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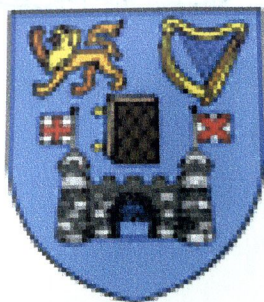
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Curing of Complex Monomer Systems: A Spectroscopic and Thermal Analysis

by
Seán J. Martin

A Thesis submitted to
The University of Dublin
for the degree of

Doctor of Philosophy



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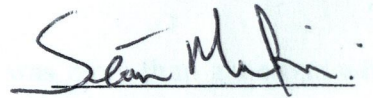
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Declaration

This thesis is submitted by the undersigned for the degree of doctor in Philosophy at the University of Dublin. It has not been submitted as an exercise for a degree at any other university.

This thesis, apart from the advice, assistance, and joint effort mentioned in the acknowledgements, is entirely my own work.

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Seán J. Martin

October 2000.

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Synopsis

This thesis describes the development of a novel methodology, which uses the high resolution liquid nuclear magnetic resonance (NMR) spectroscopic technique to continuously monitor in real time the thermal and UV-photoinitiated curing dynamics of a range of multi-component monomer systems, comprising mainly of *N*-vinyl-2-pyrrolidone / 2-hydroxyethyl methacrylate / 4 and 5-*t*-butyl-2-hydroxycyclohexyl methacrylate (NVP/HEMA/TBE). These systems are of both academic and commercial interest, in this case, in the manufacture of hydrogel contact lenses.

The technique exploits the site specific information available in liquid NMR spectra, which normally comprise resolved peaks that specifically label each of the constituents of the complex mixtures. The intensity and lineshape of these peaks can be monitored continuously as curing proceeds. Progression from liquid monomer, via a gel-like phase, towards the cured, solid polymer during UV irradiation (or thermal curing) broadens the NMR spectral lines to an extent that the resulting linewidths greatly exceed the narrow bandwidth of the NMR liquids probe (typically 4kHz). Accordingly, except for very short oligomers, the spectrometer detects only remnant monomer in the form of spectral peaks of diminishing intensity as curing proceeds. The differential conversion rates of each the individual components, continuously recorded as a function of curing time, are therefore revealed. Analysis of the changes in spectral lineshape and chemical shift provides a more microscopic picture of events at a molecular level in these curing systems. Similar real time *in situ* curing experiments are described, which were performed using the more established, though

in some ways more limited, technique of Fourier transform infrared spectroscopy (FTIR) and comparison of the results is satisfying.

The monomer conversion responses obtained from these two techniques are fitted to Douglass's model simulations generated by a new numerical implementation, which is applicable to N-component monomer mixtures. Agreement, based on published reactivity ratios of the monomer components, is good, thus validating the methodology and instilling confidence in the overall efficacy of the NMR approach.

A prerequisite for the curing experiments was a detailed spectroscopic study of each of the individual components of the systems, using liquid NMR, FTIR and UV-Vis techniques, to facilitate characteristic peak assignments in the spectra of the complex mixtures. It was also necessary to study the relaxation behaviour of the systems in order to properly establish appropriate acquisition parameters and ensure the quantitative nature of the NMR spectra recorded. Additional information regarding the molecular dynamics in these systems obtained from this work is also reported. The use of radiometry techniques, including liquid phase chemical actinometry, to measure the UV light intensities employed in the photocuring experiments is described. Finally, some measurements obtained using thermal analysis techniques, including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), conducted to examine the thermally initiated curing behaviour of some of the mixtures, are reported.

The information obtained during this study underpins an understanding of the overall curing dynamics of these composite monomer mixtures and provides important guidance in establishing suitable protocols in the manufacturing processes for production of high quality hydrogel contact lenses.

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A Study of the Thermal and Photoinduced Curing of Multi-Component Monomers and Polymers

1.1 Introduction

The facility to combine the beneficial properties of two or more component polymers to form a composite material is one of the hallmarks of polymer technology. The manufacture of composites has become an important area where the composite material is a combination of two or more polymers or a polymer of polymeric entities, which enhance the overall properties of the material. A high water content and retention, adequate mechanical strength, and a high impact resistance, acceptable mechanical integrity overall, and a high degree of homogeneity are some of the properties required for a composite material. The properties of a composite material are a function of the composition and control of differential curing rates of the various polymeric components. An understanding of the properties of a composite material is therefore a prerequisite to a successful design of the many composites used in a wide variety of practical manufacturing processes and quality tests.

1.2 Commercial Applications of Composites

The composite materials industry has been growing rapidly since the late 1940's. The industry over the past 10 years has been characterized by companies such as Johnson, and Buehler, Inc. While the first composites were designed and cast in glass as early as the 1890's, the contact lens industry began to grow after the Second World War, when Pothier was found to be the material of

Chapter One

A Study of the Thermal and Photoinitiated Curing of Multi-Component Monomer Mixtures

1.1 Introduction

The facility to combine the beneficial properties of two or more component polymers to form a composite material is one of the key strengths of polymer technology. The manufacture of contact lenses is a case in point wherein the composite material is a copolymer, terpolymer or multi-component polymer of polymer entities, which collectively generate such necessary properties as high water content and retention, adequate oxygen solubility and efficient transport, acceptable mechanical integrity, overall rapid cure rate and an optically homogeneous material.^{1,2} These properties ultimately depend upon a suitable formulation and control of differential cure rates in a complex blend of polymeric components. An understanding of the curing kinetics of key monomers in a composite is therefore a prerequisite to addressing systematically the many issues involved in developing a practical manufacturing protocol for high quality lenses.

