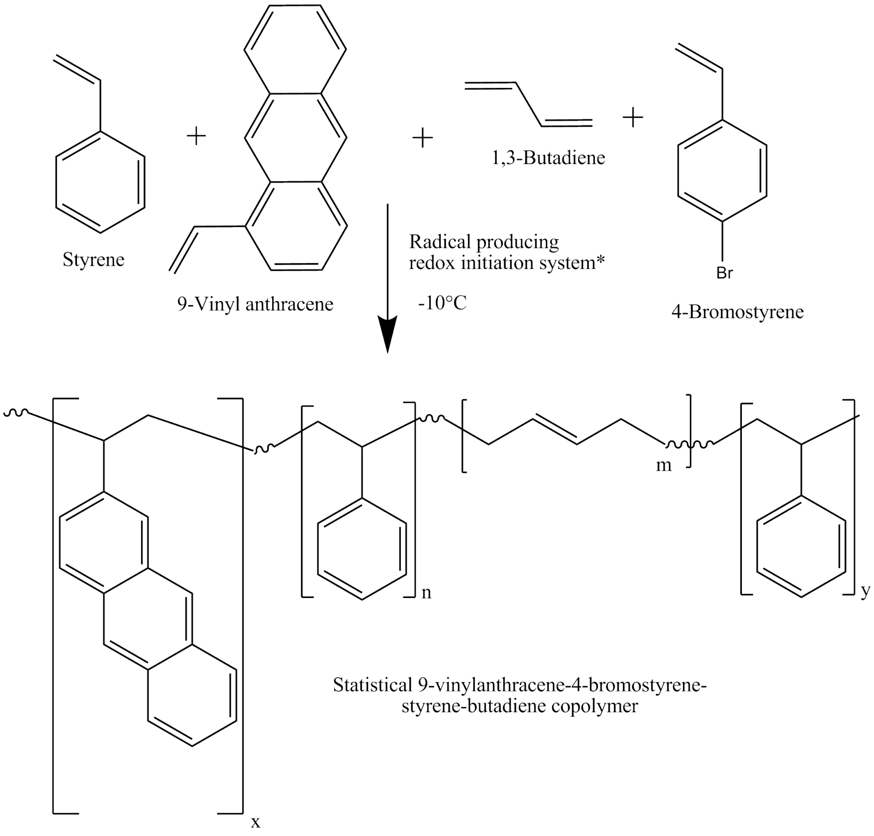


Figure 2.10: Synthesis of 9-Vinylanthracene Labelled Styrene-Butadiene Rubber Containing 4-Bromostyrene - *For details on the REDOX system please see Experimental section 6.1.4

As the previous product contained a successfully incorporated fluorophore at levels high enough to produce a visible fluorescent response, the next step was to introduce a fluorescent quencher in order to determine whether the fluorescence could be observably quenched by a heavy atom containing species randomly distributed on the same polymer chain as the fluorophore. 4-Bromostyrene was selected for use as the fluorescent quenching monomer within the SBR. As with the 9-vinylanthracene, 4-bromostyrene was chosen due to its similarity in structure with styrene as well as its commercial availability. Bromine has been shown to act as a heavy-atom quencher as described in the introduction (section 1.3.3.2) The synthesis was conducted as described in the previous method using the condenser for 1,3-butadiene and including 9-vinylanthracene but with an additional 0.2 wt% 4-bromostyrene replacing a (molar) equivalent of styrene.

Despite the 4-bromostyrene being added instead of a molar equivalent of styrene, the addition of the fluorescent and quenching monomers appears to correspond with an increase in the glass transition temperature of the products from these reactions. However the reduced 1,3-butadiene content is likely to be responsible for this change. This effect could therefore be mitigated by increasing the level of 1,3-butadiene incorporation or by increasing the 1,3-butadiene content of the monomer blend. The Tg of products could also be lowered by other changes to the synthetic method or the incorporation of Tg reducing additives (such as natural rubber) to the blend. However it was decided that fluorescence analysis would be performed on the labelled polymers before further alterations or additions to the synthesis were considered.

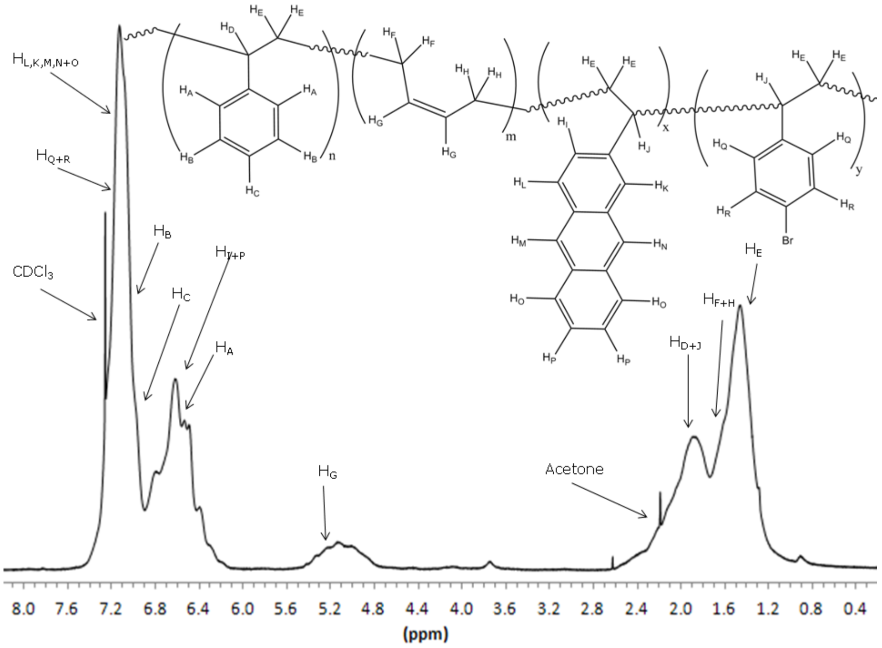


Figure 2.11: ^{1}HNMR Spectrum of SBR Containing the Fluorescent Label 9-Vinylanthracene and the Fluorescence Quencher 4-Bromostyrene - Showing the Presence of butadiene in the product

The ^{1}HNMR spectrum (Fig. 2.11) for the labelled SBR has become very complicated due to the presence of several different aromatic hydrocarbons attached to the main polymer chain. Because of the overlapping nature of the peaks associated with the various aromatic species within the polymer, the ^{1}HNMR data cannot be resolved clearly enough to show conclusively whether or not the 4-Bromostyrene has been successfully incorporated. The

^{1}HNMR data does however confirm the presence of butadiene in the product has been maintained. Although the C-Br bond does exhibit a stretching band (ν C-Br= $500 - 600$ cm^{-1}) on an IR spectrum, other bands are present within this region making it difficult to single out with certainty. Therefore elemental analysis (Tab. 2.2) was performed to confirm the presence of 4-bromostyrene within the polymer.

	C Content/%	H Content/%	N Content/%	Br Content/%
Expected	89.03	10.31	0	0.86
Discovered	77.32	7.26	ND	1.74

Table 2.2: Elemental analysis data for the SBR solid containing 9-vinylanthracene and 4-bromostyrene - ND = Not discovered within detection limits of 0.3%

The successful incorporation of 4-bromostyrene into the main polymer chain was supported by elemental analysis (Tab. 2.2) The bromine was shown to be present in the SBR following isolation from the latex and washing indicating that the 4-bromostyrene had successfully attached to the SBR. The carbon and hydrogen levels were lower than expected but the bromine content was substantially higher than expected. This was attributed to the incomplete polymerisation of all monomers in the emulsion mixture as the yield is lower than 100% and 1,3-butadiene was not present in the product at expected levels. The detection limits for the elemental analysis was 0.3% and the expected elemental contents shown in the table were calculated from the masses of reagents used.

2.5 Fluorescence Analysis

2.5.1 Free 9-Vinylanthracene

Fluorescence analysis of the free 9-vinylanthracene (in a solution of THF) was conducted to give reference data to allow comparisons with 9-vinylanthracene when bound as part of a polymer network. Steady state (i.e. constant illumination and observation as opposed to the pulsation of the illumination used in time-resolved spectroscopic methods) excitation/emission spectra (introduction 1.3.1.1) were obtained for 9-vinylanthracene (Fig. 2.12) in THF solution. These spectra show a three-pronged excitation peak with 3 maxima around 368 nm and a broad emission peak with a maximum of 428 nm. This is comparable to values previously reported in literature. [72] The spectra also show that the emission is occurring at a longer wavelength (and thus lower energy) than the excitation as is typical for fluorescence. The

Stokes shift (see introduction 1.3.1.1) between the equivalent maxima of the excitation and emission spectra is quite high and the spectral overlap (the overlap between the lower energy end of the excitation spectrum and the higher energy end of the emission spectrum) is low enough to give two distinct spectra. The three-pronged excitation peak is typical of 9-vinylanthracene with the distance between the peaks corresponding with the energy gap between the vibrational energy levels (introduction 1.5 and 1.6) for both the excited and ground states respectively. The mirror-image rule (introduction 1.3.1.1) is not obeyed, implying that transitions to the second excited state, internal conversions between the first and second excited states, or other complicated behaviour is occurring.

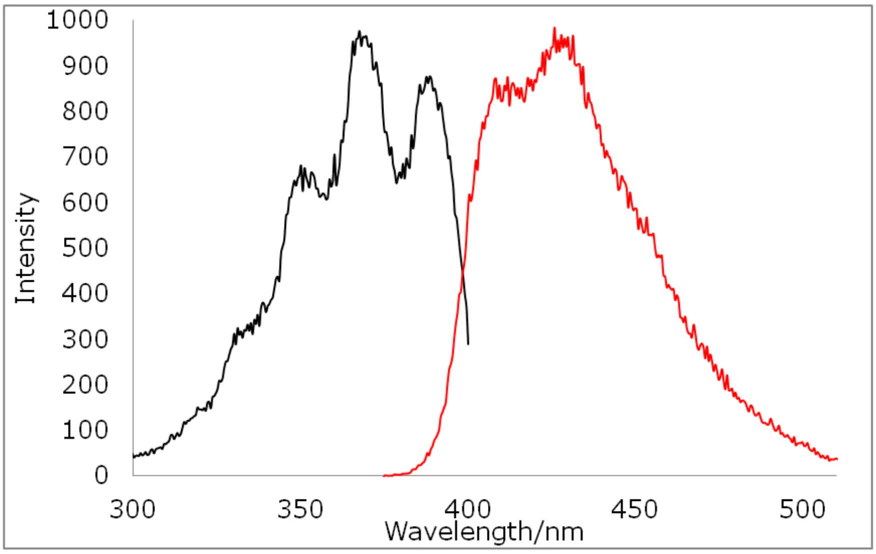


Figure 2.12: Excitation (Black) Emission (Red) Spectra for Free 9-Vinylanthracene - in THF

These data for excitation and emission maxima were used as parameters in order to obtain excited state lifetime spectra (see Introduction 1.3.1.2) for 9-vinylanthracene in the presence of different concentrations of 4-bromostyrene (Tab. 2.3) Excited state lifetime spectra are obtained using a spectrophotometer which measures the time taken between an excitation pulse of electromagnetic radiation and the detection of a photon emitted by the sample in response. This is known as time-correlated single photon counting (TCSPC). The excitation maxima measured previously was used to set the wavelength for the excitation pulse provided by the spectrophotometer and the emission maxima was used to set the monochromator on the detector. The solvent used was spectrophotometric grade tetrahydrofuran (THF) and the concentration of 9-vinylanthracene was 1x10^{-3} wt% for all readings.

The decay curves for the excited state lifetimes obtained from the spectrophotometer were analysed by fitting to exponential functions (Introduction 1.3.1.2) in order to obtain an average lifetime for the excited state in each of the solutions containing a different concentration of the fluorescence quencher. The mathematical fitting by the software employed to fit the measured decay data to an exponential model uses a least squares analysis. The confidence in the fit was assessed by the χ^2 values (Tab. 2.3) and the distribution of the residuals from the fit. The χ^2 value is obtained from the sum of squares of the difference between the data points measured for the decay and the equivalent data points on the exponential model used for fitting. The closer that this χ^2 value is to 1 the greater the confidence in the fit to the exponential model. The individual residuals from the mathematical fitting of the measured data points to the exponential model data points are also plotted for each fit and these should be randomly distributed around zero as any pattern in these residuals indicates that the mathematical model used is not appropriate for the data collected and that a different model should be used. In particular, a sloped pattern seen in the residuals with a high point at the start would indicate an additional exponential component to the data which has been unresolved by the fitting to the model used.

Fig. 2.13 shows the measured experimental data gathered by the spectrophotometer for free 9-vinylanthracene in THF as a decay curve plotted in black. The red line running through this curve is the mathematical fit for the data provided by the software using an exponential model. The closer these two lines are together the better the fit, with any deviation indicating a poor fit. The residuals are plotted below the decay curve and show the difference between the measured data points and the model data points as the number of standard deviations of the measured data points above or below the fitted curve. If the fitted curve passes through the centre of the measured data and provides a good model for it, these residuals will appear centred around zero with a similar number of points at each standard deviation above and below zero. I.e. the curve described by the mathematical fit is broadly the same as that in the experimental data. However if the residuals appear to show a pattern or exhibit runs above or below zero then the fitted curve is not describing the measured data well.

The initial data collected for the excited state lifetimes of 9-vinylanthracene fit well to the single exponential model, as 9-vinylanthracene has previously been reported to do, [74] with χ^2 within the conventionally acceptable range for fluorescent lifetimes of $0.8-1.2$[75]. However the fit begins to break down and the χ^2 values deviate from unity as the concentration of quencher increases (see appendix 6.4 for an excited state lifetime plot of 9-vinylanthracene in the presence of 4-bromostyrene.) This is not wholly unexpected as the presence of the heavy atom will change the number of environments possible for the fluorophore to occupy, and the deviation from the exponential due to collisional quenching has previously been described.[76] However the trend of the data across the lifetimes within the acceptable range of χ^2 values still serves to show that quenching is taking place.

The error associated with the measurement of excited state lifetimes shown in Tab. 2.3 was estimated from a series of repeat measurements taken on the spectrophotometer using

[4-Bromostyrene]/wt%	Exponential	Lifetime/ns	χ^2t
0	1	7.87	1.2
1x10^{-3}	1	7.54	1.2
2x10^{-3}	1	7.38	1.2
5x10^{-3}	1	7.37	1.3
1x10^{-2}	1	7.31	1.4

Table 2.3: Lifetime data for the excited state of free 9-vinylanthracene (1x10^{-3}) in the presence of different concentrations of 4-bromostyrene - in THF

the free 9-vinylanthracene (1x10^{-3} solution in THF.) The lifetimes were then calculated using the mathematical fitting process described previously. The calculated lifetimes had a maximum of 7.89 ns and a minimum of 7.81 ns, a mean of 7.86 ns and a standard deviation of 0.040 ns (equivalent to 0.5%) This level of experimental error means that some individual pairs of excited state lifetimes (particularly those above 2x10^{-3} wt%) may have differences between them that are within the error limits. However the overall trend across the entire series shows a pattern of decreasing lifetime that is outside the differences accounted for by experimental error. The difference between the lifetime calculated in the presence of 1x10^{-3} wt% 4-bromostyrene and 2x10^{-3} wt% 4-bromostyrene is likewise greater than the calculated experimental error.

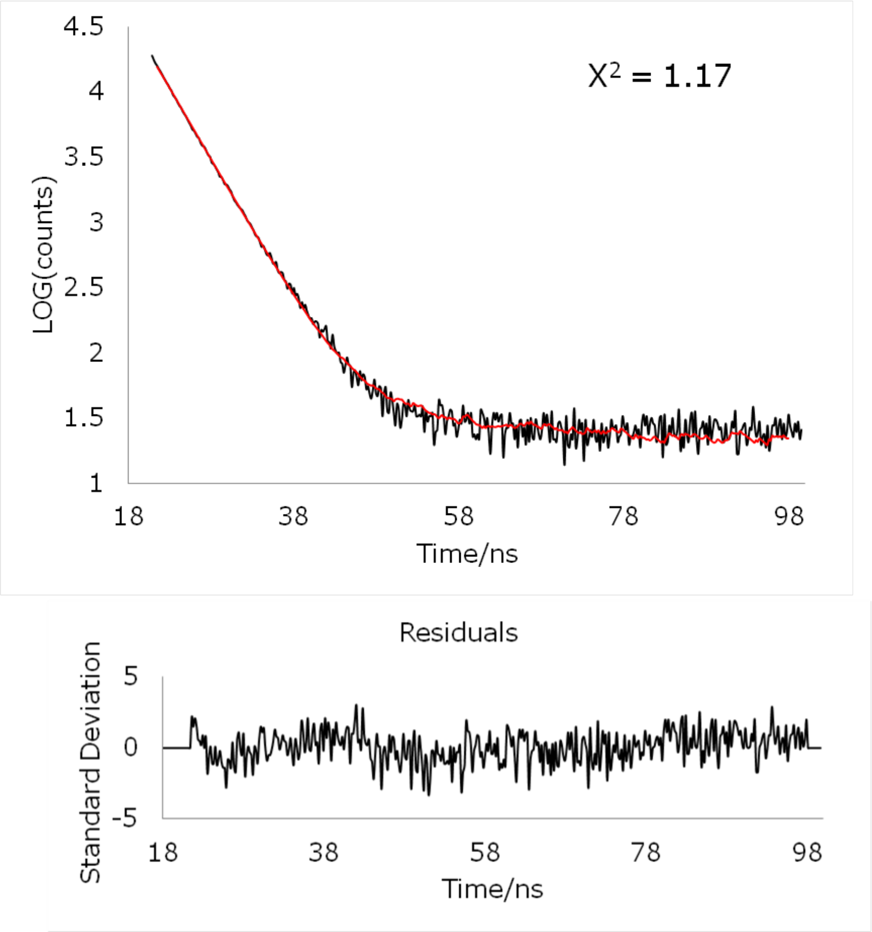


Figure 2.13: Excited State Lifetime Plot for Free 9-Vinylanthracene - Showing the mathematical fit to the single exponential in red and accompanied by a plot of the residuals from the mathematical fit.

These lifetimes (Tab. 2.3) show the quenching of fluorescence by 4-bromostyrene from 1x10^{-3} wt% which is equal to the concentration of 9-vinylanthracene used. 2x10^{-3} wt% 4-Bromostyrene, which is double the concentration of 9-vinylanthracene, gives a far greater degree of quenching still. However increasing the concentration of 4-bromostyrene beyond this amount appears to have a less obvious effect on the excited state lifetime. This ratio of 4-bromostyrene relative to 9-vinyl anthracene (2:1) is practically obtainable within the SBR solids synthesised. However these spectra were obtained in solution and therefore the chance of fluorophore-quencher encounters is governed by diffusion. In solution, when diffusion controls the rate of quenching, the overall concentration of fluorophore and quencher determines the likelihood of a quenching interaction occurring, this is also affected by temperature and pressure. However as the polymerisation reactions used to synthesise the polymer networks are random and not controlled, some areas of the network will have a concentration of fluorophore or quencher that is above or below the average. For each fluorophore, the likelihood of it being quenched is no longer dependent on diffusion because the fluorophores and quenchers are part of the polymer chain and no longer able to move freely. Quenching in a polymer network is governed by the number of quenching molecules present on the polymer chain within quenching distance of the fluorophore (introduction 1.3.3) This is referred to as the local concentration and is distinct from the overall concentration. In the polymers formed, the chance of fluorophore-quencher encounters will be governed by the local concentrations of each within the polymer network and also the mobility of the polymer chains. Furthermore oxygen is present within the solution and oxygen is known to quench the triplet states of aromatic hydrocarbons.[51] When bound within a polymer network, the fluorophore will be protected from atmospheric oxygen and the chance of excited states being quenched by oxygen will be greatly reduced. It is therefore possible that a lower concentration of 4-bromostyrene relative to 9-vinylanthracene may be needed to observe fluorescence quenching within the polymer network compared with the solutions studied due to these effects.

2.5.2 SBR-Bound 9-Vinylanthracene

As quenching of 9-vinylanthracene fluorescence by 4-bromostyrene was observed with both free in solution, the next step was to record the excited state lifetimes for the SBR bound 9-vinylanthracene both alone and in the presence of 4-bromostyrene. This will show any effect that binding has on the fluorescent response of 9-vinylanthracene and also any effect that the binding has on the ability of 4-bromostyrene to access and quench the excited state of the 9-vinylanthracene. Fluorescence was observed in these elastomers in THF solution and excitation/emission spectra (Fig. 2.14) as well as excited state lifetime spectra (Tab. 2.4) were obtained.

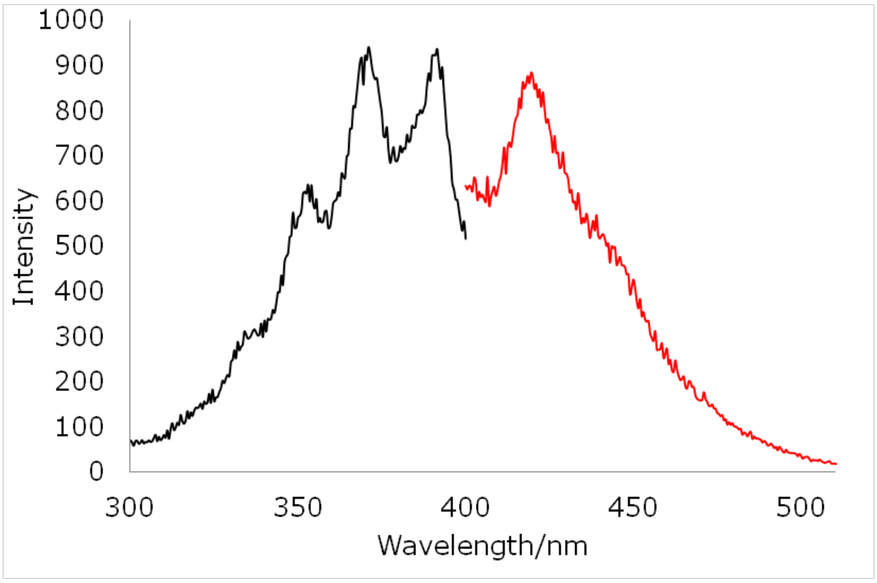


Figure 2.14: Excitation (Black) and Emission (Red) Spectra for SBR Containing 9-Vinylanthracene - in THF

The steady state spectra (Fig. 2.14) for the SBR containing 9-vinylanthracene shows a very slight decrease in excitation maximum and a slight increase in emission maximum compared with the free 9-vinylanthracene (Fig. 2.12) A sharpening of the emission peak is also seen, with the loss of the shoulder seen on the emission of free 9-vinylanthracene. This deviation from the mirror-image rule implies a change in the electronic transitions taking place (introduction 1.3.1.1) However binding to the SBR chain has had very little effect on the excitation/emission maxima. Therefore the same settings for the spectrophotometer were used to record the excited state lifetimes of SBR-bound 9-vinylanthracene as were used for the free 9-vinylanthracene previously.

Confidence in the single exponential fits were given the χ^2 values (Tab. 2.4) being close to unity and the residuals, as displayed on the excited state lifetime plot for the SBR bound 9-vinylanthracene (Fig. 2.15), being randomly distributed around zero. Once again, the χ^2 begin to deviate from unity as the heavy atom content increases. See appendix 6.5 for excited state lifetime plot for the SBR bound 9-vinylanthracene in the presence of free 4-bromostyrene.

[4-Bromostyrene]/wt%	Exponential	Lifetime/ns	χ^2t
0	1	8.12	1.2
1x10^{-3}	1	8.10	1.2
2x10^{-3}	1	7.96	1.3
5x10^{-3}	1	7.90	1.4
1x10^{-2}	1	7.92	1.4

Table 2.4: Lifetime data for the excited state of SBR-bound 9-vinylanthracene in the presence of different concentrations of free 4-bromostyrene

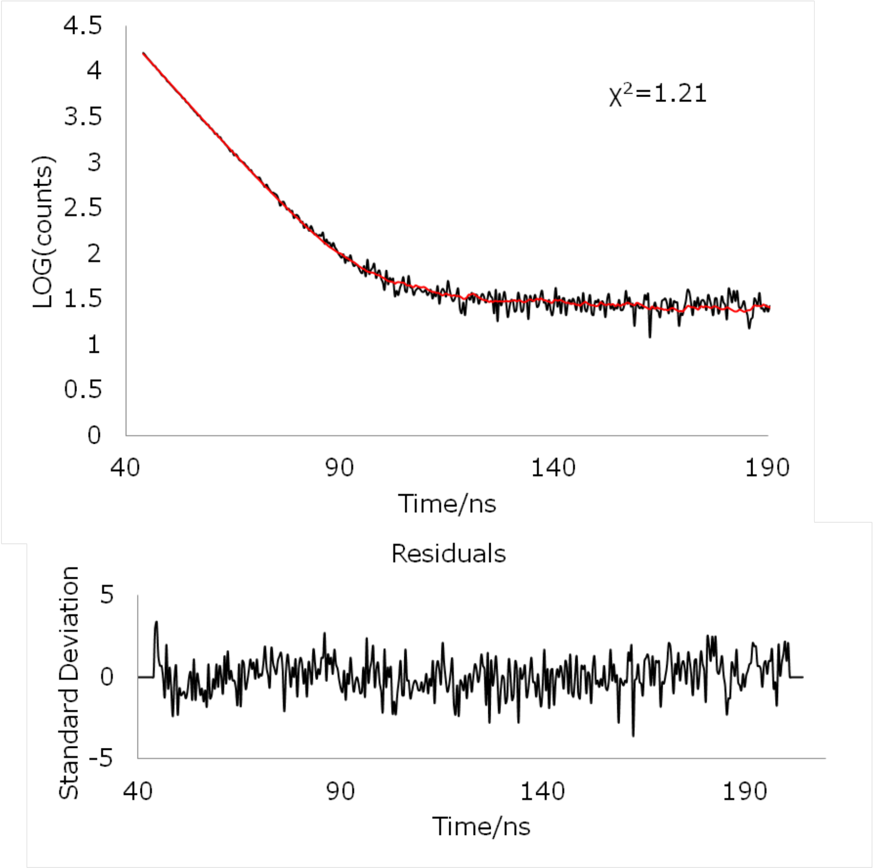


Figure 2.15: Excited State Lifetime Plot for SBR Bound 9-Vinylanthracene - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

The SBR bound 9-vinylanthracene has a lifetime (Tab. 2.4) of 8.12 ns, longer than the free 9-vinylanthracene (Tab. 2.3) which has a lifetime of 7.90 ns. Some of the readings are within error of each other (section 2.5.1) however a trend outside of error is still seen across the entire set. The quenching of fluorescence is still observed across the series but the percentage reduction in lifetime is lower than for the free 9-vinylanthracene. This is expected as binding the 9-vinylanthracene to the SBR polymer chain can hinder access of the free 4-bromostyrene to the excited state and reduce the chance of quenching. These data recorded for the bound 9-vinylanthracene used the same concentrations of polymer as used previously for the free 9-vinylanthracene but the SBR itself contained only 0.1 wt% 9-vinylanthracene. This means that the actual concentration of 9-vinylanthracene will be lower than used to record excited state lifetimes for the free 9-vinylanthracene. However the excited state lifetime is not concentration dependent and therefore should be the same for any given fluorophore alone and also for any given fluorophore:quencher ratio regardless of actual concentration.

2.5.3 SBR-Bound 9-Vinylanthracene and 4-Bromostyrene

Excited state lifetime data were also recorded for the SBR containing both 9-vinylanthracene and 4-bromostyrene as part of the polymer chain. These data are for a 1x10^{-2} wt% solution of the modified SBR, which itself contains 0.1 wt% 9-vinylanthracene and 0.2 wt% 4-bromostyrene. However, as described previously, once bound to a polymer chain, the local concentration of quencher with respect to any fluorophore may be higher or lower than the overall average. The data gave a good fit to the single exponential model (Fig. 2.16) with the residuals randomly distributed around zero. The lifetime of the excited state for this polymer in solution was 7.91 ns with a χ^2 value of 1.2 This is very similar to the excited state lifetime recorded for the SBR bound 9-vinylanthracene in the presence of free 4-bromostyrene (Tab. 2.4) This also shows a difference from the labelled SBR with no 4-bromostyrene which had an excited state lifetime of 8.12 ns (Tab. 2.4) This difference is greater than the estimated error associated with the recording of excited state lifetimes (section 2.5.1)

The lifetimes data can not be directly compared due to the bromine levels in the SBR containing both 9-vinylanthracene and 4-bromostyrene as part of the polymer chain being higher than expected (Tab. 2.2) however there is no obvious change in lifetime caused by the binding of 4-bromostyrene to SBR when compared with the same level of free 4-bromostyrene.

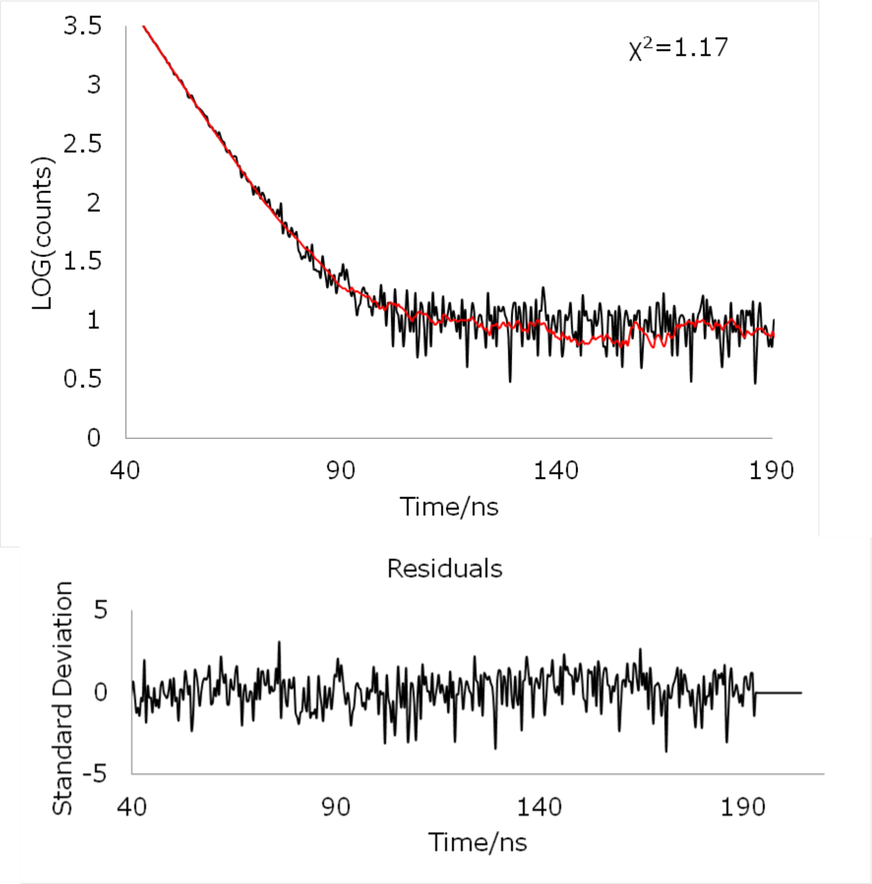


Figure 2.16: Excited State Lifetime Plot for SBR Bound 9-Vinylanthracene - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

Unfortunately, due to the opacity of the polymer itself it was not possible to acquire valid fluorescence spectra in the solid state. Fluorescence spectrophotometers work by sending a pulse or beam of light into the sample and recording the photons emitted in response, for this to be successful, the light can not deviate along either journey. Anything that causes this light to deviate by reflection, diffraction or refraction will interfere with the functioning of the spectrophotometer either by causing photons to be recorded that shouldn't be e.g. photons from the excitation pulse being directed into the detector, or by causing photons that should be recorded to be directed away from the detector. This deviation of light, known as light scattering, is caused by impurities, particulate matter, surface roughness and a variety of other sources. As the polymer is opaque and white in appearance, it must be acting as a light scatterer because the scattering of light is what causes objects to appear as white. As the polymer is scattering light, it would not be possible to obtain any worthwhile data from it by use of a spectrophotometer. Therefore it would also not be possible to observe any change in quenching of the excited state as tension is applied to the polymer.

Method	Tg*/°C	Latex Solid Content/%	Butadiene Content**/wt%
Method One	103	2	ND
Method Two	83	3	ND
Method Three	79	5	16
+ Condenser	56	10	69
+ VA	63	10	-
+ VA + BS	73	11	-

Table 2.5: Tg and solids content for SBR Polymers After Isolation from Latex - *from DSC, ** from integration of ^{1}HNMR of solid after isolation from latex N.B. Determination of the butadiene content for the final two polymers was not possible due to the complexity of the spectra and overlapping peaks. VA = 9-vinylanthracene and BS = 4-bromostyrene.

2.6 Conclusions

Cold emulsion synthesised SBR was successfully synthesised at atmospheric pressure. Data recorded using a ζ-potential analyser showed that the latices formed were colloidally stable at 25°C as shown by ζ-potential values lower than -25 mV (Fig. 2.17) although the latex formed using method one was very near the cut off point for stability of -25 mV.

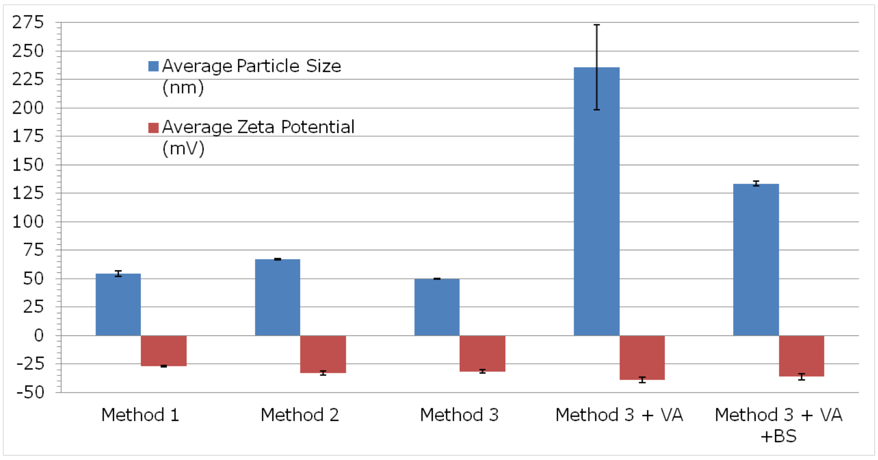


Figure 2.17: ζ Potential and Particle Size Data for SBR Latexes in a KCl Solution - ζ-Potential analyser results (red) and particle sizer data (blue) were both recorded in a KCl Solution at 25°C - VA = 9-vinylanthracene, BS = 4-bromostyrene, error bars show calculated standard error.

Stable SBR latexes were successfully synthesised at atmospheric pressure in the emulsion rig setup described (experimental 6.1.1) The SBR species synthesised using the third method described and the condenser for butadiene were shown to have butadiene present within the main chain. These rubbers had a lower Tg compared with those synthesised using method one or two (Tab. 2.5) However the range of Tg values seen in the products are still much higher than desired and the solids lack the elastic properties necessary for the continuation of the project. Both the fluorescent label (9-vinylanthracene) and the fluorescence quencher (4-bromostyrene) were successfully incorporated within SBR as confirmed by ^{1}HNMR (Fig. 2.8) and elemental analysis (Tab. 2.2) respectively.

Once precipitated from the emulsion latex, the SBR products appear opaque and slightly coloured. This opacity could have a variety of causes including surface roughness and impurities. Impurities are a likely cause, however attempts to improve the appearance by purification through reprecipitation had little effect on the opacity. The products were easily soluble in solvents such as chloroform which would make them suitable for forming solvent cast surface coatings as a possible avenue for future work.

Steady state data and excited state lifetimes were successfully obtained for the free label and also the SBR bound label in solution. The presence of 4-bromostyrene was shown to decrease the excited state lifetime of the 9-vinylanthracene both as free monomers and bound in SBR. Binding of the label to the SBR slightly increased the lifetime of the excited state but did not prevent the 4-bromostyrene from quenching it. However the iron present in the redox initiation system may also be retained within the final product and heavy metal atoms have been shown to quench fluorescence. Therefore the fluorescence data for the SBR polymers may be affected by the presence of iron. Chelation of iron by ethylenediaminetetraacetic acid (EDTA) may provide a way to remove the iron present by dialysis. However, due to the sensitivity of the spectroscopic equipment used, confidence in comparing fluorescence data across SBR polymers from different synthetic batches would not be possible. Ultimately the solid SBR species synthesised in this section were found to be unsuitable for the continuation of this project due to both the initiation system used and the opacity of the products formed.

2.7 Future Work

The appearance of the SBR polymers made them unsuitable for fluorescence analysis in the solid state which is important for the continuation of this project. However the 9-vinylanthracene worked well as a fluorophore and the 4-bromostyrene was shown to have a quenching effect on it. Further work should focus on finding a more suitable polymer network that is compatible with 9-vinylanthracene and 4-bromostyrene as these show promise as a fluorophore/quencher pair. This polymer network would ideally be flexible with good optical clarity and the synthesis should not require the use of anything that could interfere with fluorescence analysis e.g. heavy atoms. An investigation into the polymers used by industry for applications requiring optical clarity and the polymers used for fluorescence studies in literature indicated that polyacrylates would be a promising candidate to fulfil these criteria. The next chapter discusses the use of polyacrylates to form polymer networks containing 9-vinylanthracene and 4-bromostyrene and the fluorescence analysis of these polymers.

3

The Synthesis of Polyacrylate Elastomers

3.1 Introduction

Polyacrylates, also known as acrylics, are commonly used in industry. Polyacrylates are a versatile group of polymers and are often chosen for applications where optical clarity is a necessity such as glass reinforcement. As the fluorescent analysis of elastomers is a major part of this project, transparency is an essential requirement for the products formed. Polyacrylates are used for wide variety of applications from cosmetics to weather-proofing. They are stable and resistant to many chemicals and environmental effects such as heat and sunlight. As the overall aim is to produce a coating for the validation of bank notes, the ability to withstand weathering is an important consideration in the choice of material. Simple polyacrylates are often synthesized by photo-initiated radical polymerisations.[77] These UV curable polymers are simple and fast to make with a wide variety possible due to the selection of available monomers.[78] It is possible to modify these polymers, by the addition of toughening agents or other additives.[79]

Due to the optical clarity of polyacrylates, they have previously seen extensive use in fluorescence and quenching studies. The quenching of fluorescent polyacrylates has previously been exploited to develop materials which act as sensors for the quenching species such as molecular oxygen.[80] There are a few examples of polyacrylate species which contain both fluorophores and heavy-atom quenchers as part of the main polymer structure[81] however none of these materials have been studied with the goal of releasing this quenching. This chapter describes the methods for synthesis, and fluorescent analysis of elastic polyacrylate polymers containing fluorophore, heavy-atom quencher and both together.

Solution phase fluorescence spectra for the free 9-vinylanthracene in the presence of different concentrations of 4-bromostyrene were obtained previously (Section 2.5.1) The excited state lifetimes showed quenching by the heavy-atom-containing 4-bromostyrene. Fluorescence spectroscopy was utilised to measure the excited state lifetime of the fluorescent labelled polyacrylates produced in this chapter. These were then compared with the excited state lifetimes of the label in the polyacrylates which also contained the fluorescence quencher 4-bromostyrene. Both linear and cross-linked polyacrylates were synthesised with the fluorescence analysis of the linear polyacrylates performed in solution and the fluorescence analysis of the cross-linked polyacrylates performed in solid state.

3.2 Synthesis of Linear Polyacrylate Polymers

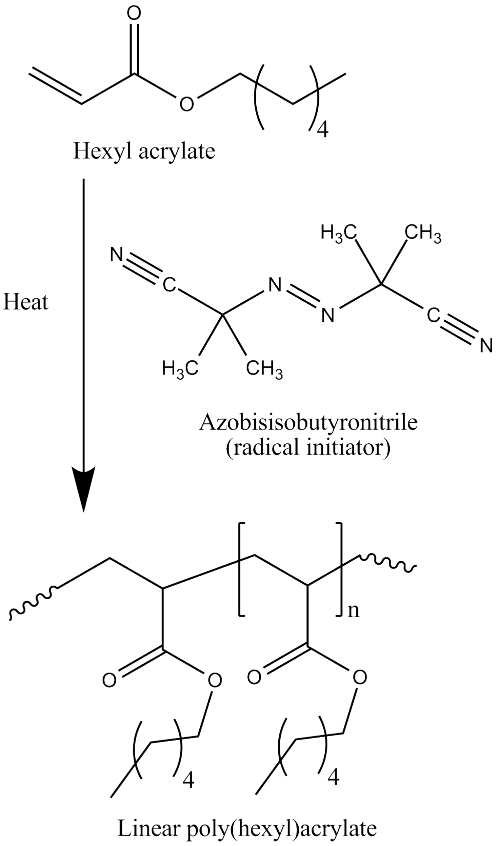


Figure 3.1: The Synthesis of Linear Polyacrylates - Initiated by Azobisisobutyronitrile (AIBN)

The formation of linear polyacrylates was achieved via thermal curing at $60°C$, initiated by AIBN. The monomer blends were degassed prior to curing using repeated freeze-pump-thaw cycles to remove oxygen prior to curing in order to prevent the termination of radicals by molecular oxygen.

9-Vinylanthracene/wt%	4-Bromostyrene/wt%	Mn	Mw
0	0	Gelled	Gelled
1	0	24300	33300
1	1	24500	36200
1	2	23500	35000
1	5	23200	34800
1	10	24600	36800

Table 3.1: GPC Data for Linear Polyacrylates - All initiated by AIBN

Molecular weights for the linear polyacrylates were obtained from GPC (Gel Permeation Chromatography) data and are shown in Tab. 3.1. These data show molecular weights around 24500 for all the polymers synthesised. Fig. 3.2 Shows the molecular weight distribution plot for the linear polyacrylate containing 1 wt% 9-vinylanthracene and no 4-bromostyrene, while Fig. 3.3 shows the molecular weight distribution plot for the linear polyacrylate containing 1 wt% 9-vinylanthracene and 10 wt% 4-bromostyrene. These represent either extreme (of 4-bromostyrene content) for the linear polyacrylates synthesised and show no obvious difference in the molecular weight distribution between them. Please see appendix Fig. 6.6 to 6.8 for the molecular weight distribution plots from the rest of the linear acrylates shown in Tab. 3.1.

The synthesis of a non-labelled linear acrylate by the same method led to the gelling[82] of the polymer. I.e. the formation of a solid polymer network that no longer behaves as a liquid or exhibits flow and contains all the remaining liquid monomer trapped within it. This is unsurprising as anthracene compounds are known to inhibit the radical polymerisation of acrylates.[45] Although the addition of 9-vinylanthracene has clearly had a large effect on the products formed, the addition of 4-bromostyrene to the reaction mixture appeared to have little effect on the molecular weight of the products formed (Tab. 3.1)

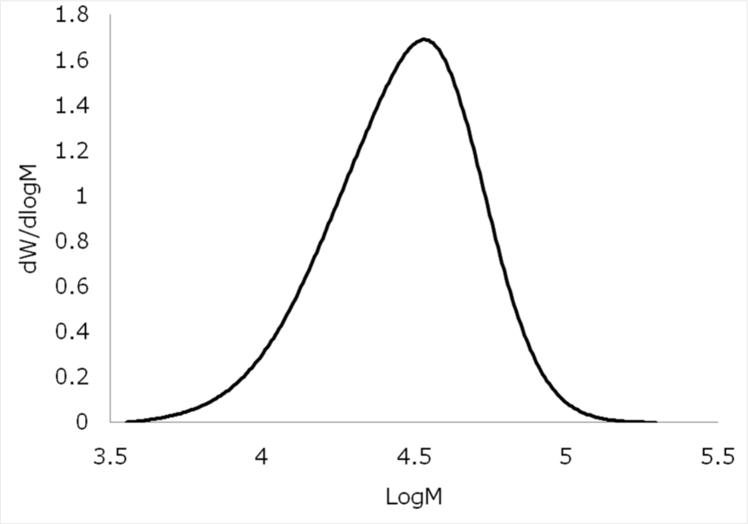


Figure 3.2: Molecular Weight Distribution Plot for Linear Polyacrylate Containing 0 wt% 4-Bromostyrene - Linear Acrylate is also labelled with 1 wt% 9-vinylanthracene

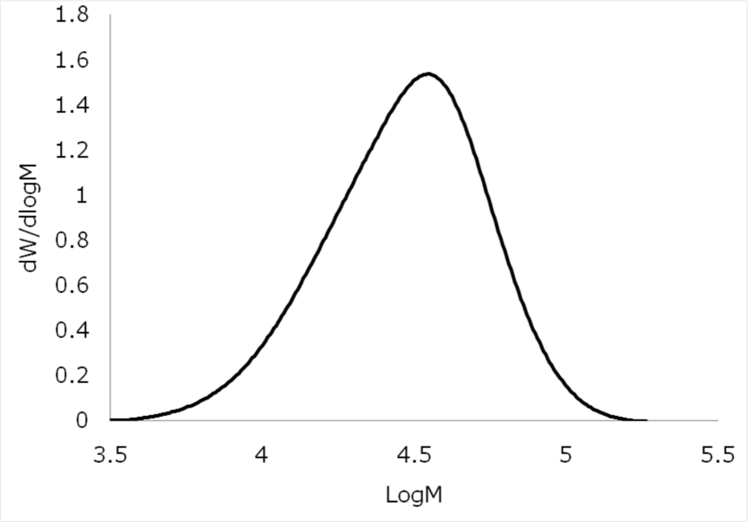


Figure 3.3: Molecular Weight Distribution Plot for Linear Polyacrylate Containing 10 wt% 4-Bromostyrene - Linear Acrylate is also labelled with 1 wt% 9-vinylanthracene

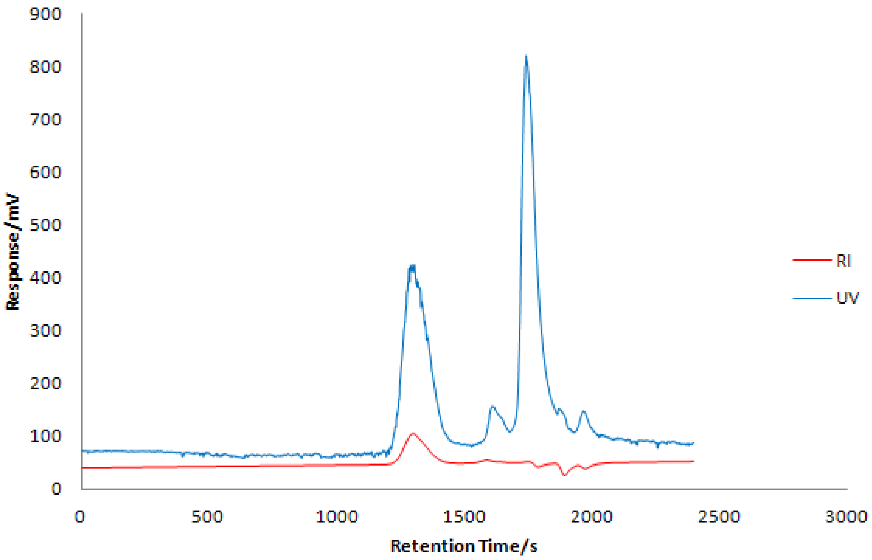


Figure 3.4: UV and RI Response Data for GPC of Linear Polyacrylate Labelled with 9-Vinylanthracene - Showing successful label attachment.

GPC data was also used to confirm the attachment of the fluorescent label to the polymer chain. This data is shown in Fig. 3.4, and compares the response obtained by the UV detector with the response from the RI detector. The UV absorber (fluorescent label) is observed to elute at the same time as the main bulk of the polymer chain showing that it is attached. If the label were not attached to the polymer, the UV response would show a peak at a much later elution time, corresponding to a molecular weight of around 205 (free 9-vinylanthracene.)

3.3 Synthesis of Cross-linked Polyacrylate Elastomers

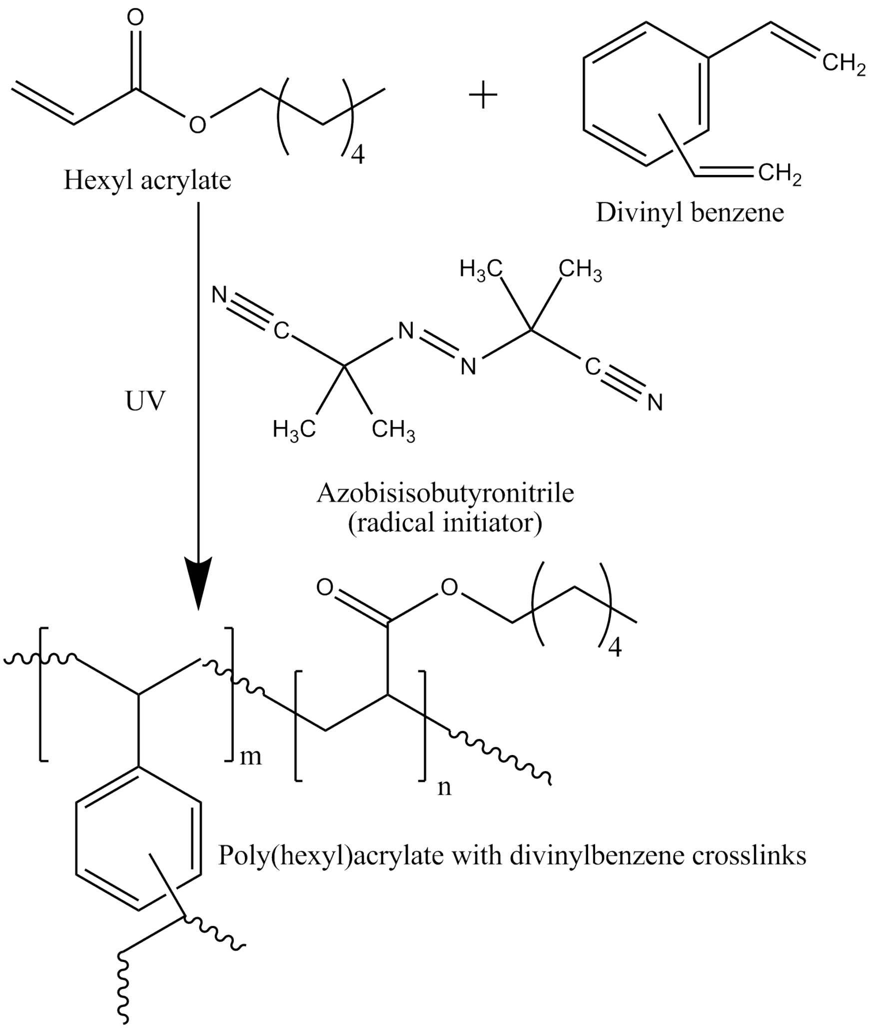


Figure 3.5: The Synthesis of DVB Cross-linked Polyacrylate Sheets - Showing the cross-linking points on the polymer chain provided by the DVB.

The cross-linking agent divinylbenzene (DVB) was confirmed to be essential for the formation of these elastomeric sheets, with curing failing in its absence. The exclusion of oxygen was also necessary to achieving polymerisation. This was achieved by bubbling the monomer blends through with nitrogen gas. Any bubbles formed were then removed by sonication and the blend injected into a mould (shown in experimental section Fig. 6.3) to minimise the access of air while curing occurred.

3.3.1 UV Initiators

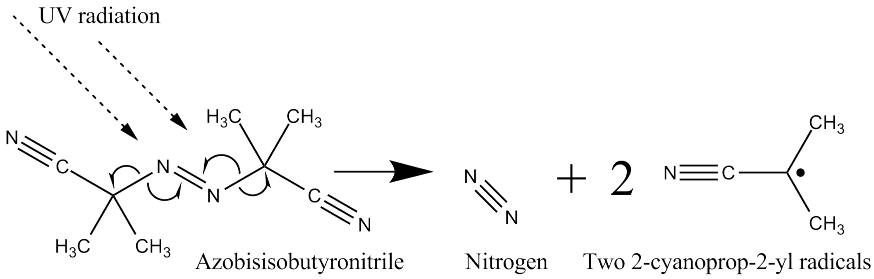


Figure 3.6: AIBN Radical Formation - Showing the release of nitrogen gas.

The elastomers formed were clear and colourless but had bubbles trapped within them. These bubbles interfered with fluorescence measurements by scattering light and also greatly reduced the tensile strength of the material. Both of these properties are undesirable for the continuation of this project. The bubbles were thought to be caused by the initiator AIBN as it produces nitrogen gas during radical formation (Fig. 3.6) which can form bubbles trapped within curing polymers. Therefore a variety of other UV initiators were evaluated (Tab. 3.2 and Fig. 3.7) for the clarity and elasticity of the products formed, as well as the time taken for complete curing.

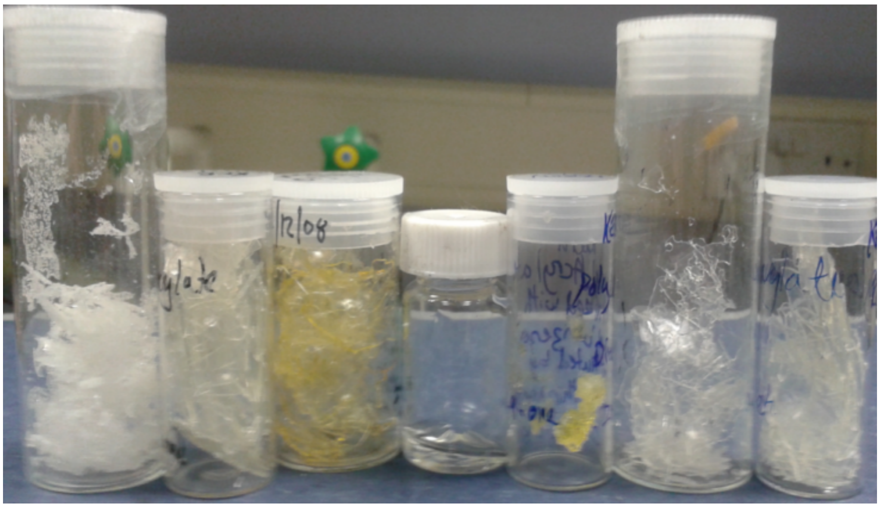


Figure 3.7: The Polyacrylate Sheets Formed Using Different Initiators - Shown left to right in the same order as they appear in Tab. 3.2

Diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) was chosen as it gave a clear, colourless product with the fewest UV exposures. Also no bubbles were formed during polymerisation with this initiator and the polymer was an even and elastic sheet. The even nature of the crosslinked sheets was determined by a visual inspection, and the sheet formed

Initiator	Exposures Required	Appearance of Product
Azobisisobutyronitrile	6	Clear and rubbery but full of bubbles
2-Methyl-4'-(methylthio)-2-morpholinopropiophenone	8	Clear and rubbery with no bubbles
2,2-Dimethoxy-2-phenylacetophenone	3	Slightly yellow and less rubbery
Isopropyl-9H-thioxanthan-9-one	-	Failed to polymerise
2-Chlorothioxanthan-9-one	10	Sticky yellow gum
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide	2	Clear and rubbery with no bubbles
2-Hydroxy-4'-(2-hydroxyethoxy-2-methylpropiophenone	6	Clear and rubbery with no bubbles

Table 3.2: A Selection of UV Initiators Along with the Number of One-Minute Exposures Required for Curing and the Appearance of the Polymer Sheet Formed

using TPO as the initiator displayed a uniform colourless appearance with no colour gradient, two-tone appearance or lumpy texture as seen in some other products shown in Fig. 3.7

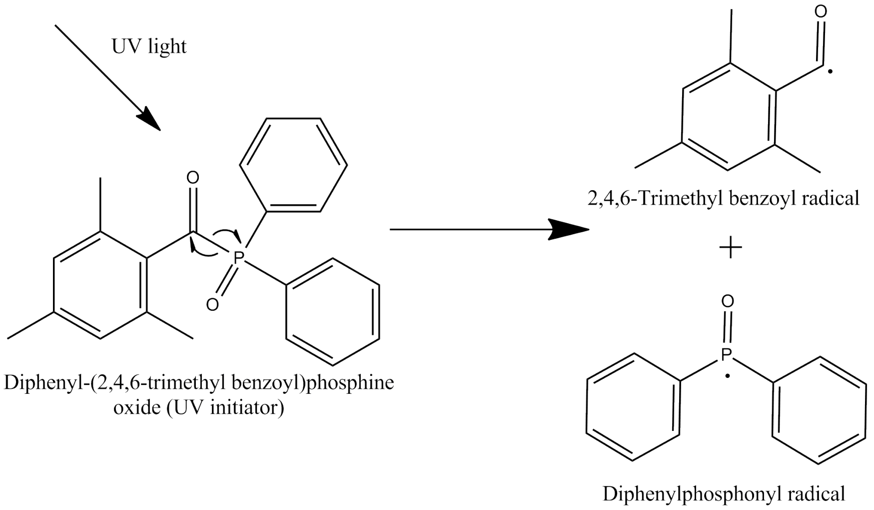


Figure 3.8: The Structure of UV Initiator Diphenyl-(2,4,6-trimethylbenzoyl)-phosphine Oxide - Showing the radical species formed by this initiator during UV exposure

TPO (Fig. 3.8) is commonly used as a UV initiator in industry. TPO absorbs photons between 370 and 420 nm and is known to photobleach.[83] The photobleaching of TPO is a desirable effect as the yellow colour of the TPO is lost during curing and does not remain in the polymer. Also the photobleaching leads to a greater depth of cure, i.e. the thickness of sheet it is possible to cure, as the UV light can pass further into the curing polymer as the yellow colour is lost. The drawback of TPO is that the radicals it forms[84] as shown in Fig. 3.8 are highly vulnerable to oxidation.[83] This should not pose a problem for any of the polymer sheets formed between quartz plates following bubbling of the monomers with nitrogen to exclude oxygen. However for any future surface coating applications, a second photoinitiator and/or oxygen scavenger (for example; benzophenone) may be required for successful curing.

3.4 Synthesis of Crosslinked Polyacrylate Elastomers Containing the Fluorescent Label 9-Vinylanthracene

A range of polymers containing different percentages (by weight) of 9-vinyl anthracene were made. Fig. 3.9 shows these polymers arranged in order of 9-vinylanthracene content from 1 wt% (left) to 0.1 wt% (right). The blue fluorescent response is clearly visible in all the polymers shown with the visible intensity decreasing along with the 9-vinylanthracene content. As the intended purpose for the polymers is in the validation of currency it is desirable that the fluorescent response should be easily visible to the naked eye to allow validation to occur in a range of situations without the need for expensive detection equipment. Many banks, shops and others with a need to validate currency will already own a UV light to enable inspection of currently used UV security features so a visible UV response would require no extra investment. All of the polymers shown would be suitable from this perspective as they are visibly fluorescent. However as the project involves the quenching of the fluorescence, it is desirable for the fluorescent label to be at the lowest useful concentration as this will give the best chance of achieving the quenching of fluorescence within these elastomers. If the level of label is much higher than needed to observe fluorescence, then the fluorescence will need to be quenched down to the minimum observable level before the quenching will be obvious. If the level of label is closer to the boundary for observable fluorescence then any quenching effect should be much more noticeable. These fluorescent labelled polymers are to be used for comparison with 4-bromostyrene containing polymers to see if quenching is observed by the naked eye. If it is, there will be a visible difference in the level of fluorescence observed between the polymers containing the same level of 9-vinylanthracene but different levels of 4-bromostyrene. Of the polymers shown in Fig. 3.9, the polymer containing 0.1 wt% 9-vinylanthracene was found to be the optimum as this still gives obvious fluorescence in response to UV light with a relatively low 9-vinylanthracene content. 0.1 wt% 9-vinylanthracene was therefore chosen as the label content for further polyacrylate synthesis.

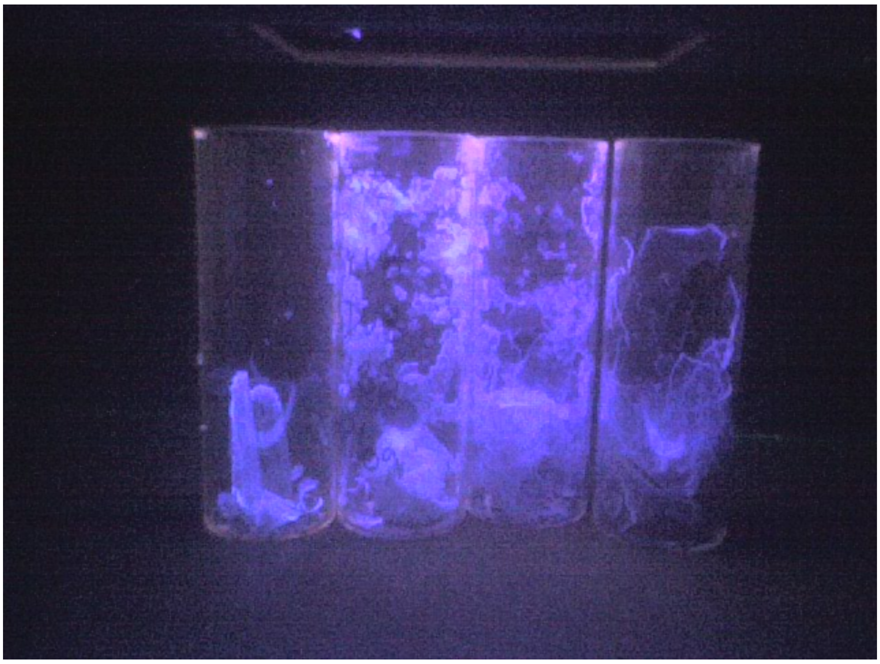


Figure 3.9: Poly(acrylate) Sheets Labelled with 9-Vinylanthracene Viewed Under UV(365 nm) Light - Containing from left to right; 1 wt%, 0.5 wt%, 0.25 wt% and 0.1 wt% 9-Vinylanthracene

3.5 Synthesis of Crosslinked Polyacrylate Elastomers Containing the Fluorescent Label 9-Vinylanthracene and the Fluorescence Quencher 4-Bromostyrene

A range of polymers containing 0.1 wt% vinyl anthracene (as determined through the previous optimisation process) and different percentages (0.1% to 1% by weight) of 4-bromostyrene were made. These were viewed under UV light (Fig. 3.10) and their appearance compared with the 0.1 wt% vinyl anthracene polymer that contained no 4-bromostyrene; this sample is shown on the far left of Fig. 3.10 The samples do appear to show quenching through a decrease in observable fluorescence as the 4-bromostyrene content increases. The sample containing 1 wt% 4-bromostyrene appears to give a less bright fluorescent response than the sample with none. However it is important to confirm spectroscopically that this is a real effect and excited state lifetime data will be needed. Fluorescence observed by the naked eye will be affected by the viewing angle and thickness of the sample. Even a relatively small increase in the thickness of a sample will make the fluorescent response appear brighter due to the greater quantity of label being viewed. Excited state lifetime data is not affected by polymer thickness or orientation and will give a more accurate determination of whether or not quenching is occurring.

Elemental analysis (Tab. 3.3) confirms the presence of bromine in the solid, cross-linked polymeric sheets (Fig. 3.10) apart from one of the lowest content (1 wt%) samples. The detection limit of bromine by elemental analysis is 0.3% so elemental analysis cannot be expected to detect the bromine content of sheets made with less than this. 4-Bromostyrene has a molecular weight of 183.05 and so comprises of 43.7% bromine. The sample containing 1 wt% 4-bromostyrene is only 0.437% bromine which is close to the detection limit of 0.3% It is therefore unsurprising that bromine has not been detected in this sample and it is very likely present at a concentration below the detection limits of elemental analysis. However the fluorescence spectroscopy is a very sensitive technique and often used to analyse fluorescent labels at concentrations around 10^{-6} M, so any quenching effect of the heavy atom present in these sheets should still be detectable by fluorescence spectroscopy even if the quencher itself cannot be detected by elemental analysis.

In the other sheets, the bromine content is higher than expected. However the DSC data in Tab. 3.3 also shows that increasing the 4-bromostyrene content of the monomer blend decreases the Tg of the resulting polymer sheet. This is a hinderance to the continuation of this project as the ability to extend the sheet is vital for the desired function of the target materials.

9-Vinylanthracene/$wt\%$	4-Bromostyrene/$wt\%$	Tg*/$°C$	C Content/%**	H Content/%**	Br Content/%**
0	0	-55	71.22	9.23	ND
1	0	-51	72.48	9.45	ND
1	1	-26	73.11	9.44	ND
2	1	-26	71.44	9.13	1.05
5	2	-23	72.94	8.68	2.48
1	10	-20	70.90	8.52	4.36

Table 3.3: Overall Results and Data for a selection of cross-linked polyacrylate elastomers - *from DSC, **from elemental analysis, (ND = Not discovered within detection limits of 0.3%)

Figure 3.10: Poly(acrylate) Sheets Labelled with 0.1 wt% 9-Vinylanthracene and Containing 4-Bromostyrene Viewed Under UV (365 nm) Light - Containing from left to right; 0 wt%, 0.1 wt%, 0.5 wt% and 1.0 wt% 4-bromostyrene

The polymer sheets formed have very little mechanical strength and even the polymers with the lower Tg values (Tab. 3.3) tear easily when tension is applied. It is essential for the polymers to withstand extension in order to evaluate its effect on the quenching of fluorescence within the polymer chains. Therefore the polymer sheets must be made more robust and elastic to allow progression of this project. Also the release of quenching will be more like to be observed in a polymer which can be extended further as greater extension will lead to greater average distance between any given fluorophore and quencher. The addition of toughening agents to the monomer blend may produce the desired properties. However it is vital to select toughening agents that will not interfere with the fluorescence analysis of the polymers. The next chapter discusses the synthesis of polyurethane acrylates with a view to enhancing the mechanical strength of the elastomers. Polyurethane acrylates were selected as toughening agents for the polyacrylate species described in this chapter because tough, elastic properties can be achieved using polyurethanes and the acrylate functionality should allow co-polymerisation with the acrylate monomers used previously. Polyurethane acrylates can also be used to form polymers with good optical clarity and so shouldn't interfere with the fluorescence analysis of the products formed.

3.6 Fluorescence Analysis

For the fluorescence analysis of the free 9-vinylanthracene, please see the previous chapter (2.5.1)

3.6.1 Linear Polyacrylate Bound 9-Vinylanthracene

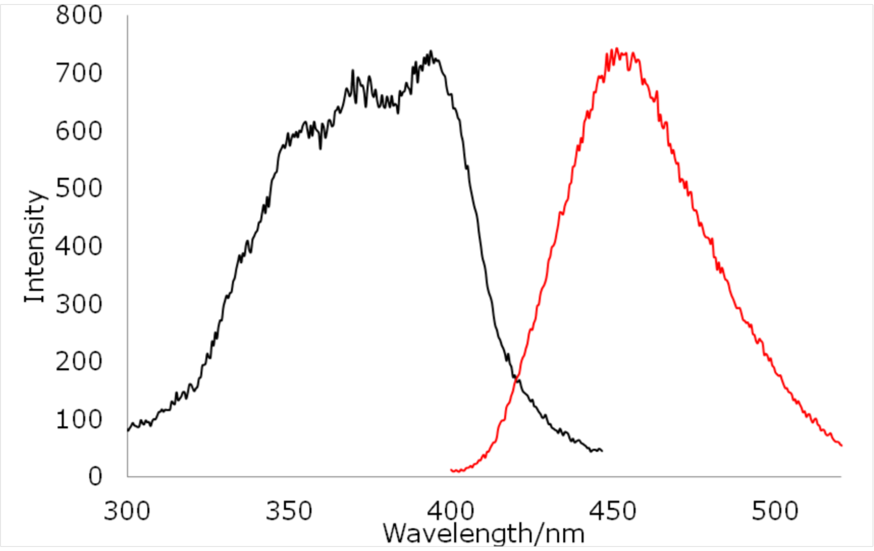


Figure 3.11: Excitation (Black) and Emission (Red) Spectra for Linear Polyacrylates Containing 9-Vinylanthracene - In toluene

A range of linear polyacrylates were synthesised to evaluate the behaviour of acrylate-bound 9-vinylanthracene in solution.

The excitation/emission spectra (Fig. 3.11) show little change in maxima compared with both the free 9-vinylanthracene (Fig. 2.12) and the SBR bound 9-vinylanthracene (Fig. 2.14) The excitation spectrum has seen a rounding off of its peak with the three maxima of the band becoming less distinct. The emission profile resembles the emission of the SBR bound 9-vinylanthracene (Fig. 2.14) with the single peak corresponding to the transition between the first excited state and the ground state still present but any other transitions seen in the excitation spectrum absent. This change in emission profile brought about by binding of the label to a polymer is not unexpected as binding can change the favourable electronic transitions responsible for the shape of the profile (introduction 1.3.1.1)

Excited state lifetime decay data (Tab. 3.4 and Tab. 3.5) were obtained for the labelled polyacrylates in both a good solvent (toluene at 25 $°C$) and a θ-solvent (cyclohexane at 34.5 $°C$) The difference in polymer conformation of the linear polyacrylate in a good solvent compared with a θ-solvent should provide an analogue for the difference between an extended and a relaxed elastomer respectively (Fig. 3.12)

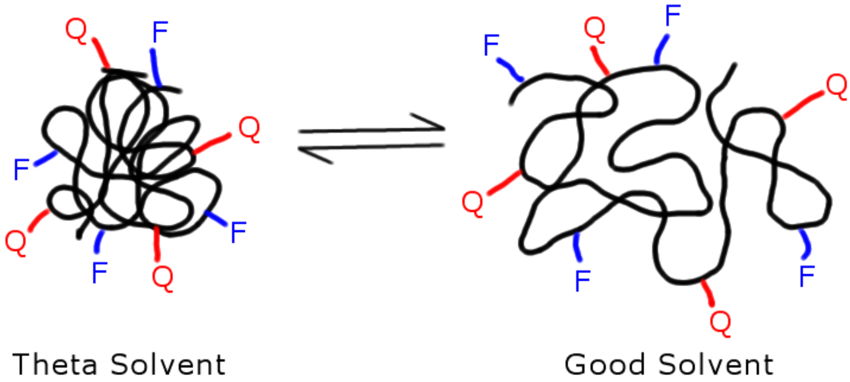


Figure 3.12: A representation of Polymer Conformation In a Good Solvent (Extended) and a θ-Solvent (Coiled) - Showing change in statistical proximity between fluorophore and quencher analogous to the chain extension in solids under tension

In a θ-solvent the polymer chains will be coiled tightly to minimise polymer-solvent interactions. This mimics the tightly packed chains in a relaxed solid and should lead to a greater degree of quenching of fluorescence as overall the heavy atoms will be in closer proximity to the fluorophores.

In a good solvent the polymer chains will be stretched out in order to maximise polymer-solvent interactions. This mimics the expanded chains in a solid under tension and should lead to a lesser degree of quenching of fluorescence as overall the heavy atoms will be statistically further away from the fluorophores and therefore more likely to be outside of the quenching distance.

Tab. 3.4 and Fig. 6.9 show that the decays observed were complex for the samples in the θ solvent with the single exponential fit breaking down, and χ^2 values deviating greatly from unity. Although the χ^2 values do not appear to increase significantly with increasing heavy atom content (Fig. 6.10) all of the χ^2 values are so far from unity that no confidence can be had in this apparent trend. Additional exponential terms led to a increase in χ^2 values so the single exponential fit was used for all data despite the low confidence in the fitting. Please see appendix 6.6.2 for the excited state lifetime plots of linear polyacrylate bound 9-vinylanthracene in the good and θ-solvent both in the presence and absence of 4-bromostyrene.

Tab. 3.5 and Fig. 6.11 show that the decays observed for the 0-2 wt% samples in the good solvent had χ^2 values near unity, with the residuals being randomly distributed around zero, giving good confidence in the fit. However, as seen in previous samples, the χ^2 values do begin

[4-Bromostyrene]/wt%	Exponentials	Lifetime/ns	χ^2
0	1	6.16	5.76
1	1	6.07	5.96
2	1	6.26	5.58
5	1	6.15	5.75
10	1	6.06	4.74

Table 3.4: Average lifetimes for the excited state of linear polyacrylate bound 9-vinylanthracene in the presence of different concentrations of 4-bromostyrene - In Cyclohexane at 34.5 °C (θ solvent)

[4-Bromostyrene]wt%	Exponentials	Lifetime/ns	χ^2
0	1	6.19	1.09
1	1	6.17	1.10
2	1	6.15	1.14
5	1	6.31	1.26
10	1	6.31	1.27

Table 3.5: Average lifetimes for the excited state of linear polyacrylate bound 9-vinylanthracene in the presence of different concentrations of 4-bromostyrene - In toluene at 25 °C (good solvent)

to deviate from unity with increasing heavy atom content and the corresponding residuals (Fig. 6.12) become less randomly distributed around zero. This gives lower confidence in the mathematical fitting and therefore the lifetime values for samples at 4-bromostyrene content of 5 wt% and above.

The χ^2 values for the same samples within the θ solvent have greatly deviated from unity ($\chi^2 > 5$) and so these lifetimes data cannot be safely compared with those from the good solvent. It is not therefore possible to assess whether quenching is occurring as a result of polymer chain collapse within the θ solvent (Fig. 3.12) The difference in calculated lifetimes is also less than the 0.5% experimental error estimated previously (section 2.5.1)

However the increase in χ^2 values for the samples within the θ solvent compared with the good solvent does itself support the collapse of the polymer chains. This is because a change in χ^2 indicates an alteration of the environment of the fluorophore. On average the lifetimes appeared to be slightly shorter for all samples in the θ solvent as compared with the good solvent. In both solvents the lifetimes appeared to decrease and then increase again with added 4-bromostyrene content. However due to the χ^2 values this cannot be confirmed for the samples in cyclohexane on statistical grounds. For the same reason, the increase in 4-bromostyrene cannot be confidently correlated with any change in the calculated lifetime of the excited state in these samples. The difference in lifetimes is also not greater than the 0.5% experimental error estimated previously for such readings (section 2.5.1) adding greater uncertainty and preventing any conclusions from being drawn.

It is possible that the local concentration of quencher, as described previously (section 2.5.1) within quenching distance of the fluorophores on the polymer chain is not high enough for quenching to be observed within these samples. Local concentration of quencher should be increased and be consistent within the solid cross-linked samples so the effect of the heavy-atom on the excited-state lifetime may be more easily observed within them. Local concentration or quencher (with respect to fluorophores) can either be increased statistically by an increase in the overall concentration of quencher or it can be a more targeted increase. This could be achieved using the same overall concentration of quencher but a decrease in the statistical distance between fluorophore and quencher however this would require greater control over the reaction.

3.6.2 Cross-linked Polyacrylate Elastomer Bound 9-Vinylanthracene

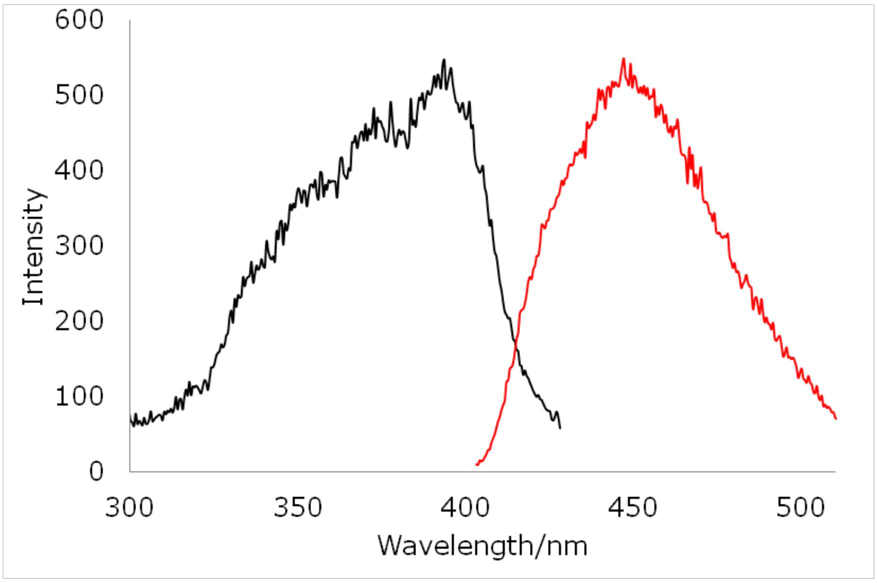


Figure 3.13: Excitation (Black) and Emission (red) Spectra for Cross-Linked Polyacrylates Containing 9-Vinylanthracene - Solid state readings.

The excitation/emission spectra (Fig. 3.13) show that the excitation maximum is around 394 nm and has all but lost its three peaked character. This implies a change in favourable electronic transitions as described in the introduction (1.3.1.1) The emission maximum has also shifted slightly to around 454 nm.

It is important to note that the intensity of emission spectra cannot be compared across the sheets containing different levels of 4-bromostyrene. This is because fluorescence spectroscopy is a very sensitive technique and even very slight changes in the thickness and orientation of the samples used can affect the amount of label present in the portion of the sample which is excited and therefore change the intensity of the emission observed. All comparisons between the fluorescence of the different sheets must come from the excited state lifetimes data as these show the decay of the excited state and are therefore unaffected by the total amount of label excited within the samples.

Tab. 3.6 shows that within the cross-linked polyacrylates, the bound 9-vinylanthracene lifetimes have increased by around 3 ns compared with the free 9-vinylanthracene (Tab. 2.3) This is probably due to the polymer matrix protecting the excited state from atmospheric oxygen. A decrease in the excited state lifetime still occurs with increasing 4-bromostyrene content across the series, however individual readings may be within the estimated error (section 2.5.1) With increasing heavy atom content, the χ^2 values again deviate from unity and the residuals become non-randomly distributed around zero, indicating reduced confidence in the mathematical fitting. Please see appendix 6.6.2 for excited state lifetimes plots of cross-linked polyacrylate bound 9-vinylanthracene with and without the presence of 4-bromostyrene (Fig. 6.13 and 6.14)

[4-Bromostyrene]/wt%	Exponentials	Lifetime	χ^2
0	1	9.49	1.2
1	1	9.44	1.2
2	1	8.95	1.3
5	1	8.51	1.5
10	1	8.49	1.7

Table 3.6: Average lifetimes for the Excited State of Cross-Linked Polyacrylate-Bound 9-Vinylanthracene in the Presence of Different Concentrations of 4-Bromostyrene

3.7 Conclusions

Linear polyacrylates were successfully synthesised and were shown by GPC to have the fluorescent label attached to the polymer chain. Fluorescence analysis did not show quenching with statistical certainty and further work is necessary for the heavy atom quenching of fluorescence to be proven to occur within these acrylic polymers. This could be due to the local concentrations of label and quencher being either too low or too high, and the difference between samples therefore difficult to observe. Quenching of the 9-vinylanthracene excited state by 4-bromostyrene was shown to occur in solution and in cross-linked sheets. However it was not possible to achieve a statistically acceptable fit for the excited state lifetime date from the linear acrylates.

Cross-linked polyacrylate elastomers were also successfully produced. They were optically clear and show the fluorescent monomer well with little to no interference. The TPO initiator (Fig. 3.8) gives an adequate depth of cure[85] (i.e. the thickness of sheet that can be successfully cured) for the thickness of the mould used to form cross-linked sheets. The products formed using the TPO initiator also exhibit excellent optical clarity with the yellow colour of the TPO being lost to photobleaching as the sheets are exposed to UV radiation.

The cross-linked sheets cure quickly and fully giving solid sheets with no residual monomer. However these elastomers are not very robust and tear easily in response to tension. These polymers are useful for displaying the fluorescence and its quenching but are less suitable to real world applications such as surface coatings due to their somewhat fragile nature and poor durability.

3.8 Future Work

The cross-linked polyacrylate elastomers had many desirable qualities for the continuation of this project and it may be possible to strengthen these polymers by the addition of toughening agents. This would overcome the disadvantages of the cross-linked polyacrylate elastomers and has the potential to produce the easily polymerisable, robust and optically clear elastomers required for this project. Polyurethane acrylates were identified as a good candidate species for toughening agents to be used in polyacrylate elastomers, and the next chapter addresses the synthesis of polyurethane acrylates. Polyurethane acrylates have the vinyl group necessary for UV initiated copolymerisation with other acrylates discussed in this chapter. They also have polyurethane functionality which can provide additional flexibility and increased tensile strength both of which are vital for the continuation of the project aims. It should also be possible to incorporate polyurethane acrylates without affecting the optical clarity, and therefore fluorescence analysis, of the elastomers formed.

4

The Synthesis of Polyurethane Acrylate Elastomers

4.1 Introduction

Polyurethane acrylates are polyurethane species with added acrylic functionality. This allows for UV curing and copolymerisation with the acrylic species described previously. These UV cured urethane-acrylic hybrid polymers tend to be optically clear and weather/chemical resistant. Due to these properties, polyurethane acrylates are commonly used in industry, and are often exploited as paints or other coatings.[86, 87] The polyurethane component of the polymers contains both hard (with a high Tg) and soft (low Tg) segments (Fig.4.1) The ratio of hard to soft segments controls the properties of the polyurethane.[88, 89] This combination grants structural strength and durability, while still allowing flexibility. A wide variety of formulations are possible with the ratio of hard:soft segments allowing control over the character of the resultant polymers.

Polyurethane elastomers are widely used in industry, including as surface coatings. Polyurethanes are synthesised by a (poly)addition reaction between a diisocyanate and a diol (or other dihydroxy species.) This means a wide variety of polyurethanes are possible. Polyurethane synthesis is usually a catalysed reaction. Stannous octanoate is commonly used but this has been shown to promote transesterification.[90] Dibutyl tin oxide is an alternative catalyst used when transesterification is not desired. The major disadvantage to polyurethanes is that they can yellow and degrade on exposure to UV radiation and other light.[91] This is more common in polyurethanes synthesised from isocyanates with aromaticity. Aliphatic polyurethanes are less commonly used and more expensive but they

have better resistance to UV and therefore colour stability. Another way around this problem is by the inclusion of UV stabilising additives to the final polymer.
Polyurethanes can be very viscous and may require the addition of a diluent for some applications such as surface coating. The diluents used are often functional, and usually acrylated species. The diluent should be compatible with the polyurethane it is to be added to. For example; simple, short-chain poly ϵ-caprolactone species could be used as a diluent for polyurethanes synthesised using poly-caprolactone diol.

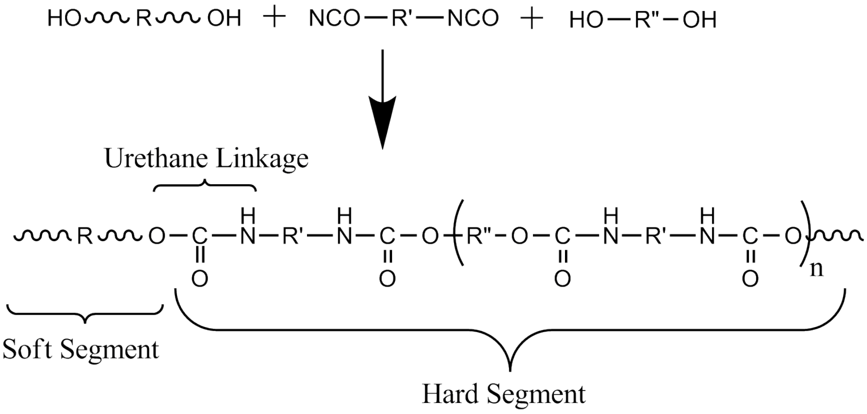


Figure 4.1: Polyurethane Formation - A general schematic for the synthesis of a polyurethane, showing the hard and soft segments as formed from the monomers.

Polyurethane acrylates are synthesised via a prepolymer. The prepolymer is formed from a polyol, a polyisocyanate and a hydroxyl functional (meth)acrylate. This prepolymer can then be polymerised by UV or thermal curing to form a homopolymer or copolymerised with other acrylate functional species. The formation of polyurethane acrylates from poly(caprolactone)diols has previously been described.[92] Polycaprolactone diols are easily synthesised and commercially available in a range of molecular weights. This allows for even greater control over the properties of the final polymer. Polyurethane acrylates can usually be synthesised without the need for solvent[93] and often have improved UV resistance compared with polyurethanes.

Fluorescent labels such as naphthalene and fluorescein are commercially available in dihydroxy-functional forms, as are various heavy atom containing species, and can be incorporated within the polyurethane chain. The hard/soft segmental morphology of the polyurethane component can also be utilised to separate the fluorescent labels and quenching monomers within the polymer. It is desirable to minimise the number of fluorophores quenched by heavy atoms within the Förster distance on the same polymer chain as these quenching interactions can not be released with the application of tension to the polymer.

This project aims to build a small library of linear polyurethane acrylate prepolymers, including some containing fluorescent labels and others containing heavy atoms. These can then be mixed with each other, or other acrylate functional species to produce a wide range of UV-curable polymer blends. The formation of prepolymers from the labels and/or quenchers should also help to separate then from each other along the polymer backbone. This means that any quenching interactions are due to chain coiling or inter-chain interactions and should be distrusted by the application of tension. If the label and quencher were too close on the same polymer chain then quenching interactions could occur even when the chain was extended under tension.

4.2 Synthesis of Linear Polyurethane Acrylate Prepolymer

For the synthesis of a polyurethane acrylate, a diol and a diisocyanate are used to form a linear prepolymer. The prepolymer is synthesised in a two step reaction under an inert atmosphere in the absence of water.

The first step involves the reaction between the polycaprolactone diol and the diisocyanate. The ratio of the two reagents is not stoichiometric and the diol is the limiting reagent with the diisocyanate in excess to give isocyanate-terminated chains. The reaction is followed by the removal of aliquots for determination of free isocyanate content via titration. The temperature of the reaction mixture is also monitored and kept below 70 $^\circ C$. As the formation of urethane linkages is an exothermic process, this can require cooling of the reaction vessel with an icebath. The temperature must be kept low to prevent allophanate formation [94] which can lead to the gelling of the reaction and the formation of solid cross-linked species with no use to this project.

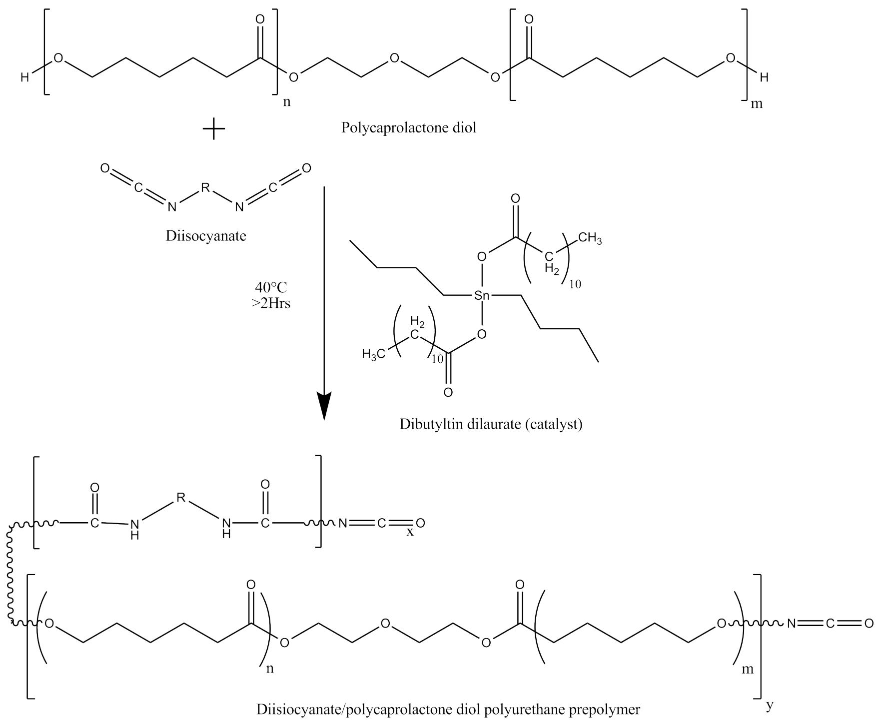


Figure 4.2: Synthesis of Linear Polyurethane Acrylate Prepolymer Step 1 - Reaction between polycaprolactone diol and diisocyanate.

The second step is the addition of a hydroxyl functional acrylate, in this case hydroxyethyl acrylate (HEA.) The HEA was added in a stoichiometric ratio to the remaining free isocyanate (NCO) groups. The determination of free NCO groups was achieved by taking samples of known weight from the reaction vessel and allowing them to react with a set volume of 1N dibutylamine. The resultant mixture was then titrated with 1N HCl to determine the remaining moles of dibutylamine and thus calculate the number of moles of dibutylamine consumed and therefore the free NCO content (Experimental 6.3.2) This method is the standard industrial practice for the determination of free NCO content[95] and is used widely in the commercial synthesis of polyurethanes.

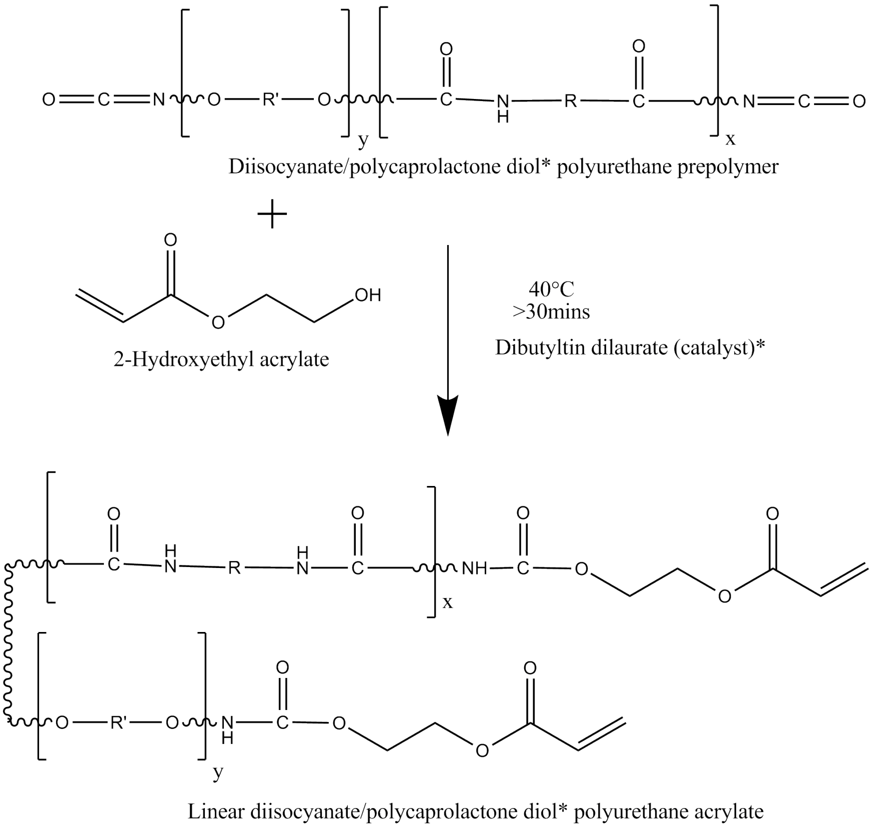
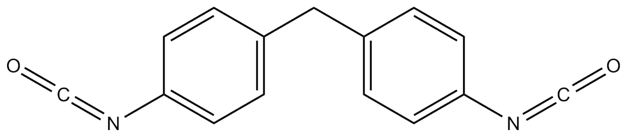


Figure 4.3: Synthesis of Linear Polyurethane Acrylate Prepolymer Step 2 - Reaction between step 1 product and hydroxyethyl acrylate. *See Fig. 4.2 for full Structure.

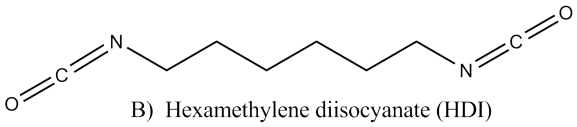
The reaction was allowed to continue until back titrations using dibutylamine, [95] (Experimental 6.3.2) as described previously, show an absence of free isocyanate groups. This results in a linear polyurethane prepolymer with acrylate functional chain ends.

4.2.1 Synthesis of Linear Polyurethane Acrylate Prepolymers from a Selection of Diisocyanates

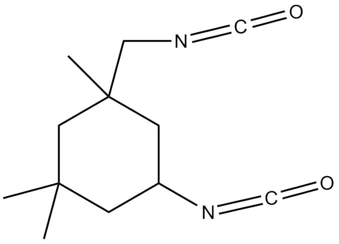
There are a wide variety of diisocyanates available with a variety of properties. Three of these (Fig.4.4) were selected for use in this project to give a range of reactivities.



A) 4,4'-Methylene diphenyl diisocyanate (MDI)



B) Hexamethylene diisocyanate (HDI)



C) Isophorone diisocyanate (IPDI)

Figure 4.4: The Structure of Three Different Diisocyanates - All commonly used in the industrial manufacture of polyurethanes.

Fig. 4.5 shows the physical appearance of the linear polyurethane acrylate prepolymers formed from the three different diisocyanates.

Figure 4.5: A Photograph of Linear Polyurethane Acrylate Prepolymers Synthesised From Various Diisocyanates - From left to right: Synthesised from MDI, synthesised from HDI, synthesised from IPDI and a gelled reaction

MDI was the first isocyanate used to form polyurethane acrylate prepolymers.

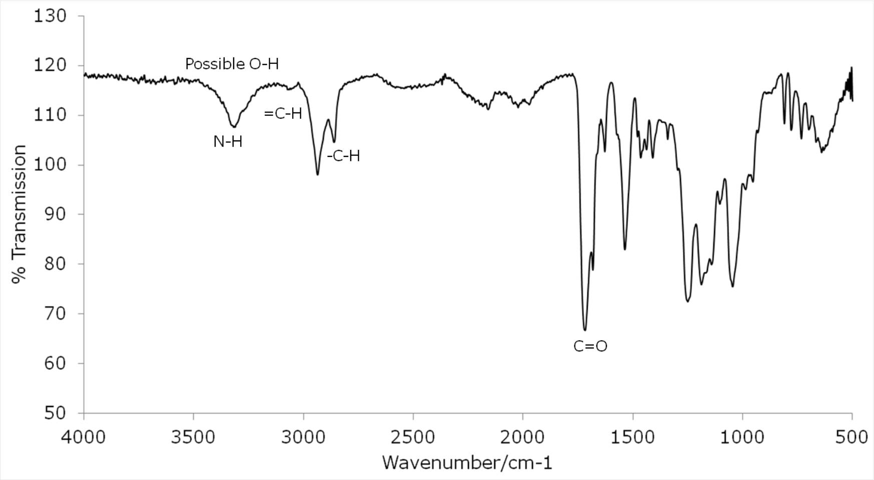


Figure 4.6: FT-IR Spectrum of Polyurethane Acrylate Synthesised from MDI - Showing the N-H bond in the urethane linkage

Fourier transform infrared spectroscopy (FT-IR) spectra of the polyurethane acrylate (Fig. 4.6) shows a reduction in the response for O-H and N=C=O bonds and the formation of an N-H bond when compared with the FT-IR spectrum of an unreacted mixture of the starting materials (Fig. 4.7) With the broad peak around 3200-3500 cm^{-1} corresponding with O-H bonds, a sharper peak at 2260-2310 cm^{-1} corresponding with N=C=O bonds. The newly formed N-H bonds correspond with a peak around 3350-3370 cm^{-1} which can be distinguished from the O-H peak by being much sharper, however the peak for the N-H bond may hide any residual O-H bond peak behind it.

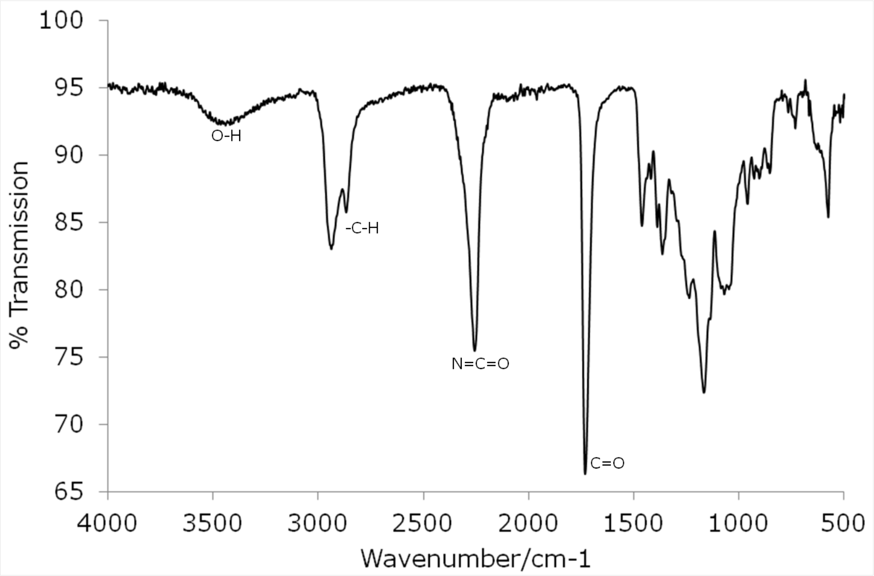


Figure 4.7: FT-IR Spectrum of an Unreacted Mixture of the Reagents Used to Synthesise a Polyurethane Acrylate - Showing the O-H bonds in the diols and the N=C=O bonds in the diisocyanate

In general, aromatic isocyanates are more reactive than their aliphatic counterparts and the MDI prepolymer formation was prone to overheating and gelling (see Fig. 4.5). Aromatic isocyanates are also known to discolour with exposure to sunlight or other sources of UV radiation.[96] This leads to a yellowing of the coating which was shown to be the case with the polyurethane acrylates formed from MDI. Although this discolouration is not indicative of a change in mechanical properties, the loss of optical clarity can interfere with the observation of fluorescence and therefore these products are not suitable for the continuation of this project.