1.2 Commercial Importance of Composite Monomer Systems

The correction of vision using contact lenses has grown into a billion dollar industry over the past 45 years, dominated by companies such as Ciba-Geigy, Johnson & Johnson, and Bausch & Lomb. While the first contact lens shapes were designed and cast in glass as early as the 1890's, the contact lens industry only began to grow after the Second World War, when PMMA was found to be a suitable material in

terms of its optical properties, biocompatibility, and 'manufacturability'. The discovery of a hydrogel material based on HEMA in the 1950's, followed by the development and patenting in 1965 of the 'spin-casting' production method,³ exploited by B&L in the United States, led to the first large scale production of HEMA lenses in 1971.^{2,4} Since then, the number of types of lenses available has increased dramatically. They are now made from a wide range of multi-component materials including a variety of hydrogel formulations, silicone acrylates, and fluoroacrylates for hard lenses. Research and development efforts on new materials and production processes continues to expand and only recently, relatively cheap disposable soft hydrogel contact lenses entered the market place for the first time. These lenses are commercially viable as a result of the 'economy of scale' of mass production and the increased automation of manufacture that were possible only when processes and protocols were optimised. Much of literature published on the curing dynamics of these systems report physical property measurements, such as hydrated water contents and modulus values from an empirically formulated range of compositions.⁵⁻⁹ A deeper fundamental understanding of the curing behaviour of the co-monomers in these multi-component systems would certainly facilitate the ability to tailor the desired material properties at the formulation stage to meet specific needs. Continued progress in the optimisation of the manufacturing protocols for existing formulations is equally critical for the development of the industry.

The novel real time NMR methodology for monitoring the thermal and photoinitiated cure dynamics of these multi-component systems, developed as part of this thesis, combined with the computer model simulations of D.C. Douglass address these challenges.

1.3 Overview of Thermal and Photocuring Processes

In these experiments curing of the multi-component systems proceeds *via* free radical addition co-polymerisation type reactions which rely on the supply of free radicals from either the thermal decomposition (thermolysis) or UV photo-activated decomposition (photolysis) of the added initiator reagents.¹⁰⁻¹³ Some degree of control over the progression of the overall curing reaction may be exerted by adjusting the concentration of the initiator species, by controlling the incident UV light intensity or by changing the temperature of the system. However, the individual conversion rates of the monomers in systems such as these can differ markedly and the composition of the polymer formed varies over the course of the reaction. This phenomenon, known as composition drift, is attributable to the varying reactivities of the monomers in the mixture. The resulting copolymer structure will therefore be a function of the reactivity ratios, or equivalently $Q-e$ values, of the components.^{14,15} The ability to continuously measure the dynamics of these processes with the progression of cure in real time, is a key step in ultimately understanding and then controlling the course of the reactions, thereby tailoring the formation of the chemical structure and ultimately achieving the synthesis of a copolymer with the physical properties that are specifically required for a particular application. The objective of this study was therefore to develop an experimental approach based on NMR spectroscopic techniques that can monitor the conversion of individual monomers over the course of a thermal or photoinitiated curing reaction. A series of papers that report the findings of the study have been published.¹⁶⁻¹⁹ This thesis now fully reports the on the work conducted and describes in detail the key findings and developments achieved.

1.4 Thesis Outline

This thesis describes the development of a novel approach which uses high resolution liquid NMR spectroscopy to continuously monitor in real time the thermal and UV-photoinitiated curing dynamics of a range of multi-component monomer systems.

The fundamentals of NMR theory, nuclear relaxation and spectroscopy, as required for subsequent data analysis, are presented in Chapter 2.

In Chapter 3, the standard experimental methods used for the spectroscopic characterisation of the individual components and of the complete composite mixtures are detailed. Modifications to the equipment that were required to achieve *in situ* UV curing are also described. Thermal analysis techniques used in some of the thermally initiated curing studies are also introduced.

The precise formulations of the multi-component monomer mixtures examined in this study are tabulated in Chapter 4. The detailed characterisation, both of the individual components and of the composite mixtures, using NMR, FTIR and UV-Visible spectroscopic techniques, are also presented. Curing-sensitive spectral lines are identified in each of the individual components of the mixtures for subsequent analysis.

The spin-lattice relaxation (T_1) response of the liquid systems are detailed in Chapter 5. Recall that T_1 establishes the recycle time used in the suite of spectral acquisition parameters in order to obviate spectral distortions and ensure the quantitative accuracy of the spectral data recorded during the NMR curing experiments. Additional information obtained from these measurements relating to the molecular dynamics in the systems is also briefly discussed.

In Chapter 6, the UV laser light source used in photoinitiated curing experiments is described, as is the light delivery system for *in situ* illumination of samples. The two radiometry techniques, based on the use of a pyroelectric Joulemeter and a liquid phase chemical actinometer, which measure the UV light intensities employed in the photocuring experiments are described.

Additionally, the experimental methodology used to monitor the real time *in situ* UV photoinitiated curing behaviour using FTIR is described. The limitations of this technique for studying multi-component systems are briefly discussed.

Chapter 7 describes the development of a novel approach which uses high resolution liquid NMR spectroscopy to continuously monitor in real time, the thermal and UV-photoinitiated curing dynamics of the range of multi-component monomer systems. Experimental procedures are discussed and data in the form of curing profiles for individual component monomers are presented as a function of curing time.

These responses are fitted to model simulations, generated by a modified numerical software program written by D.C. Douglass, which is applicable to N-component monomer mixtures. The satisfactory agreement between the theoretical and experimental data, based on published reactivity ratios for the monomers where available, is discussed.