HDI was the second diisocyanate used to form prepolymers and this gave improved UV resistance to the resultant sheets and did not lead to yellowing upon prolonged exposure to sunlight.

Again the formation of these prepolymers was confirmed by the N-H bond on the FT-IR spectrum (Fig. 4.8) although once more, this could be obscuring an O-H band corresponding to unreacted monomer. The sharp peak at 2260-2310 cm^{-1} associated with N=C=O bonds is also absent.

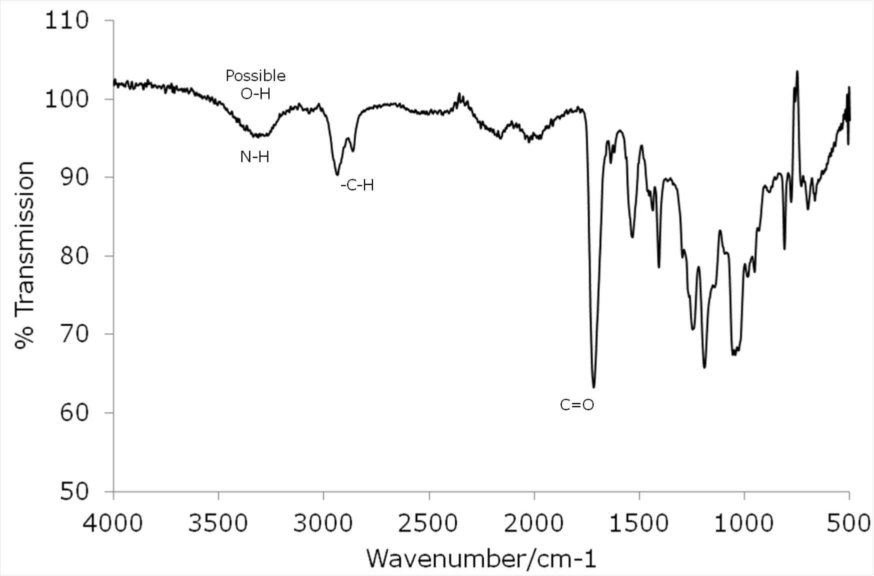


Figure 4.8: FT-IR Spectrum of Polyurethane Acrylate Synthesised from HDI - Showing the N-H bond in the urethane linkage

As HDI is a liquid, rather than a solid like MDI, DMSO is not required for solvation of the diisocyanate. However, as with the MDI, the prepolymer synthesis is very prone to the formation of waxy, unsuitable, solids (Fig. 4.5) and so a less reactive alternative was sought.

IPDI was selected as a less reactive alternative due to its bulky ring structure. The two isocyanate groups (one primary, one secondary) have different reactivities which further slows the reaction and increases selectivity.

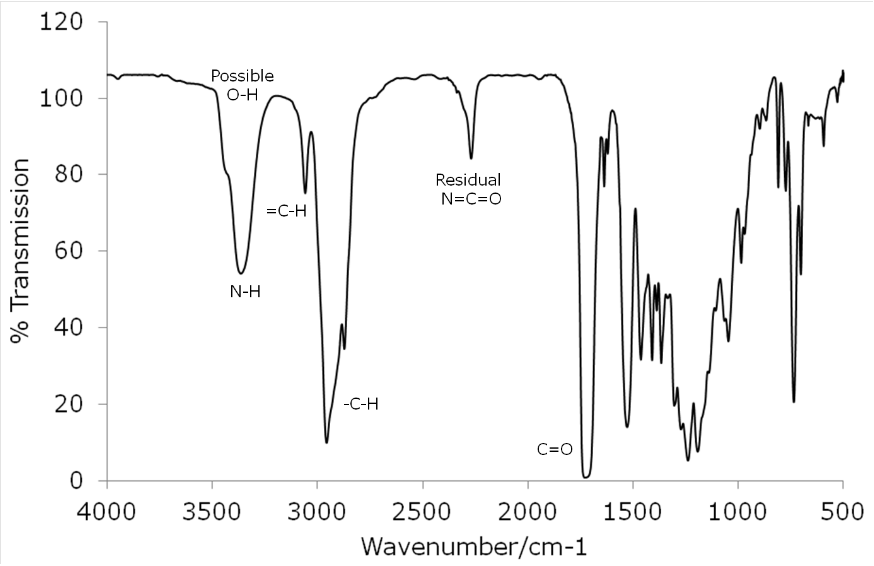


Figure 4.9: FT-IR Spectrum of Polyurethane Acrylate Synthesised from IPDI - Showing the N-H bond in the urethane linkage

As with the previous syntheses, the formation of these prepolymers was confirmed by the detection of the N-H bond on the FT-IR spectrum (Fig. 4.9) However the N-H bond now appears on the FT-IR spectrum as a bifurcated peak. This is due to the difference in bond character between the primary and secondary nature of the two different N-H bonds present in the IPDI. Again there could be a band, corresponding to O-H from residual monomers, hidden behind the N-H band. There is a sharp peak at 2260-2310 cm^{-1} associated with N=C=O bonds. However the peak is much less pronounced than would be seen in a mixture of unreacted monomers (Fig. 4.7) and so it is thought to represent a small amount of residual diisocyanate. Of the three diisocyanates, the IPDI gave the most reliable prepolymer formation without gelling of the reaction. Therefore IPDI was selected for the continuation of this project and the synthesis of all fluorescent label/quencher containing prepolymers.

4.2.2 Synthesis of Linear Polyurethane Acrylate Prepolymer Containing the Fluorescent Label 1,5-Dihydroxynaphthalene

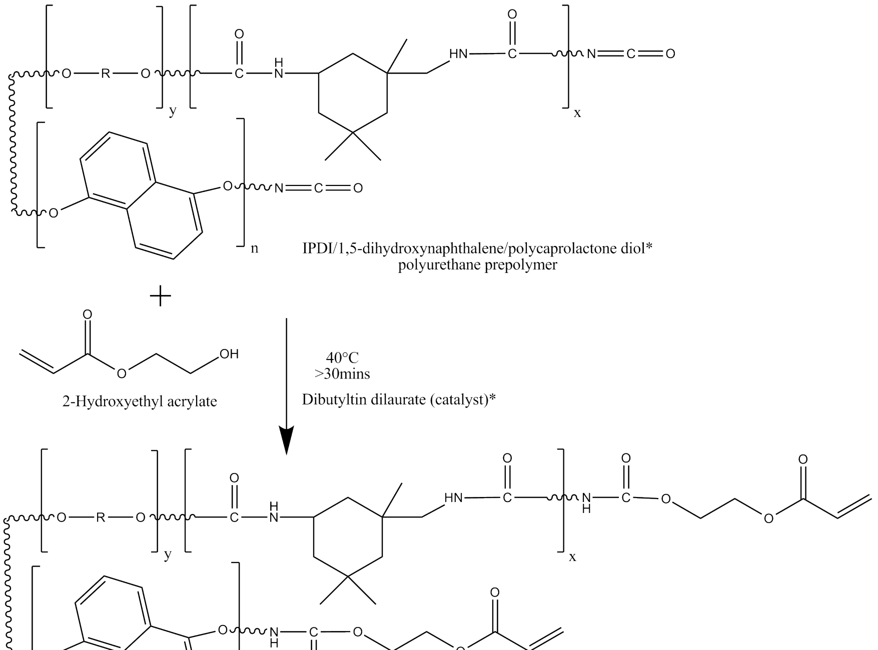


Figure 4.10: Synthesis of Linear Polyurethane Acrylate Containing the Fluorescent Label 1,5-Dihydroxynaphthalene - *See Fig. 4.2 for full structure

IPDI based linear polyurethane acrylate prepolymers containing the fluorescent label 1,5-dihydroxynaphthalene were successfully synthesised. The formation of these prepolymers was again confirmed by the detection of the N-H bond on the FT-IR spectrum (Fig. 4.11) Although again, the N-H bond peak may overlap with and conceal any O-H bond peak resulting from any residual monomer or unattached fluorescent label.

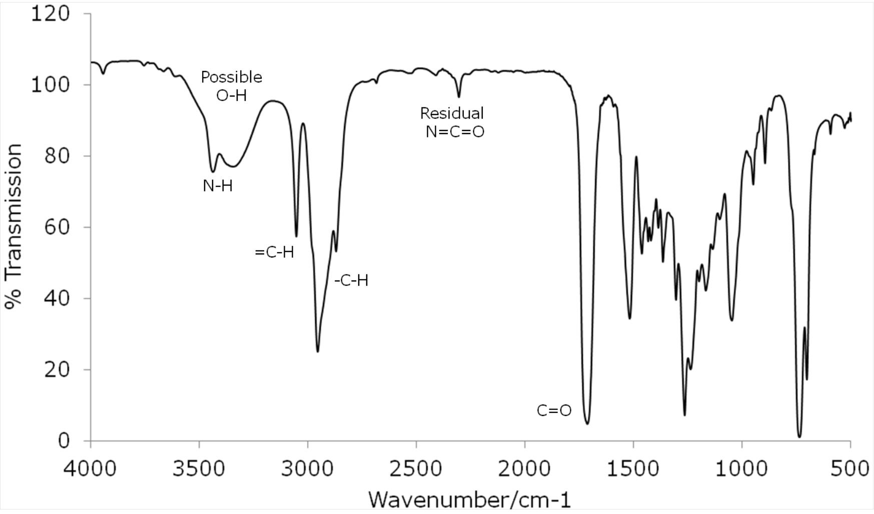


Figure 4.11: FT-IR Spectrum of 1,5-Dihydroxynaphthalene Labelled Polyurethane Acrylate Synthesised from IPDI - Showing the N-H bond in the urethane linkage

The attachment of the label to the prepolymer was confirmed by GPC by comparing the responses of both a UV and an RI detector as described in the previous chapter 3.2 The label was highly coloured and the resultant polyurethane acrylate was a deep purple/black colour (Fig. 4.12)

Figure 4.12: A Photograph of Labelled Linear Polyurethane Acrylate Prepolymers - From left to right: 1) A prepolymer containing 1,5-dihydroxynaphthalene and viewed under daylight. 2) A prepolymer containing fluorescein viewed under daylight. 3) A prepolymer containing fluorescein viewed under 365 nm UV light. 4) A prepolymer containing 3-bromo-1,2-propanediol.

The obviously coloured nature of the prepolymer formed is a concern as this could interfere with fluorescence spectroscopy or other optical techniques as well as affecting the penetration of UV light during polymerisation reactions. However any one of these prepolymers will only comprise a small part of any (otherwise colourless) prepolymer/monomer blends used. Therefore the colour of the labelled prepolymers should have minimal effect on the optical clarity of the final blend or on the UV cured solid sheets. It must also be noted that the fluorescence response of 1,5-dihydroxynaphthalene involves the emission of photons with a wavelength around 350 nm which is still within the UV segment of the electromagnetic spectrum. Therefore the fluorescent response of any polymers containing this label will only be observable with spectrophotometric equipment and not with the naked eye. The polymers labelled with 1,5-dihydroxynaphthalene can be used as proof of principle. However as the intended use for the products formed is in the day to day validation of currency, a dihydroxy functional fluorescent label that emits light within the visible part of the electromagnetic spectrum will be required. The next step was to identify such a label suitable for the syntheses described.

4.2.3 Synthesis of Linear Polyurethane Acrylate Prepolymer Containing the Fluorescent Label Fluorescein

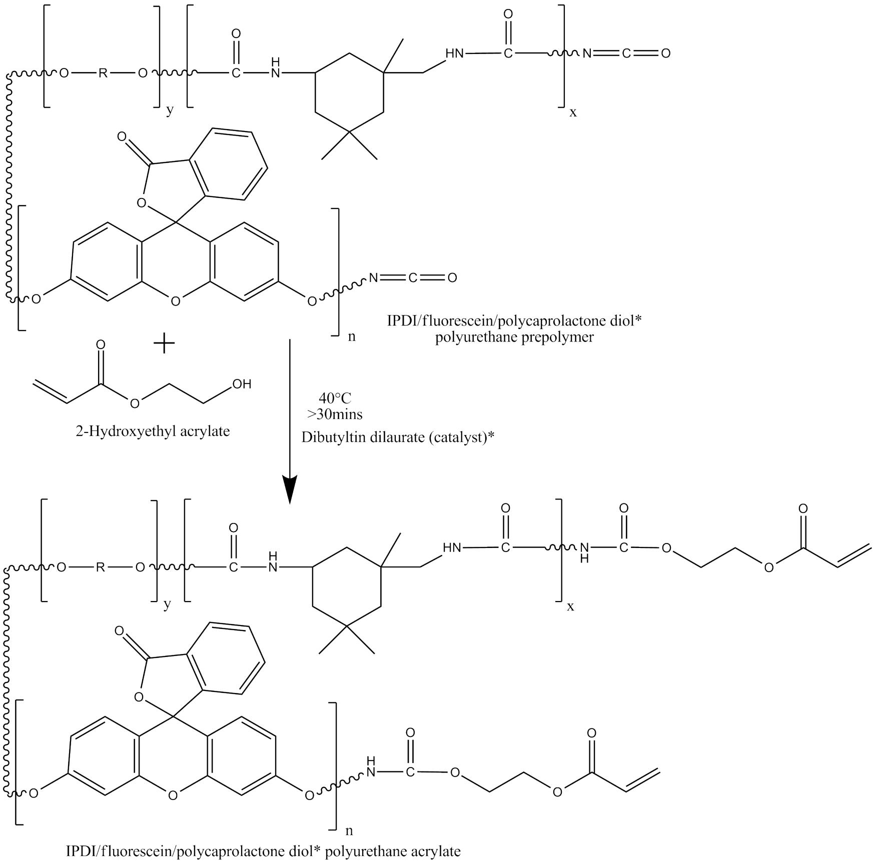


Figure 4.13: Synthesis of Linear Polyurethane Acrylate Prepolymer Containing the Fluorescent Label Fluorescein - *See Fig. 4.2 for full structure

Fluorescein is a commercially available and well characterised [97, 98] fluorescent label which emits photons with a wavelength around 517 nm. This is within the visible segment of the electromagnetic spectrum and when exposed to UV light, fluorescein visibly fluoresces a bright yellow (Fig. 4.14)

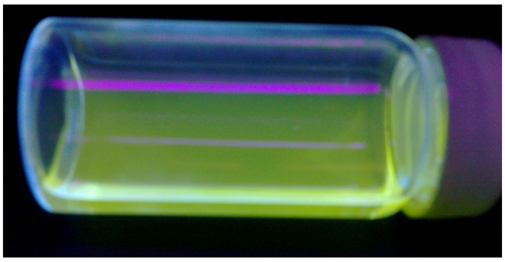


Figure 4.14: The Visible Emission of the Fluorescent Label Fluorescein - Viewed under 365 nm UV light

As with the previous syntheses, formation of these prepolymers was confirmed by the detection of the N-H bond on the FT-IR spectrum (Fig. 4.15) which again may obscure the O-H response from any residual monomer and/or label. The prepolymers are a light orange in colour (Fig. 4.12) which, as discussed previously, should not affect the optical clarity of the final polymers.

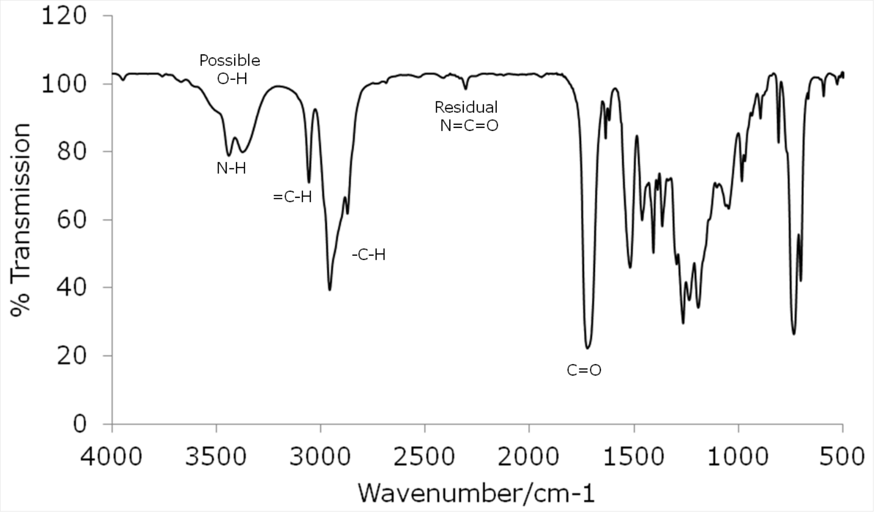


Figure 4.15: FT-IR Spectrum of Fluorescein Labelled Polyurethane Acrylate Synthesised from IPDI - Showing the N-H bond in the urethane linkage

The first attempts at producing fluorescein labelled polyurethane acrylates showed poor label attachment (Fig. 4.16) with the label washing out of the resultant polymer sheets. The method was subsequently adjusted to account for the lower reactivity of the fluorescein hydroxyl groups. Several methods were tried and it was found that if the diisocyanate was allowed to react with the fluorescein at a higher temperature before the polycaprolactone diol was added, the label was successfully incorporated within the final polyurethane acrylate. The successful attachment of the label to the main bulk of the polyurethane acrylate was shown by GPC using both an RI and a UV detector (Fig. 4.17)

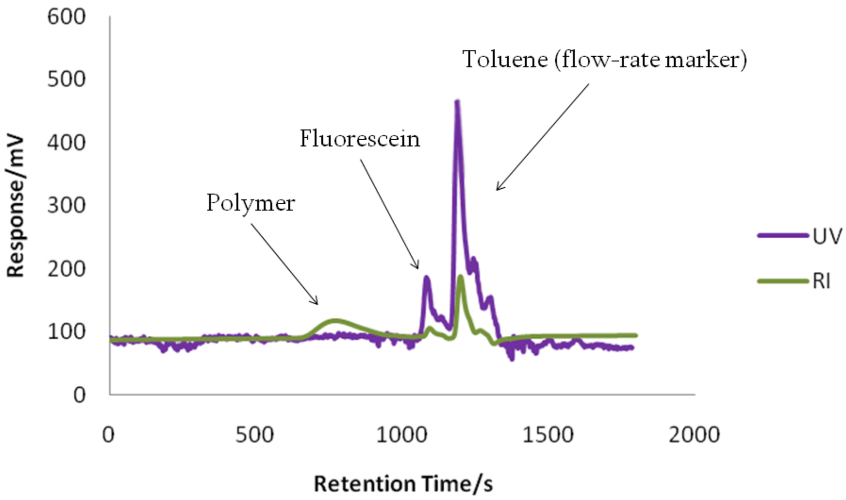


Figure 4.16: GPC Chromatogram of Fluorescein Labelled Polyurethane Acrylate Prepolymer - Method One - Showing the fluorescein not attached to the main bulk of the prepolymer

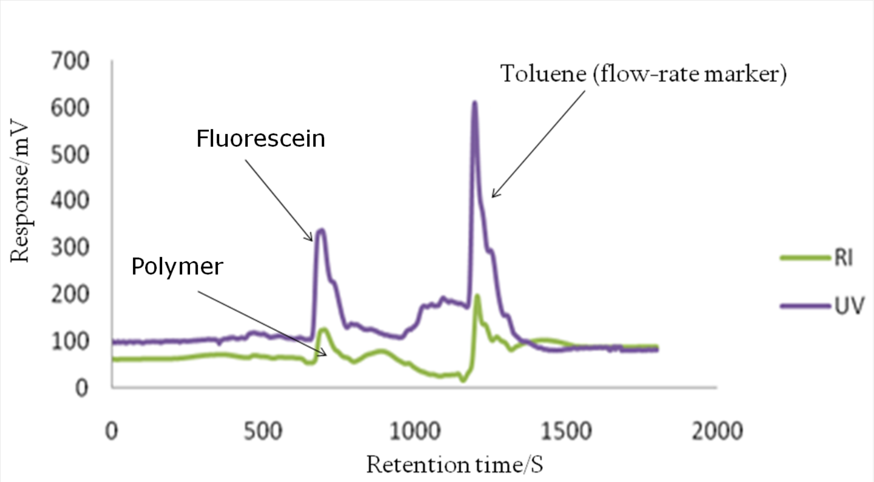


Figure 4.17: GPC Chromatogram of Fluorescein Labelled Polyurethane Acrylate Prepolymer - Method Two - Showing the fluorescein attached to the main bulk of the prepolymer

Prior to the alteration of the method, the label was seen by UV at a different retention time to that of the polyurethane acrylate seen on the RI detector (Fig. 4.16) However following the changes to the method, the UV detector showed the label eluting at the same retention time as the polyurethane acrylate (Fig. 4.17)

4.2.4 Synthesis of Linear Polyurethane Acrylate Prepolymer Containing the Fluorescence Quencher 3-Bromo-1,2-propanediol

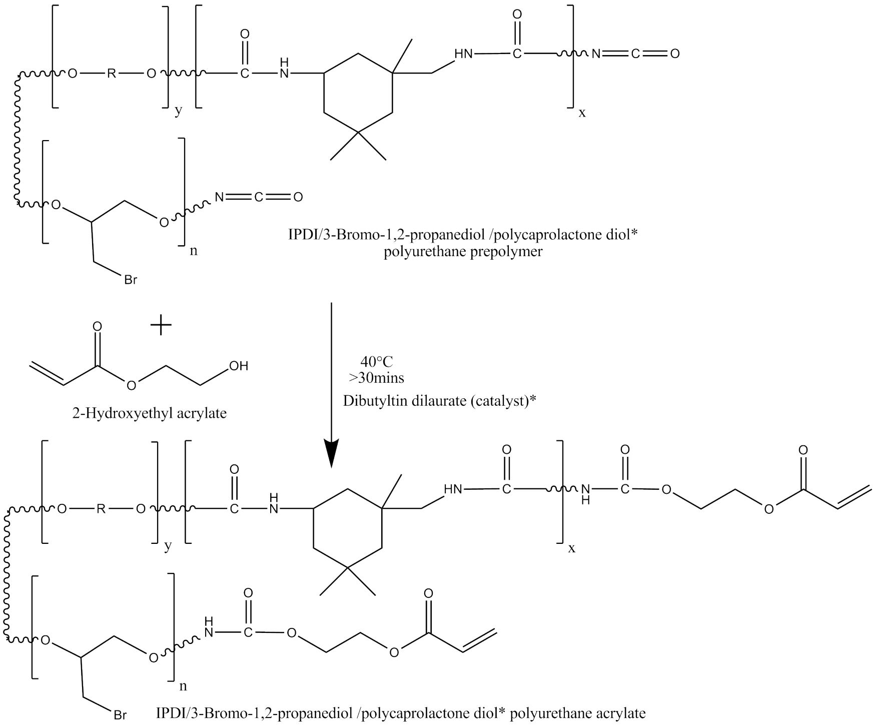


Figure 4.18: Synthesis of Linear Polyurethane Acrylate Prepolymer Containing the Fluorescence Quencher 3-Bromo-1,2-propanediol - *See Fig. 4.2 for full structure

Again, the formation of these prepolymers was confirmed by the detection of the N-H bond on the FT-IR spectrum (Fig. 4.19) A very small peak was seen corresponding to residual N=C=O groups. The N-H peak is likely to be obscuring any O-H response from residual diols.

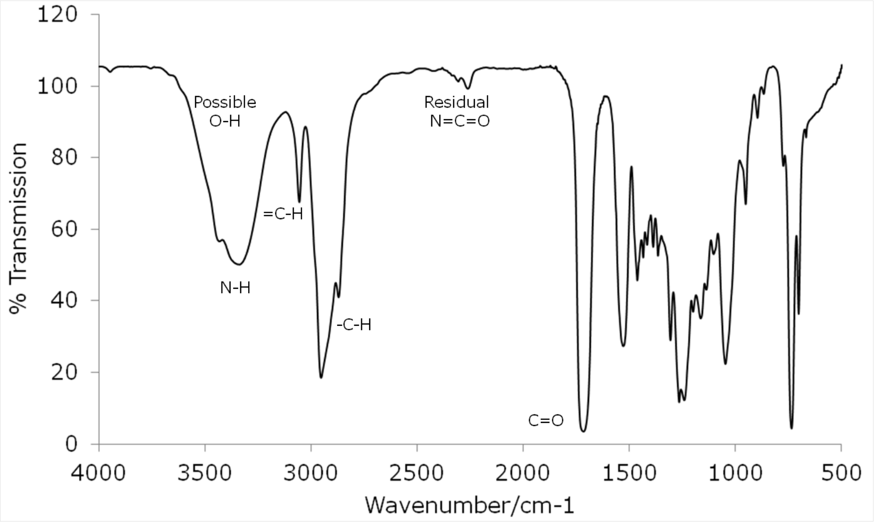


Figure 4.19: FT-IR Spectrum of 3-Bromo-1,2-propanediol Containing Polyurethane Acrylate Synthesised from IPDI - Showing the N-H bond in the urethane linkage

The presence of bromine within the polymer chain was confirmed by elemental analysis of the prepolymer following washing of the prepolymer with methanol (Tab. 4.1) The methanol washes were also submitted for elemental analysis and bromine was not detected (within detection limits of 0.3%) further confirming that the 3-bromo-1,2-propanediol is bound within the polymer.

Tab. 4.1 shows that the bromine content of the 3-bromo-1,2-propanediol containing polyurethane acrylate prepolymer was found to be 0.95 % from elemental analysis. This is much lower than the expected value of 1.96 suggesting that the 3-bromo-1,2-propanediol is not evenly distributed within the prepolymer.

Tab. 4.1 also shows that the incorporation of the 3-bromo-1,2-propanediol in the prepolymer has the effect of raising the Tg. The Tg of the heavy atom containing prepolymer was determined by DSC and found to be higher by around 5 $°C$ compared with the IPDI based polyurethane acrylate prepolymer and around 20 $°C$ higher compared with the labelled IPDI polyurethane acrylate prepolymers.

Prepolymer	Mn*	Mw*	Tg**/$^{\circ}C$	C^+/%t	H^+/%	N^+/%	Br^+/%
MDI-based	4350	3860	49.65	57.91	3.24	9.04	ND
HDI-based	2860	4350	X	53.88	2.29	8.22	ND
IPDI-based	4140	5700	-50.5	59.71	4.12	9.26	ND
1,5-Dihydroxynaphthalene labelled	4240	2800	-64.0	57.21	4.29	9.70	ND
Fluorescein Labelled	3700	4900	-65.5	59.66	5.05	9.36	ND
3-Bromo-1,2-propanediol containing	4120	4760	-45.9	55.16	4.25	9.34	0.95
Methanol wash	N/A	N/A	N/A	37.06	13.35	ND	ND

Table 4.1: Overall results and data for linear polyurethane acrylate prepolymers - *from GPC, **from DSC, $^+$ from elemental analysis (ND = Not discovered within detection limits of 0.3%)

4.2.5 UV Cured Poly(Acrylate-co-Urethane-Acrylate) Sheets

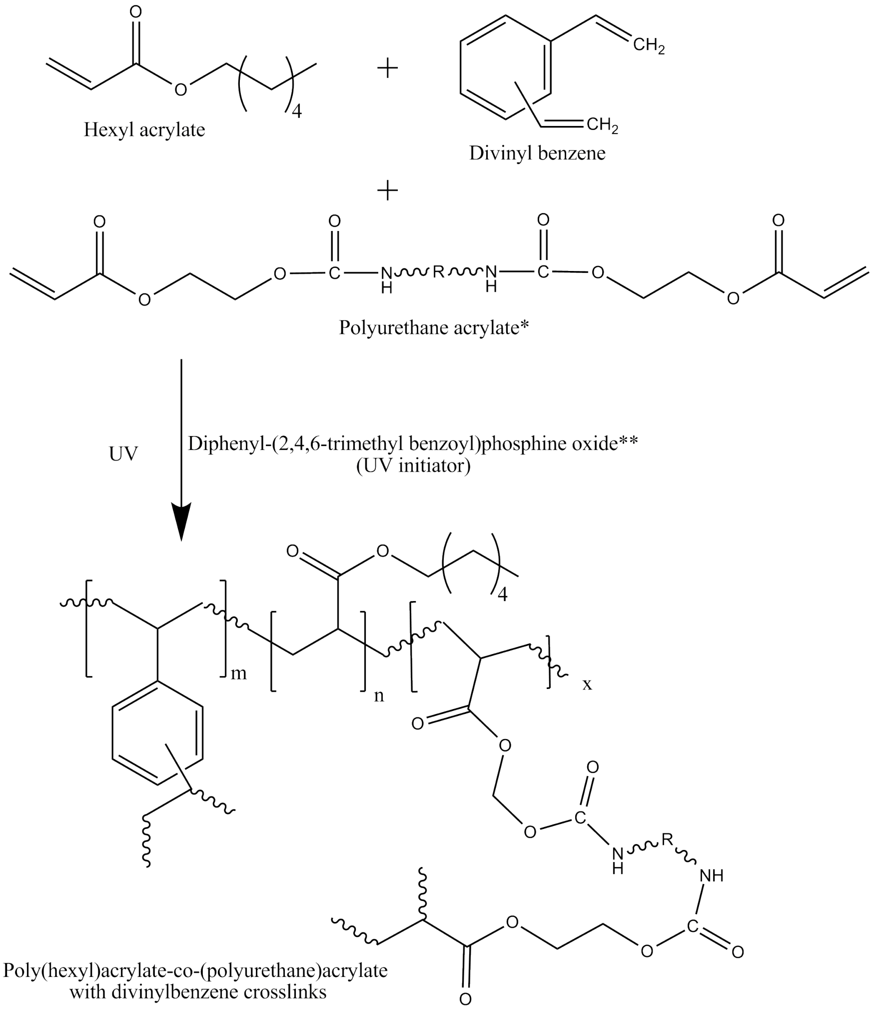


Figure 4.20: Synthesis of UV Cured Poly (Acrylate-co-Urethane-Acrylate) Solid Sheet - *Any of the linear polyurethane acrylates described previously. **See Fig. 4.2 for full structure

Urethane species were originally synthesised to act as toughening agents for acrylate polymers previously synthesised. However, upon blending it was found that the polyurethane acrylate prepolymers were immiscible with the acrylate monomers previously used. As the polyurethanes seemed a promising lead, and also appear to give clear products, they were investigated further. However, these polyurethanes are very viscous and some diluting agent (diluent) will be necessary for surface coating and other applications. Dilution will also be required to allow injection into the mould that will be used to form cross-linked species for this project.

Several other acrylate functional species were trialled as diluents for the linear polyurethane acrylate prepolymers. Commercially available poly(ethyleneglycol)diacrylates were found to be effective diluents. The blending of poly(ethyleneglycol)diacrylate with the linear polyurethane acrylate prepolymers resulted in a homogenous mixture as determined visually. It was possible to effectively bubble these blends with nitrogen in order to remove oxygen, and the mixtures were passable through a hypodermic needle allowing them to be introduced to the form used for curing (Fig. 6.3) without admitting oxygen. These blends of synthesised prepolymers and poly(ethyleneglycol)diacrylates were used to form UV cured solid sheets.

4.3 UV Cured Polyurethane Acrylate Sheets

Preliminary polymer sheets were extremely rigid and brittle. In response the crosslinking agent (divinyl benzene) content was reduced. It was eventually found that the divinylbenzene could be omitted altogether from these polymers. A range of UV cured polymers were then synthesised which had very desirable properties, with the majority having a Tg below room temperature (Tab. 4.2)

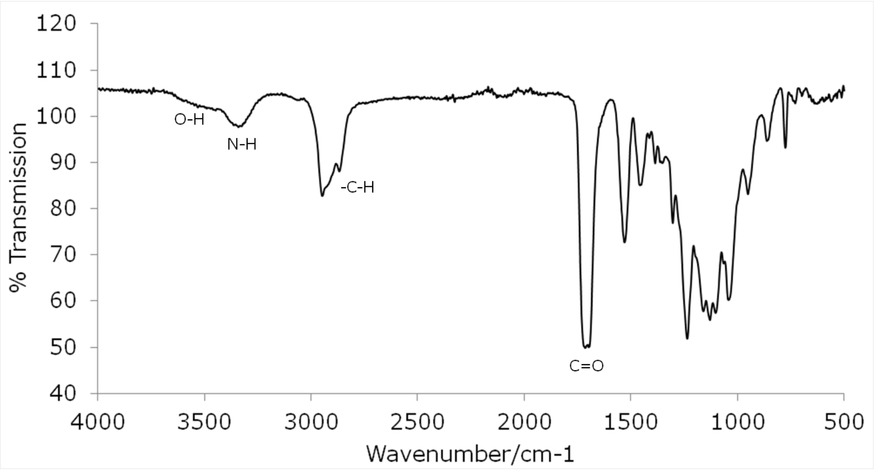


Figure 4.21: FT-IR Spectrum of a Cross-Linked Polyurethane Acrylate Sheet - Showing the N-H bond in the urethane linkage and the absence of starting materials

FT-IR spectra (Fig. 4.21) for the UV cured cross-linked polyurethane acrylate sheets show the continued presence of a peak around 3350-3370 cm^{-1} corresponding with the NH bond of urethane linkages within the polymer. There is an absence of a strong, sharp peak at 2260-2310 cm^{-1} corresponding with N=C=O bonds, indicating the lack of diisocyanate within the polymer sheet. Also the sharp peak seen in spectra of the linear polyurethane acrylate prepolymers (Fig. 4.9) around 3050 cm^{-1} corresponding with the =C-H bonds has all but disappeared showing the successful polymerisation of the majority of acrylate groups.

However there is some indication of the presence of a broad peak around 3200-3500 cm^{-1} corresponding with O-H bonds which suggests that there may be a small quantity of residual diol present or that the sample has taken on some moisture from its surroundings.

Tab 4.2 shows that the addition of the heavy atom containing species to the prepolymer was again found to raise the Tg as determined by DSC. With the Tg raised above room temperature in the sheet comprised of 70 % 3-bromo-1,2-propanediol prepolymer but below room temperature for all the other sheets formed. The presence of bromine was confirmed by elemental analysis (Tab. 4.2) only in the sheets containing greater than 10 wt% of the 3-bromo-1,2-propanediol prepolymer. However only around 0.95% of the 3-bromo-1,2-propanediol containing prepolymer is actually bromine. Therefore a sheet made with 1 wt% 3-bromo-1,2-propanediol prepolymer will only contain around 10^{-2} wt% of actual bromine. The detection limit of bromine by elemental analysis is 0.3% so elemental analysis can not be expected to detect the bromine content of sheets made with less than 3 wt% 3-bromo-1,2-propanediol prepolymer. However fluorescence spectroscopy is a very sensitive technique and often used to analyse fluorescent labels at concentrations around 10^{-6} M, so any quenching effect of the heavy atom present in these sheets should still be detectable by fluorescence spectroscopy.

4.4 Fluorescence Analysis

Steady state excitation and emission spectra were obtained for both the free and polymer-bound fluorescent labels. These give the excitation/emission maxima and allow the correct excitation and detection wavelengths to be set for the spectrophotometer used to observe the decay of the excited state. Decay curves showing the lifetime of the excited state were also recorded for both the free labels and the solid polymer sheets. The lifetimes for the polymer sheets containing increasing heavy atom content were also obtained. The intensity of emission spectra can not be compared between solid samples as the thickness and orientation of the sheets affect the amount of label present in the portion of the sample which is excited and therefore the intensity of the emission observed. Although the mould used to synthesise the polymer sheets utilises a PTFE spacer of known thickness; fluorescence spectroscopy is a very sensitive technique and could be affected by very slight variations or flaws in the PTFE spacer or quartz sheets that would be undetectable to the naked eye. All comparisons between the fluorescence of the different solid sheets must come from the excited state lifetimes data as these show the decay of the excited state and are therefore unaffected by the amount of label in the sample.

DHN-PP/wt%	F-PP/wt%	BPD-PP/wt%	Tg**/$^{\circ}C$	C^{+}/%t	H$**$/%	N$**$/%	Br$**$/%
0	0	0	-12.9	58.78	7.55	3.08	ND
1	0	0	-13.3	58.77	7.74	3.20	ND
1	0	1	-6.9	58.08	8.56	2.88	ND
1	0	2	-5.0	58.68	8.39	3.12	ND
1	0	5	-3.2	59.43	8.17	3.42	ND
0	1	0	14.4	58.92	7.85	3.52	ND
0	1	1	16.7	59	8.21	3.49	ND
0	1	10	19.0	58.09	8.50	3.59	0.46
0	1	70	29.5	58.93	8.04	3.36	0.94

Table 4.2: Overall results and data for cross-linked polyurethane acrylate polymers - DHN-PP = 1,5-Dihydroxynaphthalene labelled prepolymer, F-PP = Fluorescein labelled prepolymer and BPD-PP = 3-Bromo-1,2-propanediol containing IPDI based polyurethane acrylate prepolymer. *From DSC, ** from elemental analysis (ND = Not discovered within detection limits of 0.3%)

4.4.1 Free 1,5-Dihydroxynaphthalene

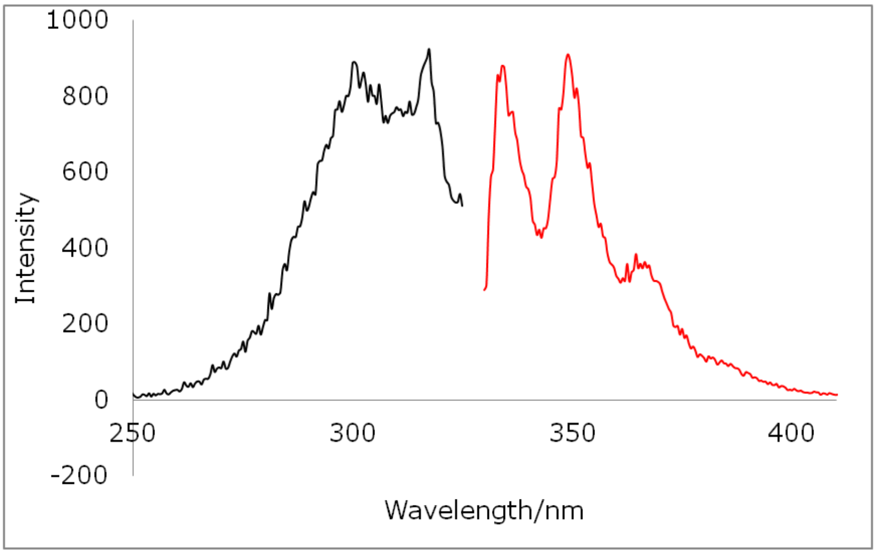


Figure 4.22: Excitation (Black) and Emission (Red) Spectra for Free 1,5-Dihydroxynaphthalene - In THF

The excitation/emission spectra (Fig. 4.22) show the free 1,5-dihydroxynaphthalene having an excitation maximum of around 315 nm and emission profile with two maxima; the slightly larger peak having a maximum of around 350 nm. These data were in line with literature values[99] and used to set the parameters for the lifetimes measurements.

It was found that the decay of the excited state of 1,5-dihydroxynaphthalene was incompatible with a single exponential mathematical fit (Fig. 4.23) with χ^2 values well beyond the acceptable range and the residuals clearly not randomly distributed around zero. A second exponential component improved the fit a little (Fig. 4.24) but still did not return values consistent with a good data fit. The triple exponential however did appear to give a good fit for the data (Fig. 4.25) with χ^2 values in the acceptable range and no obvious pattern present within the distribution of residuals. However, as noted by J. Lacowicz in Principles of Fluorescence Spectroscopy[43] most decay data can be fit using multiple exponential components and the accompanying equation (equation 1.2, introduction 1.3.1.2) and so care must be taken when using this model.

The number of exponential components used is related to the number of environments that the fluorophore is in. For very complex systems, this can mean that the lifetime components can actually follow a more continuous distribution rather than truly being discrete components.[100] Modern spectroscopy equipment and software can accurately and quickly determine all the components contributing to the average lifetime.[101] However older equipment needs the number of exponential components used for fitting to be determined based on the χ^2 values, residuals and previous knowledge of the fluorophore and system.[43] Lifetimes for 1,5-dihydroxynaphthalene are not well described in literature, however, the use of three exponential components to fit lifetime data is common across a variety of naphthalene derivatives.[102, 103] Although the components are unknown, the χ^2 values and residuals give a good level of confidence in the triple exponential fit and so it was selected for use in fitting the lifetimes data for this label.

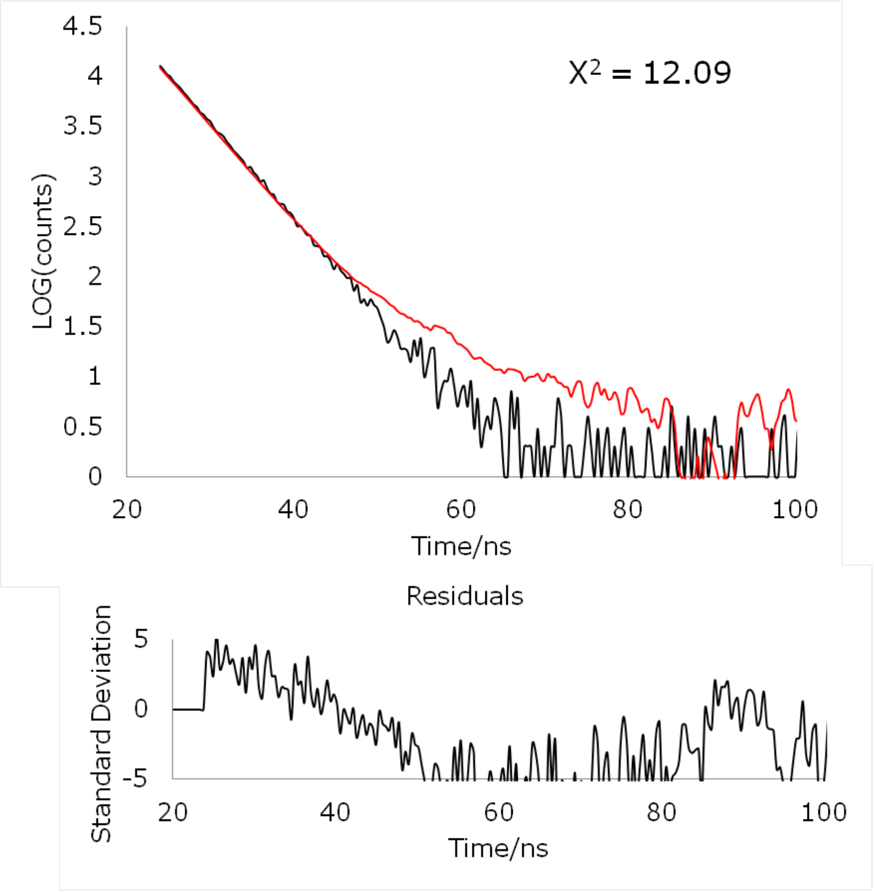


Figure 4.23: Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene - Showing the monoexponential mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit - note their non-random distribution with the slope at the start indicating decay data that has not been accounted for in the model.

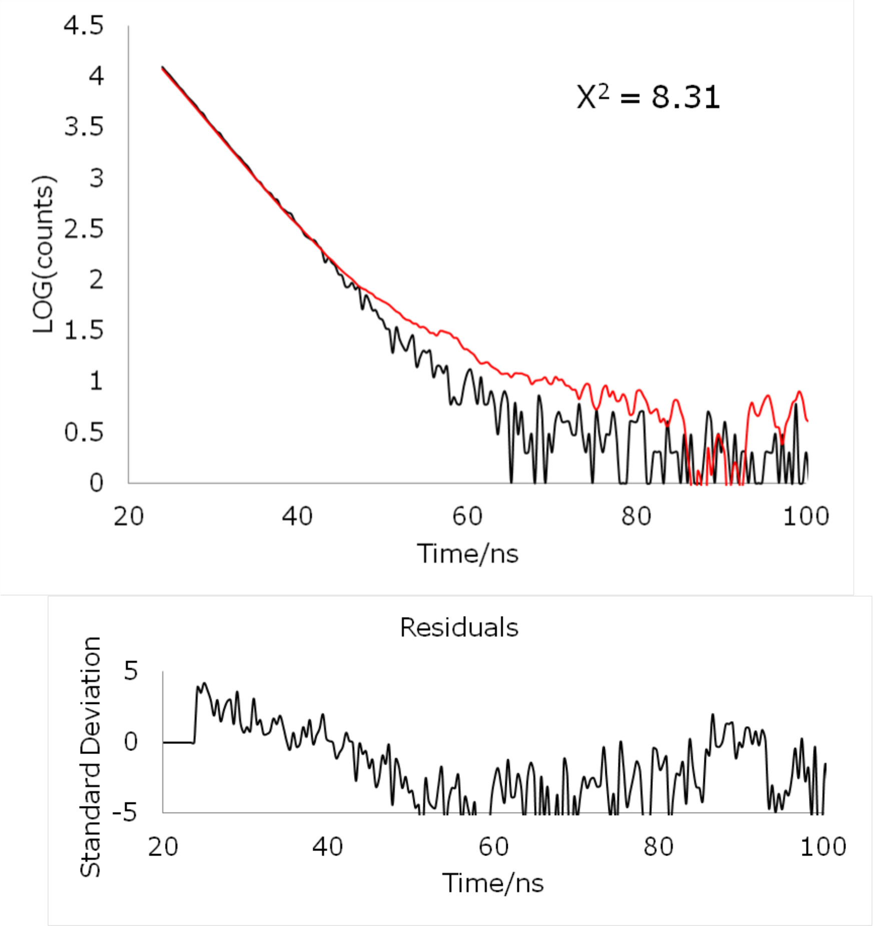


Figure 4.24: Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene - Showing the biexponential mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit - note their non-random distribution with a decay type pattern visible within them indicating a further component is present.

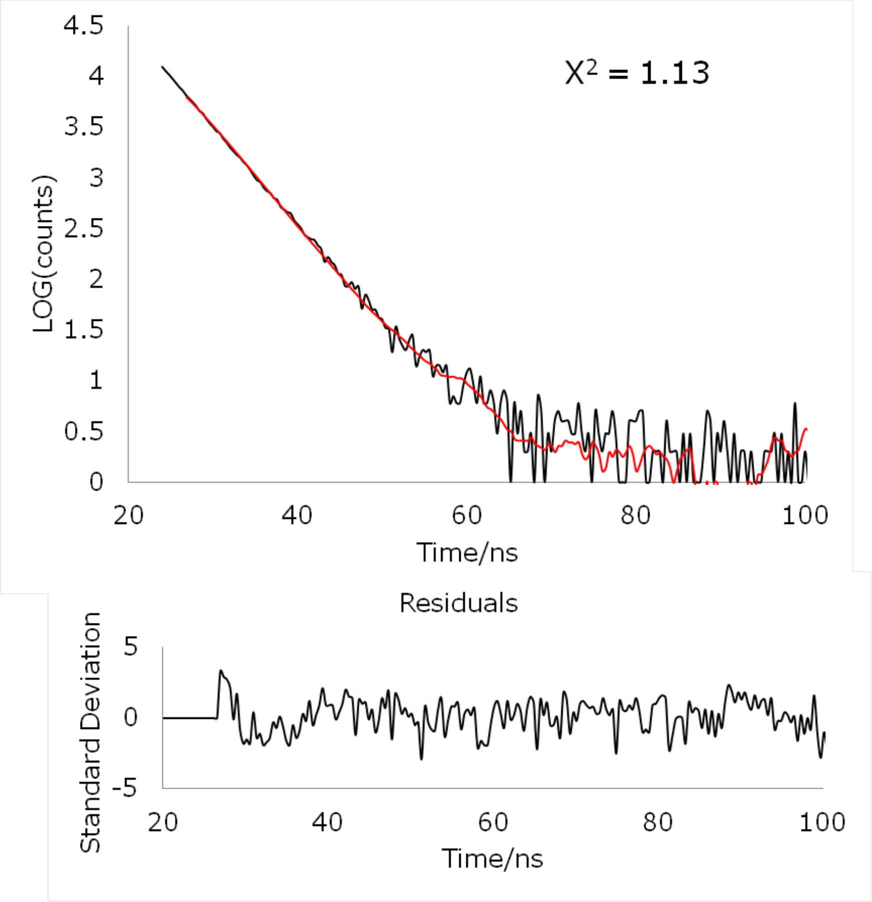


Figure 4.25: Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene - Showing the triexponential mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit - now following a random distribution.