The curing profiles observed by the NMR and FTIR methods are compared and rationalised in terms of the operating principles of the techniques. Results of thermal analysis experiments, which evaluate the effectiveness of a ramped heating protocol commonly used to cure commercial monomer systems are presented and discussed at the end of Chapter 7.

Finally, concluding comments and some suggestions for further work of

1.5 References

interest are briefly summarised in Chapter 8.

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Chapter Two

Essential NMR Theory

2.1 Introduction

This chapter introduces the essential theory for subsequent data analysis of the NMR curing experiments conducted during this study. It focuses upon NMR theory since NMR data analysis is significantly more complex than the analysis of data from DSC and FTIR techniques, which are treated routinely elsewhere.^{1,2} NMR theory is succinctly reviewed for both the classical and quantum mechanical approaches, with guidance from numerous review papers and reference texts available.²⁻¹¹

2.2 Fundamentals of NMR

2.2.1 Magnetic Moment of the Nucleus

Nuclei of odd mass number possess non-zero angular momentum or spin, I , which is quantised in units of $\hbar$. The projection of I onto the applied magnetic field direction defines the magnetic nuclear spin quantum number, $m_I = +I, I-1, I-2, \dots, -I$, which has $2I+1$ discrete values. For protons (^1H) and carbon (^{13}C) nuclei, $I = \frac{1}{2}$ and only two discrete orientations of the nuclear spin exist. Nuclei with an odd mass number have non-zero angular momentum and the spin and charge results in a nuclear magnetic moment, μ , given by

$$\mu = \gamma \hbar I \quad (2.1)$$

where γ is the gyromagnetic ratio of the nucleus. The value of γ varies for each nucleus and the sign of γ determines the relative orientation of μ with respect to I .

2.2.2 The Hamiltonian

The response of a nuclear spin system is best described in terms of a generalised Hamiltonian. The Hamiltonian, which describes the spin systems of diamagnetic non-conducting systems such as monomers and polymers, is ⁸

$$\mathcal{H}_{Total} = \mathcal{H}_Z + \mathcal{H}_{rf} + \mathcal{H}_D + \mathcal{H}_Q + \mathcal{H}_{CS} + \mathcal{H}_J + \mathcal{H}_{SR} \tag{2.2}$$

where

$\mathcal{H}_Z$ and $\mathcal{H}_{rf}$ are the Zeeman interaction and the coupling of the nuclear spins to the applied *rf* field, respectively.

$\mathcal{H}_D$ and $\mathcal{H}_Q$ are the dipolar and quadrupolar interactions respectively. Only nuclei with spin = ½ are considered in this study and hence quadrupolar interactions are not involved.

$\mathcal{H}_{CS}$, $\mathcal{H}_J$ and $\mathcal{H}_{SR}$ are the chemical shift, scalar coupling and the spin-rotation interactions, respectively. In general the scalar coupling and spin rotation terms are masked by the magnitude of the dipolar interaction in solids.

The relative magnitudes of each contribution to the Hamiltonian for liquid and solid samples using ¹H NMR techniques are presented in Table 2.1.

Table 2.1: Liquid sample vs. solid sample: ¹H NMR nuclear spin interactions in a 7.05 Tesla field.

Total Interaction	Zeeman	Dipolar	Chemical Shift	Scalar
Liquid	300 MHz	0	Isotropic single frequency	0-20 Hz
Solid	300 MHz	~ 100 kHz	0-20 ppm wide chemical shift anisotropy (Variable- Masked)	0-20 Hz (Masked)

2.2.3 The Nuclear Magnetic Resonance Condition

For a nucleus with magnetic moment μ in a constant magnetic field $\mathbf{H}_0$ along the z-axis in a Cartesian coordinate system, the interaction may be represented by the Zeeman Hamiltonian

$$\mathcal{H}_Z = -\mu \cdot \mathbf{H}_{\text{static}} \quad (2.3)$$

where $\mu = (\mu_x, \mu_y, \mu_z)$; $\mathbf{H} = (0, 0, H_0)$

Equation 2.1 becomes $\mu_z = \gamma \hbar I_z$ when $\mathbf{H}_0$ is along the z-axis, then

$$\mathcal{H}_Z = -\gamma \hbar H_0 I_z \quad (2.4)$$

The eigenvalues of this Hamiltonian are determined by the magnetic quantum number m_I and the possible Zeeman interaction energies, $(2I+1)$ are given by

$$E_{m_I} = -\gamma \hbar H_0 m_I \quad (2.5)$$

$\mathbf{H}_0$ removes the degeneracy of the nuclear magnetic energy levels and an oscillating electromagnetic field $\mathbf{H}_1(t)$ is applied orthogonal to $\mathbf{H}_0$ at the resonant frequency ω_0 . Nuclear spin transitions occur between energy levels governed by the selection rule $\Delta m_I = \pm 1$ according to

$$\Delta E = \hbar \omega_0 = \hbar \gamma H_0 \quad \text{or} \quad \omega_0 = -\gamma H_0 \quad (2.6)$$

This is the resonance condition (Figure 2.1).

From first order transition probability theory, absorption and emission are equally likely and resonance absorption is only detected in a macroscopic sample. Sustained observation of NMR absorption signals is possible because of the population difference between the two energy levels as described by the Boltzmann equation

$$\frac{N_-}{N_+} = \exp\left(-\frac{\Delta E}{kT}\right) \quad (2.7)$$

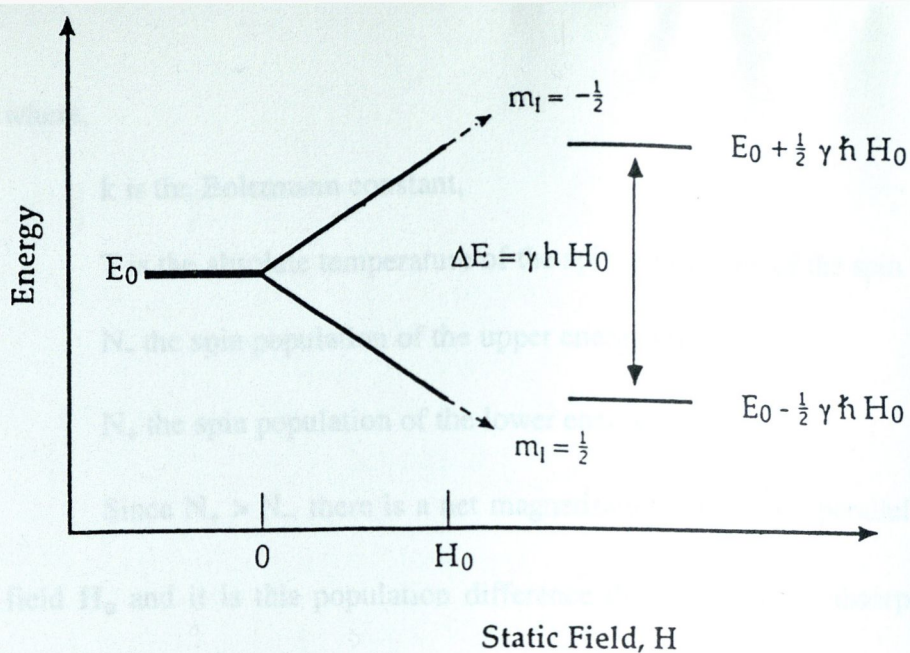


Figure 2.1. Energy level diagram showing response of nuclei with spin $= \frac{1}{2}$ in a static magnetic field H_0 .

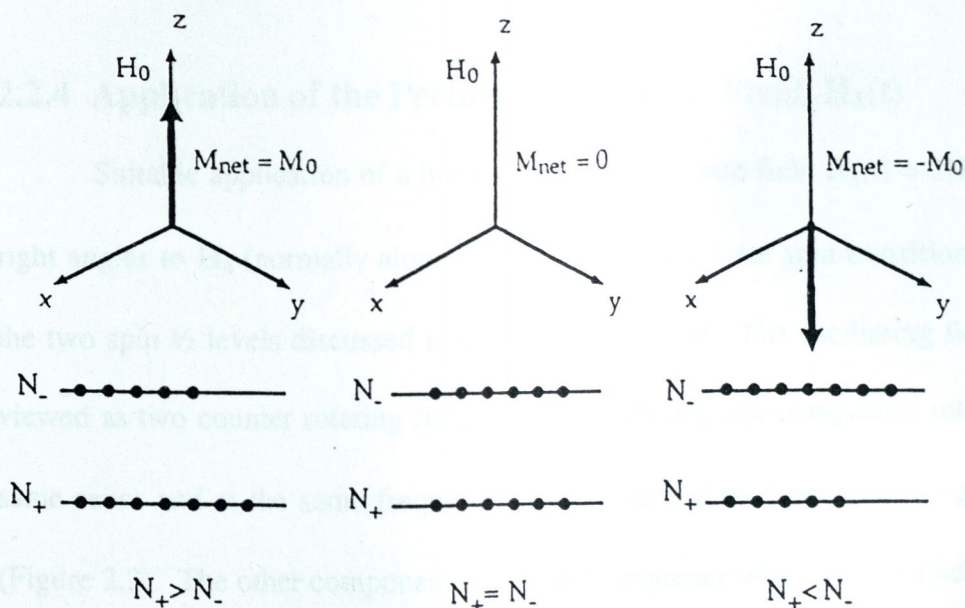


Figure 2.2. Net magnetisation in the static reference frame with respect to the Boltzmann population distribution. H_0 orientation defines z -direction.

where,

k is the Boltzmann constant,

T is the absolute temperature of the spin temperature of the spin system,

N_- the spin population of the upper energy level,

N_+ the spin population of the lower energy level.

Since $N_+ > N_-$, there is a net magnetisation $M = \sum \mu_i$ parallel to the applied field H_0 and it is this population difference that causes a net absorption of energy when nuclei are irradiated at the resonant frequency. Figure 2.2 illustrates the relationship between population differences and the net magnetisation aligned along H_0 . The spin populations quickly equilibrate with time and continued net absorption requires a separate mechanism preferentially to depopulate the higher level. This process is known as spin-lattice relaxation since relaxation occurs by loss of energy from the excited nuclear spin systems to the surrounding lattice.

2.2.4 Application of the Perturbing Magnetic Field, $H_1(t)$

Suitable application of a linear oscillating magnetic field $H_1(t) = 2H_1 \cos \omega_0 t$ at right angles to H_0 (normally along the x-axis) will stimulate spin transitions between the two spin $\frac{1}{2}$ levels discussed in the previous section. The oscillating field can be viewed as two counter rotating fields of magnitude H_1 , one component rotates in the same sense and at the same frequency as the magnetic moment precessing about H_0 (Figure 2.3). The other component rotates at a frequency which is too rapid and in the wrong direction to induce transitions and therefore can be ignored. The net effect of the static field H_0 and the oscillating field $H_1(t)$ is best visualised using a coordinate system (x', y', z') , rotating about the collinear z, z' -axes with angular velocity ω . The