Component	Pre-exponential Factor (α_i)	Component Lifetime (τ_i)/ns
1	0.180	3.84
2	0.680	7.21
3	$9.94 \text{x} 10^{-4}$	23.5

Table 4.3: Component Lifetimes of Free 1,5-Dihydroxynaphthalene

The component lifetimes of free 1,5-dihydroxynaphthalene are shown in Tab. 4.3. The pre-exponential factor (α_i) corresponds to the contribution that each component makes to the average lifetime. We can see from this table that the average lifetime of the free 1,5-dihydroxynaphthalene comes mainly (around 68%) from the component with the 7.21 ns lifetime. There is a some contribution (around 18%) from a species with a lifetime of 3.84 ns and a very small contribution (around 0.1%) from a much longer lived species with a 23.5 ns lifetime. The exact nature of these components is unknown.

The component lifetimes of free 1,5-dihydroxynaphthalene (Tab. 4.3) were used in equation 1.2 (introduction 1.3.1.2) to give an average lifetime as follows:

$$\tau = \sum_i \alpha_i \tau_i^2 / \sum_i \alpha_i \tau_i$$

$$\tau = 3.85x10^{-17}/5.61x10^{-9}$$

$$\tau = 6.86x10^{-9}$$

This method to calculate the average lifetime as described by equation 1.2 (introduction 1.3.1.2) was used for all lifetime data reported using a multi exponential fit.

Tab. 4.4 shows that the average lifetime of the free 1,5-dihydroxynaphthalene decreasing as the 3-bromo-1,2-propanediol content increases up to 5x10^{-3} 3-bromo-1,2-propanediol. At higher 3-bromo-1,2-propanediol content, the average lifetime appears to increase again. However, as seen in the acrylate polymers (Tab. 3.6) the increase in 3-bromo-1,2-propanediol is also accompanied by a deviation of χ^2 values from unity and also the deviation from random distribution of the residuals from the mathematical fit (example lifetime plot shown in Appendix Fig. 6.15) For these reasons, statistical confidence in the mathematical fitting and resultant average lifetimes is not possible for the free 1,5-dihydroxynaphthalene in the presence of high levels (1x10^{-2}) of 3-bromo-1,2-propanediol.

[3-Bromo-1,2-Propanediol]/wt%	Exponential	Average Lifetime/ns	χ^2
0	3	6.86	1.1
1x10^{-3}	3	6.64	1.1
2x10^{-3}	3	6.39	1.2
5x10^{-3}	3	6.41	1.2
1x10^{-2}	3	6.73	1.3

Table 4.4: Average lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol

The error associated with the measurement of excited state lifetimes shown in Tab. 4.4 was estimated again due to the different number of exponential components used in the mathematical fit. As before, the experimental error was calculated from a series of repeat measurements taken on the spectrophotometer using the free 1,5-Dihydroxynaphthalene ($1x10^{-3}$ solution in THF.) The lifetimes were then calculated using the mathematical fitting process described previously and equation 1.2 (introduction 1.3.1.2) The calculated lifetimes had a maximum of 6.92 ns, a minimum of 6.86 ns, a mean of 6.90 ns and a standard deviation of 0.034 ns. This error was equivalent to 0.5% which is the same as the experimental error calculated previously (section 2.5.1) for the lifetimes measured and fitted to the single exponential model. This similarity gives increased confidence in the estimation of error for this type of measurement.

Tab. 4.5 shows the average lifetimes of the free 1,5-dihydroxynaphthalene in the presence of prepolymer bound 3-bromo-1,2-propane diol. As with the free 3-bromo-1,2-propane diol (Tab. 4.4) the increase in content of prepolymer bound 3-bromo-1,2-propane diol initially corresponds with a reduction in the average lifetime of the 1,5-dihydroxynaphthalene excited state. This reduction is much greater than the estimated experimental error which gives confidence that this is a real effect. At levels higher than $5x10^{-3}$wt%, the average lifetime again appears to increase. However, as with the free 3-bromo-1,2-propanediol (Tab. 4.4) the χ^2 values are also seen to deviate from unity as the heavy atom content increases. The distribution of residuals from the mathematical fit also begin to lose their random nature (example lifetime plot shown in appendix Fig. 6.16) Therefore it is not statistically certain that the subsequent increase in lifetime is a real effect. Component lifetimes are given in the appendix Tab. 6.11 and Tab. 6.12 These show that most of the change seen in the lifetime is coming from the main component (lifetime around 7.2 ns) with the other two components changing only slightly. The component lifetimes also show the breakdown of the mathematical fit at higher levels of 3-bromo-1,2-propane diol through the decrease in all pre-exponential factors. This decrease shows that the mathematical model describes less of the data.

While the χ^2 values appear to increase as the lifetime decreases, the increase in χ^2 is attributed to the heavy atom content. The lifetime components are related to the number of environments that the fluorophore can be in[100] and the greater the heavy atom content, the more environments are possible. This means that as the heavy atom content increases, the components contributing to the excited state lifetime become less discrete and decay data deviates further from the mathematical model which is based on discrete components.

[3-Bromo-1,2-Propanediol Prepolymer]/wt%	Exponential	Average Lifetime/ns	χ^2
0	3	6.86	1.1
$1\text{x}10^{-3}$	3	6.77	1.1
$2\text{x}10^{-3}$	3	6.60	1.2
$5\text{x}10^{-3}$	3	6.69	1.2
$1\text{x}10^{-2}$	3	6.68	1.4

Table 4.5: Average lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol prepolymer

4.4.2 Linear Polyurethane Acrylate Bound 1,5-Dihydroxynaphthalene

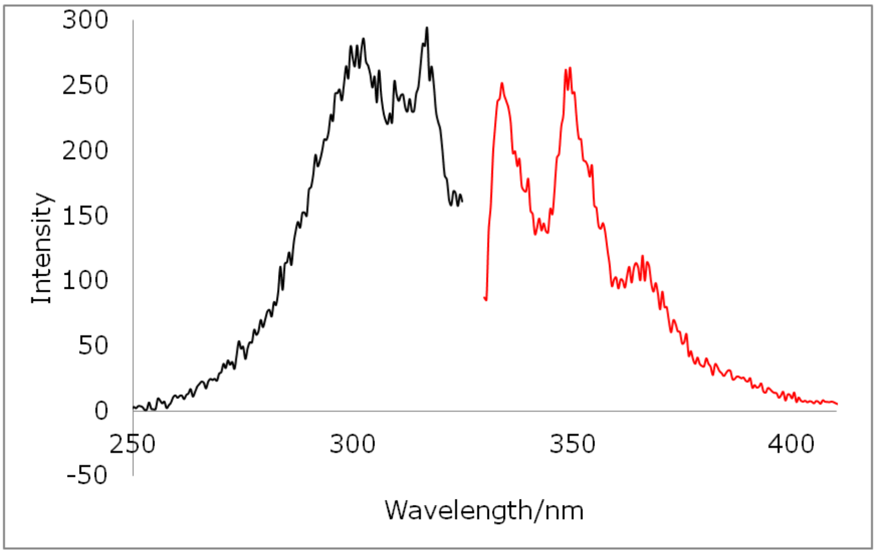


Figure 4.26: Excitation (Black) and Emission (Red) Spectra for Linear Polyurethane Acrylate Prepolymer Bound 1,5-Dihydroxynaphthalene - in THF

The excitation/emission spectra (Fig. 4.26) show the linear polyurethane acrylate bound 1,5-dihydroxynaphthalene having an excitation maximum of 310 nm and emission maximum of 350 nm. This is very similar to the free 1,5-dihydroxynaphthalene (Fig. 4.22) and the profile of the excitations/emissions is also unchanged. This shows that the character of the 1,5-dihydroxynaphthalene fluorescence and the electronic transitions favoured are unaltered by incorporation within the prepolymer.

[3-Bromo-1,2-Propanediol]/wt%	Exponential	Average Lifetime/ns	χ^2
0	3	6.83	1.1
1x10^{-3}	3	6.82	1.1
2x10^{-3}	3	6.65	1.2
5x10^{-3}	3	6.83	1.3
1x10^{-2}	3	7.50	1.3

Table 4.6: Average lifetimes for the excited state of prepolymer bound 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol

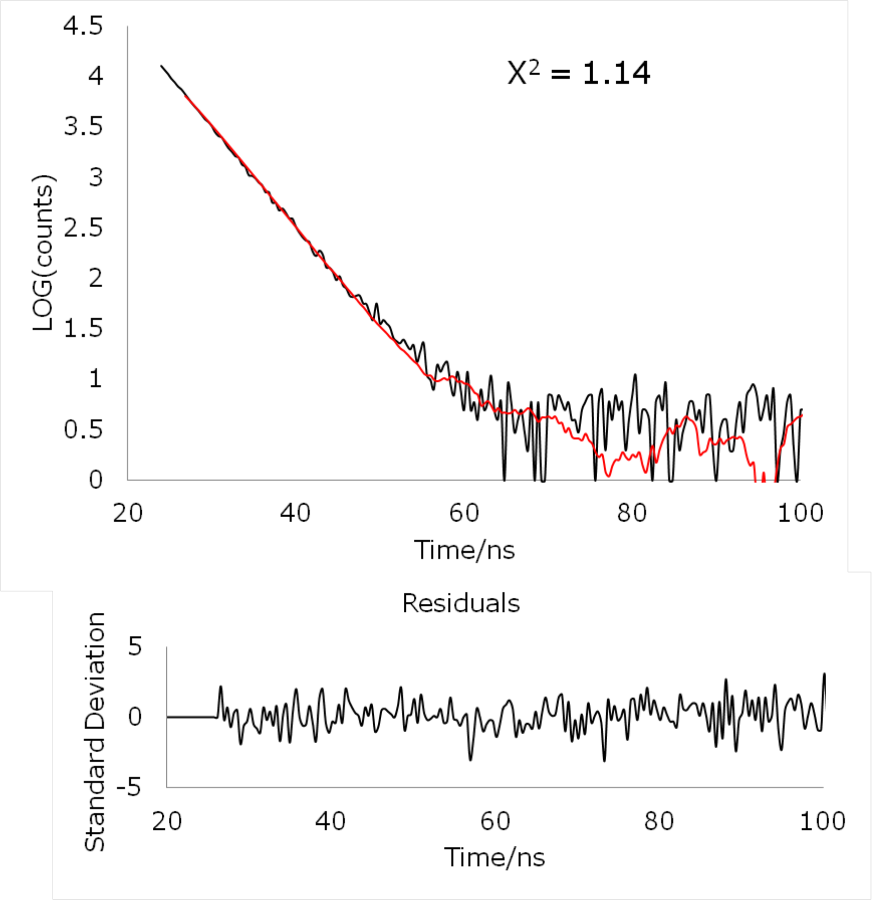


Figure 4.27: Excited State Lifetime Plot for Prepolymer Bound 1,5-Dihydroxynaphthalene - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

Tab 4.6 shows that the linear polyurethane acrylate prepolymer bound 1,5-dihydroxynaphthalene was found to have an average lifetime almost unchanged from the free 1,5-dihydroxynaphthalene (Tab. 4.4) indicating that binding within a prepolymer hasn't affected the longevity of the excited state. The component lifetimes (Fig. 6.13 and Fig. 6.14) are similarly unchanged by binding within the prepolymer.

The average lifetime decreases with increasing concentrations of 3-bromo-1,2-propanediol. The changes are greater than the experimental error estimated previously (section 4.4.1) showing that the decrease in lifetime is a real effect. Component lifetimes are given in Appendix Tab. 6.11 and Tab. 6.12 These show that most of the change seen in the lifetime is again resulting from the main component (with a lifetime around 7 ns) with the other two components barely changing. The component lifetimes also show the breakdown of the mathematical fit at higher levels of quencher with the decrease in all pre-exponential factors indicating the mathematical model is no longer providing a good fit to the data.

The χ^2 values are close to unity for both the free (Fig. 4.25) and bound (Fig. 4.27) 1,5-dihydroxynaphthalene in the absence of quencher. However when quencher is present the data is more complex and once again χ^2 begins to deviate from unity and the residuals from the mathematical fits lose their random distribution (example lifetime plots shown in appendix Fig. 6.17 and Fig. 6.18)

[3-Bromo-1,2-Propanediol Prepolymer]/wt%	Exponential	Average Lifetime/ns	χ^2
0	3	6.83	1.1
1x10^{-3}	3	6.69	1.2
2x10^{-3}	3	6.22	1.2
5x10^{-3}	3	6.64	1.3
1x10^{-2}	3	6.77	1.4

Table 4.7: Average lifetimes for the excited state of prepolymer bound 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol prepolymer

As with the free 1,5-dihydroxynaphthalene, the data shows the lifetime decreasing slightly with the addition of free 3-bromo-1,2-propanediol. This shows that the labelled prepolymer is quenched by the free 3-bromo-1,2-propanediol (Tab. 4.6) in low concentrations. However the lifetime subsequently increases again upon addition of further 3-bromo-1,2-propanediol.

The prepolymer bound 3-bromo-1,2-propanediol (Tab. 4.7) gives very similar results. The binding of 3-bromo-1,2-propanediol appears to have reduced its efficacy as a quencher, however it is probable that this is the result of the increase in molecular weight resulting in a lower proportion of the quencher being the heavy atom species. As with the free 3-bromo-1,2-propanediol, the differences in lifetime are greater than the estimated error (section 2.5.1) however the confidence in the fit is lost at the highest levels of prepolymer bound 3-bromo-1,2-propanediol.

4.4.3 UV Cured Polyurethane Acrylate Bound 1,5-Dihydroxynaphthalene

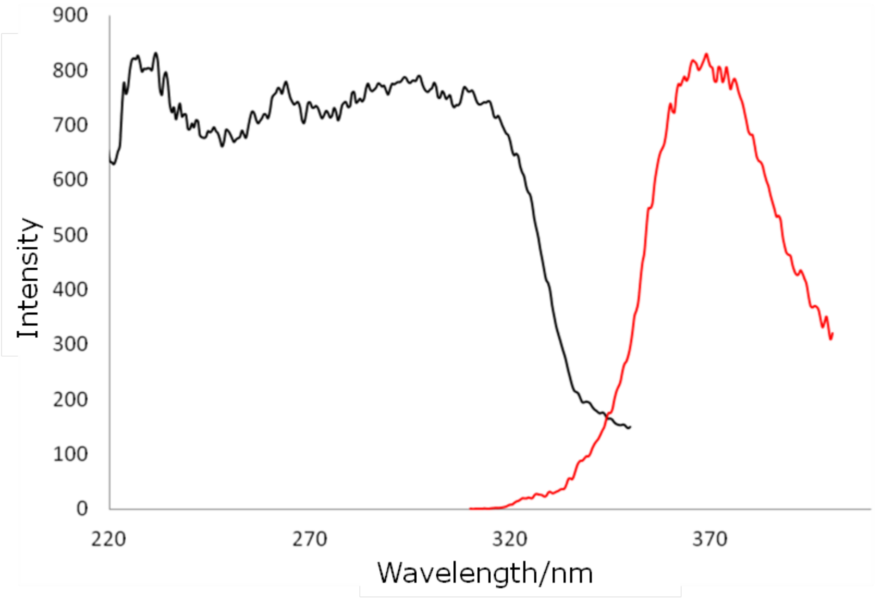


Figure 4.28: Excitation (Black) and Emission (Red) Spectra for Cross-Linked Polyurethane Acrylate Bound 1,5-Dihydroxynaphthalene - Solid state readings

The excitation/emission spectra (Fig. 4.28) shows the cross-linked polyurethane acrylate bound 1,5-Dihydroxynaphthalene having a broad excitation maximum of around 270 nm and emission maximum of 370 nm. This is an increase in the wavelengths of both maxima compared with the unbound label (Fig. 4.22) The appearance of the peaks is also changed with both spectra broadened and with both excitation and emission maxima appearing over a wider range. This broadening, especially apparent in the excitation spectrum, is attributed to the wide variety of environments it is possible for the label to occupy within the polymer matrix compared with those possible in solution.

The lifetimes for the excited state (Tab. 4.8) show a decrease in the lifetime upon incorporation of the quencher that is much greater than the error calculated previously (section 4.4.1) However the χ^2 and residuals distributions begin to move away from acceptable values as the quencher content increases which gives reduced confidence in the fit at higher levels. Overall, the lifetimes for the excited state are vastly increased by incorporation within the cross-linked polymer sheet which is not unexpected as binding a fluorophore within a polymer network is known to increase the lifetime of its excited state.[104] This is likely due to the polymer shielding the excited state from molecular oxygen and reduced chance of encounter with any quenching species due to reduced mobility within the local environment. The component lifetimes (appendix Fig. 6.15) all show an increase, with a much greater contribution to the average lifetime coming from the most long-lived component (around 24 ns) This component is now a major contributor to the average lifetime indicating that the environment responsible for this component has been greatly increased by the incorporation within the polymer matrix. Interestingly the contribution from this long-lived component decreases with increasing quencher concentration which implies that although this component is long-lived it is not a product of quenching brought about by the heavy atom.

3-Bromo-1,2-Propanediol Prepolymer/wt%	Exponentials	Average Lifetime/ns	χ^2
0	3	20.57	1.2
1	3	17.22	1.2
2.5	3	17.66	1.3
5	3	21.62	1.4

Table 4.8: Average lifetime Data for the Excited State of Cross-Linked Polyurethane Acrylate Bound 1,5-Dihydroxynaphthalene in the Presence of Different Levels of 3-Bromo-1,2-Propanediol

4.4.4 Free Fluorescein

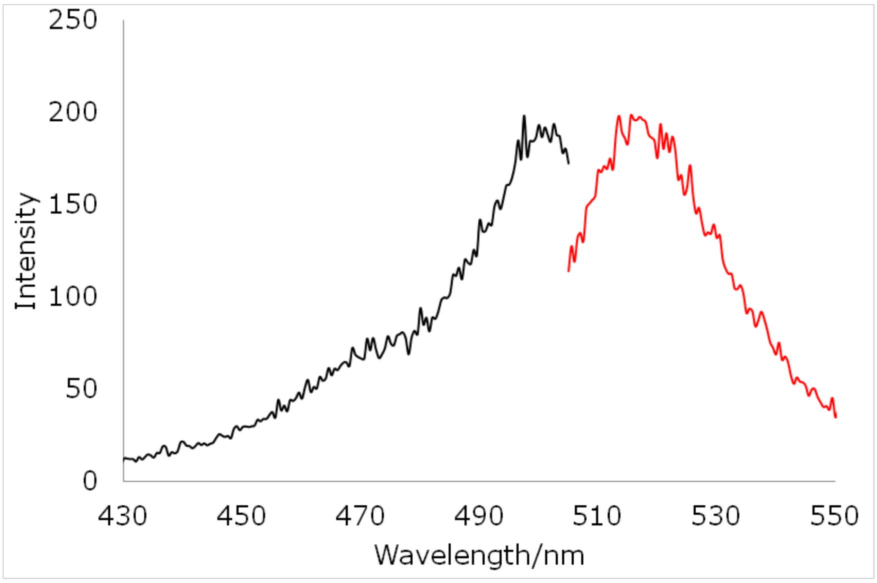


Figure 4.29: Excitation (Black) and Emission (Red) Spectra for Free Fluorescein - Solution phase readings; spectrophotometric grade ethanol.

The excitation/emission spectra (Fig. 4.29) show the free fluorescein having an excitation maximum of 500 nm and emission maximum of 517 nm. Both spectra show a single peak corresponding to the transition between the ground state and the first excited state. These results are in agreement with values reported in the literature.[105] These data were used to set the parameters for the lifetimes measurements.

Tab. 4.9 shows that the data for the lifetime of the excited state for free fluorescein fit very well with the single exponential mathematical model. The χ^2 values are near unity and the random distributions of the residuals around zero (Fig. 4.30) also give a good degree of confidence in the mathematical fitting. These data agree with previously described for fluorescein which show single exponential fit giving a lifetime of around 4 ns. [98, 106, 107] Unlike previous sample groups, the χ^2 values are not seen to deviate from unity with increasing heavy atom content and the residuals from the mathematical fit retain their random character at even the highest (1x10^{-2}) levels of 3-bromo-1,2-propanediol (example lifetime plot shown in Appendix Fig. 6.19) However there seems to be little, if any, decrease in the lifetime of the excited state when the heavy atom containing molecules are present (Tab. 4.9) Increasing the concentration of heavy atom containing molecules also seems to have very little, if any, effect. The small changes seen are well within the error associated with the recording of this type of data (section 2.5.1) and so no conclusions can be drawn from this set of results.

BPD/wt%	Exponential	Lifetime/ns	χ^2
0	1	4.24	0.89
$1x10^{-3}$	1	4.24	1.0
$2x10^{-3}$	1	4.23	1.0
$5x10^{-3}$	1	4.22	0.9
$1x10^{-2}$	1	4.21	0.9

Table 4.9: Average lifetimes for the excited state of free fluorescein in the presence of different concentrations of 3-bromo-1,2-propanediol - BPD = 3-Bromo-1,2-Propanediol

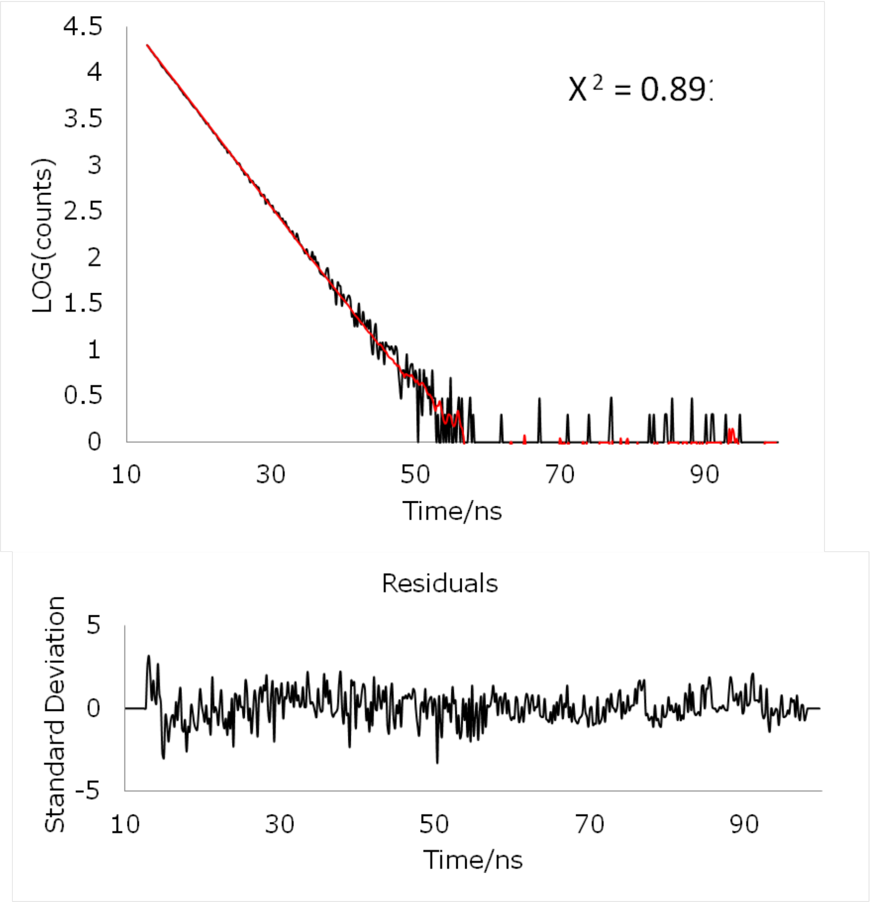


Figure 4.30: Excited State Lifetime Plot for Free Fluorescein - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

Tab. 4.10 shows that binding the 3-bromo-1,2-propanediol within a polyurethane acrylate prepolymer has little to no effect on its action as a quencher. As with the free 3-bromo-1,2-propanediol (Tab. 4.9) there is no observed decrease in the lifetime of the fluorescein excited state when the heavy atom containing molecules are present. Any difference seen in lifetime is smaller than differences accounted for by the experimental error calculated previously (section 2.5.1) Once again, the data for the lifetimes of the fluorescein excited state fit very well with the single exponential mathematical model. The χ^2 values are near unity for all samples within this group and the random distributions of the residuals around zero (example lifetime plot shown in Appendix Fig. 6.20) giving a good degree of confidence in the mathematical fitting.

BPD-PP/wt%	Exponential	Lifetime/ns	χ^2
0	1	4.24	0.89
1x10^{-3}	1	4.25	0.9
2x10^{-3}	1	4.25	1.0
5x10^{-3}	1	4.25	1.0
1x10^{-2}	1	4.22	1.0

Table 4.10: Average lifetimes for the excited state of free fluorescein in the presence of different concentrations of 3-bromo-1,2-propanediol prepolymer. - BPD-PP = 3-Bromo-1,2-Propanediol Prepolymer

4.4.5 Linear Polyurethane Acrylate Bound Fluorescein

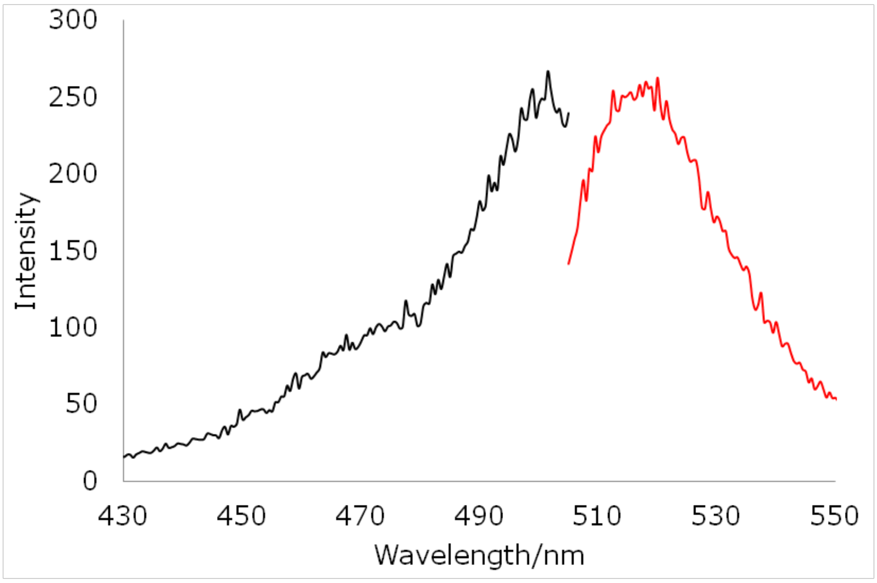


Figure 4.31: Excitation (Black) and Emission (Red) Spectra for Linear Polyurethane Acrylate Prepolymer Bound Fluorescein - Excitation spectrum recorded with emission set to 510 nm and emission spectrum recorded with excitation set to 460 nm.

The excitation/emission spectra (Fig. 4.31) show the linear polyurethane acrylate bound fluorescein having an excitation maximum of 500 nm and emission maximum of 517 nm. Both spectra have a single peak corresponding to the electronic transition between the ground state and the first excited state. The excitation is slightly higher and the emission unchanged from the free fluorescein (Fig. 4.29) The profile of the excitations/emissions is also unchanged, indicating that the character of the fluorescence from this label is unaltered by its incorporation within the prepolymer and the favoured electronic transitions are unchanged.

Tab. 4.11 shows that the lifetimes calculated for the linear polyurethane acrylate prepolymer bound fluorescein samples are shorter than those for the free fluorescein (Fig. 4.9) at all concentrations of 3-bromo-1,2-propane diol. These differences are much greater than would be accounted for by the calculated experimental error (section 2.5.1) Therefore it must be the case that binding of fluorescein within the prepolymer has had the effect of increasing the longevity of the excited state. This is attributed to the prepolymer providing protection of the excited state from atmospheric oxygen. The presence of free 3-bromo-1,2-propane diol appears to increase the lifetime of the excited state of bound fluorescein outside of the 0.5% estimated error. However subsequent increase in the wt% of 3-bromo-1,2-propane diol has little to no effect on the excited state lifetimes of the bound fluorescein with all changes well within error of each other. It is thought that the initial change in excited state lifetime upon addition of 3-bromo-1,2-propane diol is due to quenching. However the lack of increase in quenching seen with increased 3-bromo-1,2-propane diol content is attributed to the effect of the heavy atom containing species on the rigidity of the polymer. As heavy atom content increases, the prepolymer becomes less flexible. This could lead to a greater degree of protection of the excited state from oxygen which would prevent the mechanism of heavy atom quenching (introduction 1.3.3.2) from occurring.

[3-Bromo-1,2-Propanediol]/wt%	Exponential	Lifetime/ns	χ^2
0	1	3.74	1.2
$1x10^{-3}$	1	3.90	1.2
$2x10^{-3}$	1	3.90	1.2
$5x10^{-3}$	1	3.93	1.2
$1x10^{-2}$	1	3.90	1.3

Table 4.11: Average lifetimes for the excited state of prepolymer bound fluorescein in the presence of different concentrations of 3-bromo-1,2-propanediol

For all but the highest content ($1x10^{-2}$) of 3-bromo-1,2-propane diol (example lifetime plots shown in Appendix Fig. 4.32 and Fig. 6.21) the χ^2 values are around unity and residuals distributed randomly around zero indicating a good level of confidence in the mathematical fit to the single exponential model.

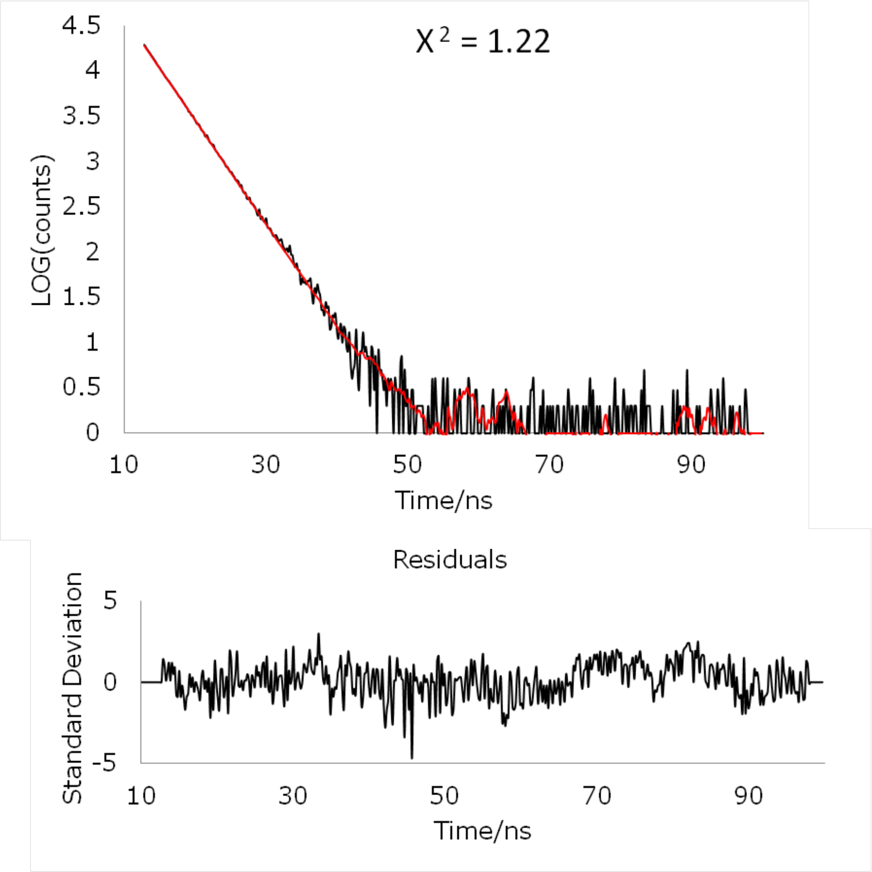


Figure 4.32: Excited State Lifetime Plot for Prepolymer Bound Fluorescein - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

Tab. 4.12 shows that the binding of 3-bromo-1,2-propane diol within a linear polyurethane acrylate prepolymer has prevented the increase in lifetime of the excited state seen in the samples containing free 3-bromo-1,2-propane diol (Tab. 4.11) This is to be expected as these polymers contain a lower overall heavy atom content than those containing free 3-bromo-1,2-propane diol. Once again, changing the wt% of 3-bromo-1,2-propane diol containing prepolymer has little to no effect on the excited state lifetimes of the bound fluorescein with any differences accounted for by the estimated experimental error (section 2.5.1) At the higher contents (above 5x10^{-3} wt%) of 3-bromo-1,2-propane diol the χ^2 values begin to deviate from unity (Fig. 4.33) indicating a decreased level of confidence in the mathematical fit to the single exponential. The residuals (Fig. 4.33) also appear to have begun to lose their random character with short runs above and below zero showing a possible pattern starting to emerge.

[3-Bromo-1,2-Propanediol Prepolymer]/wt%	Exponential	Lifetime/ns	χ^2
0	1	3.74	1.2
$1\text{x}10^{-3}$	1	3.71	1.2
$2\text{x}10^{-3}$	1	3.72	1.2
$5\text{x}10^{-3}$	1	3.71	1.3
$1\text{x}10^{-2}$	1	3.72	1.4

Table 4.12: Average lifetimes for the excited state of free fluorescein in the presence of different concentrations of 3-bromo-1,2-propanediol prepolymer.

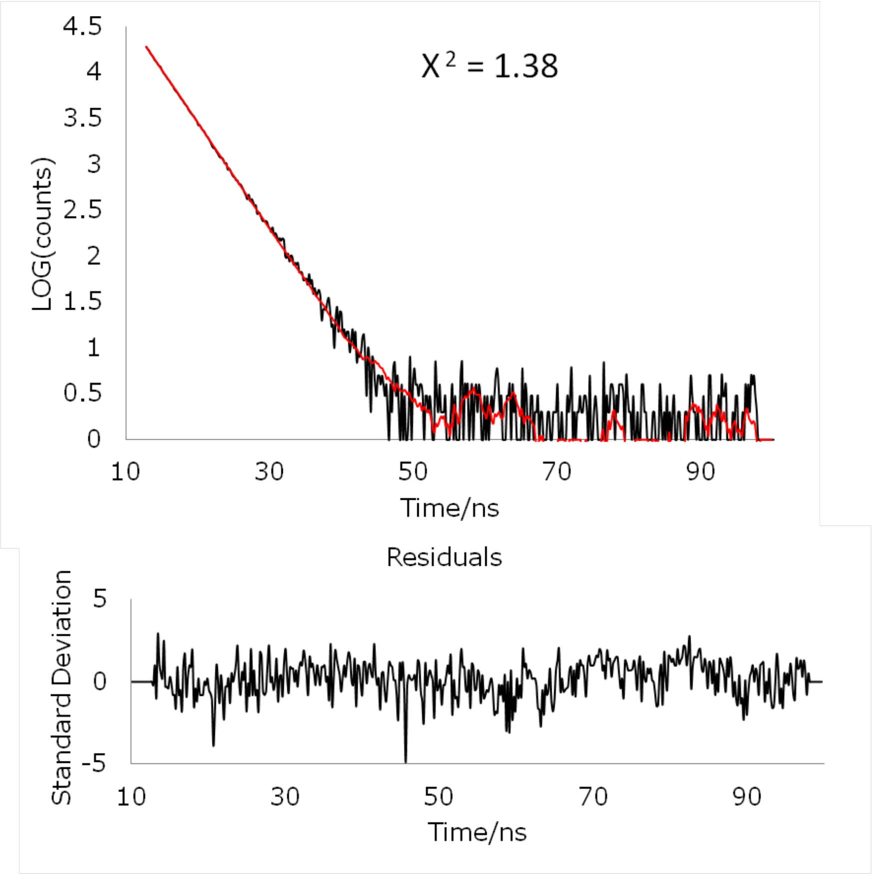


Figure 4.33: Excited State Lifetime Plot for Prepolymer Bound Fluorescein in the Presence of $1\text{x}10^{-2}$wt% 3-Bromo-1,2-propane diol Linear Polyurethane Acrylate Prepolymer - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit which show the possible start of a pattern with runs above and below zero

4.4.6 UV Cured Polyurethane Acrylate Bound Fluorescein

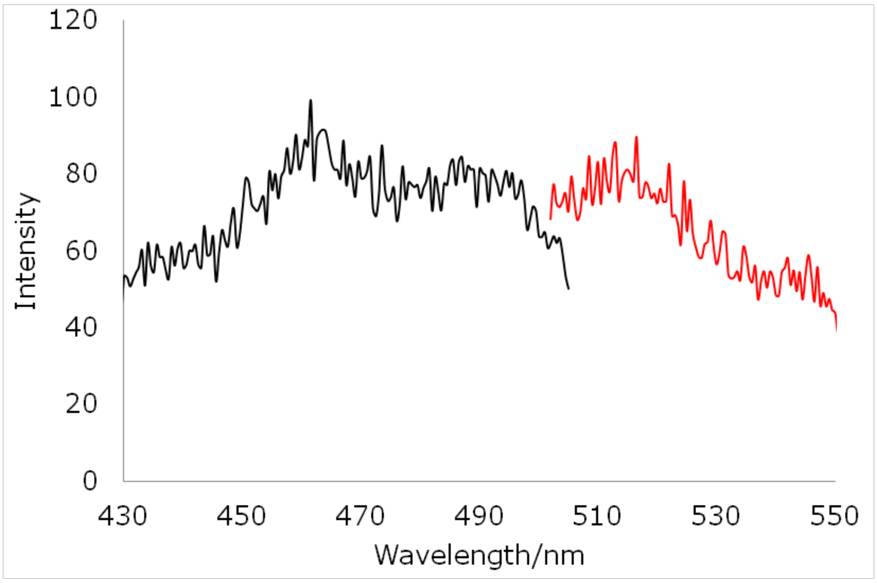


Figure 4.34: Excitation (Black) and Emission (RED) Spectra for UV Cured Polyurethane Acrylate Bound Fluorescein - Solid State Readings

As with the 1,5-dihydroxynaphthalene (Fig. 4.28,) the excitation and emission spectra for UV cured polyurethane acrylate bound fluorescein (Fig. 4.34) show a broadening of the peaks compared with the solution phase spectra for the free (Fig. 4.29) and linear prepolymer bound fluorescein (Fig. 4.31) This is not unexpected as incorporation within a polymer chain allows energy transfer along that chain and can affect favourable electronic transitions.[108]

Tab. 4.13 appears to show that increasing the heavy atom content of the cross-linked polymer sheets increases the excited state lifetime. This is the opposite effect to expected as the quenching of fluorescence corresponds with a decrease in the excited state lifetime. For the sheets with low (1 wt%) or no 3-bromo-1,2-propanediol prepolymer content, the χ^2 values are close to unity (Fig. 4.35) giving good confidence in the mathematical fit to the single exponential model.

However, once again, as heavy atom content increases (above 3 wt%) the χ^2 values begin to deviate substantially from unity and residuals are very obviously no longer distributed randomly around zero (Fig. 4.36) indicating a decreased level of confidence in the mathematical fit to the single exponential.

3-Bromo-1,2-Propanediol Prepolymer/wt%	Exponentials	Lifetime/ns	χ^2
0	1	3.85	0.9
1	1	3.89	0.8
3	1	3.89	1.6
10	1	4.48	3.6

Table 4.13: Lifetime data for the excited state of 1 wt% fluorescein prepolymer labelled cross-linked polyurethane acrylates containing different levels of 3-bromo-1,2-propanediol prepolymer

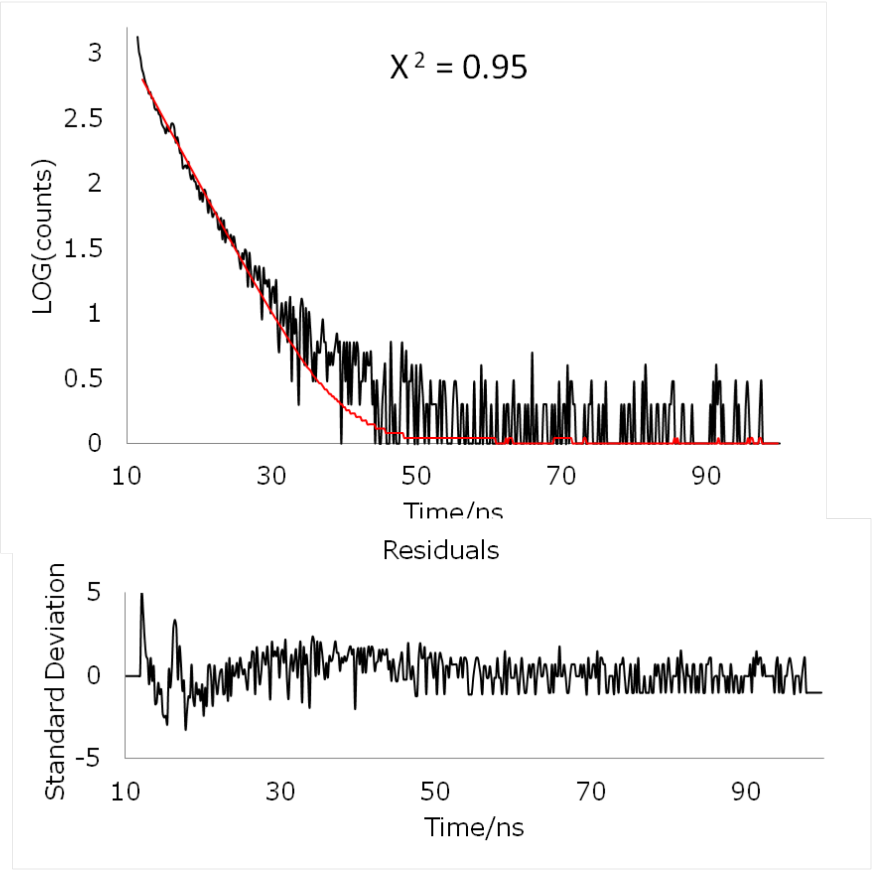


Figure 4.35: Excited State Lifetime Plot for Fluorescein Labelled Cross-Linked Polyurethane Acrylate - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

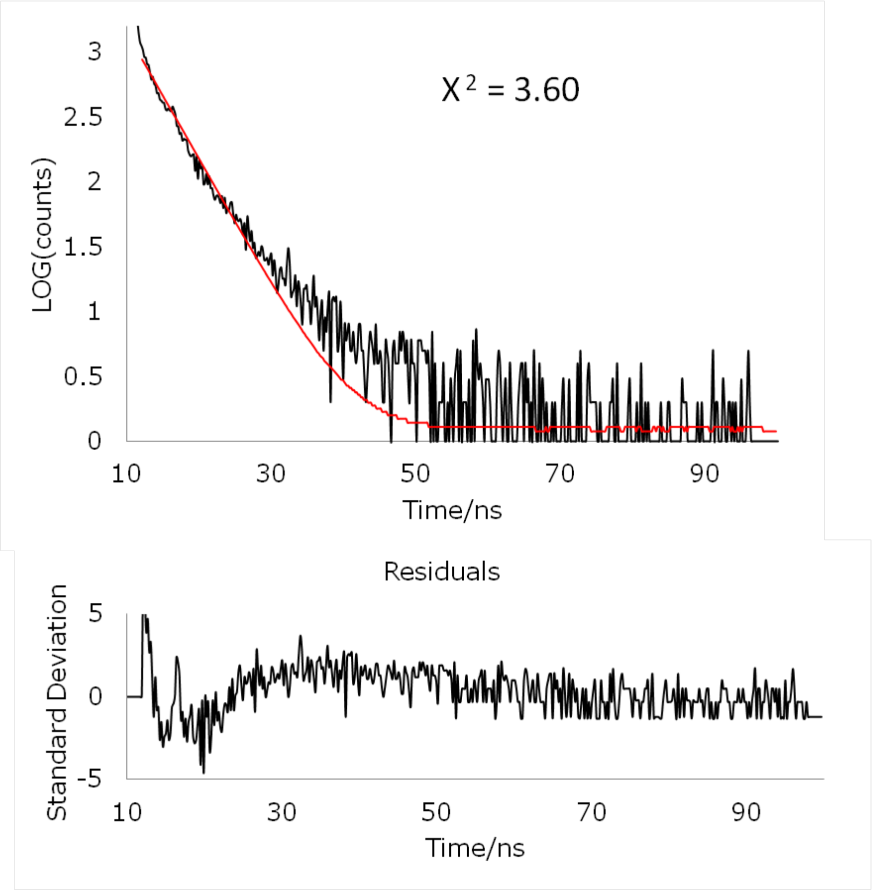


Figure 4.36: Excited State Lifetime Plot for Fluorescein Labelled Cross-Linked Polyurethane Acrylate Containing 10 wt% 3-Bromo-1,2-propanediol - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit - note the residuals have lost their random nature and show a decay-like pattern within them.

Fig. 4.37 shows a photograph of the fluorescein-labelled cross-linked polyurethane acrylate sheets which also appear to show increased fluorescence with increasing heavy atom content.

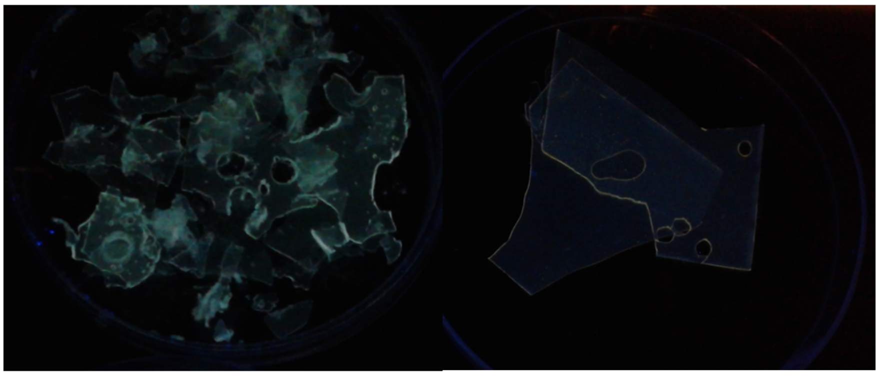


Figure 4.37: A Photograph of Fluorescein Labelled Cross-Linked Polyurethane Sheets Viewed Under UV Light (365 nm) - Both contain 1 wt% fluorescein prepolymer. The left sample was made with 70 wt% 3-bromo-1,2-propanediol prepolymer. The right sample was made with 10 wt% 3-bromo-1,2-propanediol prepolymer

If the lifetime is increasing with added heavy atom, this is the opposite of the expected effect and could be due to a change in the degree of light scattering or otherwise brought about by change in the microstructure of the films. Examination of cross-sections of the film by transmission electron microscopy (TEM)[109] or scanning electron microscopy (SEM)[110] may provide useful information about the microstructure, however this is outside the scope of this project. The opacity and physical properties alter with the addition of the heavy atom containing species. Therefore it is possible that as the heavy atom content increases, the corresponding increase in glassiness of the sample is reducing permeation of molecular oxygen throughout the polymer matrix and subsequently reducing its access to the excited state fluorescein. This will prevent the mechanism of quenching (introduction 1.3.3) which relies on atmospheric oxygen. It is also possible that the crossing to the triplet state brought about by the presence of the heavy atoms is increasing the triplet population to the point where triplet-triplet encounters are likely. This could give rise to delayed fluorescence (i.e. fluorescence observed after the removal of the light source) resulting from triplet-triplet annihilation.[111]

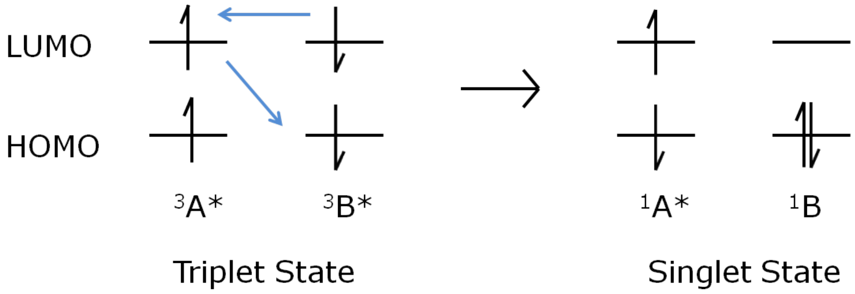


Figure 4.38: A schematic of triplet-triplet annihilation - Showing the formation of two singlets (one ground state and one excited) from two excited state triplets.

Inter-system crossing (as shown on the Jablonski diagram; introduction Fig. 1.5) from the single to the triplet state involves flipping the spin of the excited electron. This means that the return of this electron to the ground state (which would result in fluorescence) becomes spin forbidden. In order to return to the ground state, a change in spin orientation (which may accompany phosphorescence) would need to occur. However if two triplet states encounter then it may be possible for them to form two singlet states as shown in Fig 4.38. Of the two singlet groups formed, on is in the ground state. However the other is still in an excited state but it is now able to relax to the ground state, giving rise to fluorescence. This fluorescence is termed ”delayed fluorescence” because it is dependent on first inter-system crossing, then the encounter rate between suitable triplets, and can therefore occur some time after the light source that caused the original excitation has been removed. If this effect is occurring in the samples tested, it would explain why the lifetime of the excited state appears to be increasing along with the concentration of heavy atom. Heavy atom quenching relies on intersystem crossing to the triplet state and quenching of the subsequent phosphorescence (introduction 1.3.3.2) therefore some triplets are necessary for this type of quenching to occur. It may be that there is an optimum level of heavy atom concentration for quenching. This would be a concentration that leads to enough intersystem crossing to allow quenching to occur but not enough to create a high enough triplet population that triplet-triplet encounters are likely.