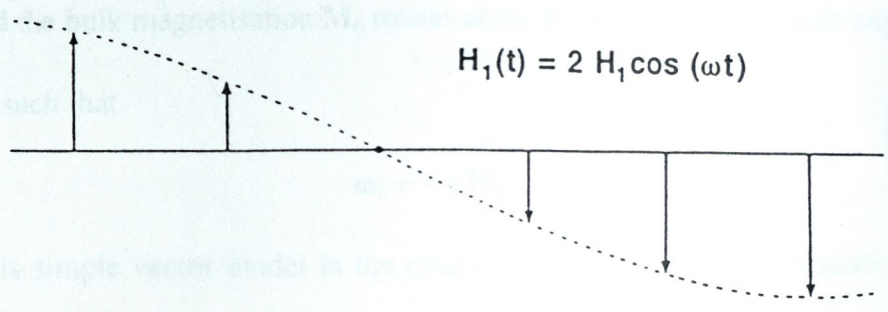
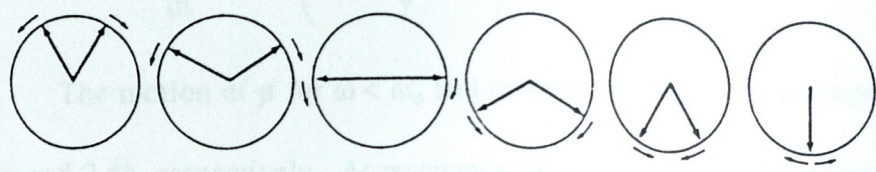


Figure 2.3. A linear oscillating magnetic field $H_1(t)$ split into two counter rotating magnetic fields of magnitude H_1 . Rotation is in the x-y plane, angular frequency ω .

component of $\mathbf{H}_1(t)$ with the correct direction and frequency defines the rotating x' -axis (Figure 2.4a). The equation of motion of the magnetic moment in the rotating field viewed from this rotating frame is

$$\frac{d\boldsymbol{\mu}}{dt} = \gamma \boldsymbol{\mu} \otimes \left(\mathbf{H}_0 + \frac{\omega}{\gamma} + \mathbf{H}_1 \right) = \gamma \boldsymbol{\mu} \otimes \mathbf{H}_{\text{effective}} \quad (2.8)$$

The motion of $\boldsymbol{\mu}$ for $\omega < \omega_0$ and on-resonance ($\omega = \omega_0$) are depicted in Figure 2.4a and 2.4b, respectively. At resonance, $\mathbf{H}_{\text{effective}} = \mathbf{H}_1$ and the magnetic moment $\boldsymbol{\mu}$ and the bulk magnetisation $\mathbf{M}_0$ rotates about $\mathbf{H}_1$ in the z' - y' plane with angular velocity ω_1 such that

$$\omega_1 = -\gamma \mathbf{H}_1 \quad (2.9)$$

This simple vector model in the rotating frame is a convenient visualisation of how the net magnetisation can be manipulated by the application of rf pulses $\mathbf{H}_1(t)$ of variable duration. If the pulse is applied for a duration t , then $\mathbf{M}_0$ will rotate through an angle θ , given by

$$\theta = \gamma H_1 t \quad (2.10)$$

Two pulse lengths of particular interest are $\theta = \pi/2$ (90° pulse) and $\theta = \pi$ (180° pulse), which are the basis for more complicated pulse sequences used to measure relaxation times in the study of molecular motions (Figure 2.5) (*see Chapter 3*).

2.3 Relaxation Processes

2.3.1 Spin-Lattice Relaxation (T_1)

Spin-lattice relaxation describes how the higher energy level of the perturbed spin system preferentially depopulates by transferring excess of magnetic energy or

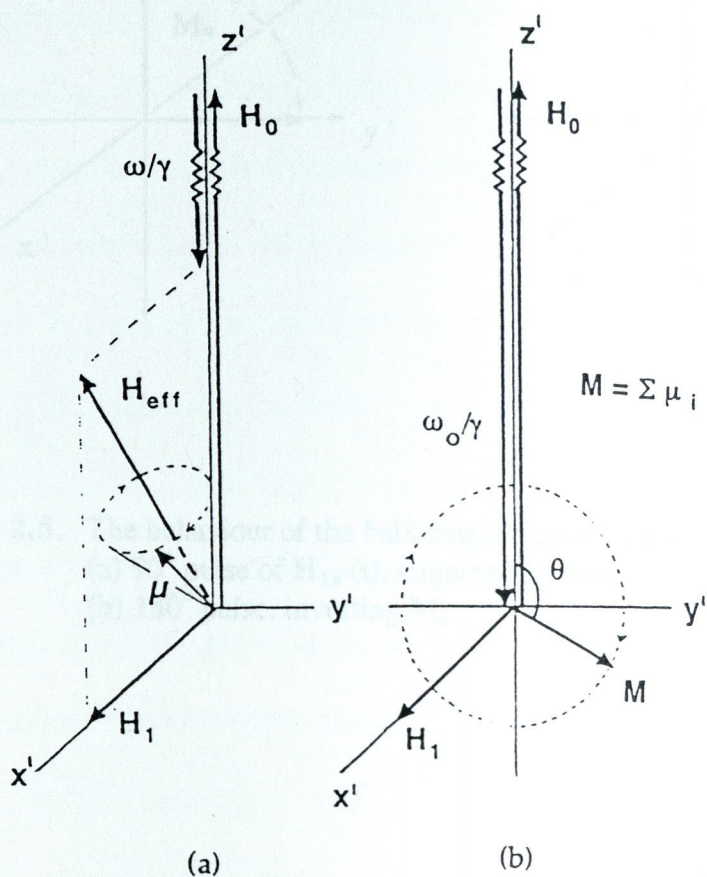


Figure 2.4. (a) Precession of nuclear dipole under influence of $H_{\text{effective}}$. Rotational reference frame is (x', y', z') , angular frequency $\omega < \omega_0$.
 (b) Circular motion of the net magnetisation vector in the $z'-y'$ plane when $\omega = \omega_0$, at resonance.