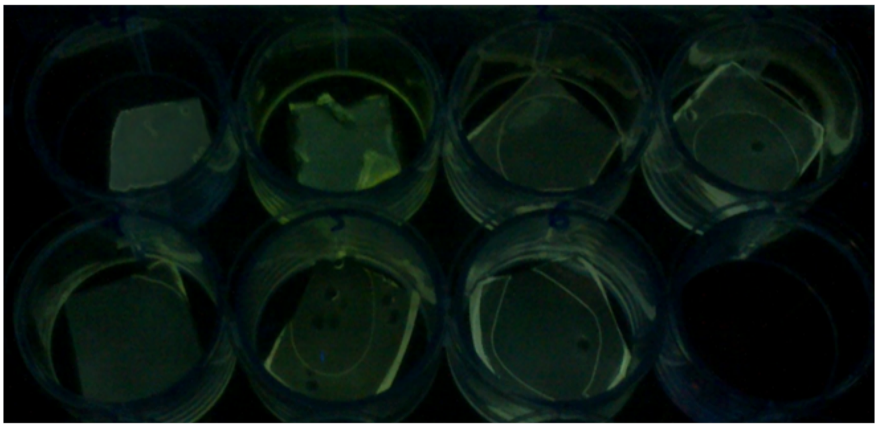


Figure 4.39: A Photograph of a Cross-Linked Polyurethane Sheet Containing 1wt% Fluorescein Labelled Polyurethane Acrylate and Doped with Various Brominated Solvents. Viewed Under UV Light (365 nm) - From left to right and top to bottom; 1) undoped reference 2) 3-bromo-1,2-propane diol 3) 1-bromonaphthalene 4) 2-bromopropane 5) 1-bromobutane 6) ethyl-2-bromoisobutyrate and 7) bromobenzene.

A brief experiment was performed to quickly and visually determine whether bromine atoms are causing an increase in the fluorescence seen from the fluorescein label. A crosslinked polyurethane acrylate sheet containing no 3-bromo-1,2-propanediol but containing 1 wt% fluorescein labelled polyurethane acrylate was doped with a variety of brominated solvents. This was to rule out the specific structure of the 3-bromo-1,2-propanediol being the cause of the observed increase in fluorescence. The resultant doped samples were viewed under UV light (see Fig. 4.39) and did appear to have increased fluorescence. However due to the toxic nature of the dopants used, lifetimes could not be safely recorded for these samples in the open sample holder used in the spectrophotometer.

4.5 Conclusions

Several linear polyurethane acrylates were successfully synthesised, including some containing fluorescent labels (fluorescein and 1,5-dihydroxynaphthalene) and fluorescent quencher (3-bromo-1,2-propanediol.) These polyurethane acrylates are viscous and so diluents are required to form thin sheets and exclude oxygen successfully for UV curing. Butyl acrylate was found to be immiscible with these polyurethanes. Several other acrylic species were tried and poly(ethyleneglycol)diacrylates were found to be effective diluents for these polyurethane acrylates. These were then blended with the polyurethanes made previously to give a range of UV curable monomer blends. The yellowing of the polyurethane acrylate sheets with UV curing has been avoided by the use of an aliphatic diisocyanate. The removal of aromaticity from the polyurethane has yielded optically clear elastomeric sheets. However some yellowing may still be seen due to the colour of the fluorescent label. Yellowing can also occur from over-exposure in the UV oven. The effects of long term (but less intense) UV exposure have not been thoroughly investigated as this is outside the scope of this project.

The first attempts at producing fluorescent polyurethane acrylates showed poor label attachment. The method was subsequently adjusted to account for the lower reactivity of the fluorescent/quenching diols. Several methods were tried and it was found that if the diisocyanate was allowed to react with the fluorescent or quenching diol before the polycaprolactone diol was added, the label can be successfully incorporated within the final polyurethane acrylate. The successful attachment of the label to the main bulk of the polyurethane acrylate was shown by GPC using both an RI and a UV detector. The addition of the fluorescent labelled urethane acrylates to the blends led to the successful synthesis of fluorescent solid polyurethanes. The sheets containing fluorescein showed a visible yellow fluorescence when placed under a UV lamp (Fig. 4.37) but the fluorescence of those containing 1,5-dihydroxynaphthalene is only observable by spectroscopic equipment. This incorporation of the fluorescent labelled urethane acrylates to the blends had limited side effects in the finished UV cured sheets. However the addition of the fluorescent quencher containing urethane acrylates to the blends led to increased Tg and brittleness in the UV cured sheets.

The excited state lifetimes for the free and prepolymer-bound labels appeared to show quenching of the 1,5-dihydroxynaphthalene for up to twice as much heavy atom containing as fluorescent species, and little to no change in lifetime for the fluorescein. The excited state lifetimes for the free and prepolymer-bound labels also appeared to show that the initial binding of the labels to the linear polyurethane acrylates had little effect on the average lifetime of the excited state. However the subsequent crosslinking into the solid sheets drastically increased the average lifetime of the excited state of the 1,5-dihydroxynaphthalene. The excited state lifetimes for the 1,5-dihydroxynaphthalene labelled sheets appeared to show a slight decrease in lifetime corresponding with double the content of quencher with respect to the label, as was seen in solution. Fluorescein labelled sheets were observed to show an increase in excited state lifetime with the addition of the heavy atom containing species. This was attributed to either triplet-triplet annihilation or the inability of atmospheric oxygen to permeate the polymer sheets and act as a quencher. This effect would increase as the Tg and rigidity of the sheets increase with the amount of 3-bromo-1,2-propanediol included. If the lack of oxygen within the sheets is responsible for the lack of quenching observed, reducing the glassiness of the polymer sheet should alleviate this effect. If the cause is triplet-triplet annihilation then a label less prone to delayed fluorescence could solve the problem. It is also possible that an optimum ratio of label : quencher may exist that produces quenching but not delayed fluorescence. The polymers synthesised in this chapter could also lead to a product with the opposite effect to the original plan. I.e. a fluorescent polymer that shows a reduction rather than an increase in fluorescence in response to mechanical tension. Such a polymer would still fulfill the objective of this project by exhibiting a specific fluorescent response to a mechanical stimulus and would be a useful product for security applications.

4.6 Future Work

Some of the fluorescent polymer sheets synthesised in this chapter showed a degree of quenching of the excited state following addition of heavy atom containing species. The next stage of this project will be to attempt to reduce this quenching by applying tension to the quenched sheets. In order to have the best chance of achieving this, the polymers would still need to be elastic even when higher levels of fluorescent quenchers are added. However this was not the case with the polyurethane acrylates synthesised in this chapter which became rigid and glassy when the heavy atom containing species were incorporated. Therefore it is necessary to synthesise polymers with greater elasticity than the polyurethane acrylates synthesised in this chapter. The use of highly elastic polymers would mean that the reduction in elasticity with increasing heavy atom content still results in an easily extendable polymer sheet. These changes should also help to increase the permeation of oxygen into the polymer sheets thereby increasing the access of oxygen to the fluorescent labels. The next chapter addresses the synthesis of highly elastic polyurethanes from polyether polyols and the addition of fluorescent labels and quenchers to these species.

Both of the labels discussed in this chapter are compatible with the synthesis of polyurethanes and will be used in the next chapter. 1,5-dihydroxynaphthalene will be investigated further because of the observed reduction in the excited state lifetime of this label in the presence of heavy atom containing species. Fluorescein will be investigated further because of the bright and visible nature of its fluorescence and the large amount of previous work using this label, including incorporation of fluorescein within polyurethanes.[112]

5

The Synthesis of Polyurethane Elastomers

5.1 Introduction

As explained in the previous chapter, aliphatic diisocyanates are favoured for surface coating applications over aromatic diisocyanates as they are more UV-resistant. Although polyurethanes are commonly synthesised via a prepolymer, the one-shot bulk polymerisations of polyurethanes has also previously been described.[113] The one-shot polymerisation of 1,4-butanediol with IPDI catalysed by dibutyltin dilaurate as described by Da-Kong Lee and Hong-Bing Tsai[114] informs the general synthesis of such polymers and formed the basis for the method used in this project.

As these polyurethanes are formed using a catalyst rather than a UV initiator, the absence of oxygen from the monomer mixture is not required for successful curing. Therefore the polymers are to be formed in situ on petri dishes from the catalysed monomer mixture. Dry polytetrafluoroethylene (PTFE) spray, used as a release agent, will allow the removal of the cured polymer sheet from the petri dish. The intended use for the products formed in this project are surface coating applications. However the fluorescence analysis required for the continuation of the project is more easily conducted on solid polymer sheets rather than surface coatings. In particular the coating of paper may interfere with the fluorescence analysis due to the use of optical brighteners in most papers. It is the intention of this project to provide proof of principle with regard to the quenching and subsequent release of quenching prior to the development of the exact formulation to be used in the desired applications.

This chapter discusses the in-situ synthesis of polyurethane elastomers from an aliphatic diisocyanate (IPDI) and a polyether polyol (Voranol) using 1,4-butanediol as a chain extender. The triol structure of the polyether polyol used provides branching points for the polymer chain, forming a solid network without the requirement for the addition of cross-linking agents. Similar polyurethanes containing fluorescent labels, fluorescent quenchers and a combination of the two will then be synthesised. As in the previous chapter, this will be accomplished by the incorporation of dihydroxy functional fluorescent labels/quenchers. Following the unexpected results from the fluorescence studies in the previous chapter, 4-bromoresorcinol is also introduced as a second heavy-atom containing diol as its aromatic structure more closely resembles the 4-bromostyrene previously shown to quench fluorescence (section 2.5.1) Fluorescence analysis of the resultant elastomers will also be conducted.

5.2 Synthesis of IPDI Terminated Prepolymers from Fluorescent and Heavy Atom Diols

In the previous chapter, there were difficulties in incorporating the fluorescent labels into the polymer. This was attributed to the comparatively low reactivity of the hydroxyl groups in these monomers and solved by the synthesis of prepolymers (section 4.2.3) Therefore the method for synthesis of Voranol-based polyurethanes containing fluorescent labels also proceeded via a prepolymer. The prepolymers were formed by reacting the dihydroxy functional label with an excess of IPDI to form discrete, short-chains comprising of the label flanked on either side by IPDI.

It was found that the 3-bromo-1,2-propanediol did not need to be incorporated within an IPDI terminated prepolymer prior to formation of the polyurethanes and, being a liquid, it mixed well with the monomer blend to form a homogeneous mixture prior to curing. This was determined visually by the lack of observed phase-separation. However there were difficulties in dissolving the solid 4-bromoresorcinol into the monomer mix and phase-separation was observed, therefore a 4-bromoresorcinol prepolymer was also synthesised.

5.2.1 Synthesis of IPDI Terminated Fluorescein Prepolymer

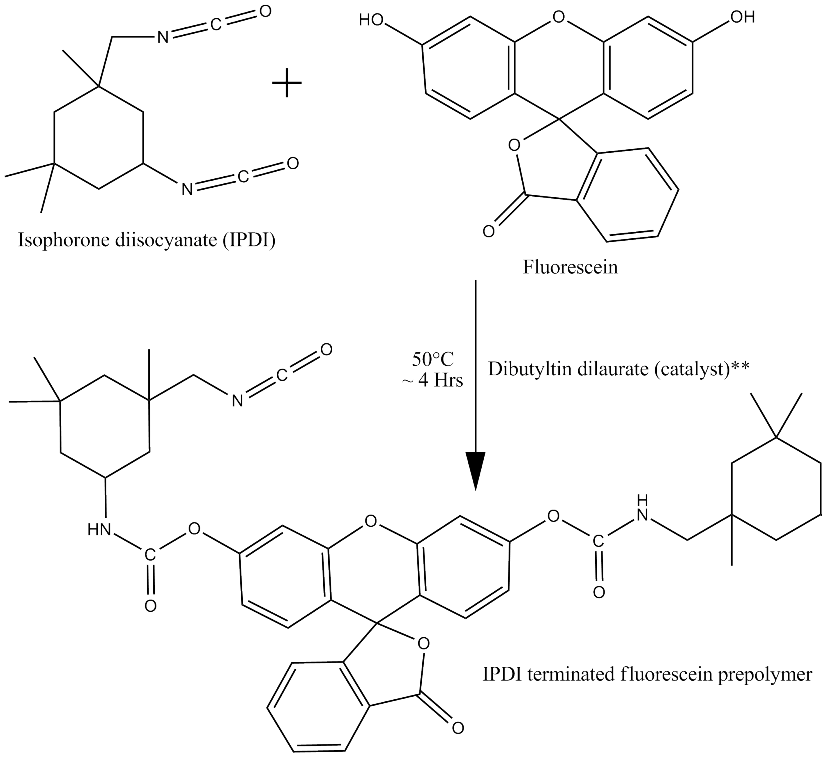


Figure 5.1: IPDI Terminated Fluorescein Prepolymer Synthesis - *See Fig. 4.2 for full structure.

Aside from the change in appearance of the reaction mixture, the successful synthesis of the IPDI terminated prepolymer from the fluorescein was confirmed by FT-IR. The FT-IR spectrum (Fig. 5.2,) shows the overwhelming presence of N=C=O groups corresponding with the major peak around 2260-2310 cm^{-1}. The absence of an obvious broad peak around 3200-3500 cm^{-1} indicates the lack of O-H groups which would correspond to unreacted fluorescein. However a small presence of O-H from residual monomers may be hidden behind the N-H band. The band around 3700 cm^{-1} is unknown but is suspected to be a combination band resulting from the N=C=O groups.

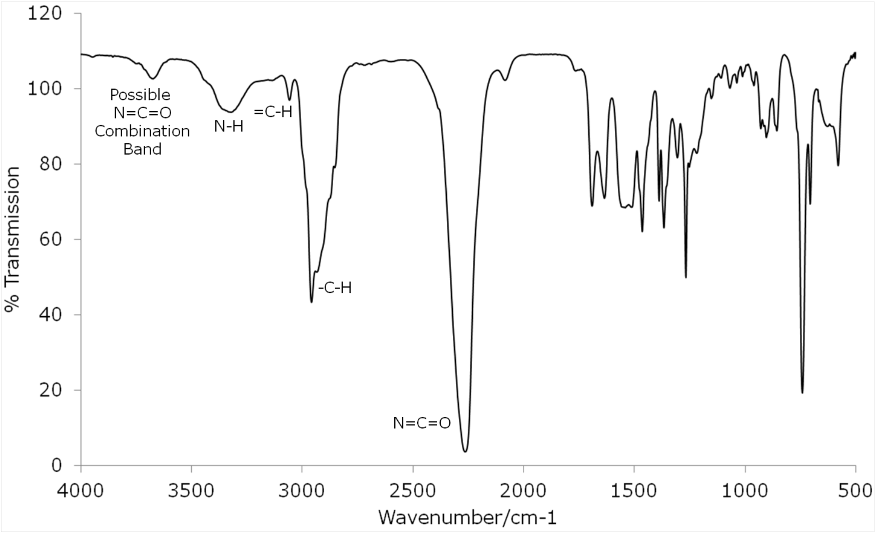


Figure 5.2: FT-IR Spectrum of IPDI Terminated Fluorescein Prepolymer - Showing the presence of N=C=O bonds and a lack of O-H bonds

The ^{1}HNMR does not confirm the presence of the N-H proton from the urethane linkage however the O-H proton that would indicate the presence of unreacted label is also absent.

5.2.2 Synthesis of IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer

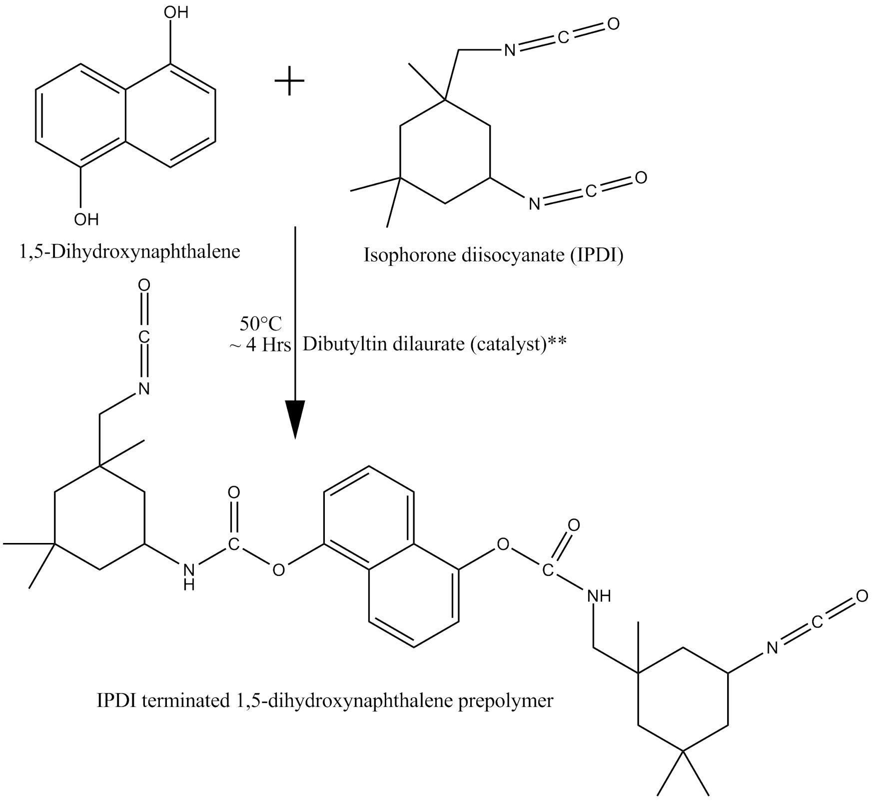


Figure 5.3: Synthesis of IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer

- *See Fig. 4.2 for full structure.

Again, the successful synthesis of the IPDI terminated prepolymer from 1,5-dihydroxynaphthalene was confirmed by FT-IR. As previously, the Ft-IR spectrum (Fig. 5.4) shows the presence of N=C=O groups and the lack of O-H groups which would correspond to unreacted 1,5-dihydroxynaphthalene. The unknown band around 3700 cm^{-1} is still present and is suspected to be a combination band resulting from the N=C=O groups.

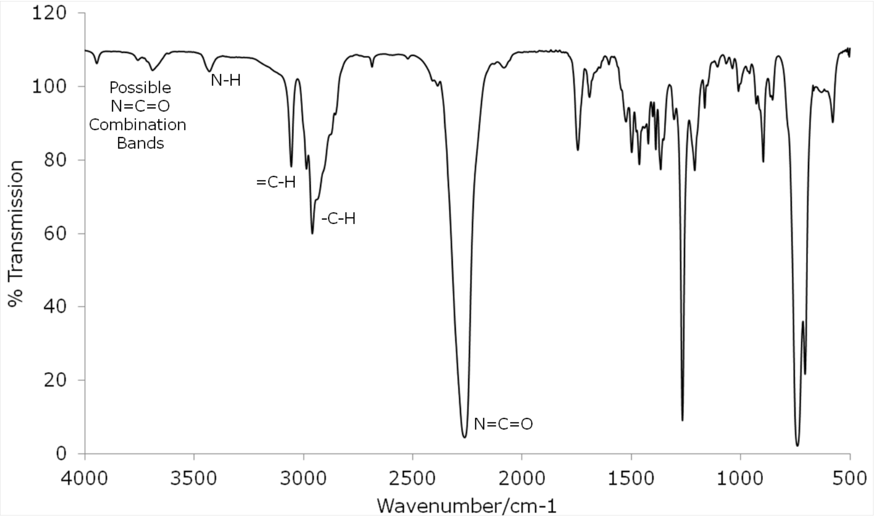


Figure 5.4: FT-IR Spectrum of IPDI Terminated 1,5-Dihydroxynaphthalene Pre-polymer - Showing the presence of N=C=O bonds and a lack of O-H bonds

The ^{1}HNMR (Fig. 5.5) shows the presence of aromatic protons corresponding to the fluorescent label, and although the N-H proton from the urethane linkage is not seen, neither is the O-H proton that would indicate residual label.

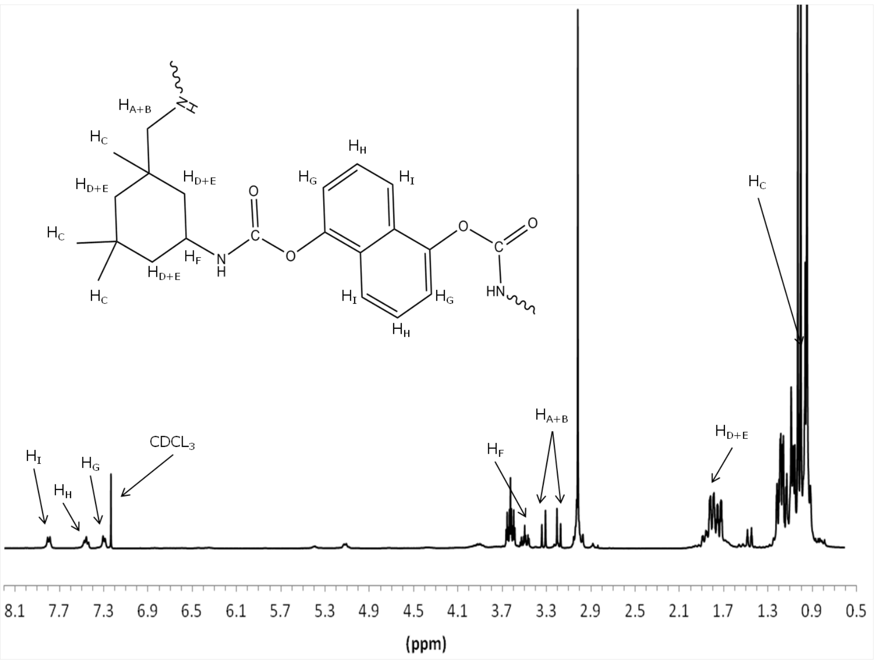


Figure 5.5: ^{1}HNMR Spectrum of IPDI Terminated 1,5-Dihydroxynaphthalene Pre-polymer - Showing the presence of aromatic protons

5.2.3 Synthesis of IPDI Terminated 4-Bromoresorcinol Prepolymer

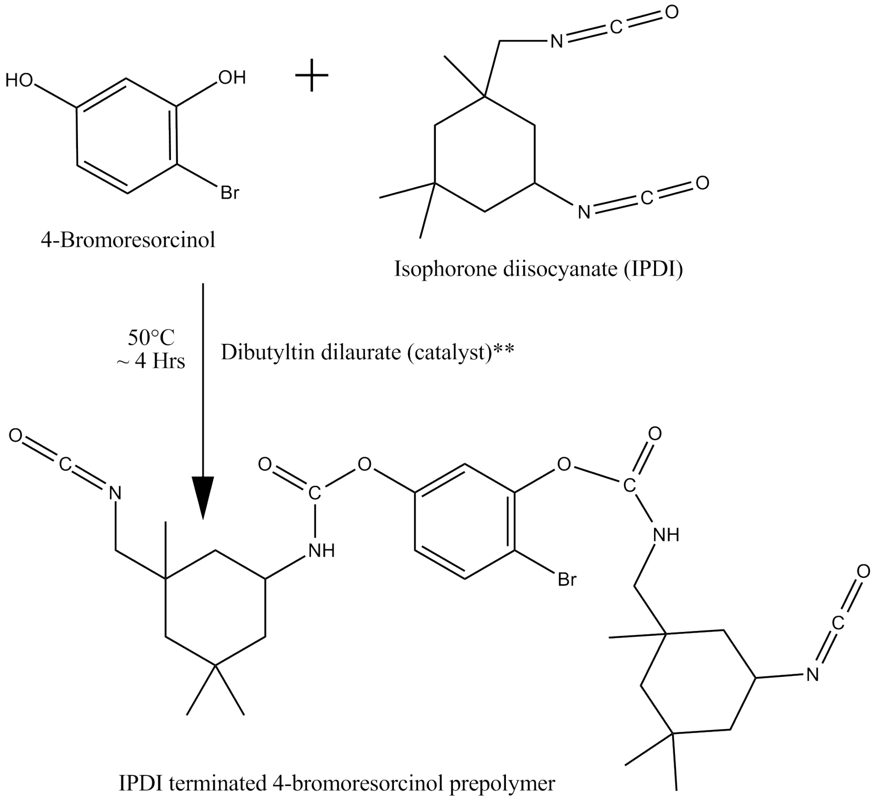


Figure 5.6: Synthesis of IPDI Terminated 4-Bromoresorcinol Prepolymer - *See Fig. 4.2 for full structure.

The successful synthesis of the IPDI terminated prepolymer from 4-bromoresorcinol was again confirmed by FT-IR. The FT-IR spectrum (Fig. 5.7) shows the presence of N=C=O groups and the lack of a strong peak from O-H groups which would correspond to unreacted 4-bromoresorcinol. However, again there may be a small amount of residual monomer causing an O-H peak that is obscured by the N-H band. The unknown band around 3700 cm^{-1} suspected to be a combination band resulting from the N=C=O groups is still observed.

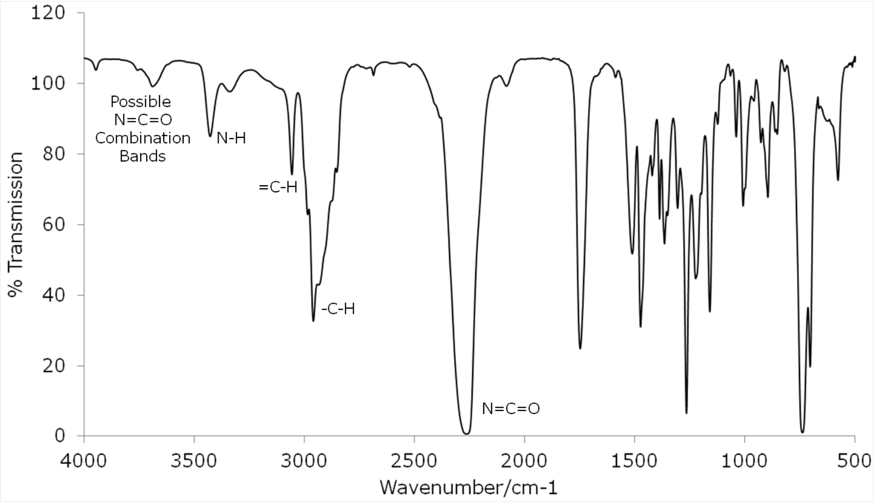


Figure 5.7: FT-IR Spectrum of IPDI Terminated 4-Bromoresorcinol Prepolymer - Showing the presence of N=C=O bonds and a lack of O-H bonds

The ^{1}HNMR (Fig. 5.8) again shows the presence of aromatic protons corresponding to the 4-bromoresorcinol. Although the N-H proton from the urethane linkage is not seen, neither is the O-H proton from residual diol.

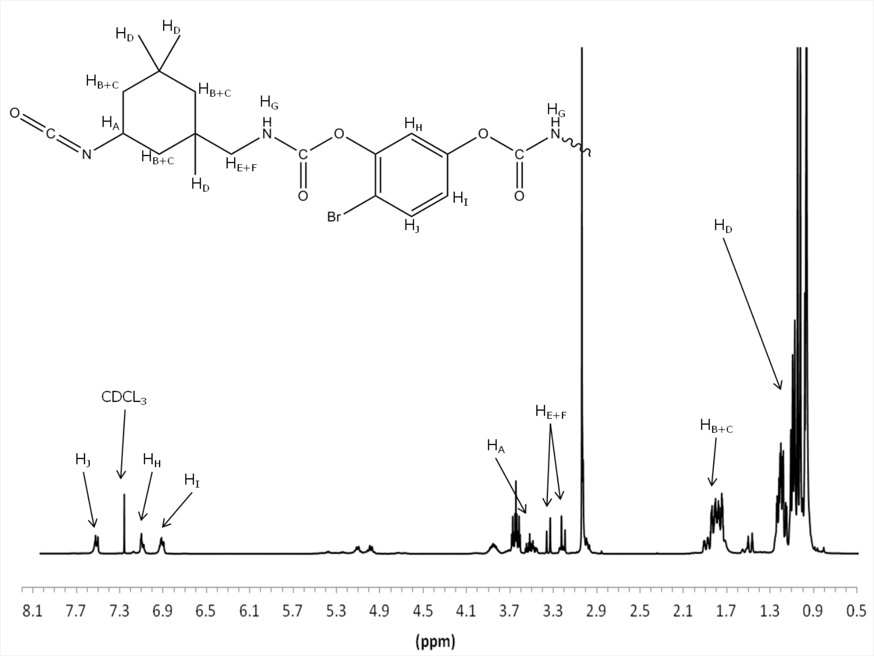


Figure 5.8: ^{1}HNMR Spectrum of IPDI Terminated 4-Bromoresorcinol Prepolymer - Showing the presence of aromatic protons

Tab. 5.1 shows that the bromine content of the 4-bromoresorcinol prepolymer was slightly higher than the expected value (6.83) However this difference is within the detection limits of bromine for elemental analysis (0.3%)

Prepolymer	C*/%	H*/%	N*/%	Br*/%
Fluorescein	65.53	9.24	12.95	ND
1,5-Dihydroxynaphthalene	67.50	8.89	12.80	ND
4-Bromoresorcinol	59.40	7.91	9.34	6.59

Table 5.1: Overall results and data for IPDI terminated prepolymers - *from elemental analysis (ND = Not discovered within detection limits of 0.3%)

5.3 Voranol Polyurethane Elastomers

Voranol is the brand name for a range of triol polyether polyols produced by the Dow chemical company. Voranol 3322, the variant used for this project, was supplied with an nominal molecular weight of 3660. Prior to incorporation within a polyurethane formulation, the precise molecular weight of the batch used must be known. The molecular weight of Voranol was calculated from the hydroxyl value which was determined by back titration with acetic anhydride[115] as is standard practice in industry. The molecular weight of the Voranol used was found to be 3742 gmol^{-1} which as Voranol contains three hydroxyl groups per unit, corresponds to an equivalent weight for the hydroxyl of 1247 g i.e. 1247 g of Voranol would provide one mole of OH groups. The equivalent weight of hydroxyl for 1,4-butanediol and the equivalent weight of isocyanate for IPDI were calculated directly from the molecular formulae as these are both discrete compounds whose exact formulae are known. The prepolymers described previously were synthesised using a slight excess of IPDI. Therefore the exact equivalent weights of isocyanate for the prepolymers also needed to be determined by back titration, this time with with dibutylamine (Experimental 6.3.2) which is also standard practice in industry.

To ensure complete curing, the monomer composition of the polyurethane was calculated to give an overall ratio of 1.05 NCO groups for every 1 OH group. The hydroxyl functional portion of the monomer blend was comprised of a ratio of one 1,4-butanediol OH group to every ten Voranol OH groups.

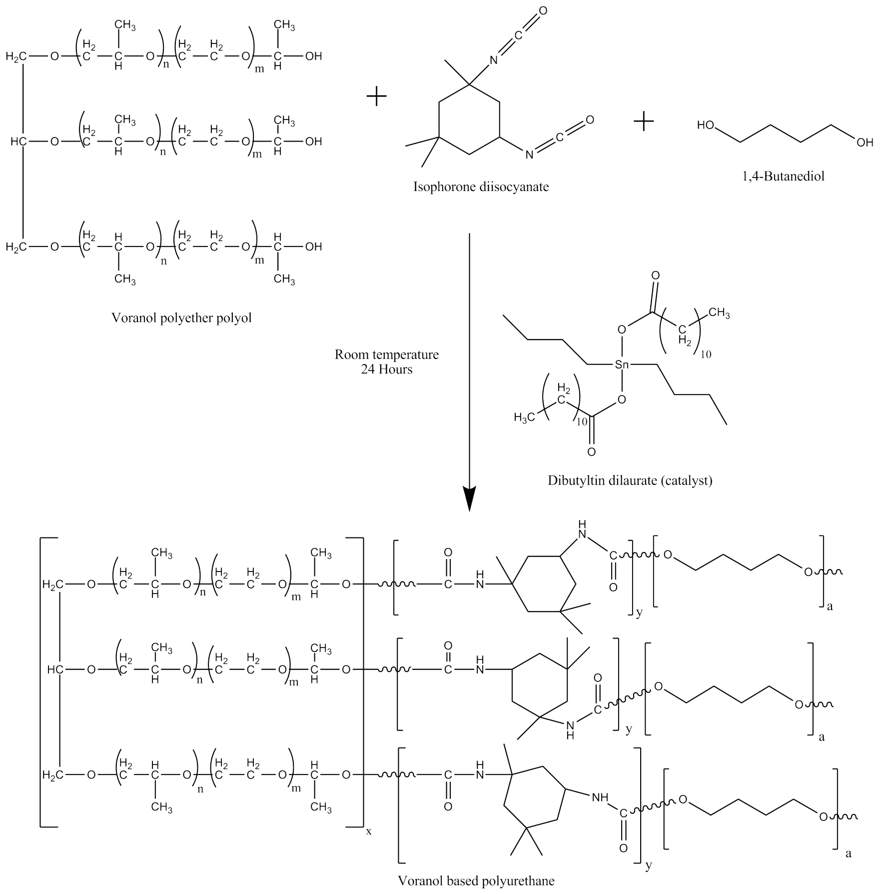


Figure 5.9: Synthesis of a Voranol based polyurethanes - *See Fig. 4.2 for full structure.

A wide range of polyurethane elastomers were successfully produced. Compared with the UV-cured polyurethane acrylate polymers (3.3) these polyurethanes took a much greater time to cure, with a minimum of 24 hours required. The polyurethanes were very similar in appearance to the polyurethane acrylate polymer sheets formed previously however they were more elastic and had a Tg of around -63 °C (Tab. 5.2) compared with the Tg of around -13 °C for the unlabelled UV-cured polyurethane acrylates (Tab. 4.2)

FT-IR data (Tab. 5.10) confirms the complete curing of polyurethanes by the absence of the characteristic sharp peak at 2260-2310 cm^{-1} corresponding with N=C=O bonds that would indicate the presence of residual IPDI or IPDI-terminated prepolymers. A broad peak around 3200-3500 cm^{-1} corresponding with O-H bonds would indicate residual diol or polyol monomers or the presence of moisture. This may be present on the spectrum but hidden by an overlapping N-H band. The example spectrum shown is for the unlabelled, non-heavy atom containing sample but all FT-IR spectra for the polyurethanes synthesised gave the same results. The unknown band around 3700 cm^{-1} has now vanished, supporting the theory that was a combination band resulting from the N=C=O groups.

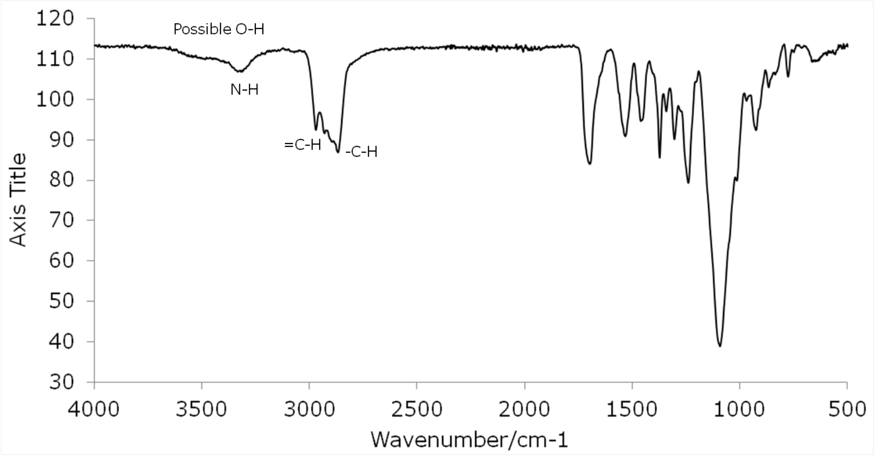


Figure 5.10: FT-IR Spectrum of a Voranol based polyurethane - Showing the absence of residual O-H and N=C=O bands.

All polyurethanes were synthesised from a blend of Voranol and IPDI with labels and quenchers incorporated as needed. The labelled polyurethanes were synthesised using either IPDI terminated 1,5-dihydroxynaphthalene prepolymer (Fig. 5.3) or IPDI terminated fluorescein prepolymer (Fig. 5.1)

Heavy atom containing fluorescence-quenched polyurethanes were synthesised using either 3-bromo-1,2-propanediol or IPDI terminated 4-bromoresorcinol prepolymer. A range of polyurethanes were made using both the fluorescein (Tab. 5.2) and the 1,5-dihydroxynaphthalene (Tab. 5.3) Each of the two labels was paired with both the 3-bromo-1,2-propanediol and the IPDI terminated 4-bromoresorcinol prepolymer (Fig. 5.6) to produce four different label/quencher pairings within the library of polyurethanes synthesised.

Fluorescein Prepolymer/wt%	BPD/wt%	BrR-PP/wt%	Tg/°C*	C$^+$/%	H$^+$/%	N$^+$/%	Br$^+$/%
0	0	0	-63.2	60.84	10.04	3.02	ND
0.1	0	0	-63.2	60.79	10.11	3.01	ND
0.1	1	0	-63.1	60.22	10.02	3.17	1.15
0.1	5	0	-60.03	59.43	9.47	4.04	3.24
0.1	10	0	-57.8	57.28	9.36	4.20	5.72
0.1	0	1	-61.2	60.98	10.7	3.68	0.53
0.1	0	2.5	-59.1	60.67	10.53	3.90	1.33
0.1	0	5	-60.5	60.17	10.09	4.50	2.38

Table 5.2: Overall results and data for fluorescein labelled Voranol based polyurethanes - *from DSC, $^+$ from elemental analysis (ND = Not discovered within detection limits of 0.3%) BPD = 3-Bromo-1,2-propanediol, BrR-PP = IPDI terminated 4-Bromoresorcinol prepolymer.

1,5-DHN Prepolymer/wt%	BPD/wt%	BrR-PP/wt%	Tg/°C*	C^+/%	H^+/%	N^+/%	Br^+/%
0	0	0	-63.2	60.84	10.04	3.02	ND
0.1	0	0	-63.3	60.7	10.13	3.13	ND
0.1	1	0	-62.2	60.36	10.19	3.17	0.84
0.1	5	0	-62.2	58.86	9.99	3.46	2.30
0.1	10	0	-59.0	57.33	9.47	4.23	7.51
0.1	0	1	-63.1	60.22	10.21	2.67	2.41
0.1	0	2.5	-62.9	60.27	9.96	3.53	2.68
0.1	0	5	-57.8	60.17	10.12	4.32	3.59

Table 5.3: Overall results and data for 1,5-dihydroxynaphthalene labelled Voranol based polyurethanes - *from DSC, $^+$ from elemental analysis (ND = Not discovered within detection limits of 0.3%) BPD = 3-Bromo-1,2-propanediol, BrR-PP = IPDI terminated 4-Bromoresorcinol prepolymer.

Tab. 5.2 and Tab. 5.3 show the overall DSC and elemental analysis data for a range of the polymers formed, with the samples being split into fluorescein labelled polyurethanes and 1,5-dihydroxynaphthalene labelled polyurethanes. The results show that these values follow broadly the same trends as in the polyurethane acrylate polymers. The elemental analysis data shown in both tables confirms the presence of bromine within the polymer sheets and absence of bromine in methanol washes. These data, along with the FT-IR spectra and appearance of polymers formed show the complete curing of the polyurethane sheets.

The DSC data for the polyurethanes show that increasing the heavy atom content of these polymers does not affect the Tg to the same extent as it did in the polyurethane-acrylate polymers (Tab. 4.2) although increasing heavy atom content still leads to a slight increase in Tg especially for the 3-bromo-1,2-propanediol. As the 3-bromo-1,2-propanediol was incorporated into the monomer blend directly, rather than via a prepolymer, a greater heavy atom content was attainable. The 4-bromoresorcinol content was limited by the constraints of the formulation required for curing which demanded a 1.05:1 overall NCO:OH ratio. Also the 3-bromo-1,2-propanediol has a lower relative molecular mass than the IPDI terminated 4-bromoresorcinol prepolymer and so the same wt% corresponds to a higher heavy atom content.

5.4 Fluorescence Analysis

For the excitation/emission data recorded for free fluorescein and 1,5-dihydroxynaphthalene and their lifetimes in the presence of free 3-bromo-1,2-propanediol please see the previous chapter.

Steady state excitation and emission spectra were obtained for all of the polymer-bound fluorescent labels. The excitation/emission maxima from these were used to set the correct excitation and detection wavelengths for the spectrophotometer used to observe the decay of the excited state. Decay curves showing the lifetime of the excited state were also recorded for both the free labels in the presence of the 4-bromoresorcinol and for the solid polymer sheets. The lifetimes for the polymer sheets containing increasing heavy atom content were also obtained. Again it is important to note that the intensity of emission spectra can not be compared between solid samples. The thickness and orientation of the sheets affect the amount of label present in the portion of the sample which is excited and therefore the intensity of the emission observed. This is especially important for the polymer sheets synthesised in this chapter as they were cast onto petri dishes rather than being formed in a mould using a spacer of known thickness. All comparisons between the fluorescence of the different solid sheets must de drawn from the excited state lifetimes data as these show the decay of the excited state and are therefore unaffected by the amount of label in the sample.

5.4.1 Free 1,5-Dihydroxynaphthalene

Tab. 5.4 shows data for the excited state lifetime of free 1,5-dihydroxynaphthalene in the presence of different concentrations of unbound 4-bromoresorcinol. The results show that increasing the concentration of 4-bromoresorcinol has the effect of reducing the excited state lifetime. These differences are greater than the experimental error estimated for this type of measurement (section 4.4.1) This shows that 1,5-dihydroxynaphthalene is quenched by the 4-bromoresorcinol. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all but the highest ($1\text{x}10^{-2}$) concentration of 4-bromoresorcinol (Fig. 5.11) The component lifetimes (Appendix 6.16) show that, as with the 3-bromo-1,2-propanediol, the majority of the decrease in lifetime is coming from the major component with a lifetime around 7 ns.

[4-Bromoresorcinol]/wt%	Exponential	Average Lifetime/ns	χ^2
0	3	6.86	1.1
1x10^{-3}	3	6.82	1.1
2x10^{-3}	3	6.78	1.2
5x10^{-3}	3	6.61	1.2
1x10^{-2}	3	6.53	1.3

Table 5.4: Average lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of 4-bromoresorcinol

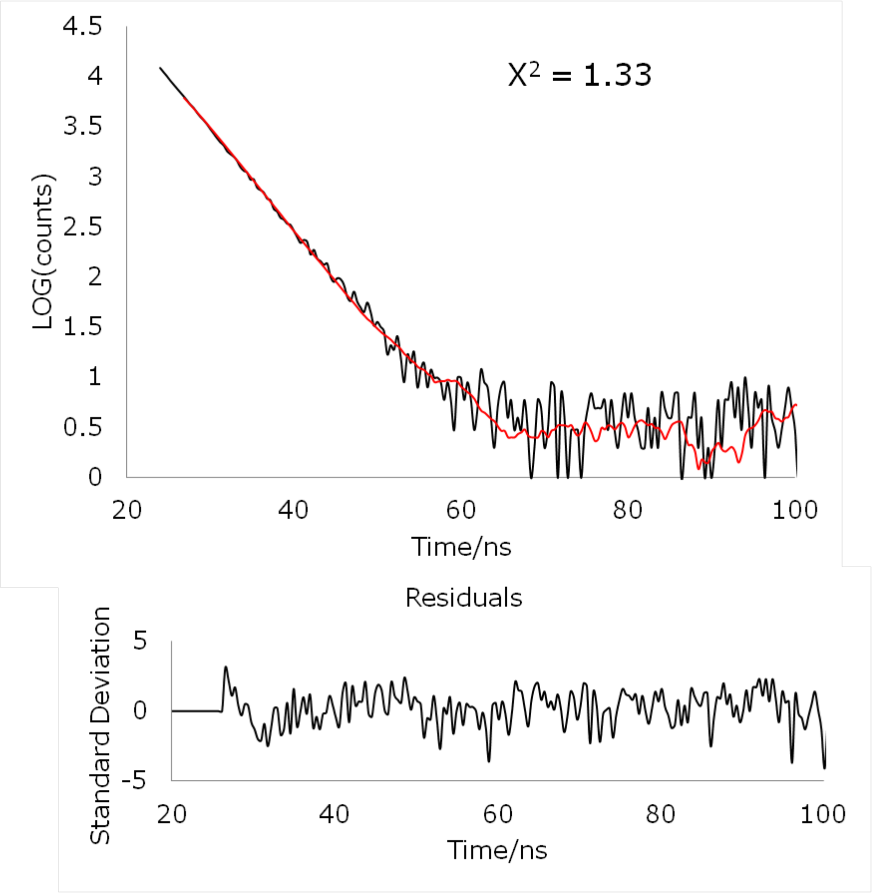


Figure 5.11: Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene in the Presence of 1x10^{-2}wt% 3- 4-Bromoresorcinol - Showing the mathematical fit in red and accompanied by a plot of the residuals from the triple exponential mathematical fit.

Tab. 5.5 shows data for the excited state lifetime of free 1,5-dihydroxynaphthalene in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer. The results show that increasing the concentration of IPDI terminated 4-bromoresorcinol has the effect of reducing the excited state lifetime. At higher levels, and across the whole series, the change in excited state lifetime is also greater than the experimental error estimated previously (section 4.4.1) This shows that 1,5-dihydroxynaphthalene is quenched by the IPDI terminated 4-bromoresorcinol prepolymer. Although the reduction in the excited state lifetime is not as pronounced as that seen with the unbound 4-bromoresorcinol (Tab. 5.4) this is not unexpected as the prepolymer has a greater molecular weight and the same wt% of quencher corresponds to a lower overall heavy atom content. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plot shown in appendix Fig. 6.22)

[4-Bromoresorcinol]/wt%	Exponential	Average Lifetime/ns	χ^2
0	3	6.86	1.1
1x10^{-3}	3	6.86	1.1
2x10^{-3}	3	6.84	1.2
5x10^{-3}	3	6.77	1.2
1x10^{-2}	3	6.65	1.2

Table 5.5: Average lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer

5.4.2 IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer

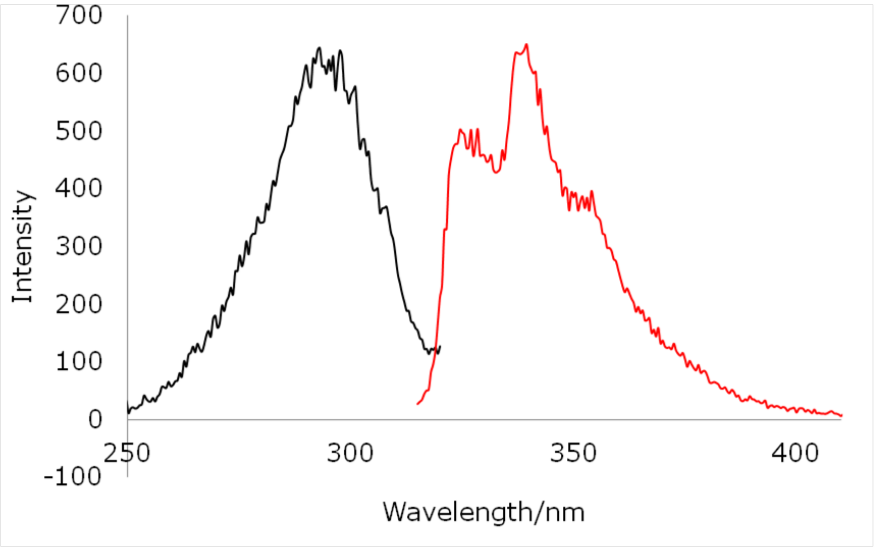


Figure 5.12: Excitation (Black) and Emission (Red) Spectra for IPDI terminated 1,5-Dihydroxynaphthalene Polyurethane Prepolymer - in THF

The excitation/emission spectra (Fig. 5.12) for the IPDI terminated 1,5-dihydroxynaphthalene prepolymer shows an excitation maximum of 298 nm and emission maximum of 340 nm. These values are slightly lower than for the free 1,5-dihydroxynaphthalene (Fig. 4.22) and the profile of the excitation curve is narrowed to a single peak with the multi-peaked character of the emission curve greatly reduced. This indicates that incorporation within a prepolymer has altered the favourable electronic transitions for the 1,5-dihydroxynaphthalene.