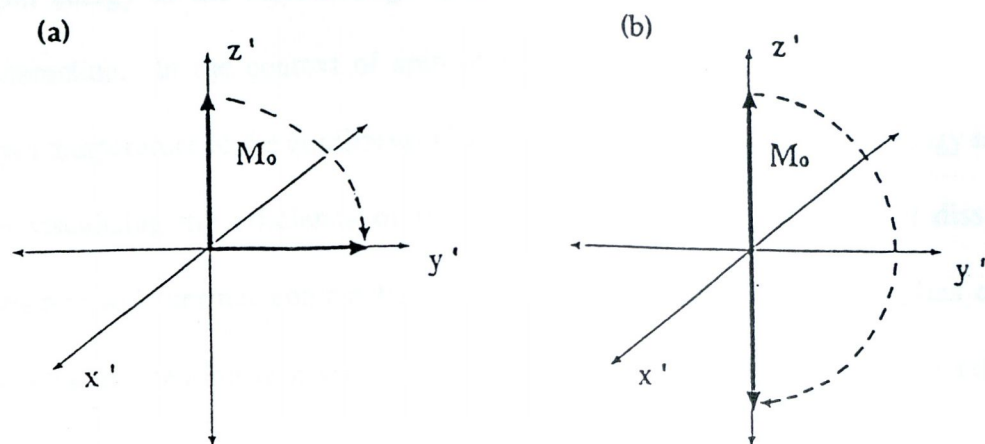


Figure 2.5. The behaviour of the bulk magnetisation, in resonant rotating frame,
 (a) 90° pulse of $H_{1x'}(t)$, aligning M_0 along y' ,
 (b) 180° pulse, inverting M_0 .

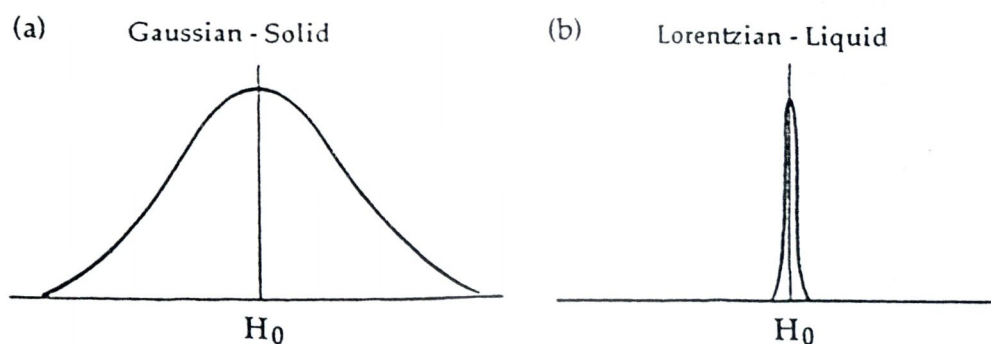


Figure 2.6. Schematic line-shapes resulting from the distribution of local fields H_{loc} about the static field H_0 .
 (a) Typical line shape for solids, exhibiting a Gaussian distribution.
 (b) Typical liquid line-shape, Lorentzian in nature.

spin energy to the surroundings, (collectively known as the lattice) *via* a phonon interaction. In the context of spin temperature,¹² spin-lattice relaxation returns the spin temperature to the equilibrium lattice temperature. This thermal analogy is useful in visualising the efficiency of the relaxation process in terms of heat dissipation, where good thermal contact between the lattice and spin systems implies efficient relaxation resulting in a short relaxation time T_1 , which characterises the relaxation process. T_1 is the spin-lattice relaxation time.

The relationship between T_1 and molecular motion can be visualised as follows: Components of localised magnetic fields, fluctuating at or near the Larmor precession frequency provide the necessary perturbation to induce transitions between spin levels. The origin of these fluctuating fields are nuclear spins attached to the monomer molecules (or oligomers or polymer chains), undergoing molecular motion at the NMR resonance frequency. Spin-lattice relaxation is most efficient (T_1 is short) for molecular motions at or near the resonance frequency. The dominant interactions are dipole in nature for spin $\frac{1}{2}$ systems. For nuclei with electric quadrupole moments, the dominant process is the interaction of the nuclear electric quadrupole with local electric field gradients. The time dependence of M_z including Larmor precession and the effects of spin-lattice relaxation, which is presumed to be exponential, is given by the first Bloch equation¹³ in differential form

$$\frac{dM_z}{dt} = -\gamma(H \otimes M)_z + \frac{(M_0 - M_z)}{T_1} \quad (2.11)$$

2.3.2 Spin-Spin Relaxation (T_2) and Spectral Lineshapes

The theoretical approach used to describe the precession of the magnetisation in a magnetic field in its simplest form assumes that there are no mutual interactions

between neighbouring dipoles. Dipolar interactions lead to a distribution of local fields, $\mathbf{H}_{\text{loc}}$, within the sample and each dipole precesses with a frequency defined by $\mathbf{H}_0 + \mathbf{H}_{\text{loc}}$. In effect, $\mathbf{H}_{\text{loc}}$ generates a local distribution about $\mathbf{H}_0$ (Figure 2.6). In solids the distribution is broad while in liquids neighbouring contributions are averaged spatially to zero, or close to zero, resulting in a narrow resonance, resembling that for isolated spins (*see Table 2.1*). These distributions are mimicked in the spectral lineshapes of solids and liquids (Table 2.2).