Tab. 5.6 shows data for the excited state lifetime of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of unbound 3-bromo-1,2-propanediol. The results show that increasing the concentration of 3-bromo-1,2-propanediol has the effect of reducing the excited state lifetime up to 1x10^{-2} wt% at which point the excited state lifetime begins to increase again. These differences are greater than would be accounted for by the experimental error estimated in section 4.4.1 The excited state lifetimes for the IPDI terminated 1,5-dihydroxynaphthalene prepolymers are greatly increased when compared with the excited state lifetimes for free 1,5-dihydroxynaphthalene in the presence of the same concentrations of 3-bromo-1,2-propanediol (Fig. 4.5) The capping of the 1,5-dihydroxynaphthalene at both ends with IPDI has more than doubled the excited state lifetime of the label. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plots shown in appendix Fig. 6.23 and Fig. 6.24) The component lifetimes for the IPDI terminated 1,5-dihydroxynaphthalene prepolymer (appendix 6.18, 6.19

and 6.20 show that the increase has come mainly from a large increase in contribution from the long-lived component (23.5 ns) which has remained unchanged in its longevity. This implies that the changes to the fluorophore environment from incorporation within this prepolymer has increased the number of fluorophores that exist in the environment corresponding to the long-lived component. The longevity of the other two components has increased which implies that they are protected in some way, possibly by reduced access to natural quenchers such as oxygen.

3-Bromo-1,2-propanediol/$wt\%$	Exponentials	Average Lifetime	χ^2
0	3	13.41	1.0
1x10^{-3}	3	13.37	1.0
2x10^{-3}	3	13.22	1.1
5x10^{-3}	3	13.16	1.1
1x10^{-2}	3	13.32	1.2

Table 5.6: Lifetimes for the excited state of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of 3-bromo-1,2-propanediol

Tab. 5.7 shows data for the excited state lifetime of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of unbound 4-bromoresorcinol. The results show that increasing the concentration of 4-bromoresorcinol has the effect of reducing the excited state lifetime with the change in lifetime far greater than the calculated error associated with such readings (section 4.4.1) This shows that quenching of the excited state by the heavy atom containing species is taking place. The excited state lifetimes for the IPDI terminated 1,5-dihydroxynaphthalene prepolymers are still greatly increased when compared with the excited state lifetimes for free 1,5-dihydroxynaphthalene. However the 4-bromoresorcinol has decreased the excited state lifetime to a greater degree than the 3-bromo-1,2-propanediol (Fig. 5.6) The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plot shown in Appendix Fig. 6.25)

Tab. 5.8 shows data for the excited state lifetime of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer. The results show that increasing the concentration of IPDI terminated 4-bromoresorcinol prepolymer has the effect of reducing the excited state lifetime

4-Bromoresorcinol]/$wt\%$	Exponentials	Average Lifetime	χ^2
0	3	13.41	1.0
1x10^{-3}	3	12.76	1.1
2x10^{-3}	3	12.30	1.2
5x10^{-3}	3	12.23	1.1
1x10^{-2}	3	11.93	1.2

Table 5.7: Lifetimes for the excited state of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of 4-bromoresorcinol

beyond the differences accounted for by experimental error (section 4.4.1) This pattern continues up to 1x10^{-2} wt% at which point the excited state lifetime begins to increase again. The excited state lifetimes for the IPDI terminated 1,5-dihydroxynaphthalene prepolymers are still greatly increased when compared with the excited state lifetimes for free 1,5-dihydroxynaphthalene however the IPDI terminated 4-bromoresorcinol prepolymer has decreased the excited state lifetime to a greater degree than the free 4-bromoresorcinol (Tab. 5.7) This is surprising as the IPDI terminated 4-bromoresorcinol prepolymer contains less heavy atom than the same wt% of unbound 4-bromoresorcinol. Once again, the χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plot shown in Appendix Fig. 6.26)

Overall for the IPDI terminated 1,5-dihydroxynaphthalene prepolymer, the IPDI terminated 4-bromoresorcinol prepolymer provides the greatest degree of quenching, reducing the average lifetime of the excited state by nearly 1.8 ns.

4-Bromoresorcinol Prepolymer]/$wt\%$	Exponentials	Average Lifetime	χ^2
0	3	13.41	1.0
1x10^{-3}	3	12.08	1.1
2x10^{-3}	3	11.80	1.0
5x10^{-3}	3	11.59	1.0
1x10^{-2}	3	11.63	1.2

Table 5.8: Lifetimes for the excited state of IPDI terminated 1,5- dihydroxynaphthalene prepolymer in the presence of different concentrations of 4-bromoresorcinol prepolymer.

5.4.3 Voranol Polyurethane Bound 1,5-Dihydroxynaphthalene

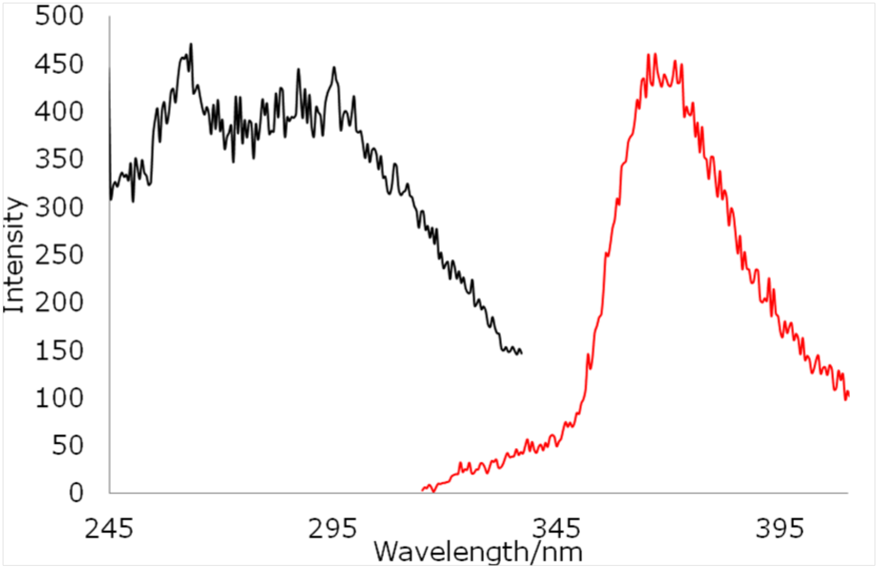


Figure 5.13: Excitation/Emission Spectra for Voranol Based Polyurethanes Labelled with 1,5-Dihydroxynaphthalene - Solid state readings.

The solid state excitation/emission spectra (Fig. 5.13) for Voranol based polyurethanes labelled with 1,5-dihydroxynaphthalene show a very broad excitation maximum between 254 and 300 nm with an emission maximum of 365 nm. The emission maximum is higher than for the free 1,5-dihydroxynaphthalene (Fig. 4.22) with the multi-peaked character of the emission curve lost and only a single peak observed corresponding to the electronic transition between the first excited state and the ground state. The profile of the excitation curve has widened to a much broader single peak.

Tab 5.9 shows data for the excited state lifetime of Voranol based polyurethanes labelled with 1,5-dihydroxynaphthalene containing different wt% of 3-bromo-1,2-propanediol. The results show that increasing the 3-bromo-1,2-propanediol content of the polymer has the effect of reducing the excited state lifetime up to 10 wt% at which point the excited state lifetime begins to increase again. The excited state lifetimes for the 1,5-dihydroxynaphthalene bound within Voranol based polyurethanes are greatly increased when compared with the excited state lifetimes for both free 1,5-dihydroxynaphthalene (Tab. 4.4) and the IPDI terminated 1,5-dihydroxynaphthalene prepolymer (Tab. 5.6) This is expected as binding labels within a polymer matrix protects the excited state from oxygen present in the atmosphere and an increase in excited state lifetime has been seen in all polymer bound labels analysed previously when compared with the free label in solution. The component lifetimes (Fig. 6.21 and Fig. 6.22) again show that the increase in average lifetime is coming mainly from an increase in longevity in the shorter-lived two components as well as an increase in contribution from the longest-lived component. The subsequent decrease in average lifetime following the addition of quencher also follows this trend. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for samples containing 2 wt% 3-bromo-1,2-propanediol or lower (Fig. 5.14) However both the χ^2 and residuals deviate from statistically acceptable values for samples containing 5 wt% 3-bromo-1,2-propanediol or higher (example lifetime plot shown in Appendix Fig. 6.27)

3-Bromo-1,2-propanediol/$wt\%$	Exponentials	Average Lifetime	χ^2
0	3	20.53	1.1
1	3	18.50	1.2
2	3	17.37	1.1
5	3	17.26	1.3
10	3	18.54	1.4

Table 5.9: Lifetimes for the excited state of 1,5-dihydroxynaphthalene labelled Voranol based polyurethanes containing different concentrations of 3-bromo-1,2-propanediol

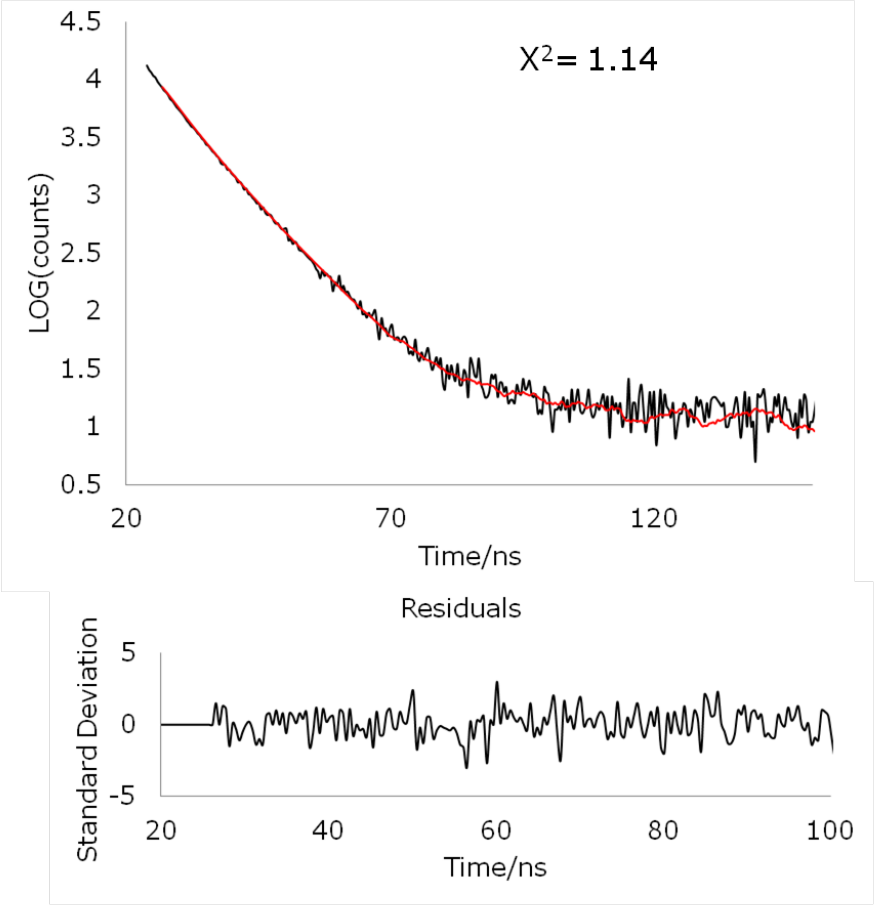


Figure 5.14: Excited State Lifetime Plot for 1,5-Dihydroxynaphthalene Labelled Voranol Based Polyurethane - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

Tab. 5.10 shows data for the excited state lifetime of Voranol based polyurethanes labelled with 1,5-dihydroxynaphthalene containing different wt% IPDI terminated 4-bromoresorcinol prepolymer. The results show that increasing the concentration of 4-bromoresorcinol has the effect of reducing the excited state lifetime for all samples well beyond the levels accounted for by the error calculated previously (section 4.4.1) The excited state lifetimes for the Voranol based polyurethanes labelled with 1,5-dihydroxynaphthalene containing different wt% IPDI terminated 4-bromoresorcinol prepolymer are broadly similar to those observed for samples containing different concentrations of 3-bromo-1,2-propanediol (Tab. 5.9) However the 4-bromoresorcinol prepolymer achieves a much greater degree of quenching at high concentrations (5 wt%) than the 3-bromo-1,2-propanediol. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all but the highest content (5 wt%) of IPDI terminated 4-bromoresorcinol prepolymer (example lifetime plot shown in Appendix Fig. 6.28)

4-Bromoresorcinol prepolymer/$wt\%$	Exponentials	Average Lifetime	χ^2
0	3	20.53	1.1
0.1	3	19.33	1.1
1	3	17.48	1.1
2.5	3	14.33	1.2
5	3	12.93	1.3

Table 5.10: Lifetimes for the excited state of 1,5-dihydroxynaphthalene labelled Voranol based polyurethanes containing different concentrations of 4-bromoresorcinol prepolymer

Overall, as in the polyurethane acrylate sheets synthesised in the previous chapter, incorporation into the solid sheet has greatly increased the lifetime of the 1,5-dihydroxynaphthalene excited state. Quenching is observed by the shortening of the lifetime as 3-bromo-1,2-propanediol is added although, again, the lifetimes begin to increase after a certain level of 3-bromo-1,2-propanediol is reached (Tab. 5.9) However the deviation of χ^2 values from unity mean that confidence in this increase is low. The Voranol based solid sheets containing 4-bromoresorcinol appear to show an even greater degree of quenching (Tab. 5.10) despite the lower levels possible within the formulations. Although the lower levels used may explain why an increase in lifetimes at high levels of 4-bromoresorcinol is not seen as it is with the 3-bromo-1,2-propanediol.

5.4.4 Free Fluorescein

Tab. 5.11 shows data for the excited state lifetime of free fluorescein in the presence of different concentrations of unbound 4-bromoresorcinol. The results show that increasing the concentration of 4-bromoresorcinol has the effect of reducing the excited state lifetime. This shows that fluorescein is quenched by the 4-bromoresorcinol. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all excited state lifetime values (Fig. 5.15) The differences in lifetime between individual samples are within calculated experimental error of each other (section 2.5.1) however greater differences are seen across the entire series.

[4-Bromoresorcinol]/wt%	Exponential	Lifetime/ns	χ^2
0	1	4.24	0.9
1x10^{-3}	1	4.22	1.1
2x10^{-3}	1	4.17	1.0
5x10^{-3}	1	4.15	1.0
1x10^{-2}	1	4.11	1.0

Table 5.11: Average lifetimes for the excited state of free fluorescein in the presence of different concentrations of 4-bromoresorcinol

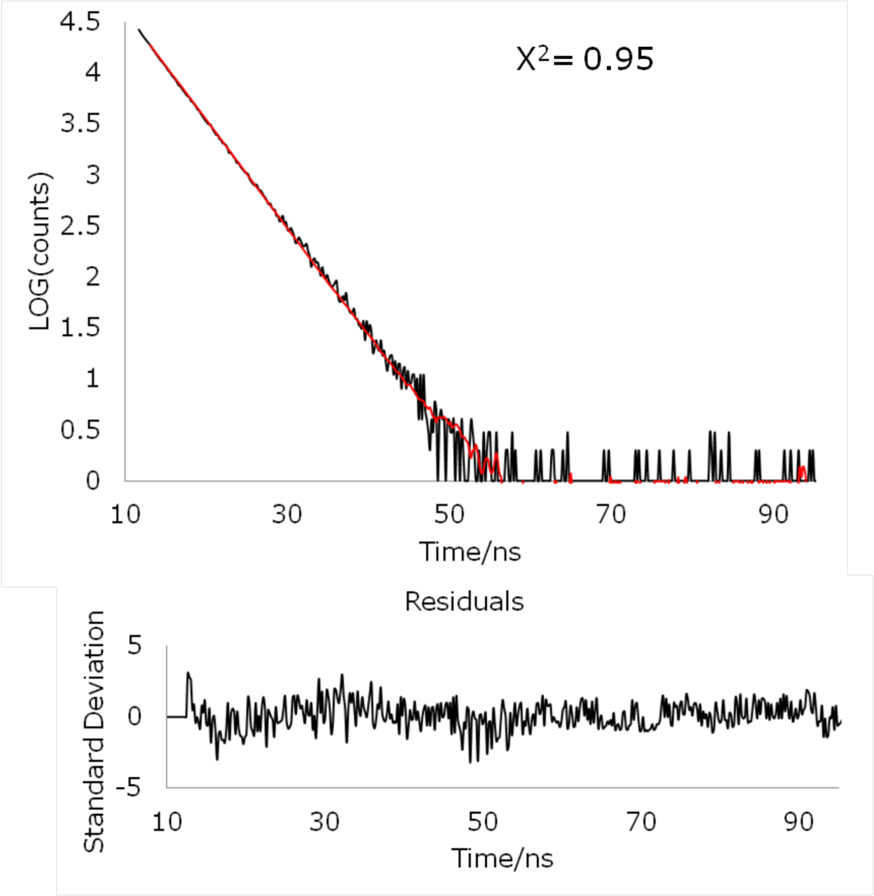


Figure 5.15: Excited State Lifetime Plot for Free Fluorescein in the Presence of 1x10^{-2}wt% 4-bromoresorcinol - Showing the mathematical fit in red and accompanied by a plot of the residuals from the triple exponential mathematical fit.

Tab. 5.12 shows data for the excited state lifetime of free fluorescein in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer. The results show that increasing the concentration of IPDI terminated 4-bromoresorcinol has the effect of reducing the excited state lifetime. However the reduction in the excited state lifetime is not as pronounced as that seen in with the unbound 4-bromoresorcinol (Tab. 5.11) this is not unexpected as the prepolymer has a greater molecular weight and the same wt% of quencher corresponds to a lower overall heavy atom content. The reduction in lifetime is not greater than the estimated error for such readings (section 2.5.1) for any results but the two extremes. This means that no strong conclusions about degree of quenching can be drawn from this set of data The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plot shown in Appendix Fig. 6.29)

BRR-PP/wt%	Exponential	Lifetime/ns	χ^2
0	1	4.24	0.9
1x10^{-3}	1	4.25	1.0
2x10^{-3}	1	4.24	0.9
5x10^{-3}	1	4.22	0.9
1x10^{-2}	1	4.19	0.9

Table 5.12: Average lifetimes for the excited state of free fluorescein in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer

- BRR-PP = IPDI terminated 4-bromoresorcinol prepolymer

Overall the effect on the excited state lifetime is much less pronounced for the fluorescein than for the 1,5-dihydroxynaphthalene in the presence of the same concentrations of 4-bromoresorcinol and its prepolymer.

5.4.5 IPDI Terminated Fluorescein Prepolymer

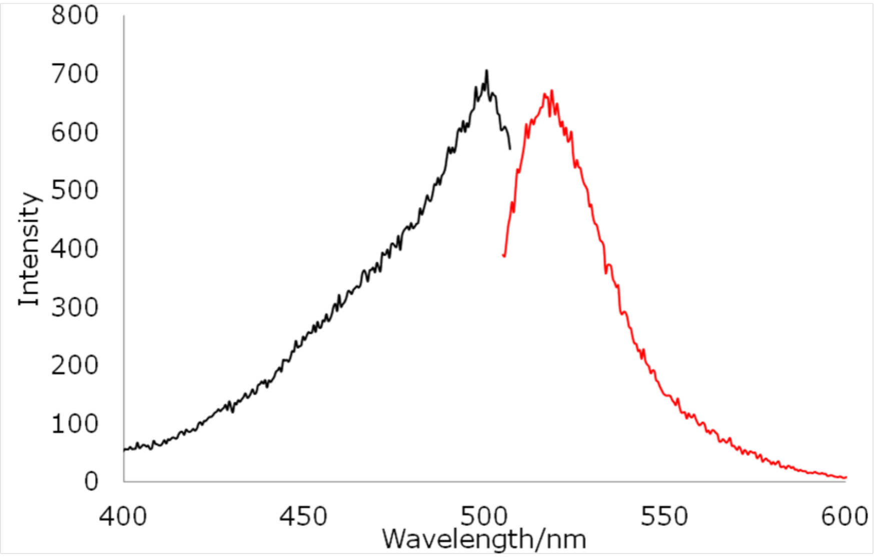


Figure 5.16: Excitation/Emission Spectra for IPDI Terminated Fluorescein Prepolymer - Solution in spectrophotometric grade THF.

The excitation/emission spectra (Fig. 5.16) for the IPDI terminated fluorescein prepolymer show an excitation maximum of 495 nm and emission maximum of 520 nm. This is a slight decrease in excitation maximum and increase in emission maximum compared with the values for free fluorescein (Fig. 4.29) The profile of both curves is slightly sharper and less broad than those of the free fluorescein.

Tab. 5.13 shows data for the excited state lifetime of IPDI terminated fluorescein prepolymer in the presence of different concentrations of unbound 3-bromo-1,2-propanediol. The results show that increasing the concentration of 3-bromo-1,2-propanediol has the effect of slightly increasing the excited state lifetime. However this increase is much smaller than the experimental error calculated previously (section 2.5.1) and so may not be a real effect. The excited state lifetimes for the IPDI terminated fluorescein prepolymers are also slightly reduced when compared with the excited state lifetimes for free fluorescein in the presence of the same concentrations of 3-bromo-1,2-propanediol (Fig. 4.10) Both of these effects are the opposite to those observed in the IPDI terminated 1,5-dihydroxynaphthalene prepolymer (Tab. 5.6) The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plots shown in Appendix Fig. 6.30 and Fig. 6.31)

Tab. 5.14 shows data for the excited state lifetime of IPDI terminated fluorescein prepolymer in the presence of different concentrations of unbound 4-bromoresorcinol. The results show that increasing the concentration of 4-bromoresorcinol has the effect of slightly

3-Bromo-1,2-propanediol/$wt\%$	Exponentials	Lifetime	χ^2
0	1	4.09	1.0
1x10^{-3}	1	4.08	1.2
2x10^{-3}	1	4.08	1.0
5x10^{-3}	1	4.09	1.1
1x10^{-2}	1	4.10	0.9

Table 5.13: Lifetimes for the excited state of IPDI terminated fluorescein prepolymer in the presence of different concentrations of 3-bromo-1,2-propanediol

reducing the excited state lifetime up to 1x10^{-2} wt% at which point a slight increase in excited state lifetime is observed. The decrease in lifetime across the series is greater than the estimated experimental error (section 2.5.1) but the subsequent increase is not. The excited state lifetimes for the IPDI terminated fluorescein prepolymers are still slightly shorter than the excited state lifetimes for free fluorescein. The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plot shown in appendix Fig. 6.32)

4-Bromoresorcinol/$wt\%$	Exponentials	Lifetime	χ^2
0	1	4.09	1.0
1x10^{-3}	1	4.08	1.0
2x10^{-3}	1	4.03	1.0
5x10^{-3}	1	4.01	1.1
1x10^{-2}	1	4.02	1.1

Table 5.14: Lifetimes for the excited state of IPDI terminated fluorescein prepolymer in the presence of different concentrations of 4-bromoresorcinol

Tab. 5.15 shows data for the excited state lifetime of IPDI terminated fluorescein prepolymer in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer. The results show that increasing the concentration of IPDI terminated 4-bromoresorcinol prepolymer has the effect of slightly reducing the excited state lifetime up to 1x10^{-2}

wt% at which point the excited state lifetime begins to increase again. However these changes are smaller than the estimated error for such readings (section 2.5.1) and so can not be used to draw any conclusions. The excited state lifetimes for the IPDI terminated fluorescein prepolymers are still slightly decreased when compared with the excited state lifetimes for free fluorescein. Again, the χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all samples (example lifetime plot shown in Appendix Fig. 6.33)

4-Bromoresorcinol Prepolymer]/$wt\%$	Exponentials	Lifetime	χ^2
0	1	4.09	1.0
1x10^{-3}	1	4.10	1.1
2x10^{-3}	1	4.08	1.2
5x10^{-3}	1	4.07	1.1
1x10^{-2}	1	4.08	1.1

Table 5.15: Lifetimes for the excited state of IPDI terminated fluorescein prepolymer in the presence of different concentrations of 4-bromoresorcinol prepolymer.

Overall the data shows that the IPDI terminated fluorescein prepolymer excited state shows little to no quenching by either the 4-bromoresorcinol, the IPDI terminated 4-bromoresorcinol prepolymer or the 3-bromo-1,2-propanediol. The χ^2 values and distribution of residuals give good confidence in the mathematical fit for all values.

5.4.6 Voranol Polyurethane Bound Fluorescein

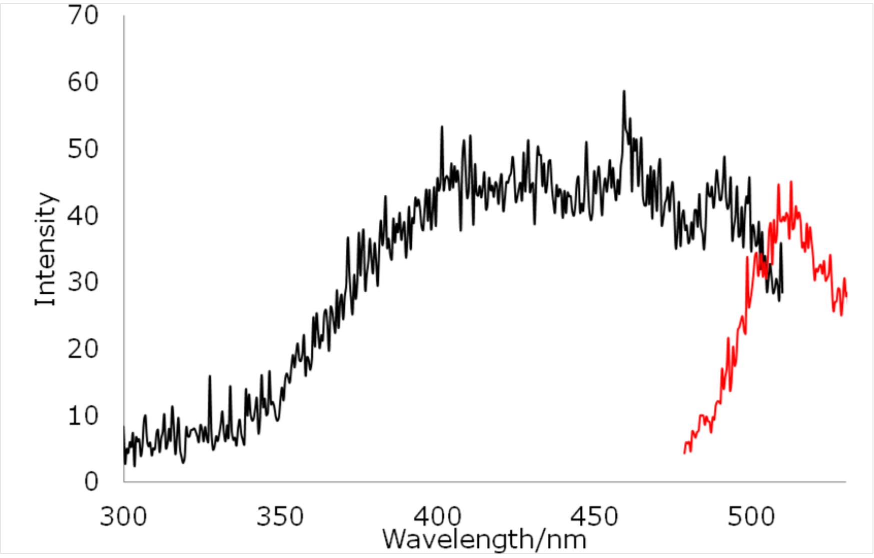


Figure 5.17: Excitation (Black) and Emission (Red) Spectra for Voranol Based Polyurethanes Labelled with Fluorescein - Solid state readings.

The solid state excitation/emission spectra (Fig. 5.17) for Voranol based polyurethanes labelled with fluorescein show a very broad excitation maximum between 400 and 500 nm with an emission maximum of 520 nm. As with the 1,5-dihydroxynaphthalene (Fig. 5.13,) the excitation/emission spectra for the solid Voranol sheets containing fluorescein show a pronounced broadening of the excitation peak compared with both the free fluorescein (Fig. 4.29) and the prepolymer bound fluorescein (Fig. 5.16) This is thought to be a result of binding within a polymer chain allowing energy transfer along that chain.[108]

Tab 5.16 shows data for the excited state lifetime of Voranol based polyurethanes labelled with fluorescein containing different wt% of 3-bromo-1,2-propanediol. The results show that increasing the 3-bromo-1,2-propanediol content of the polymer has the effect of greatly increasing the excited state lifetime. This difference is much greater than could be accounted for by experimental error as estimated in section 2.5.1 This is the opposite effect to expected and the reverse of the trend seen in the Voranol based polyurethanes labelled with 1,5-dihydroxynaphthalene (Fig. 5.9) The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for samples containing 2 wt% 3-bromo-1,2-propanediol or lower (Fig. 5.18) However, as with the Voranol based polyurethanes labelled with 1,5-dihydroxynaphthalene, both the χ^2 and residuals deviate from statistically acceptable values for samples containing 5 wt% 3-bromo-1,2-propanediol or higher (example lifetime plot shown in Appendix Fig. 6.34)

3-Bromo-1,2-propanediol/$wt\%$	Exponentials	Lifetime	χ^2
0	1	4.09	1.2
1	1	4.18	1.2
2	1	4.24	1.2
5	1	4.75	1.3
10	1	5.07	1.4

Table 5.16: Lifetimes for the excited state of fluorescein labelled Voranol based polyurethanes containing different concentrations of 3-Bromo-1,2-propanediol.

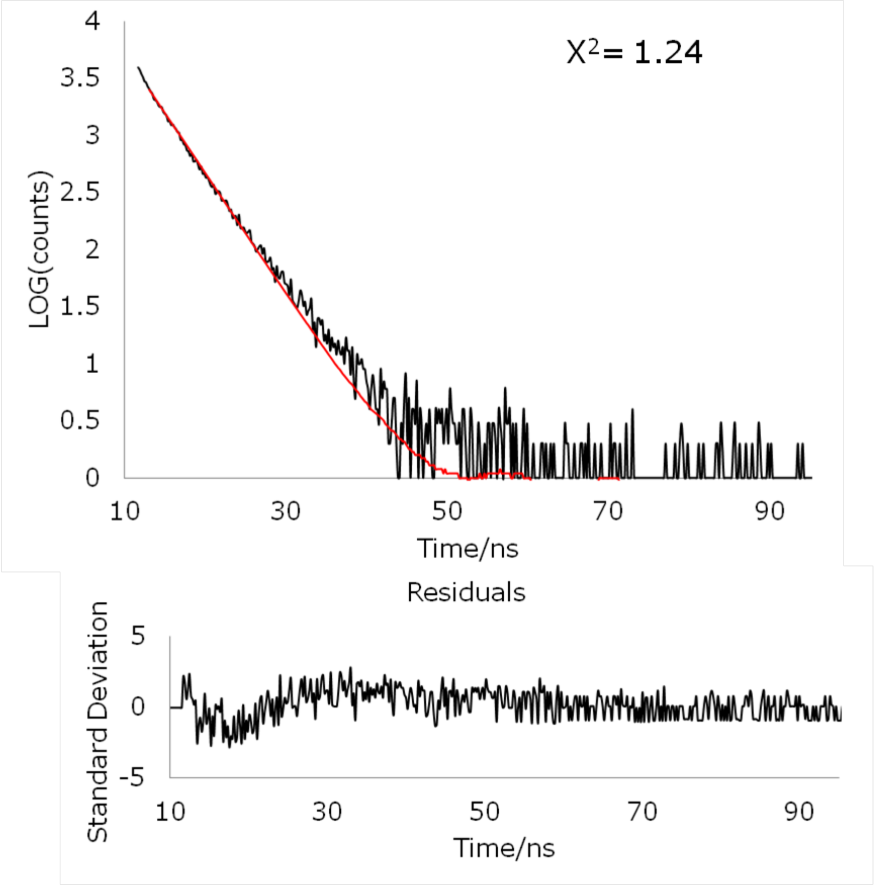


Figure 5.18: Excited State Lifetime Plot for Fluorescein Labelled Voranol Based Polyurethane - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

Tab. 5.17 shows data for the excited state lifetime of Voranol based polyurethanes labelled with fluorescein and containing different wt% IPDI terminated 4-bromoresorcinol prepolymer. The results show that increasing the concentration of 4-bromoresorcinol prepolymer has the effect of increasing the excited state lifetime. The excited state lifetimes for the Voranol based polyurethanes labelled with fluorescein containing different wt% IPDI terminated 4-bromoresorcinol prepolymer are broadly similar to those observed for samples containing different concentrations of 3-bromo-1,2-propanediol (Tab. 5.16) However the 4-bromoresorcinol prepolymer does not increase the excited state lifetime to the same degree at high concentrations (5 wt%) as the 3-bromo-1,2-propanediol .The χ^2 values are near unity and the residuals from the mathematical fit are randomly distributed around zero giving good confidence in the mathematical fit for all but the highest content (5 wt%) of IPDI terminated 4-bromoresorcinol prepolymer (example lifetime plot shown in appendix Fig. 6.35) The differences in lifetimes across the series are greater than estimated error (section 2.5.1) however some individual pairs of results may be within error of each other.

4-Bromoresorcinol Prepolymer/wt%	Exponentials	Lifetime	χ^2
0	1	4.09	1.2
0.1	1	4.12	1.1
1	1	4.25	1.1
2	1	4.23	1.2
5	1	4.25	1.3

Table 5.17: Lifetimes for the excited state of fluorescein labelled Voranol based polyurethanes containing different concentrations of 4-bromoresorcinol prepolymer.

Overall, the fluorescein labelled Voranol based polyurethane sheets did not show any quenching with the addition of 4-bromoresorcinol or 3-bromo-1,2-propanediol (Tab. 5.17 and 5.16) In fact the excited state lifetimes were observed to increase with the addition of the heavy atom containing species. This effect was more pronounced in the sheets containing 3-bromo-1,2-propanediol however this may be because higher levels of 3-bromo-1,2-propanediol were possible to achieve within the formulation limits. The increase in lifetime was attributed to the promotion of the triplet state by the heavy atom leading to delayed fluorescence. Fluorescein and its derivatives have previously been shown to exhibit delayed fluorescence when bound within polymers.[116, 117, 118]

5.5 Conclusions

The formation of solid, branched polyurethanes was successful. A wide range of polyurethane sheets were successfully synthesised, including some containing fluorescent labels (fluorescein and 1,5-dihydroxynaphthalene) and fluorescence quenchers (1,2-bromopropanediol and 4-bromoresorcinol) and some containing both. The dry PTFE spray worked well as a release agent and allowed the polymers to be easily lifted away from the petri dish moulds used. Voranol was selected as the main polyol as it has multiple OH groups which allow for branching to occur. It was also posited that Voranol, being a polyether polyol, would grant increased elasticity to the products and this proved to be the case. 1,4 Butane diol was also selected for the flexibility granted to solid sheets made using it.

There were initial problems with the incorporation of fluorescent/quenching species into these sheets. These did not always mix in well and cure along with the other reagents in the blend and in some cases this led to unsuccessful curing of the sheets. This problem was solved by using the fluorescent label/fluorescence quencher to form prepolymers with isophorone diisocyanate prior to the formation of polymer sheets. It was found that the initial sheets formed, even if successfully cured, still contained a very uneven distribution of label/quencher. Various mixing processes were tried however some led to the polyurethanes curing in the sample tubes prior to the addition of catalyst. This was attributed to residual catalyst in the prepolymers from their synthesis. As rigorous mixing was still required to blend the viscous prepolymers with the other reagents, the order of reagent addition was found to be very important. The IPDI and IPDI terminated prepolymers were mixed in a sample tube and agitated using a vortex machine to mix them well with each other prior to the addition of the diols. This allowed the prepolymers to be mixed with the less viscous IPDI without danger of premature curing. Once all the isocyanate species were fully mixed together, the Voranol and butanediol were then added to the mixture which could then be agitated again for a shorter time to blend them together prior to curing. This method led to the even distribution of the different monomers as judged by eye.

As seen in the polyurethane acrylates, the 1,5-dihydroxynaphthalene excited state showed an increase in lifetime when bound within a polymer matrix. Once again this was attributed to the protection of the excited state from atmospheric oxygen. Quenching is observed by the shortening of the 1,5-dihydroxynaphthalene excited state lifetime when 3-bromo-1,2-propanediol is incorporated within the polyurethane sheets although the lifetimes begin to increase after a certain level of 3-bromo-1,2-propanediol is reached. The Voranol based solid sheets containing 4-bromoresorcinol appear to show an even greater degree of quenching than those containing 3-bromo-1,2-propanediol despite the lower levels possible within the parameters of the formulations. Although the lower levels used may explain why an increase in lifetime at high levels of 4-bromoresorcinol is not seen as it is with the 3-bromo-1,2-propanediol.

The excited state lifetimes for the fluorescein labelled sheets were once again observed to increase with the addition of the heavy atom containing species. As the polyurethane sheets are much less glassy than the polyurethane acrylates synthesised in the previous chapter, this was attributed to triplet-triple annihilation. The increase in elasticity and reduction in glassiness should allow oxygen to better penetrate the solid sheets. Therefore the effect observed is less likely to be due to the access of oxygen to the excited state. It may be possible to mitigate this effect by using a different fluorescent label. It may also be possible to take advantage of this effect to produce a fluorescent polymer that shows a reduction rather than an increase in fluorescence in response to mechanical tension. Unfortunately, due to time constraints, these avenues of research are to be left for future work and not pursued within this project.

5.6 Future Work

5.6.1 Elastomers

Further research towards the development of polymers which exhibit a specific fluorescent response to mechanical stimuli would be of great interest to the development of new security features. Of the elastomers synthesised, the Voranol based polyurethanes are by far the most promising in terms of properties and so should form the starting point for any future work. The flexibility, durability and optical clarity of these materials give them a good chance of displaying the desired effect and their chemistry allows for the incorporation of a variety of labels and quenchers.

5.6.2 Fluorescence

Progression of this work would involve the investigation of the excited state lifetime of samples while they are subjected to tension. It would be interesting to see if and how the lifetime of the quenched 1,5-dihydroxynaphthalene labelled samples changed with mechanical stimuli. The development of a method for applying measured and repeatable tension to a polymer sample while within the sample holder of a spectrophotometer would be a requirement for this.

The use of alternative heavy atom quenchers would be interesting to see and it may be possible to achieve a greater degree of quenching using other commercially available quenching diols or diisocyanates. As the best results with regard to the quenching of the excited state lifetime came from the 9-vinylanthracene/bromostyrene combination, the synthesis of a dihydroxy functional anthracene monomer for use in conjunction with 4-bromoresorcinol or other aromatic quenching species would be a promising avenue for future research. Such materials should also exhibit fluorescence within the visible part of the electromagnetic spectrum which is greatly desirable for the intended applications.

The use of fluorescent or quenching diisocyanates, when paired with fluorescent or quenching diols would also allow for phase separation between the label and quencher within the polyurethane. It would be possible to incorporate the label in the soft segment and the quencher in the hard segment or vice versa. This may be a strategy that would help to further research in this area by creating a greater statistical distance between fluorophores and quenchers when the polymer is stretched out and the chains extended. It would also be possible to use either the label or quencher as a chain linkage in a crosslinked polyurethane network. This technique has been described previously for fluorescein[112, 119] but not paired with a quencher incorporated on the polymer backbone.

The polymers labelled with fluorescein displayed an increase in fluorescence lifetime with increasing heavy atom content. Although this was the opposite of the intended effect, further work could be undertaken in this area. Phosphorescent lifetimes could be acquired to help fully understand the results seen. These materials could also still be useful for security applications in the intended way but with the change observed under tension being an increase in visible fluorescence rather than a decrease. Fluorescence analysis of the elastomers made in this chapter while under tension would be the next step for this work.

6

Experimental

6.1 Synthesis of Styrene-Butadiene Polymers

6.1.1 Materials

All reagents were obtained from Sigma-Aldrich and used as received unless listed below. All solvents were laboratory reagent grade, obtained from the departmental chemical stores and sourced from Fisher. Both styrene (Bp 41 °C) and 4-bromostyrene (Bp 49.5 °C) inhibited by tert-butyl catechol were washed three times with 100 ml 10 % NaOH $_{(aq.)}$ and three times with 200 ml deionised water to remove the inhibitor before drying with $MgSO_4$ and distilling under reduced pressure. Deionised water was obtained from a Millipore Direct-Q 3 ultrapure water system.

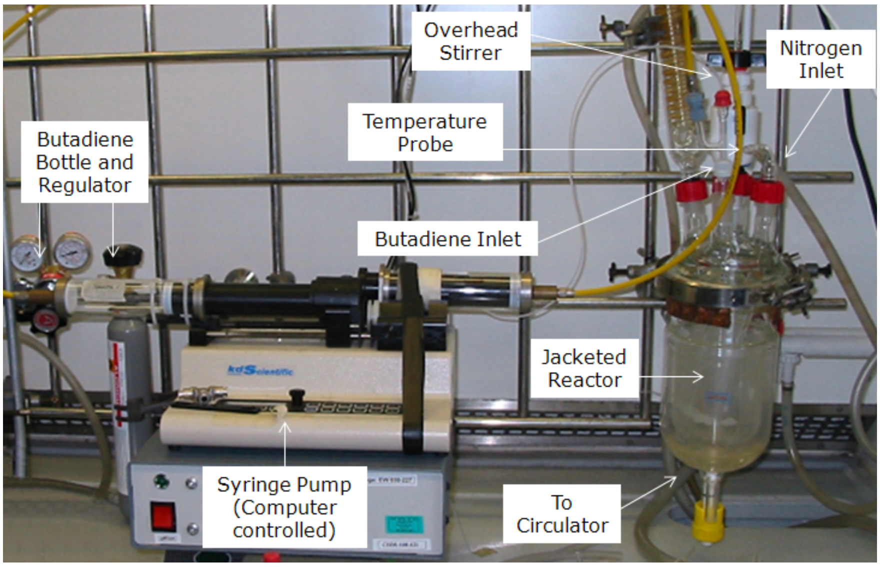


Figure 6.1: The Apparatus Used for Emulsion Polymerisation - The computer controlling the syringe pump and temperature controlled circulators not pictured

For the synthesis of SBR in this project, an emulsion rig (Fig. 6.1) was used. This comprised of a Radleys jacketed reactor fitted with an overhead stirrer and cooled to -10 °C by a Haake DC 30 circulator bath filled with ethanol. For those reactions using a condenser for the 1,3-butadiene, a separate circulator was used to cool the heat exchange column.

6.1.2 Method One

The reaction vessel was initially charged with the styrene 0.2 mol (21 g) 500 ml deionised water, SDS surfactant and the initiation system described by Vandenberg and Hulse [67] and still used in industry (Tab. 6.1) Then 1,3-Butadiene gas 1 mol (54 g) was delivered by a computer controlled Precidor Type 5003, Infors HT infusion pump comprising of two 100 cm^3 glass syringes which alternately fill from the gas cylinder and empty into the reaction vessel. The reaction was performed under a nitrogen atmosphere and monitored by a temperature probe. The reaction was allowed to proceed for 24 hours before the product was isolated by precipitation into acetone followed by filtering and repeated washes with cold acetone. The polymer was then dried in vacuo at room temperature for 48 hours to give a bright white solid. This system utilises water as the heat transfer medium, SDS as the surfactant and a cumene hydroperoxide redox system as the initiator.

Yield: 16%
Solid content: 2% (12.6% expected)
Butadiene Content: Either not present and product is polystyrene or content is too low to determine.

Reagent	Parts by weight
Styrene	25
1,3-Butadiene	75
Sodium dodecyl sulfate	5
Sodium hydroxide	0.061
Cumene hydroperoxide	0.17
Iron(II) Sulfate	0.017
Sodium pyrophosphate decahydrate	1.5
d-Fructose	0.5

Table 6.1: Reagents for SBR synthesis

Particle Size: 54 nm
^{1}*H-NMR* (250 MHz, $CDCl_3$): δ 7.139 (2H, m, aromatic); δ 7.022 (2H, m, aromatic); δ 6.656 (2H, s, aromatic); δ 1.897 (1H, s, CH); δ 1.442 (2H, s, CH_2)
pH: 7.24
Melting Point: 198-200 °C
Elemental analysis: Carbon 91.16; Hydrogen 7.39
Expected: Carbon 89.66; Hydrogen 10.34

6.1.3 Method Two

As above but with Aerosol OT replacing the SDS as the surfactant and the addition of 2.2 mmol (2.5 g) cyclodextrin to the reaction mixture as an aid to butadiene solubility.
Yield: 24%
Solid content: 3% (12.6% expected)
Butadiene Content: Either not present and product is polystyrene or content is too low to determine.
Particle Size: 67 nm
^{1}*H-NMR* (250 MHz, $CDCl_3$): δ 7.123 (2H, m, aromatic); δ 7.007 (2H, m, aromatic); δ 6.542 (2H, s, aromatic); δ 1.769 (1H, s, CH); δ 1.438 (2H, s, CH_2)
pH: 7.23

Melting Point: 197-199 °C
Elemental analysis: Carbon 90.71; Hydrogen 7.44
Expected: Carbon 89.66; Hydrogen 10.34

6.1.4 Method Three

As above but this system utilises water as the heat transfer medium, Aerosol OT as the surfactant and a different cumene hydroperoxide redox system as the initiator as widely used in industry and described in the Encyclopedia of Chemical Processing. [70] Aerosol OT was kept as the surfactant, replacing the SFS used in the cited recipe as the Aerosol OT works much better under the reaction conditions used.
Yield: 40%

Reagent	Parts by weight
Styrene	25
1,3-Butadiene	75
Aerosol OT	5
Cumene hydroperoxide	0.17
Iron(II) Sulfate	0.017
EDTA	0.06
SFS	0.1

Table 6.2: Reagents for SBR synthesis

Solid content: 5% (12.6% expected)
Butadiene Content: 16% from NMR data (expected 75%)
Particle Size: 50 nm
^{1}*H-NMR* (250 MHz, $CDCl_3$): δ 7.084 (2H, m, aromatic); δ 6.916 (2H, m, aromatic); δ 6.644 (2H, s, aromatic); δ 5.0742 (2H, m, vinyl); δ 1.855 (1H, s, CH); δ 1.813 (4H, m, CH_2); δ 1.439(2H, m, CH_2)
pH: 7.23
Melting Point: 184-187 °C
Elemental analysis: Carbon 80.89; Hydrogen 7.36

Expected: Carbon 89.66; Hydrogen 10.34

6.1.5 Method Three With 1,3-Butadiene Condenser

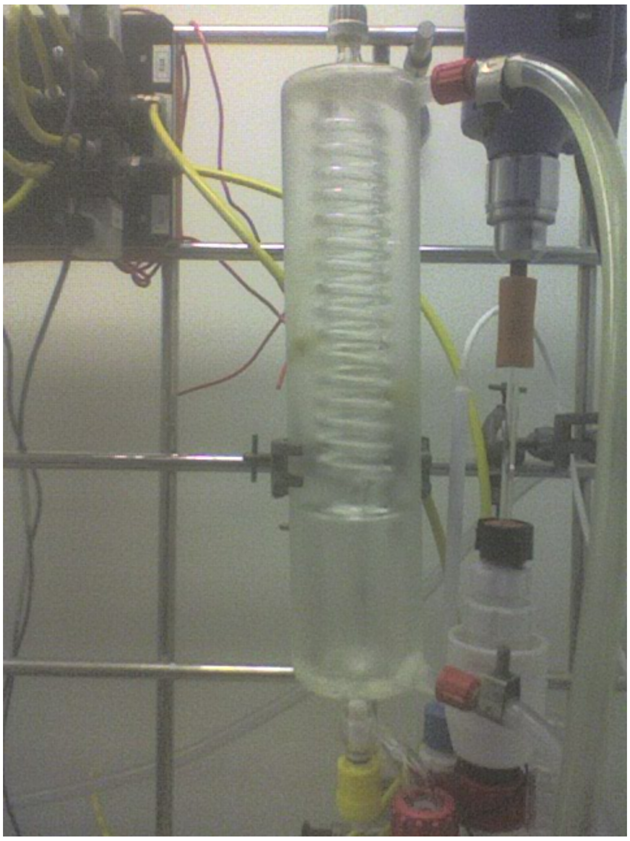


Figure 6.2: Condenser for 1,3-Butadiene - With cladding removed to display the heat exchanger

As previous method but with 1,3-butadiene gas being condensed into a liquid prior to addition to the reaction mixture. As can be seen in Fig. 6.2 the butadiene condenser allows for the passage of the butadiene gas through a spiral heat exchange column which is surrounded by circulating ethanol cooled to -10 °C . This allows the butadiene gas to condense visibly in the reservoir at the bottom of the heat transfer spiral. The tap can then be opened and the liquid butadiene allowed to flow into the reaction vessel. The 1,3-butadiene enters at the top as it has a vapour density of 1.87 relative to air and so will travel down the column without need for pumping.
Yield: 79%
Solid content: 10% (12.6% expected)

Butadiene Content: 69% from NMR data (expected 75%)
^{1}*H-NMR* (250 MHz, $CDCl_3$): δ 7.235 (2H, m, aromatic); δ 7.169 (2H, m, aromatic); δ 7.013 (2H, s, aromatic); δ 5.340 (2H, m, vinyl); δ 1.947 (1H, s, CH); δ 1.899 (4H, m, CH_2); δ 1.743(2H, m, CH_2)
pH: 7.24
Melting Point: 162-164 °C
Elemental analysis: Carbon 74.17; Hydrogen 7.30
Expected: Carbon 89.66; Hydrogen 10.34

6.1.6 SBR Containing 9-Vinylanthracene

As above, but using 0.2 mol (20.6 g) of styrene and with the addition of 3.7 mmol (0.75 g) 9-vinylanthracene (1 wt%) The product was an off-white solid that following isolation was stored in a sample tube wrapped in tinfoil to protect the fluorescent label.
Yield: 79%
Solid content: 10% (12.7% expected)
*Butadiene Content:*Not determinable from NMR data (expected 75%)
Particle Size: 236 nm
^{1}*H-NMR* (250 MHz, $CDCl_3$): δ 7.198 (9H, m, aromatic); δ 6.604 (5H, m, aromatic); δ 4.972 (2H, m, vinyl); δ 1.908 (6H, m, CH); δ 1.449 (4H, m, CH_2);
pH: 7.25
Melting Point: 162-165 °C
Elemental analysis: Carbon 75.11; Hydrogen 7.24
Expected: Carbon 89.79; Hydrogen 10.21

6.1.7 SBR Containing 9-Vinylanthracene and 4-Bromostyrene

As above, but using 0.19 mol (19.7 g) of styrene and with the addition of 8.2 mmol (1.5 g) 4-bromostyrene along with the 3.7 mmol (0.75 g) 9-vinylanthracene. Again, the product was an off-white solid that following isolation was stored in a sample tube wrapped in tinfoil to protect the fluorescent label.
Yield: 78%
Solid content: 10% (12.9% expected)
Butadiene Content: Not determinable from NMR data (expected 75%)
Particle Size: 133 nm

^{1}*H-NMR* (250 MHz, $CDCl_3$): δ 6.924 (13H, m, aromatic); δ 6.701 (5H, m, aromatic); δ 4.960 (2H, m, vinyl); δ 1.981 (7H, m, CH); δ 1.409 (4H, m, CH_2);
pH: 7.24
Melting Point: 164-167 °C
Elemental analysis: Carbon 77.32; Hydrogen 7.26; Bromine 1.74
Expected: Carbon 89.03; Hydrogen 10.11; Bromine 0.86

6.2 Synthesis of Acrylate Polymers

6.2.1 Materials

All reagents were obtained from Sigma-Aldrich and used as received unless listed below. 4-bromostyrene (Bp 49.5 °C) inhibited by tert-butyl catechol was washed three times with 100 ml 10 % NaOH $_{(aq)}$ and three times with 200 ml deionised water to remove the inhibitor before drying with $MgSO_4$ and distilling under reduced pressure. DBA (Bp 159 °C) and hexylacrylate (Bp 88 °C) were washed three times with 100 ml 5% NaOH $_{(aq.)}$ then three times with 300 ml deionised water before being distilled from CaH_2 under reduced pressure. AIBN was recrystallised from diethyl ether. Deionised water was obtained from a Millipore Direct-Q 3 ultrapure water system. All solvents were laboratory reagent grade, obtained from the departmental chemical stores and sourced from Fisher.

6.2.2 Synthesis of Linear Acrylate Polymer

Hexylacrylate (25 g, 0.16 mol) and the thermal initiator AIBN (25 mg, 0.15 mmol) were added to a clean, dry glass ampoule with a quick-fit connector. A Schlenk line (vacuum gas manifold) was used to perform freeze-pump thaw degassing cycles on the contents of the ampoule to remove oxygen prior to curing. The ampoule was then attached to a port on the Schlenk line connected to a high vacuum pump fitted with a liquid nitrogen cooled cold trap. Each cycle comprised of the following steps.

- Closing of all taps connecting the ampoule to the vacuum line
- Complete freezing of the contents of the ampoule using a Dewar of liquid nitrogen
- Opening of the taps connecting the ampoule to the vacuum line to allow evacuation of the ampoule's atmosphere. This was judged by the reduction of the pressure across the line to 10^{-4} mbar.

- Closing of all taps connecting the ampoule to the vacuum line
- Complete thawing of the contents of the ampoule using a beaker of room temperature water - degassing of the monomer blend occurs in this step and should be visible as bubbles rising through the liquid

Each ampoule was subjected to at least three freeze-pump-thaw cycles with additional cycles undertaken as needed until bubbles were not observed during the thawing step. Then the neck of the ampoule was sealed using a blowtorch and the sealed ampoule removed from the Schlenk line. The ampoule was then placed in a thermostated water bath at 60 °C and allowed to react for 24 hours. The monomer blend containing no fluorescent label gelled.

6.2.3 Synthesis of Labelled Linear Acrylate Polymer

As above but with the monomer blend comprising of hexylacrylate (24.75 g, 0.158 mol), 9-vinylanthracene (0.25 g, 1.22 mmol) and the thermal initiator AIBN (25 mg, 0.15 mmol) The clear, colourless product was isolated by precipitation into a 4:1 mix of methanol:deionised water. The solvent mixture was then decanted off, the precipitation repeated with fresh solvent and then the polymer dried in vacuo at room temperature for 12 hours and stored in a foil wrapped bottle.
Yield: 93%
Molecular Weight: $M_n = 24300$, $M_w = 33300$

6.2.4 Synthesis of Labelled Linear Acrylate Polymer Containing 4-Bromostyrene

As above but with the monomer blend comprising of 9-vinylanthracene (0.25 g, 1.22 mmol) and the thermal initiator AIBN (25 mg, 0.15 mmol) with quantities of hexylacrylate and 4-bromostyrene as shown in Tab. 6.3 with results.

Hexylacrylate	4-Bromostyrene	Yield/%	M_n	M_w
24.50 g, 0.157 mol	0.25 g, 1.37 mmol	92	24500	36200
24.25 g, 0.155 mol	0.5 g, 2.73 mmol	93	23500	35000
23.50 g, 0.150 mol	1.25 g, 6.83 mmol	89	23200	34300
22.25 g, 0.142 mol	2.5 g, 13.66 mmol	90	24600	36800

Table 6.3: Monomer Blends for Synthesis of Labelled Linear Acrylate Polymer Containing 4-Bromostyrene

6.2.5 Synthesis of Cross-linked Polyacrylate Elastomers

6.2.5.1 Equipment

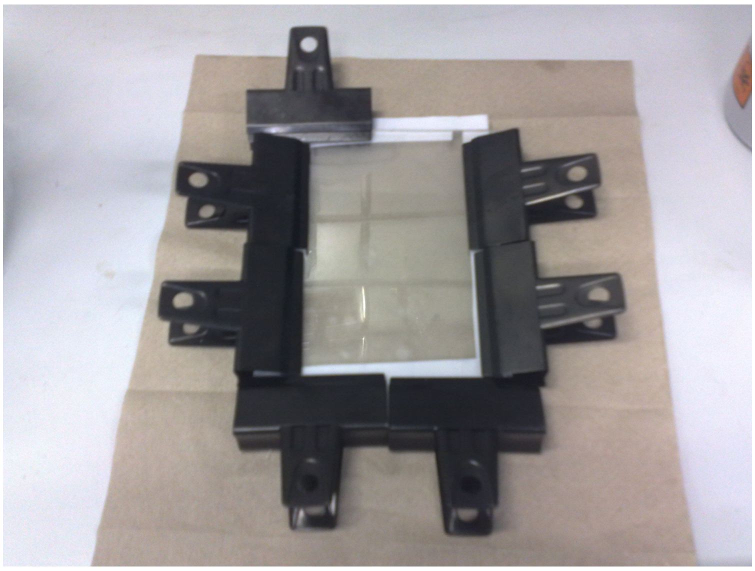


Figure 6.3: The form used to contain the monomer blend for UV curing - Showing the crystal plates and the PTFE spacer between them

The polymers were formed as sheets between two UV-transmissive quartz plates using a PTFE spacer (Fig. 6.3) The crystal plates were covered by a thin disposable sheet of polyethylene terephthalate (PET) held in place by Scotchguard mounting spray and cleaned with methanol. This allows for easy release of the polymer sheets once formed and prevents damage to the quartz plates. The PET sheets were changed and the quartz plates cleaned and dried between each synthesis.

6.2.5.2 Polyhexyl Acrylate Elastomer

Hexylacrylate (6.2 g, 39.7 mmol) and divinylbenzene (0.31 g, 2.4 mmol) were added to a sample tube and bubbled with nitrogen gas for half an hour to remove any oxygen. Then AIBN (65 mg, 0.4 mmol) was added, the sample tube capped and the contents sonicated to remove any bubbles. The monomer blend was transferred to the form (Fig. 6.3) using a syringe fitted with a hypodermic needle to reduce exposure to air. The PTFE spacer had a small channel cut into it to allow for ease and speed of injection. The reaction mixture was then initiated in a UV oven with a series of one minute exposures, the crystal plates and polymer inside were turned over and allowed to cool briefly between each exposure.

As the AIBN formed products containing bubbles, several UV initiators were substituted for the AIBN using the previous method and diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) was chosen for the speed of polymerisation and properties of the products formed.

IR: 2929 cm^{-1} (C-H); 2859 cm^{-1} (C-H); 1730 cm^{-1} (C=O); 1454 cm^{-1} (C-H bend); 1158 cm^{-1} (C-O)

Elemental analysis: Carbon 71.22; Hydrogen 9.23

Expected: Carbon 70.28; Hydrogen 10.22

6.2.5.3 Polyhexyl Acrylate Labelled with 9-vinylanthracene

As above and using TPO but with 6.14 g (39.3 mmol) hexylacrylate and the addition of 9-vinylanthracene (65 mg , 0.32 mmol)

IR: 2926 cm^{-1} (C-H); 2857 cm^{-1} (C-H); 1729 cm^{-1} (C=O); 1455 cm^{-1} (C-H bend); 1159 cm^{-1} (C-O)

Elemental analysis: Carbon 72.48; Hydrogen 9.45

Expected: Carbon 70.31; Hydrogen 10.22

6.2.5.4 Polyhexyl Acrylate Labelled with 9-Vinylanthracene, Quenched with 4-Bromostyrene

As previously but with the monomer blend comprising of divinylbenzene (0.31 g, 2.4 mmol,) 9-vinylanthracene (65 mg, 0.32 mmol) and the UV initiator TPO with quantities of hexylacrylate and 4-bromostyrene as shown in Tab. 6.4 with results.

IR: 2927 cm^{-1} (C-H); 2857 cm^{-1} (C-H); 1728 cm^{-1} (C=O); 1451 cm^{-1} (C-H bend); 1158

cm^{-1} (C-O)

6.3 Polyurethane Acrylate Polymers

All solvents except the dimethylsulfoxide (DMSO 99.9%; anhydrous with SureSeal cap from Aldrich) were laboratory reagent grade, obtained from the departmental chemical stores and sourced from Fisher. All reagents were obtained from Sigma-Aldrich and used as received unless listed below. The polycaprolactone diol used has average molecular weight of 530.

6.3.1 Linear Polyurethane Acrylate Prepolymer Synthesis

The properties of polyurethanes are governed by the soft segment content. This can be set at the desired weight fraction and the following calculations used to establish the reagent quantities:

$$SoftSegmentContent = W_S/W_S + W_H \qquad \text{(Equation 9.1)}$$

Where W_S is the weight of the soft segment and W_H is the weight of the hard segment.

$$SoftSegmentContent = W_S/(W_S + W_I + (W_S/M_N + W_I/M_I)M_D) \quad \text{(Equation 9.2)}$$

Where W_I is the weight of diisocyanate, M_I is the molar mass of the diisocyanate, M_N is the molar mass of the diol and M_D is the molar mass of the acrylate.

It is essential to use completely dry reagents and exclude water from the reaction vessel to prevent unwanted side reactions and foaming.

6.3.2 MDI Based Linear Polyurethane Acrylate Prepolymer Synthesis

Using Equation 9.2 (6.3.1) to calculate the mass of MDI required to give 50% soft segment content.

Hexylacrylate	4-Bromostyrene	C	C expected	H	H expected	Br	Br expected
6.08 g, 38.9 mmol	65 mg, 0.36 mmol	73.11	70.35	9.44	10.11	ND	0.43
6.01 g, 38.5 mmol	0.13 g, 0.71 mmol	71.44	70.17	9.13	10.06	1.05	0.85
5.82 g, 37.2 mmol	0.33 g, 1.78 mmol	72.94	69.67	8.68	9.88	2.48	2.08
5.49 g, 35.1 mmol	0.65 g, 3.55 mmol	70.90	68.89	8.52	9.61	4.37	3.96

Table 6.4: Monomer blends for synthesis of labelled cross-linked acrylate polymer containing 4-bromostyrene

$$0.5 = 53/53 + W_I + (53/530 + W_I/250.25)116.12$$

Which solves to give $W_I = 44.13$ which is then used in Equation 9.1 (6.3.1) to calculate W_D, the desired mass of HEA to be added.

$$0.5 = 53/53 + (44.13 + W_D)$$

Which solves to give $W_D = 8.87$ (76.4 mmol)

A 500 ml flange flask with a four neck lid was washed, dried overnight and the centre neck fitted with a PTFE coated paddle for an overhead stirrer using a PTFE bung with a hole the right size for the stirrer shaft. The flange flask was then clamped together with PTFE spacer between the flask and the lid to ensure a tight fit and prevent damage. The other necks were fitted with a nitrogen bubbler, a temperature probe and a stopper. The flask was then purged with nitrogen and 53 g (0.1 mol) polycaprolactone diol added and heated under a nitrogen atmosphere to 80°C using a paraffin filled oil bath and a stirrer hotplate. The stirrer paddle shaft was attached to a high powered overhead stirrer and the contents of the flask stirred vigorously. The flask was kept at 80°C for two hours before being cooled to 40°C.

Meanwhile MDI (44g, 0.18 mol) was added to a round-bottomed flask under a nitrogen atmosphere. The reagent bottle containing the remainder of the MDI was also purged with nitrogen before returning to storage. This MDI was then dissolved in minimal DMSO (around 30 ml.) Once the polycaprolactone diol had cooled to 40°C, the solvated MDI was added by funnel through the stoppered neck of the flange flask with the flask being open to air for the shortest possible time. After the reagents had mixed well, 2-3 drops of dibutyltin dilaurate was added to catalyse the reaction. As the reaction is exothermic the temperature of the mixture may rise as the reagents react. The temperature is monitored via the probe. It is important to avoid the exothermic reaction carrying the mixture above 70°C, as this could cause the reaction mixture to gel. If the reaction mixture reached 55°C the oil bath was removed and an acetone icebath used to cool the reaction vessel. Once the reaction returned to 40°C, the oil bath was used again. The reaction was allowed to proceed for two hours at 40°C with vigorous stirring maintained throughout.

After two hours, the free NCO content of the prepolymer was determined by back titration using dibutylamine and hydrochloric acid as is standard industrial practice [95]. This was achieved by removing three samples ($\sim$ 2 g) of the polyurethane, recording their mass and adding them each to a conical flask. The flasks were then purged with nitrogen and 20 cm^3 of 1N dibutylamine (DBA) in toluene added to each. The mixtures were swirled, capped and heated gently for 10 minutes to encourage complete reaction before allowing to cool and titrating with 1N HCl in toluene using bromocresol green (yellow/green at end point) as an indicator. Blank values were obtained and determined by the direct titration of 20 cm^3 of 1N DBA plus 10 cm^3 of toluene with 1N HCl using a few drops of bromocresol green as an indicator. Both the sample and the blank titre values were only accepted if they agreed within 0.1 cm^3. The titre values were then used in the following equation:

$$\text{NCO } molg^{-1} = T_B - T_I M_{HCL}/1000/W_I \qquad \text{(Equation 9.3)}$$

Where T_B is the blank titre, T_I is the sample titre and W_I is the mass of sample used. This equation gives the moles of free NCO per g of sample. The titrations were run in triplicate so the outcome of Equation 9.3 (6.3.2) was averaged for the three values obtained. This value was then multiplied by the total mass of the reaction mixture (minus the amount removed for titration samples) to give the total free NCO content of the entire reaction mixture in moles. This should roughly agree with the outcome of Equation 9.1 (6.3.1) and if it is much greater then the reaction would be allowed to proceed for half an hour before titrations were performed again. Once the free NCO content is in line with the expected value, a stoichiometric quantity of HEA (8.54 g, 73.5 mmol) was then added and the reaction allowed to continue at 40°C.

Another sample was checked by back titration half an hour after the addition of the hydroxyl ethyl acrylate to ensure that there were no isocyanate groups remaining and the polymer chain ends were all acrylated. If NCO was still present, a stoichiometric quantity of HEA was added again and the reaction continued for another half hour before another set of titrations. If the sample titration values matched with the value for the blanks then the product was collected and stored in the freezer to be isolated by precipitation into 2-propanol as required.

Molecular Weight: $M_n = 4350$, $M_w = 3860$

Elemental Analysis: Carbon 67.91; Hydrogen 3.24; Nitrogen 9.04

Expected: Carbon 68.69; Hydrogen 4.51; Nitrogen 9.37

IR: 3317 cm^{-1} (N-H); 2939 cm^{-1} (C-H); 2872 cm^{-1} (C-H); 1725 cm^{-1} (C=O);1542 cm^{-1} (C=C)

6.3.3 HDI Based Linear Polyurethane Acrylate Prepolymer Synthesis

As previous but using HDI (38.2 g, 0.23 mol), HEA (15.1 g, 0.13 mol) and no DMSO.
Molecular Weight: $M_n = 2860$, $M_w = 4350$
Elemental Analysis: Carbon 53.88; Hydrogen 2.2; Nitrogen 8.22
Expected: Carbon 66.24; Hydrogen 4.86, Nitrogen 8.02
IR: 3325 cm^{-1} (N-H); 2941 cm^{-1} (=C-H); 2873 cm^{-1} (C-H); 1727 cm^{-1} (C=O); 1536 cm^{-1} (C=C)

6.3.4 IPDI Based Linear Polyurethane Acrylate Prepolymer Synthesis

As previous but using IPDI (42.4 g, 0.19 mol), HEA (10.4 g, 89.6 mmol) and no DMSO.
Molecular Weight: $M_n = 4140$, $M_w = 5700$
Elemental Analysis: Carbon 59.71; Hydrogen 4.12; Nitrogen 9.26
Expected: Carbon 62.25; Hydrogen 7.94; Nitrogen 10.12
IR: 3441 cm^{-1} (N-H); 3376 cm^{-1} (N-H); 3062 cm^{-1} (=C-H)
2961 cm^{-1} (C-H); 2868 cm^{-1} (C-H); 1738 cm^{-1} (C=O); 1522 cm^{-1} (C=C)

6.3.5 1,5-Dihydroxynaphthalene Labelled IPDI Linear Polyurethane Acrylate Prepolymer Synthesis

As previous but using HEA (8.47 g, 72.9 mmol) with 1,5-Dihydroxynaphthalene (2.12 g, 13.2 mmol) added as a chain extender following the 2 hour reaction between the polycaprolactone diol and the IPDI. Following the addition of 1,5-Dihydroxynaphthalene, the reaction was allowed to proceed for a further half an hour at 40°C before aliquots were removed for titration as previously described.
Molecular Weight: $M_n = 4240$, $M_w = 2800$
Elemental Analysis: Carbon 57.21; Hydrogen 4.29; Nitrogen 9.70
Expected: Carbon 63.14; Hydrogen 7.86; Nitrogen 10.08
IR: 3452 cm^{-1} (N-H); 3362 cm^{-1} (N-H); 3058 cm^{-1} (=C-H); 2963 cm^{-1} (C-H); 2877 cm^{-1}

(C-H); 1725 cm^{-1} (C=O); 1528 cm^{-1} (C=C)

6.3.6 Fluorescein Labelled IPDI Linear Polyurethane Acrylate Prepolymer Synthesis

The flange flask was set up as previously described but heated to 80°C containing only nitrogen and then allowed to cool to 50 °C. Fluorescein (2.12 g, 6.38 mmol) and IPDI (42.4 g, 0.19 mol) were then added to the flask and mixed well before 2-3 drops of dibutyltin dilaurate was added to catalyse the reaction. The reaction was allowed to proceed at 50 °C, ensuring the temperature did not rise above 70 °C. During this time, the polycaprolactone diol (50.9 g, 96 mmol) was separately dried in vacuo at 60°C in a clean dry beaker. After two hours, the reaction was allowed to cool to 40 °C before the dry polycaprolactone diol (50.9 g, 96 mmol) was added and the reaction was allowed to proceed for two hours at 40°C before aliquots were removed for titration as previously described. This reaction used (10.6 g, 91.5 mmol) HEA.
Molecular Weight: $M_n = 3700$, $M_w = 4900$
Elemental Analysis: Carbon 59.66; Hydrogen 5.05; Nitrogen 9.36
*Expected:*Carbon 62.60; Hydrogen 7.77; Nitrogen 9.70
IR: 3451 cm^{-1} (N-H); 3389 cm^{-1} (N-H); 3062 cm^{-1} (=C-H); 2962 cm^{-1} (C-H); 2878 cm^{-1} (C-H); 1733 cm^{-1} (C=O); 1528 cm^{-1} (C=C)

6.3.7 3-Bromo-1,2-propanediol Containing IPDI Linear Polyurethane Acrylate Prepolymer Synthesis

As previous but using 3-Bromo-1,2-propanediol (2.12 g, 13.7 mmol) in place of fluorescein and HEA (11.1 g, 95.6 mmol)
Molecular Weight: $M_n = 4120$, $M_w = 4760$
Elemental Analysis: Carbon 55.16; Hydrogen 4.25; Nitrogen 9.34; Bromine 0.95
*Expected:*Carbon 60.63; Hydrogen 7.80; Nitrogen 9.61; Bromine 1.96
IR: 3448 cm^{-1} (N-H); 3369 cm^{-1} (N-H); 3061 cm^{-1} (=C-H); 2959 cm^{-1} (C-H); 2878 cm^{-1} (C-H); 1731 cm^{-1} (C=O); 1541 cm^{-1} (C=C)

6.3.8 Synthesis of Crosslinked Polyurethane Acrylate Elastomers

The polymers were formed as sheets between two UV-transmissive quartz plates using a PTFE spacer (Fig. 6.3) as previously described. 70 mg TPO was weighed out into a sample tube and 2 g poly(ethylene glycol) diacrylate (average molecular weight 700) added. The sample tube was capped and the reagents vortexed to blend. 5 g IPDI based polyurethane acrylate prepolymer was then added and the mixture vortexed again. The reagents were bubbled through with nitrogen gas using clean, dry needle for half an hour to remove any oxygen. The sample tube was then capped and the contents sonicated to drive out any bubbles. The monomer mixture was then injected in between coated crystal plates cured in a UV oven as described previously.
Elemental Analysis: Carbon 58.78; Hydrogen 3.08; Nitrogen 7.55
Expected: Carbon 58.34; Hydrogen 5.33; Nitrogen 6.61
IR: 3369 cm^{-1} (N-H); 2927 cm^{-1} (C-H); 2865 cm^{-1} (C-H); 1716 cm^{-1} (C=O)

6.3.9 Synthesis of 1,5-Dihydroxynaphthalene Labelled Crosslinked Polyurethane Acrylate Elastomers

As previous but using 4.65 g IPDI based polyurethane acrylate prepolymer and 0.35 g 1,5-dihydroxynaphthalene labelled IPDI based polyurethane acrylate prepolymer.
Elemental Analysis: Carbon 58.77; Hydrogen 3.20; Nitrogen 7.74
Expected: Carbon 58.21; Hydrogen 5.34; Nitrogen 6.63
IR: 3363 cm^{-1} (N-H); 2949 cm^{-1} (C-H); 2873 cm^{-1} (C-H); 1715 cm^{-1} (C=O); 1529 cm^{-1} (C=C)

6.3.10 Synthesis of 1,5-Dihydroxynaphthalene Labelled 3-Bromo-1,2-propanediol Containing Crosslinked Polyurethane Acrylate Elastomers

As previously but using quantities of IPDI based polyurethane acrylate prepolymer and 3-Bromo-1,2-propanediol containing IPDI based polyurethane acrylate prepolymer as shown in Tab. 6.5 with results.
IR: 3341 cm^{-1} (N-H); 2948 cm^{-1} (C-H); 2797 cm^{-1} (C-H); 1715 cm^{-1} (C=O); 1531 cm^{-1}

(C=C)

6.3.11 Synthesis of Fluorescein Labelled Crosslinked Polyurethane Acrylate Elastomers

As previous but using 4.65 g IPDI based polyurethane acrylate prepolymer and 0.35 g fluorescein labelled IPDI based polyurethane acrylate prepolymer
Elemental Analysis: Carbon 58.92; Hydrogen 3.52; Nitrogen 7.85
Expected: Carbon 58.33; Hydrogen 5.38; Nitrogen 6.63
IR: 3363 cm^{-1} (N-H); 2948 cm^{-1} (C-H); 2873 cm^{-1} (C-H); 1712 cm^{-1} (C=O); 1529 cm^{-1} (C=C)

6.3.12 Synthesis of Fluorescein Labelled 3-Bromo-1,2-propanediol Containing Crosslinked Polyurethane Acrylate Elastomers

As previously but using quantities of IPDI based polyurethane acrylate prepolymer and 3-Bromo-1,2-propanediol containing IPDI based polyurethane acrylate prepolymer as shown in Tab. 6.6 with results.
IR: 3342 cm^{-1} (N-H); 2949 cm^{-1} (C-H); 2869 cm^{-1} (C-H); 1713 cm^{-1} (C=O); 1529 cm^{-1} (C=C)

6.4 Polyurethane Polymers

6.4.1 Materials

All reagents were obtained from Sigma-Aldrich and used as received unless listed below. All solvents were laboratory reagent grade, obtained from the departmental chemical stores and sourced from Fisher. Voranol 3322 was supplied by Dow Chemical Company and dried in vacuo for 24 hours at 60 °C prior to use.

IPDI-PP	BPD-PP	C	C expected	H	H expected	N	N expected	Br	Br expected
4.30 g	0.35 g	58.08	57.98	2.88	5.35	8.56	6.64	ND	0.048
3.95 g	0.7 g	58.68	57.75	3.12	5.35	8.39	6.64	ND	0.095
2.90 g	1.75 g	59.43	57.07	3.42	5.37	8.17	6.66	ND	0.24

Table 6.5: Monomer blends for synthesis of 1,5-dihydroxynaphthalene labelled cross-linked polyurethane acrylate polymer with 3-bromo-1,2-propanediol - IPDI-PP = IPDI based polyurethane acrylate prepolymer, BPD-PP = 3-Bromo-1,2-propanediol containing IPDI based polyurethane acrylate prepolymer, exp = expected value.

IPDI-PP	BPD-PP	C	C expected	H	H expected	N	N expected	Br	Br expected
4.30 g	0.35 g	59.00	58.11	3.49	5.39	8.21	6.62	ND	0.048
2.90 g	1.75 g	58.09	57.20	3.59	5.41	8.50	6.64	0.46	0.24
1.15 g	3.5 g	58.93	56.06	3.36	5.45	8.04	6.66	0.94	0.48

Table 6.6: Monomer blends for synthesis of fluorescein labelled cross-linked polyurethane acrylate polymer with 3-bromo-1,2-propanediol - IPDI-PP = IPDI based polyurethane acrylate prepolymer, BPD-PP = 3-Bromo-1,2-propanediol containing IPDI based polyurethane acrylate prepolymer

6.4.2 Synthesis of IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer

The flange flask was set up as previously described and heated to 80 °C containing only nitrogen and then allowed to cool to 50 °C. 1,5-dihydroxynaphthalene (8.0 g, 50 mmol) and IPDI (33.35 g, 0.15 mol) were added to the vessel. Once the reagents were well mixed, 2-3 drops of dibutyltin dilaurate were added. And the reaction allowed to proceed at 50 °C for 2 hours. As before, care was taken to not allow the reaction temperature to exceed 70 °C and vigorous stirring was maintained throughout the reaction. After 2 hours, the reaction mixture was titrated for free NCO content as previously described (6.3.2) and the values recorded to allow accurate formulation for subsequent solid sheets.
Elemental Analysis: Carbon 65.50; Hydrogen 8.89; Nitrogen 12.80
Expected: Carbon 66.80; Hydrogen 7.57; Nitrogen 10.17
IR: 3430 cm^{-1} (N-H); 3055 cm^{-1} (=C-H); 2985 cm^{-1} (C-H); 2959 cm^{-1} (C-H); 2262 cm^{-1} (N=C=O); 1602 cm^{-1} (C=C)
^{1}*H-NMR* (400 MHz, $CDCl_3$): δ 7.832 (2H, m, aromatic); δ 7.492 (2H, m, aromatic); δ 7.299 (2H, m, aromatic); δ 3.543 (1H, t, CH); δ 3.402 (2H, dd, CH_2); δ 1.839 (6H, m, CH_2); δ 1.211 (3H, m, CH, CH_2)

6.4.3 Synthesis of IPDI Terminated Fluorescein Prepolymer

As previous but with IPDI (33.35 g, 0.15 mol) and fluorescein (16.62 g, 50 mmol)
Elemental Analysis: Carbon 65.53; Hydrogen 9.24; Nitrogen 12.95
Expected: Carbon 67.31; Hydrogen 6.67; Nitrogen 8.41
IR: 3321 cm^{-1} (N-H); 3056 cm^{-1} (=C-H); 2957 cm^{-1} (C-H); 2263 cm^{-1} (N=C=O); 1609 cm^{-1} (C=C)
^{1}*H-NMR* (400 MHz, $CDCl_3$): δ 3.540 (1H, t, CH); δ 3.302 (2H, dd, CH_2); δ 1.789 (6H, m, CH_2); δ 1.156 (3H, m, CH, CH_2)

6.4.4 Synthesis of IPDI Terminated 4-Bromoresorcinol Prepolymer

As previous but with IPDI (33.35 g, 0.15 mol) and 4-bromoresorcinol (9.45 g, 50 mmol)
Elemental Analysis: Carbon 59.40; Hydrogen 7.91; Nitrogen 9.34; Bromine 6.59

Expected: Carbon 58.93; Hydrogen 6.96; Nitrogen 9.82; Bromine 9.33
IR: 3426 cm^{-1} (N-H); 3056 cm^{-1} (=C-H); 2958 cm^{-1} (C-H); 2262 cm^{-1} (N=C=O); 1599 cm^{-1} (C=C)
^{1}*H-NMR* (400 MHz, $CDCl_3$): δ 7.683 (H, m, aromatic); δ 7.138 (1H, m, aromatic); δ 76.944 (1H, m, aromatic); δ 3.502 (1H, t, CH); δ 3.398 (2H, dd, CH_2); δ 1.799 (6H, m, CH_2); δ 1.202 (3H, m, CH, CH_2)

6.4.5 Synthesis of Crosslinked Polyurethane Elastomers

The Voranol 3322 was back titrated using acetic anhydride to determine the hydroxyl value using the standard industry method as described by Lubrizol [115] which was found to be 45. This was used to calculate the equivalent weight of OH groups (this is the mass required to give one mole of OH.) As the molecular formula of isophorone diisocyanate is discreet and known, the equivalent weight of NCO groups can be calculated without the need for titrations. However the IPDI terminated prepolymers required titrating for exact NCO content as described previously (section 6.3.2) The mass of IPDI and IPDI prepolymers used were calculated to give a total NCO content of 1.05 times the total OH content (calculated from the mass of Voranol and 1,4-Butanediol used.)

Voranol (5 g, 1.34 mmol), 1,4-butanediol (0.5 g, 5.5 mmol) and IPDI (1.76 g, 7.9 mmol) were added to a sample tube which was capped and vortexed to mix the reagents. Once the reagents were well blended, the reaction mixture was sonicated to remove any bubbles. 2-3 drops dibutyltin dilaurate was added and the reaction mixture swirled gently to mix before being immediately poured onto a pre-prepared petri dish coated with PTFE dry release spray. The petri dish was gently tilted to provide an even coating on the whole surface. The petri dish containing the reaction mixture was left to cure for 48 hours in a vented fume cupboard. Once the reaction was complete, the polymer was released from the petri dish to give a clear, colourless elastomeric sheet.
Elemental Analysis: Carbon 60.84; Hydrogen 10.04; Nitrogen 3.02
Expected: Carbon 61.17; Hydrogen 9.79; Nitrogen 3.06
IR: 3316 cm^{-1} (N-H); 2969 cm^{-1} (C-H); 2866 cm^{-1} (C-H); 1093 cm^{-1} (C-O)

6.4.6 Synthesis of 1,5-Dihydroxynaphthalene Labelled Crosslinked Polyurethane Elastomers

IPDI (1.74 g, 7.83 mmol) and IPDI terminated 1,5-dihydroxynaphthalene prepolymer (0.015 g) were added to a sample tube which was capped and vortexed to mix the reagents well and solvate the prepolymer within the IPDI. Once the isocyanate functional reagents were well blended, Voranol (5 g, 1.34 mmol) and 1,4-butanediol (0.5 g, 5.5 mmol) were added to the reaction mixture which was then briefly vortexed and sonicated to remove any bubbles. 2-3 drops dibutyltin dilaurate was added and the reaction mixture poured onto a petri dish and cured as described previously.
Elemental Analysis: Carbon 60.70; Hydrogen 10.13; Nitrogen 3.13
Expected: Carbon 61.26; Hydrogen 9.77; Nitrogen 3.22
IR: 3309 cm^{-1} (N-H); 3032 cm^{-1} (=C-H); 2970 cm^{-1} (C-H); 2871 cm^{-1} (C-H); 1600 cm^{-1} (C=C) 1095 cm^{-1} (C-O)

6.4.7 Synthesis of 1,5-Dihydroxynaphthalene labelled 3-Bromo-1,2-propanediol containing Crosslinked Polyurethane Elastomers

As previously but using quantities of IPDI, IPDI terminated 1,5-dihydroxynaphthalene prepolymer and 3-Bromo-1,2-propanediol as shown in Tab. 6.7 with results.
IR: 3327 cm^{-1} (N-H); 3040cm^{-1} (=C-H); 2968 cm^{-1} (C-H); 2869 cm^{-1} (C-H); 1594 cm^{-1} (C=C) 1095 cm^{-1} (C-O)

6.4.8 Synthesis of 1,5-Dihydroxynaphthalene Labelled 4-Bromoresorcinol Containing Crosslinked Polyurethane Elastomers

As previously but using quantities of IPDI and IPDI-terminated 4-bromoresorcinol and 1,5-dihydroxynaphthalene prepolymers as shown in Tab. 6.8 with results.
IR: 3329 cm^{-1} (N-H); 3028 cm^{-1} (=C-H); 29868 cm^{-1} (C-H); 1595cm^{-1} (C=C) 1097 cm^{-1} (C-O)

IPDI	DHN-PP	BPD	C	C exp	H	H exp	N	N exp	Br	Br exp
1.88 g,8.46 mmol	0.14 g	0.08 g, 0.52 mmol	60.36	60.92	10.19	9.69	3.17	3.35	0.84	0.54
2.4 g, 10.8 mmol	0.16	0.43 g, 2.77 mmol	58.86	59.61	9.99	9.38	3.46	3.80	2.30	2.61
3.26 g, 14.7 mmol	0.19	1.0 g,6.45 mmol	57.33	58.0	9.47	9.0	4.23	4.37	7.51	5.18

Table 6.7: Monomer blends for synthesis of 1,5-dihydroxynaphthalene labelled cross-linked polyurethane polymer with 3-bromo-1,2-propanediol - DHN-PP = IPDI terminated 1,5-dihydroxynaphthalene prepolymer, BPD = 3-Bromo-1,2-propanediol, exp = expected value

IPDI	DHN-PP	BRR-PP	C	C exp	H	H exp	N	N exp	Br	Br exp
1.54 g, 6.93 mmol	0.14 g	0.54 g	60.22	61.03	10.21	9.68	2.67	3.40	2.41	0.46
1.24 g, 5.58 mmol	0.16 g	1.36 g	60.27	60.74	9.96	9.56	3.53	3.68	2.68	1.09
0.61 g, 2.74 mmol	0.18 g	3.05 g	60.17	60.23	10.12	9.35	4.32	4.12	3.59	2.15

Table 6.8: Monomer blends for synthesis of 1,5-dihydroxynaphthalene labelled cross-linked polyurethane polymer with 4-bromoresorcinol - BRR-PP = IPDI terminated 4-bromoresorcinol prepolymer, DHN-PP = IPDI terminated 1,5-dihydroxynaphthalene prepolymer, exp = expected value

6.4.9 Synthesis of Fluorescein Labelled Crosslinked Polyurethane Elastomers

As previous but using 1.4 g (6.30 mmol) IPDI and 0.37 g IPDI terminated fluorescein prepolymer.
Elemental Analysis: Carbon 60.79; Hydrogen 10.11, Nitrogen 3.01
Expected: Carbon 61.21; Hydrogen 9.84, Nitrogen 3.09
IR: 3328 cm^{-1} (N-H); 3022 cm^{-1} (=C-H); 2969 cm^{-1} (C-H); 2869 cm^{-1} (C-H); 1611 cm^{-1} (C=C) 1095 cm^{-1} (C-O)

6.4.10 Synthesis of Fluorescein Labelled 3-Bromo-1,2-propanediol Containing Crosslinked Polyurethane Elastomers

As previously but using quantities of IPDI and 3-bromo-1,2-propanediol as shown in Tab. 6.9 with results.
IR: 3328 cm^{-1} (N-H); 3018 cm^{-1} (=C-H); 2969 cm^{-1} (C-H); 2870 cm^{-1} (C-H); 1603 cm^{-1} (C=C) 1096 cm^{-1} (C-O)

6.4.11 Synthesis of Fluorescein Labelled 4-Bromoresorcinol Containing Crosslinked Polyurethane Elastomers

As previously but using quantities of IPDI and IPDI-terminated 4-bromoresorcinol prepolymer as shown in Tab. 6.10 with results.
IR: 3319 cm^{-1} (N-H); 3016 cm^{-1} (=C-H); 2970 cm^{-1} (C-H); 2870 cm^{-1} (C-H); 1599 cm^{-1} (C=C) 1097 cm^{-1} (C-O)

6.5 Polymer Characterisation

6.5.1 ^{1}HNMR

^{1}HNMR spectra were obtained using either a Bruker AMX-400 or a Bruker AC-250 spectrometer at room temperature. All spectra were analysed using TopSpin software and were

IPDI	F-PP	BRR-PP	C	C exp	H	H exp	N	N exp	Br	Br exp
1.52 g, 6.84 mmol	0.38 g	0.08 g, 0.52 mmol	60.22	60.89	10.02	9.75	3.17	3.22	1.15	0.55
2.44 g, 11.0 mmol	0.42 g	0.45 g, 2.90 mmol	59.43	59.73	9.47	9.37	4.04	4.11	3.24	2.63
2.79 g, 12.6 mmol	0.5 g	1.0 g, 6.45 mmol	57.28	57.91	9.36	9.06	4.20	4.25	5.72	5.27

Table 6.9: Monomer blends for synthesis of fluorescein labelled cross-linked polyurethane polymer with 3-bromo-1,2-propanediol - F-PP = IPDI terminated fluorescein prepolymer, BPD = 3-Bromo-1,2-propanediol, exp = expected value

IPDI	F-PP	BRR-PP	C	C exp	H	H exp	N	N exp	Br	Br exp
1.35 g, 6.07 mmol	0.4 g	0.56 g	60.98	61.08	10.70	9.71	3.68	3.51	0.53	0.47
1.06 g, 4.77 mmol	0.42 g	1.4 g	60.67	60.79	10.53	9.58	3.90	3.80	1.33	1.10
0.38g, 1.71 mmol	0.46 g	3.2 g	60.17	60.26	10.09	9.36	4.50	4.26	2.38	2.21

Table 6.10: Monomer blends for synthesis of fluorescein labelled cross-linked polyurethane polymer with 4-bromoresorcinol - BRR-PP = IPDI terminated 4-bromoresorcinol prepolymer, F-PP = IPDI terminated fluorescein prepolymer, exp = expected value

normalised using the solvent peak. ^{1}HNMR samples were made up using 40-50 mg of polymer dissolved in 1 ml of deuterated chloroform and filtered into a 7 mm NMR sample tube.

6.5.2 GPC

Gel permeation chromatography was performed using a Waters 515 HPLC pump, a Gilson234 autoinjector, an Erma ERC-7512 RI detector and a Waters Millipore Lambda-max LC model 481 Spectrophotometer. Average molecular weights were recorded for all samples relative to polystyrene standards. GPC grade THF was used as the eluent and all samples were run at room temperature with a flow rate of 1 ml/min^{-1}. The high molecular weight samples (SBR and linear polyacrylate) were run on 2x30 cm mixed-E (3 μ) PL-gel columns from Polymer Laboratories UK, these columns have an effective range of $10^1 - 10^6$. Lower molecular weight samples (polyurethane acrylate and polyurethane prepolymers) run on 3x30 cm mixed-B (10 μ) PL-gel columns from Polymer Laboratories UK, these columns have an effective range of $10^1 - 10^3$. Both column sets were fitted with a guard column and all samples were run at room temperature.

6.5.3 Elemental Analysis

Elemental analysis for carbon, hydrogen and nitrogen was carried out automatically using a Perkin-Elmer 2400 CHNS/0 series 2 elemental analyser and 5 mg of each sample was used for analysis. The bromine content of samples required 10 mg and was achieved through the classical Schöniger flask combustion method. Tolerance on all the results is 0.3%.

6.5.4 FT-IR

All FT-IR spectra were recorded at room temperature from 500-4000 cm^{-1} using a Perkin-Elmer spectrum 100 FT-IR spectrometer at room temperature. All spectra were compiled from 4 scans using Perkin-Elmer Spectrum software. All samples were analysed directly using a Perkin-Elmer universal diamond ATR (attenuated total reflectance) accessory with a spectral resolution of 4 cm^{-1}.

6.5.5 DSC

The Tg of samples were recorded using a Perkin-Elmer Pyris 1 differential scanning calorimeter with Perkin-Elmer Pyris software. The heat flow curves for all samples were recorded over two heating cycles with a cooling cycle in between held at the minimum temperature for 5 minutes to equilibrate. The ramp rate for both heating cycles was 10 °C per minute and the cooling cycle rate was 40 °C per minute. The minimum temperature for all samples was set to -90 °C. Thermal gravimetric analysis using a Perkin-Elmer Pyris 1 thermal gravimetric analyser was used to ensure that the maximum temperature for each sample was set below the decomposition temperature of the polymer in order to protect the instrument.

6.5.6 Particle Sizing/ζ-potential

Particle sizing and ζ-potential analysis were conducted using a Brookhaven Instruments Corporation Zetapals Zeta potential analyser using Brookhaven Instruments Corporation Zetapals/Zetaplus software. Samples were made up in a 1 mmol $KCl_{(aq)}$ solution for ζ-potential readings and a 10 mmol $KCl_{(aq)}$ solution for particle size readings. The samples were sonicated and filtered before analysis to remove any dust or bubbles and a 1 cm pathlength cuvette was used for all readings. All analyses were recorded in triplicate with ten runs per reading for ζ-potentials.

6.6 Fluorescence Analysis

6.6.1 Steady State (Excitation/Emission)

Excitation/Emission data were recorded using a Perkin-Elmer LS-50 spectrophotometer using FLWinlab software. Solid samples were analysed using a sliding vertical sample mounting. Liquid samples were analysed using a UV transmissive quartz cell with pathlength 1 cm. Liquid samples contained 1x10^{-2} gcm^{-2} polymer or 1x10^{-2} gcm^{-3} free label. All samples were made up from more concentrated stock solutions using an Eppendorf autopipettor to reduce error. The Eppendorf autopipettor was calibrated monthly and the calibration checked using an analytical balance before use. The pipettor was used in accordance with standard operating procedures as published by pipette manufacturers. [120] [121] Spectrophotometric grade THF was used to solvate all polymers, free 9-vinylanthracene and free 1,5-dihydroxynaphthalene and spectrophotometric grade methanol was used to solvate free fluorescein.

6.6.2 Excited State Lifetime Determination

Excited state lifetimes data were recorder using a Edinburgh Instruments System 199 Spectrophotometer, processing of the data was performed using IBH v 4.2 software. Lifetime determination using mathematical fitting was conducted in accordance with Equation 1.1

(Section 1.3.1.2) and the average lifetime calculated using Equation 1.2 (Section 1.3.1.2) for the multi-exponential fits of samples containing 1,5-dihydroxynaphthalene. Solid samples were analysed using an 90° angled sample holder with non-reflective coating. Liquid samples were analysed using a UV transmissive quartz cell with pathlength 1 cm. Liquid samples contained 1x10^{-2} gcm^{-2} polymer or 1x10^{-2} gcm^{-3} free label with the concentration of heavy atom containing species variable. All samples were made up from more concentrated stock solutions using an Eppendorf autopipettor to reduce error. Spectrophotometric grade THF was used to solvate all polymers, free 9-vinylanthracene and free 1,5-dihydroxynaphthalene. Spectrophotometric grade methanol was used to solvate free fluorescein.

Lifetimes data were recorded using a source nanoLED providing an excitation pulse of 370 nm (9-vinylanthracene labelled samples,) 195 nm (1,5-dihydroxynaphthalene labelled samples,) and 495 nm (fluorescein labelled samples,) and a detection monochromator set to λmax as determined by the steady state data shown for each sample.

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Appendix

Appendix to The Synthesis of Styrene-Butadiene Elastomers

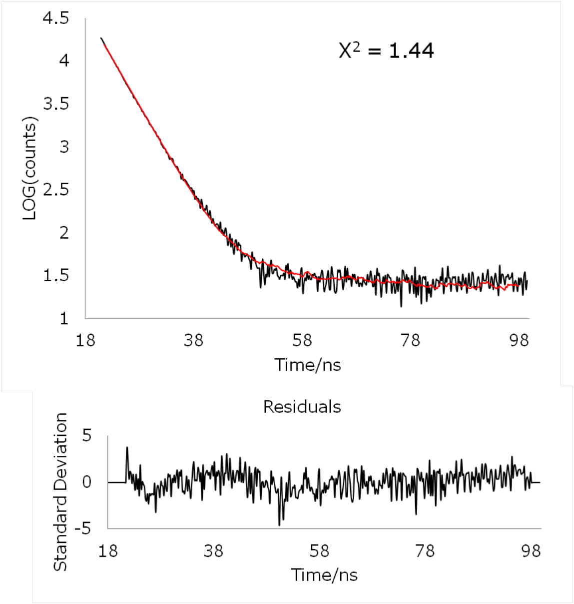

Figure 6.4: Excited State Lifetime Plot for Free 9-Vinylanthracene in the Presence of 1x10^{-2} wt% 4-Bromostyrene - Showing the mathematical fit to the single exponential in red and accompanied by a plot of the residuals from the mathematical fit.