Table 2.2. Normalised lineshape functions.⁶

Function Type	Normalised Lineshape
Lorentzian	$L(\nu) = \frac{\delta\nu}{\pi} \left(\delta\nu^2 + (\nu - \nu_0)^2 \right)^{-1}$
Gaussian	$G(\nu) = \sqrt{2\pi\sigma^2} \exp\left\{ \frac{-(\nu_0 - \nu)^2}{2\sigma^2} \right\}$

Note: $\delta\nu$: halfwidth maxim of the lineshape; σ : standard deviation; ν_0 : frequency offset.

In the time domain, it is convenient to visualise the behaviour of the magnetisation $\mathbf{M}_0 = \sum \mu_i$ after a 90° pulse that initially aligns $\mathbf{M}_0$ along the y-axis. The constituent moments μ_i , experience the local field distribution and their initial phase coherence is progressively destroyed due to the corresponding distribution of precession frequencies. Therefore $\mathbf{M}_T$, the transverse magnetisation decays to zero, typically in a time of $10 \mu\text{s}$ for a rigid solid and of the order of milliseconds for a liquid. The characteristic spin-spin relaxation time, T_2 is often assumed to be exponential and the corresponding Bloch equation describes the behaviour of the transverse magnetisation as follows

$$\frac{dM_{x,y}}{dt} = -\gamma(\mathbf{H} \otimes \mathbf{M})_{x,y} - \frac{M_{x,y}}{T_2} \quad (2.12)$$

T_2 monitors the local spatial and temporal nature of neighbouring spins and is a sensitive probe of the local molecular environment in solid systems. T_2 is dominantly determined by dipole-dipole interactions. Under favourable conditions T_2 may be estimated by observing the decay of the magnetisation following a 90° pulse, known as the free induction decay (FID). Other cases require the use of more sophisticated pulse sequences.

2.3.3 Rotating Frame Relaxation ($T_{1\rho}$)

Nuclear T_1 spin-lattice relaxation probes motion in the megahertz range as the recovery of the magnetisation occurs in the large static H_0 field which determines the energy level separation (ΔE). Motion can be probed at lower frequencies while retaining the sensitivity of the T_1 experiment. Recall that the signal-to-noise ratio is proportional to the square of the measured frequency. An ingenious approach which allows the motion at lower frequencies to be examined while retaining the sensitivity of high field polarisation was devised by Slichter and Ailion.¹⁴ They established the magnetisation M_0 in H_0 and then spin-locked M_0 along H_1 and monitored the subsequent decay with a characteristic rotating frame relaxation time $T_{1\rho}$. This is, in effect, a T_1 experiment performed at a lower field strength H_1 which is sensitive to lower motional frequencies in the kilohertz range.

2.3.4 The Bloembergen, Purcell and Pound (BPP) Theory

Bloembergen, Purcell and Pound (BPP) described nuclear magnetic relaxation of liquids in terms of T_1 and T_2 ¹⁵ and this was later extended to $T_{1\rho}$.¹⁶ The principal assumptions on which the theory is based are as follows:

- (i) Isotropic random motion of spins for which the Hamiltonian is averaged to zero.
- (ii) A single correlation time τ_c to characterise molecular motions responsible for relaxation.

The correlation time $\tau_c = (2\pi\nu_c)^{-1}$ characterises the time taken for a molecular entity (such as a molecular moiety, a monomer unit, an oligomer or a polymer chain or side-group) to move, rotate or translate from one site to another. Modifications of both assumptions are required for polymeric systems in the solid state.

Initially motional behaviour can be described in terms of an ideal correlation function as

$$G(\tau) = G(0) \exp\left(-\frac{\tau}{\tau_c}\right) \quad (2.13)$$

where $G(0)$ defines the initial position of the molecule at an arbitrary time and $G(\tau)$ is the position at a time later τ .

This parameter can be viewed as a memory function which has an assumed exponential dependence with a time constant τ_c . Fourier transformation of the correlation function results in a spectral distribution of the motional frequencies, given by

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(i\omega\tau) d\tau = G(0) \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (2.14)$$

where a is a constant and $J(\omega)$, the power spectrum, is a measure of the power available at frequency ω which interacts with the spin system. In Figure 2.7 the spectral density functions at three representative correlation times (τ_c) with respect to