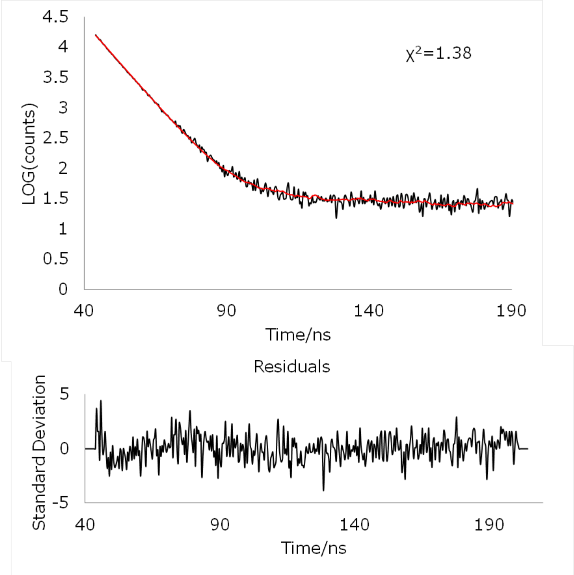

Figure 6.5: **Excited State Lifetime Plot for SBR Bound 9-Vinylanthracene in the Presence of 1x10^{-2} wt% 4-Bromostyrene** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

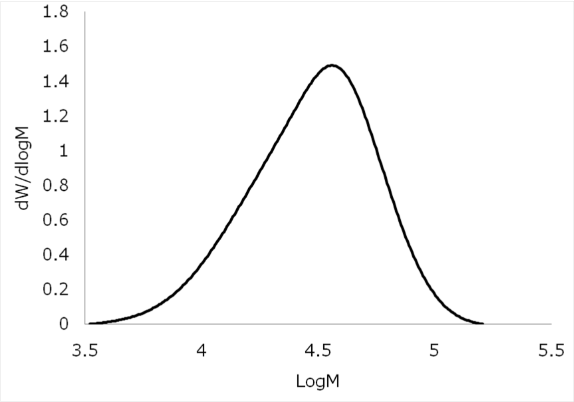

Figure 6.6: Molecular Weight Distribution Plot for Linear Polyacrylate Containing 1 wt% 4-Bromostyrene - Linear Acrylate is also labelled with 1 wt% 9-vinylanthracene

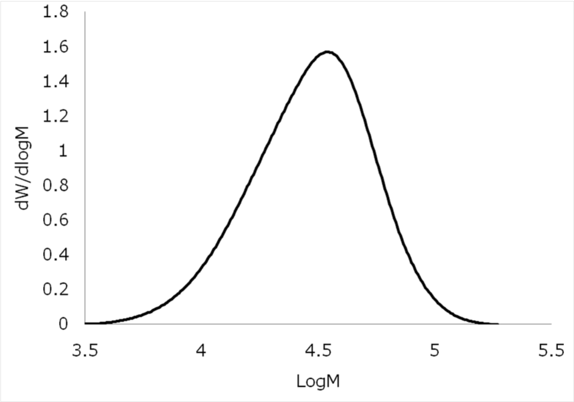

Figure 6.7: Molecular Weight Distribution Plot for Linear Polyacrylate Containing 2 wt% 4-Bromostyrene - Linear Acrylate is also labelled with 1 wt% 9-vinylanthracene

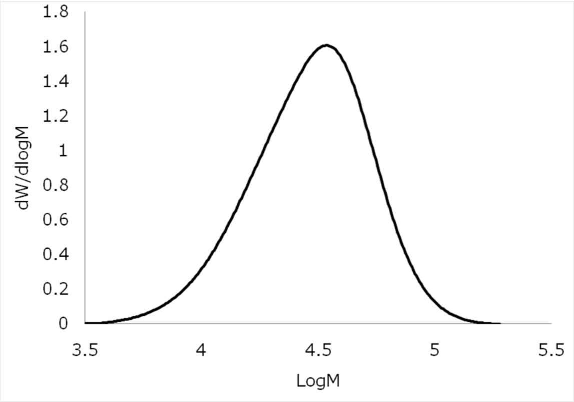

Figure 6.8: Molecular Weight Distribution Plot for Linear Polyacrylate Containing 5 wt% 4-Bromostyrene - Linear Acrylate is also labelled with 1 wt% 9-vinylanthracene

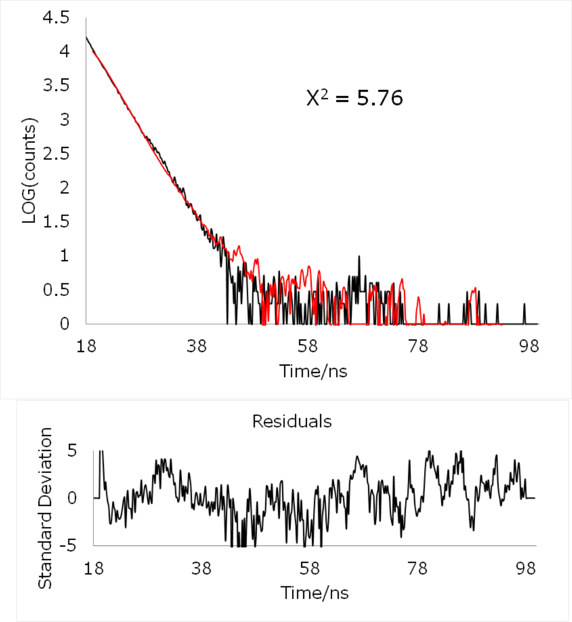

Figure 6.9: **Excited State Lifetime Plot for Linear Polyacrylate Bound 9-Vinylanthracene in Cyclohexane at 34.5 °C (θ-solvent)** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

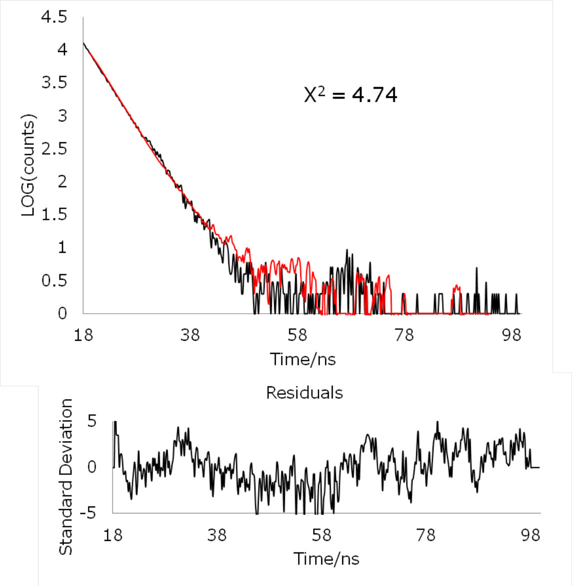

Figure 6.10: **Excited State Lifetime Plot Linear Polyacrylate Bound 9-Vinylanthracene in the Presence of 10 wt% 4-Bromostyrene in Cyclohexane at 34.5 °C (θ-solvent)** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

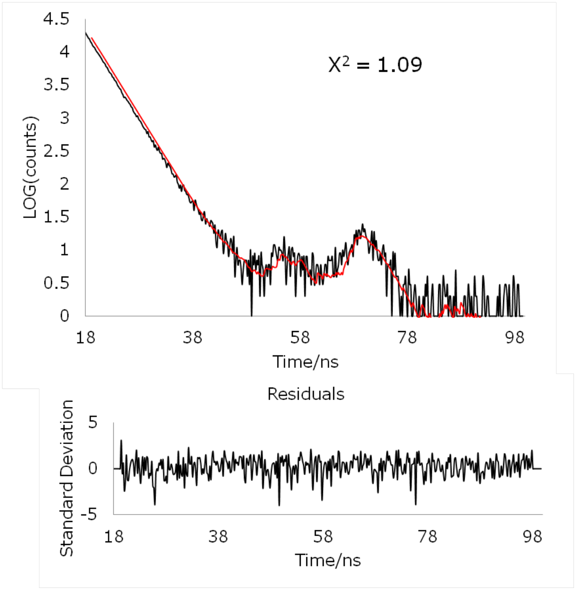

Figure 6.11: **Excited State Lifetime Plot for Linear Polyacrylate Bound 9-Vinylanthracene in Toluene (good solvent)** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

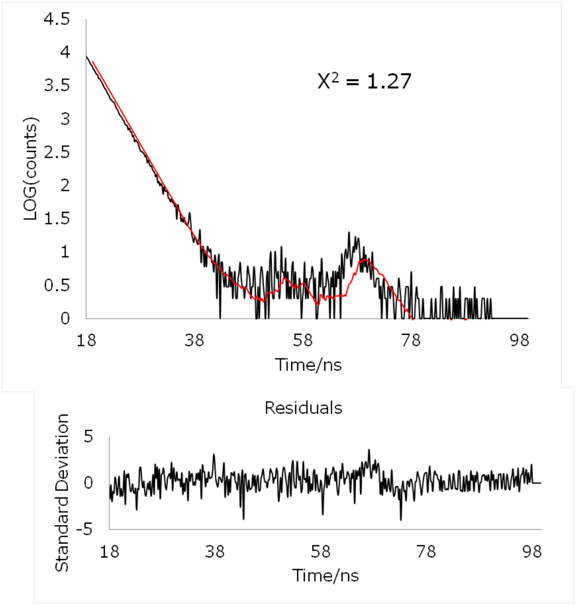

Figure 6.12: **Excited State Lifetime Plot for Linear Polyacrylate Bound 9-Vinylanthracene in the Presence of 10 wt% 4-Bromostyrene in Toluene (good solvent)** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

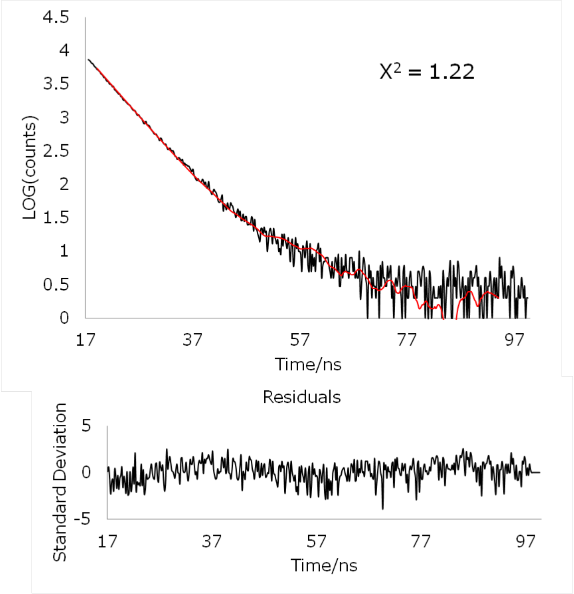

Figure 6.13: **Excited State Lifetime Plot for Cross-Linked Polyacrylate Bound 9-Vinylanthracene -** Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

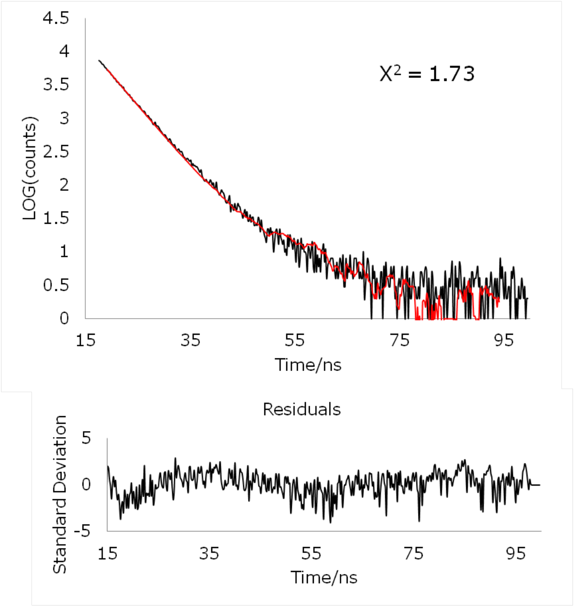

Figure 6.14: **Excited State Lifetime Plot for Cross-Linked Polyacrylate Bound 9-Vinylanthracene with 5 wt% 4-Bromostyrene -** Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

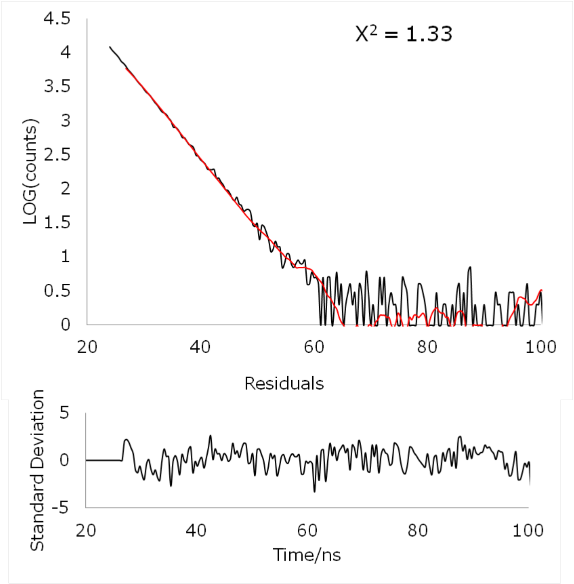

Figure 6.15: **Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propane diol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the triple exponential mathematical fit.

For this and all other component lifetime tables; (τ_i) is the calculated lifetime of the component, and α_i is the pre-exponential factor which corresponds to the contribution that component makes to the average lifetime.

[3-Bromo-1,2-Propanediol]/wt%	Component	α_i	τ_i/ns
0	1	0.180	3.84
0	2	0.680	7.21
0	3	9.94x10^{-4}	23.5
1x10^{-3}	1	0.180	3.81
1x10^{-3}	2	0.672	6.97
1x10^{-3}	3	9.87x10^{-4}	23.4
2x10^{-3}	1	0.178	3.80
2x10^{-3}	2	0.669	6.69
2x10^{-3}	3	9.79x10^{-4}	23.1
5x10^{-3}	1	0.169	3.81
5x10^{-3}	2	0.653	6.70
5x10^{-3}	3	9.78x10^{-4}	23.1
1x10^{-2}	1	2.19$10^{-2}$	3.80
1x10^{-2}	2	0.343	6.71
1x10^{-2}	3	7.78x10^{-4}	23.1

Table 6.11: Component lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol

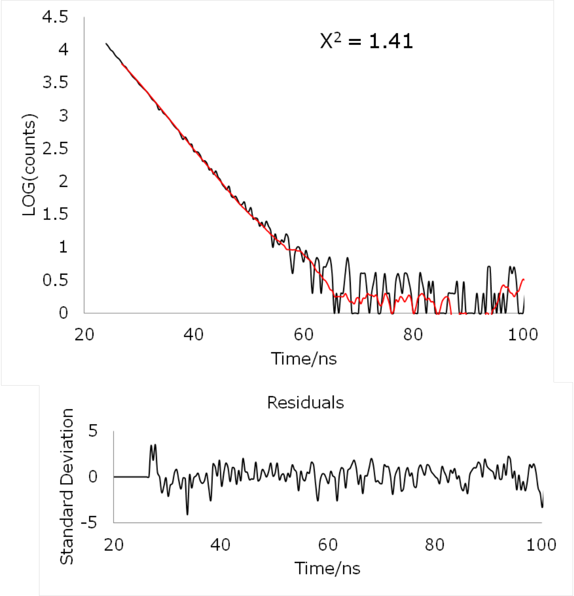

Figure 6.16: **Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propane diol Linear Polyurethane Acrylate Prepolymer** - Showing the triple exponential mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

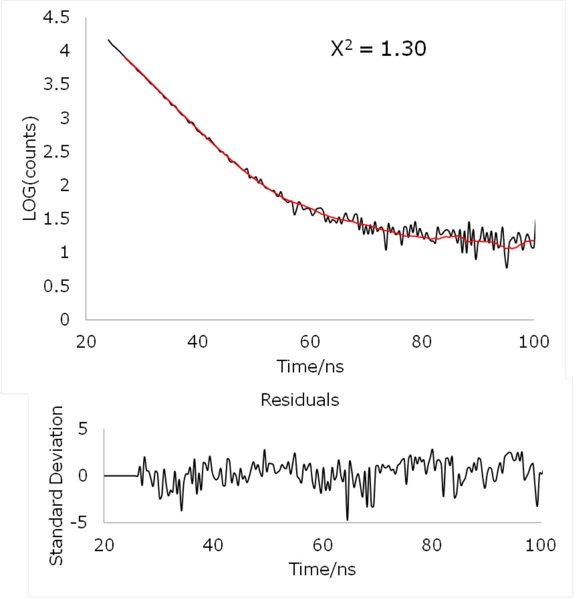

Figure 6.17: **Excited State Lifetime Plot for Prepolymer Bound 1,5-Dihydroxynaphthalene in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propane diol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

[3-Bromo-1,2-Propanediol Prepolymer]/wt%	Component	α_i	τ_i/ns
0	1	0.180	3.84
0	2	6.80	7.21
0	3	9.94x10^{-4}	23.5
1x10^{-3}	1	0.180	3.82
1x10^{-3}	2	0.679	7.11
1x10^{-3}	3	9.85x10^{-4}	23.5
2x10^{-3}	1	0.177	3.82
2x10^{-3}	2	0.674	6.93
2x10^{-3}	3	9.81x10^{-4}	23.4
5x10^{-3}	1	0.138	3.82
5x10^{-3}	2	0.664	6.93
5x10^{-3}	3	9.67x10^{-4}	23.4
1x10^{-2}	1	9.99x10^{-2}	3.82
1x10^{-2}	2	0.461	6.92
1x10^{-2}	3	7.83x10^{-4}	23.4

Table 6.12: Component lifetimes for the Excited State of Free 1,5-Dihydroxynaphthalene in the Presence of Different Concentrations of 3-Bromo-1,2-propanediol Prepolymer

[3-Bromo-1,2-Propanediol]/wt%	Component	α_i	τ_i/ns
0	1	0.179	3.83
0	2	0.616	7.22
0	3	9.45x10^{-4}	23.3
1x10^{-3}	1	0.178	3.83
1x10^{-3}	2	0.615	7.20
1x10^{-3}	3	9.43x10^{-4}	23.2
2x10^{-3}	1	0.176	3.82
2x10^{-3}	2	0.588	7.03
2x10^{-3}	3	9.17x10^{-4}	23.0
5x10^{-3}	1	0.102	3.82
5x10^{-3}	2	0.576	7.03
5x10^{-3}	3	9.10x10^{-4}	23.4
1x10^{-2}	1	5.73x10^{-3}	3.84
1x10^{-2}	2	8.02x10^{-2}	7.04
1x10^{-2}	3	8.95x10^{-4}	23.5

Table 6.13: Component lifetimes for the excited state of prepolymer bound 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol

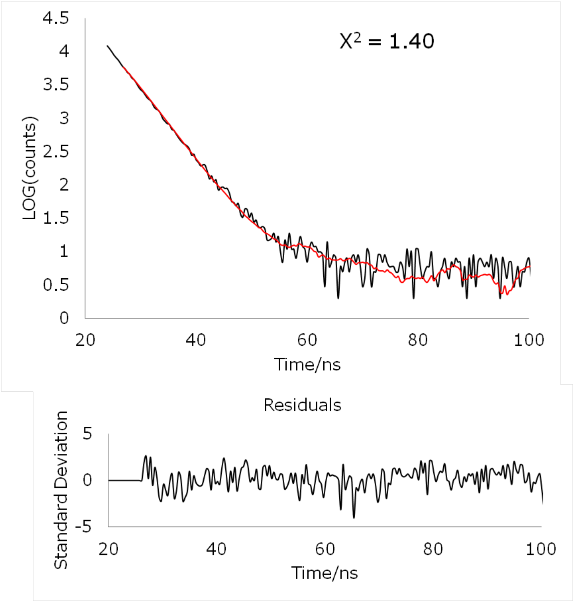

Figure 6.18: **Excited State Lifetime Plot for Prepolymer Bound 1,5-Dihydroxynaphthalene in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propanediol Linear Polyurethane Acrylate Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

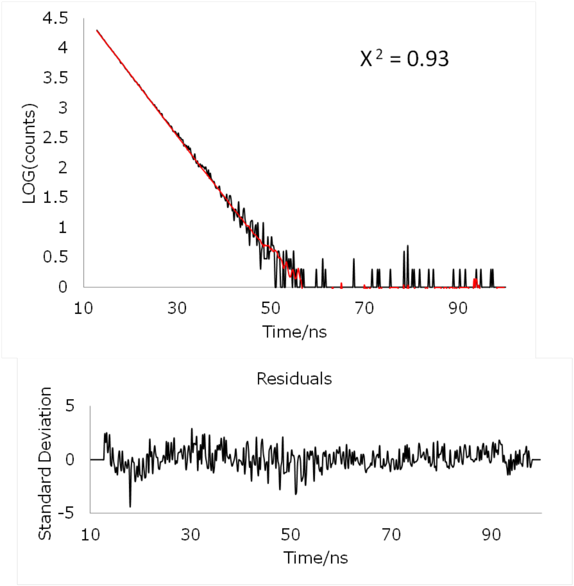

Figure 6.19: **Excited State Lifetime Plot for Free Fluorescein in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propane diol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

[3-Bromo-1,2-Propanediol Prepolymer]/wt%	Component	α_i	τ_i/ns
0	1	0.179	3.83
0	2	0.616	7.22
0	3	9.45x10^{-4}	23.3
1x10^{-3}	1	0.178	3.82
1x10^{-3}	2	0.615	7.05
1x10^{-3}	3	9.38x10^{-4}	23.2
2x10^{-3}	1	0.177	3.82
2x10^{-3}	2	0.502	6.61
2x10^{-3}	3	8.68x10^{-4}	23.1
5x10^{-3}	1	1.56x10^{-2}	3.83
5x10^{-3}	2	0.426	6.61
5x10^{-3}	3	6.63x10^{-4}	23.1
1x10^{-2}	1	9.32x10^{-3}	3.83
1x10^{-2}	2	0.131	6.62
1x10^{-2}	3	5.98x10^{-4}	23.4

Table 6.14: Component lifetimes for the excited state of prepolymer bound 1,5-dihydroxynaphthalene in the presence of different concentrations of 3-bromo-1,2-propanediol prepolymer

[3-Bromo-1,2-Propanediol Prepolymer]/wt%	Component	α_i	τ_i/ns
0	1	$2.34 \mathrm{x} 10^{-3}$	3.93
0	2	0.380	8.37
0	3	0.384	24.7
1	1	$2.12 \mathrm{x} 10^{-3}$	3.92
1	2	0.286	8.05
1	3	0.122	24.3
2.5	1	$1.53 \mathrm{x} 10^{-3}$	3.93
2.5	2	0.184	8.05
2.5	3	$8.57 \mathrm{x} 10^{-2}$	24.5
5	1	$9.44 \mathrm{x} 10^{-4}$	3.92
5	2	$5.03 \mathrm{x} 10^{-2}$	8.06
5	3	$7.89 \mathrm{x} 10^{-2}$	24.5

Table 6.15: Component lifetimes for the Excited State of Cross-Linked Polyurethane Acrylate Bound 1,5-Dihydroxynaphthalene in the Presence of Different Levels of 3-Bromo-1,2-Propanediol

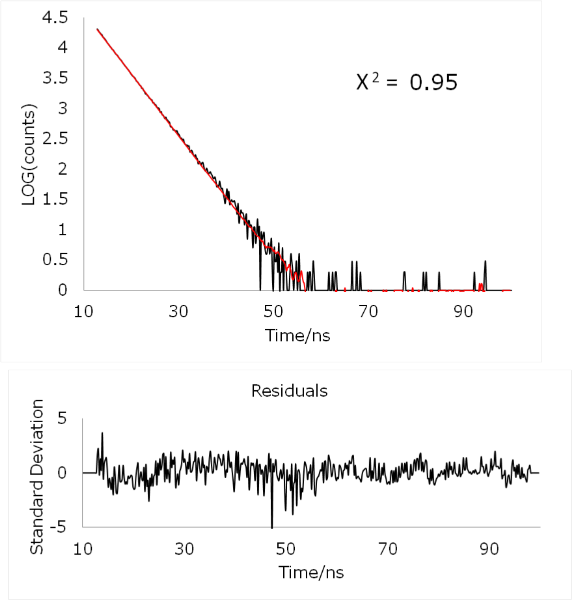

Figure 6.20: **Excited State Lifetime Plot for Free Fluorescein in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propane diol Linear Polyurethane Acrylate Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

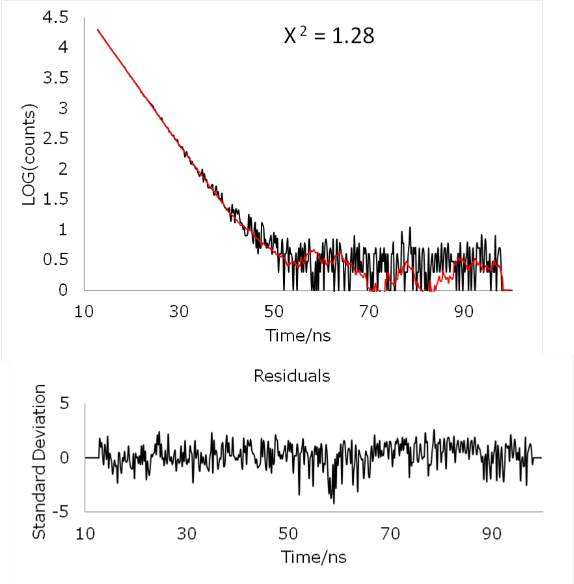

Figure 6.21: **Excited State Lifetime Plot for Prepolymer Bound Fluorescein in the Presence of 1x10^{-2}wt% 3-Bromo-1,2-propane diol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

[4-Bromoresorcinol]/wt%	Component	α_i	τ_i/ns
0	1	0.183	3.84
0	2	0.679	7.22
0	3	$9.28\text{x}10^{-4}$	23.5
$1\text{x}10^{-3}$	1	0.184	3.84
$1\text{x}10^{-3}$	2	0.669	7.19
$1\text{x}10^{-3}$	3	$9.28\text{x}10^{-4}$	23.5
$2\text{x}10^{-3}$	1	0.183	3.83
$2\text{x}10^{-3}$	2	0.663	7.15
$2\text{x}10^{-3}$	3	$9.19\text{x}10^{-4}$	23.5
$5\text{x}10^{-3}$	1	0.174	3.83
$5\text{x}10^{-3}$	2	0.628	6.96
$5\text{x}10^{-3}$	3	$8.04\text{x}10^{-4}$	23.4
$1\text{x}10^{-2}$	1	0.153	3.82
$1\text{x}10^{-2}$	2	0.509	6.91
$1\text{x}10^{-2}$	3	$6.87\text{x}10^{-4}$	23.3

Table 6.16: Component lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of 4-bromoresorcinol

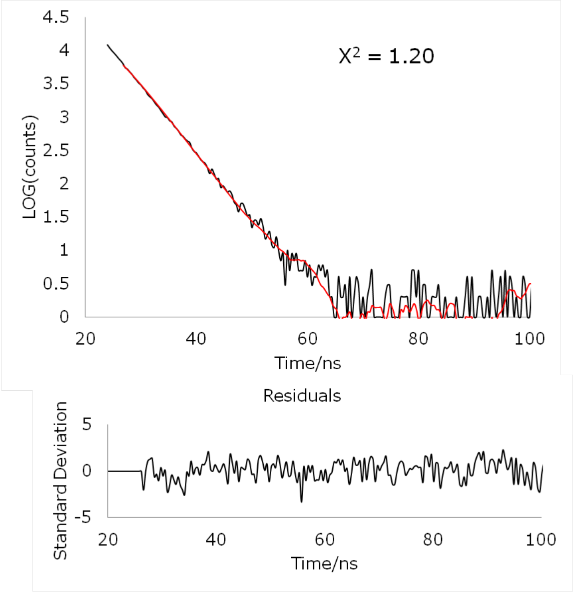

Figure 6.22: **Excited State Lifetime Plot for Free 1,5-Dihydroxynaphthalene in the Presence of 1x10^{-2}wt% 3- IPDI terminated 4-Bromoresorcinol Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the triple exponential mathematical fit.

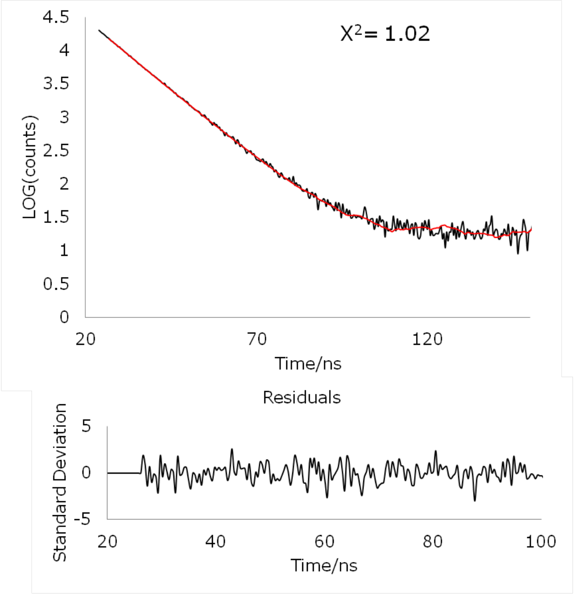

Figure 6.23: **Excited State Lifetime Plot for IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer** - Showing the triple exponential mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

[4-Bromoresorcinol Prepolymer]/wt%	Component	α_i	τ_i/ns
0	1	0.183	3.84
0	2	0.679	7.22
0	3	$9.28\text{x}10^{-4}$	23.5
$1\text{x}10^{-3}$	1	0.182	3.83
$1\text{x}10^{-3}$	2	0.679	7.22
$1\text{x}10^{-3}$	3	$9.26\text{x}10^{-4}$	23.5
$2\text{x}10^{-3}$	1	0.181	3.83
$2\text{x}10^{-3}$	2	0.676	7.19
$2\text{x}10^{-3}$	3	$9.25\text{x}10^{-4}$	23.5
$5\text{x}10^{-3}$	1	0.163	3.82
$5\text{x}10^{-3}$	2	0.656	7.08
$5\text{x}10^{-3}$	3	$9.11\text{x}10^{-4}$	23.5
$1\text{x}10^{-2}$	1	0.141	3.81
$1\text{x}10^{-2}$	2	0.591	6.94
$1\text{x}10^{-2}$	3	$8.42\text{x}10^{-4}$	23.4

Table 6.17: Component lifetimes for the excited state of free 1,5-dihydroxynaphthalene in the presence of different concentrations of IPDI terminated 4-bromoresorcinol prepolymer

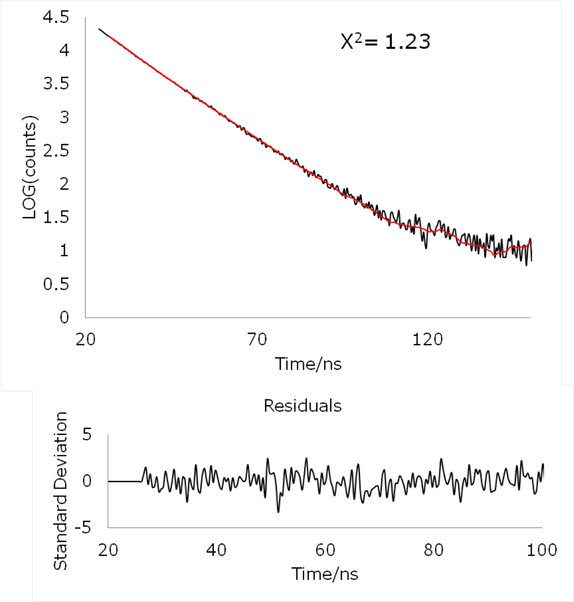

Figure 6.24: **Excited State Lifetime Plot for IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer in the Presence of 1x10^{-2} wt% 3-Bromo-1,2-propanediol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

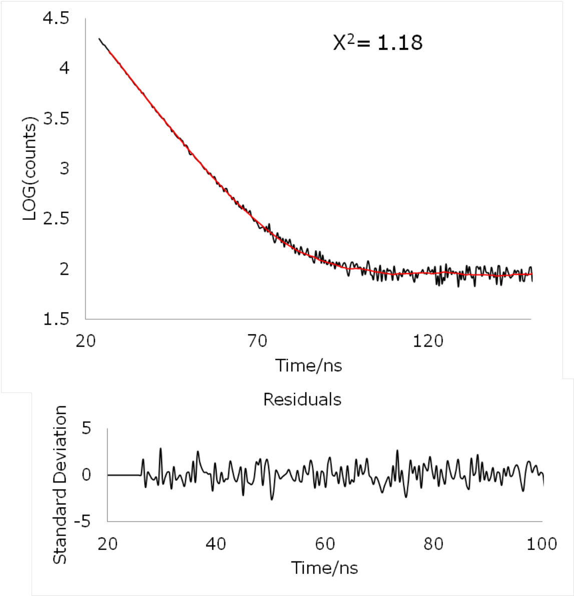

Figure 6.25: **Excited State Lifetime Plot for IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer in the Presence of 1x10^{-2} wt% 4-Bromoresorcinol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

[3-Bromo-1,2-propanediol]/wt%	Component	α_i	τ_i/ns
0	1	8.93x10^{-2}	3.95
0	2	0.622	8.35
0	3	0.123	23.6
1x10^{-3}	1	8.93x10^{-2}	3.94
1x10^{-3}	2	0.621	8.02
1x10^{-3}	3	0.120	23.5
2x10^{-3}	1	8.92x10^{-2}	3.94
2x10^{-3}	2	0.616	8.02
2x10^{-3}	3	0.120	23.5
5x10^{-3}	1	8.71x10^{-2}	3.94
5x10^{-3}	2	0.615	7.92
5x10^{-3}	3	0.119	23.4
1x10^{-2}	1	8.52x10^{-2}	3.93
1x10^{-2}	2	0.554	7.89
1x10^{-2}	3	0.114	23.4

Table 6.18: Component lifetimes for the excited state of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of 3-bromo-1,2-propanediol

[4-Bromoresorcinol]/wt%	Component	α_i	τ_i/ns
0	1	9.93x10^{-2}	3.95
0	2	0.622	8.35
0	3	0.123	23.6
1x10^{-3}	1	8.83x10^{-2}	3.95
1x10^{-3}	2	0.608	7.89
1x10^{-3}	3	0.105	23.5
2x10^{-3}	1	8.69x10^{-2}	3.94
2x10^{-3}	2	0.586	7.46
2x10^{-3}	3	9.27x10^{-2}	23.4
5x10^{-3}	1	8.49x10^{-2}	3.92
5x10^{-3}	2	0.504	7.01
5x10^{-3}	3	8.19x10^{-2}	23.3
1x10^{-2}	1	8.13x10^{-2}	3.92
1x10^{-2}	2	0.504	7.01
1x10^{-2}	3	8.19x10^{-2}	2.33

Table 6.19: Component lifetimes for the excited state of IPDI terminated 1,5-dihydroxynaphthalene prepolymer in the presence of different concentrations of 4-bromoresorcinol

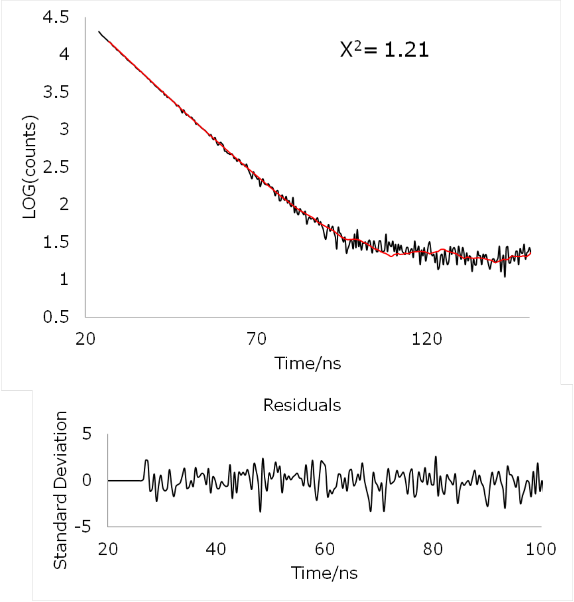

Figure 6.26: **Excited State Lifetime Plot for IPDI Terminated 1,5-Dihydroxynaphthalene Prepolymer in the Presence of 1x10^{-2} wt% 4-Bromoresorcinol Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

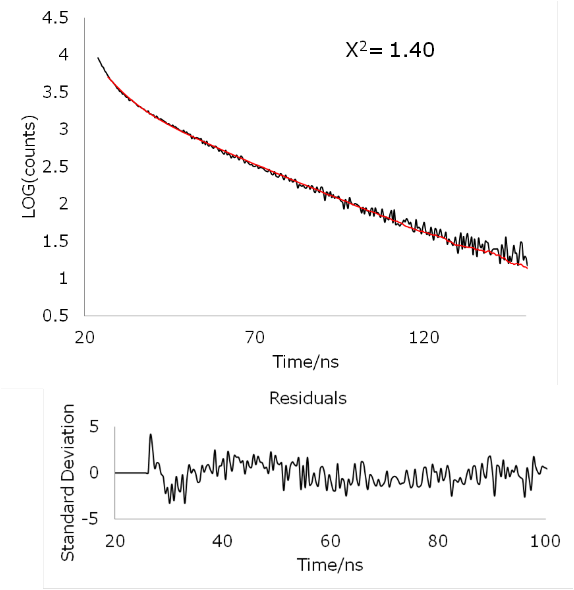

Figure 6.27: **Excited State Lifetime Plot for 1,5-Dihydroxynaphthalene Labelled Voranol Based Polyurethane containing 10 wt% 3-Bromo-1,2-propanediol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

[4-Bromoresorcinol Prepolymer]/wt%	Component	α_i	τ_i/ns
0	1	$8.93\text{x}10^{-2}$	3.95
0	2	0.622	8.35
0	3	0.123	23.6
$1\text{x}10^{-3}$	1	$8.89\text{x}10^{-2}$	3.94
$1\text{x}10^{-3}$	2	0.619	7.85
$1\text{x}10^{-3}$	3	$8.90\text{x}10^{-2}$	23.4
$2\text{x}10^{-3}$	1	$8.84\text{x}10^{-2}$	3.93
$2\text{x}10^{-3}$	2	0.606	7.28
$2\text{x}10^{-3}$	3	$8.49\text{x}10^{-2}$	23.3
$5\text{x}10^{-3}$	1	$8.74\text{x}10^{-2}$	3.93
$5\text{x}10^{-3}$	2	0.593	7.02
$5\text{x}10^{-3}$	3	$8.02\text{x}10^{-2}$	23.2
$1\text{x}10^{-2}$	1	$7.92\text{x}10^{-2}$	3.92
$1\text{x}10^{-2}$	2	0.496	6.94
$1\text{x}10^{-2}$	3	$6.93\text{x}10^{-2}$	23.2

Table 6.20: Component lifetimes for the excited state of IPDI terminated 1,5- dihydroxynaphthalene prepolymer in the presence of different concentrations of 4-bromoresorcinol prepolymer

[3-Bromo-1,2-propanediol]/wt%	Component	α_i	τ_i/ns
0	1	$3.39\text{x}10^{-2}$	4.11
0	2	0.311	11.8
0	3	0.259	25.7
$1\text{x}10^{-3}$	1	$3.37\text{x}10^{-2}$	4.10
$1\text{x}10^{-3}$	2	0.310	9.69
$1\text{x}10^{-3}$	3	0.159	25.5
$2\text{x}10^{-3}$	1	$3.33\text{x}10^{-2}$	4.09
$2\text{x}10^{-3}$	2	0.307	9.36
$2\text{x}10^{-3}$	3	0.125	25.2
$5\text{x}10^{-3}$	1	$3.10\text{x}10^{-2}$	4.09
$5\text{x}10^{-3}$	2	0.302	9.25
$5\text{x}10^{-3}$	3	0.121	25.2
$1\text{x}10^{-2}$	1	$1.78\text{x}10^{-2}$	4.09
$1\text{x}10^{-2}$	2	0.155	9.23
$1\text{x}10^{-2}$	3	$8.76\text{x}10^{-2}$	25.1

Table 6.21: Component lifetimes for the excited state of 1,5-dihydroxynaphthalene labelled Voranol based polyurethanes containing different concentrations of 3-bromo-1,2-propanediol

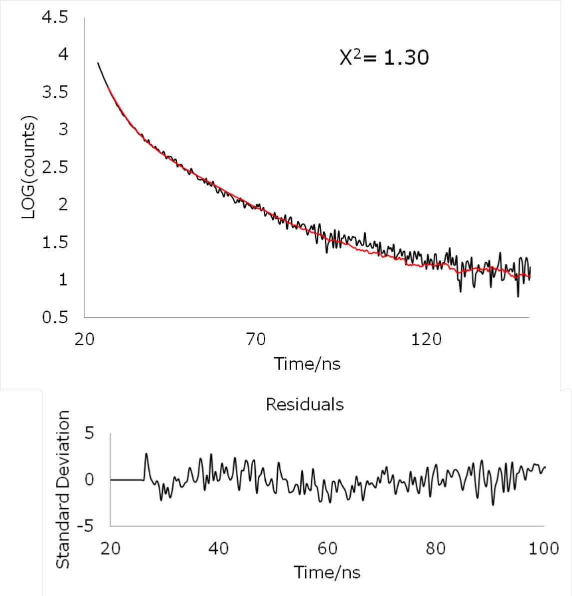

Figure 6.28: Excited State Lifetime Plot for 1,5-Dihydroxynaphthalene Labelled Voranol Based Polyurethane containing 5 wt% 4-Bromoresorcinol Prepolymer - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

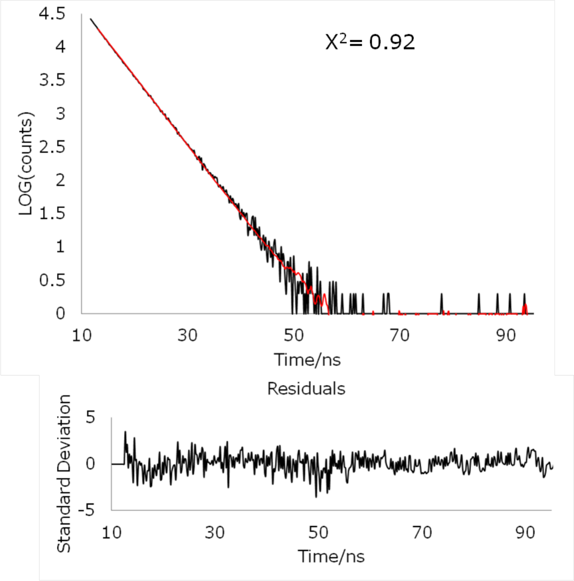

Figure 6.29: Excited State Lifetime Plot for Free Fluorescein in the Presence of 1x10^{-2}wt% IPDI Terminated 4- bromoresorcinol Prepolymer - Showing the mathematical fit in red and accompanied by a plot of the residuals from the triple exponential mathematical fit.

[4-Bromoresorcinol Prepolymer]/wt%	Component	α_i	τ_i/ns
0	1	$3.39\text{x}10^{-2}$	4.11
0	2	0.311	11.8
0	3	0.259	25.7
$1\text{x}10^{-3}$	1	$3.23\text{x}10^{-2}$	4.10
$1\text{x}10^{-3}$	2	0.310	10.2
$1\text{x}10^{-3}$	3	0.192	25.6
$2\text{x}10^{-3}$	1	$3.20\text{x}10^{-2}$	4.09
$2\text{x}10^{-3}$	2	0.295	9.27
$2\text{x}10^{-3}$	3	0.120	25.4
$5\text{x}10^{-3}$	1	$3.17\text{x}10^{-2}$	4.08
$5\text{x}10^{-3}$	2	0.276	8.34
$5\text{x}10^{-3}$	3	$5.50\text{x}10^{-2}$	25.2
$1\text{x}10^{-2}$	1	$2.22\text{x}10^{-2}$	4.06
$1\text{x}10^{-2}$	2	0.193	7.23
$1\text{x}10^{-2}$	3	$2.85\text{x}10^{-2}$	25.2

Table 6.22: Component lifetimes for the excited state of 1,5-dihydroxynaphthalene labelled Voranol based polyurethanes containing different concentrations of 4-bromoresorcinol prepolymer

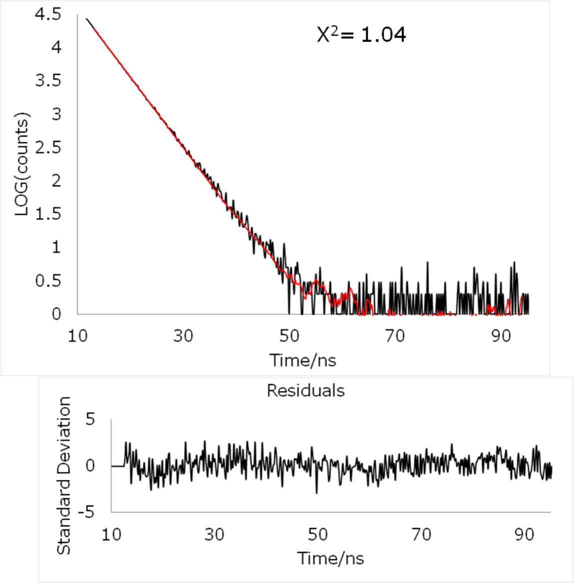

Figure 6.30: **Excited State Lifetime Plot for IPDI Terminated Fluorescein Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

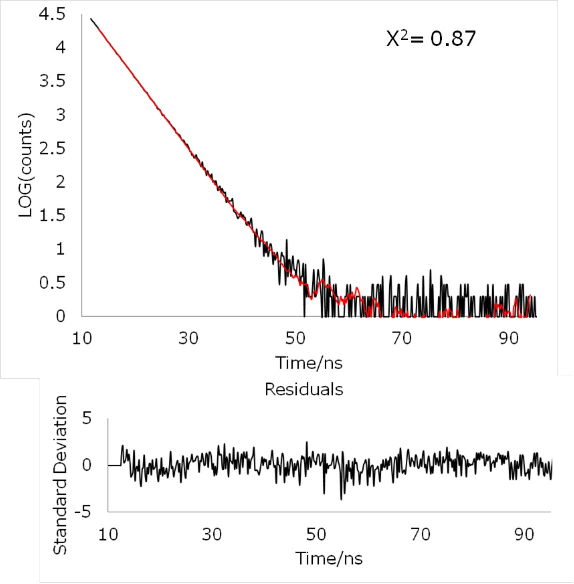

Figure 6.31: **Excited State Lifetime Plot for IPDI Terminated Fluorescein Prepolymer in the Presence of 1x10^{-2} wt% 3-Bromo-1,2-propanediol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

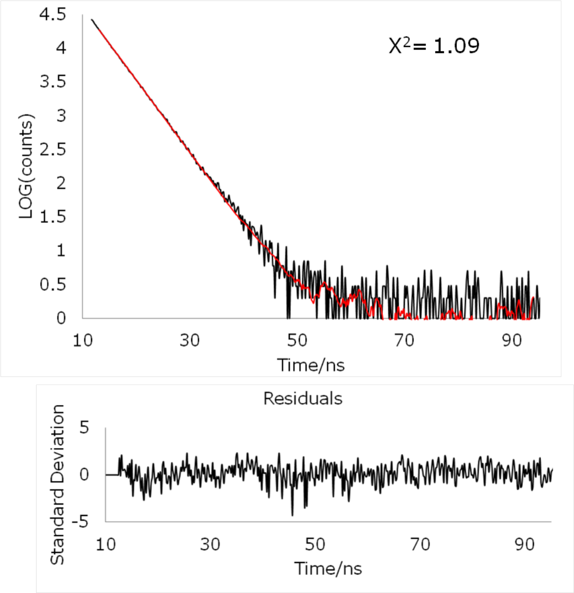

Figure 6.32: **Excited State Lifetime Plot for IPDI Terminated Fluorescein Prepolymer in the Presence of 1x10^{-2}wt% 4-Bromoresorcinol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

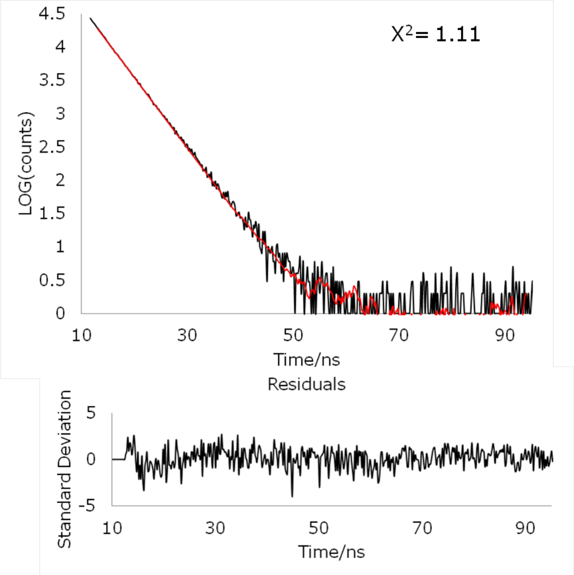

Figure 6.33: **Excited State Lifetime Plot for IPDI Terminated Fluorescein Prepolymer in the Presence of 1x10^{-2}wt% 4-Bromoresorcinol Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

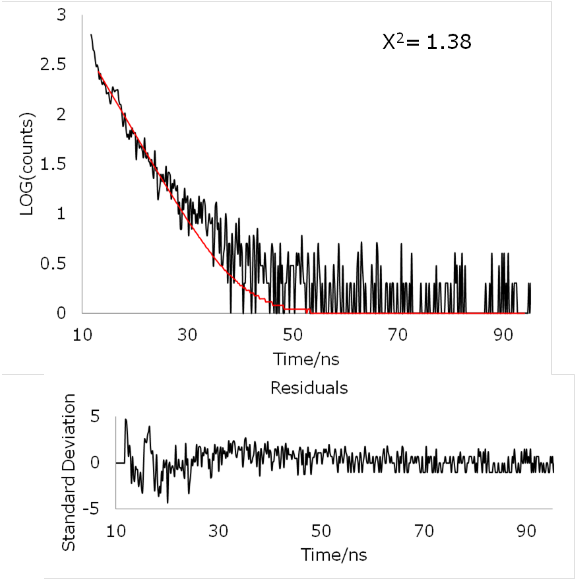

Figure 6.34: **Excited State Lifetime Plot for Fluorescein Labelled Voranol Based Polyurethane containing 10 wt% 3-Bromo-1,2-propanediol** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.

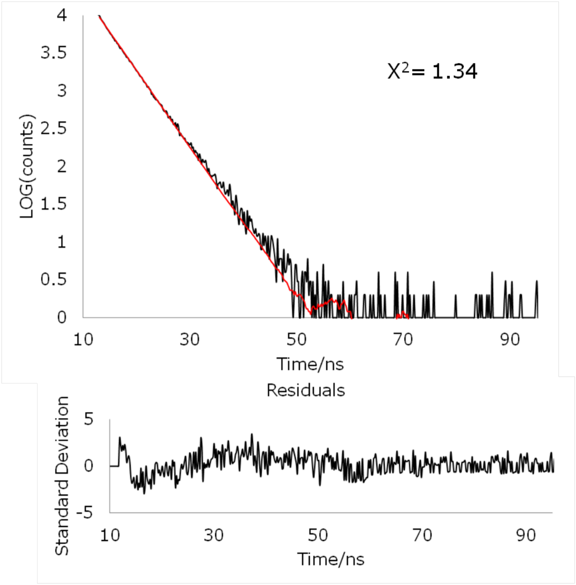

Figure 6.35: **Excited State Lifetime Plot for Fluorescein Labelled Voranol Based Polyurethane containing 5 wt% 4-Bromoresorcinol Prepolymer** - Showing the mathematical fit in red and accompanied by a plot of the residuals from the mathematical fit.