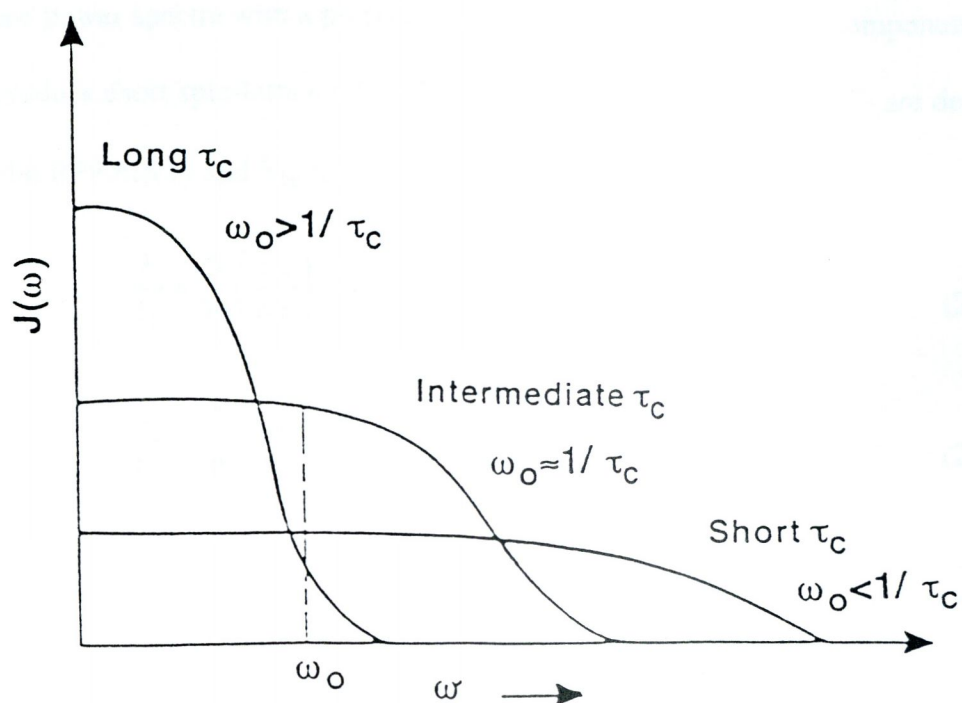


Figure 2.7. Spectral density function $J(\omega)$, for long, medium and short τ_c . Amplitude at ω_o gives indication on the extent of interaction with the nuclear spins.

ω are presented. Since only molecular motions in the region of the precession frequency will enable efficient spin-lattice energy transfer, long and short τ_c 's will result in long T_1 values as the coupling to the lattice is weak. Intermediate τ_c 's will produce power spectra with a preponderance of the required frequency component and thus produce short spin-lattice relaxation times. Expressions for T_1 and T_2 are derived from the BPP theory and $T_{1\rho}$ is derived from extended BPP theory:¹⁶

$$\frac{1}{T_1} = \frac{3}{20} \left(\frac{\mu_o}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r^6} \left\{ \frac{2\tau_c}{1 + \omega_o^2 \tau_c^2} + \frac{8\tau_c}{1 + 4\omega_o^2 \tau_c^2} \right\} \quad (2.15)$$

$$\frac{1}{T_2} = \frac{3}{40} \left(\frac{\mu_o}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r^6} \left\{ 6\tau_c + \frac{10\tau_c}{1 + \omega_o^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_o^2 \tau_c^2} \right\} \quad (2.16)$$

$$\frac{1}{T_{1\rho}} = cH_L^2 \left\{ \frac{\tau_L}{1 + 4\omega_l^2 \tau_c^2} \right\} \quad (2.17)$$

where $\omega_l = \gamma H_l$; c is a constant and $H_l \gg H_L$, the local field.

A plot of T_1 , T_2 and $T_{1\rho}$ for a low temperature secondary relaxation and the glass transition of a model polymer system is shown in Figure 2.8. Under extreme narrowing conditions, *i.e.* liquid systems – very rapid motion, all three relaxation rates theoretically converge. In general terms, the characteristic relaxation times behave as follows:

- a) non-viscous liquid: $T_1 = T_{1\rho} = T_2$
- b) viscous liquid: $T_1 > T_{1\rho} = T_2$
- c) non-rigid solid: $T_1 \gg T_{1\rho} > T_2$
- d) rigid solid: $T_1 \gg T_{1\rho} \gg T_2$

Approximate expressions that may be used to extract the correlation time or frequency from such experimental data are described in Table 2.3.

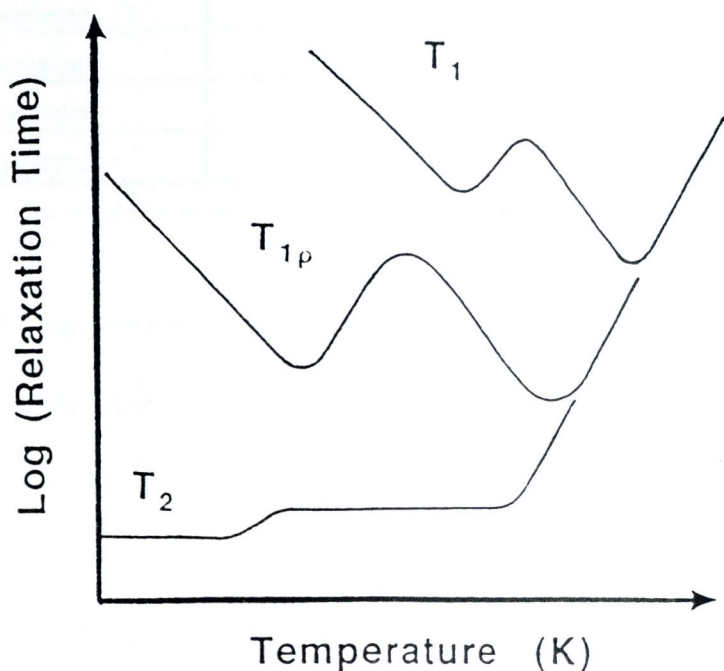


Figure 2.8. Relaxation times, T_1 , T_2 and $T_{1\rho}$, plotted as a function of temperature for an ideal polymer system. The low temperature transition is typical of side-chain or segmental main-chain motion. The high temperature transition is the glass transition. Convergence of the three relaxation times is predicted for short τ_c .

Table 2.3: Broad-line proton expressions used to calculate ν_c in each relaxation regime. S-A implies that Slichter-Ailion conditions apply.

NMR Feature	Expression for ν_c	Range of ν_c (Hz)
T_1 minimum	$2^{1/2} \nu_o$	$4 \times 10^6 - 4 \times 10^8$
S-A region	$1/2\pi T_{1\rho}$	$10 - 10^3$
$T_{1\rho}$ minimum	$\gamma H_1 / 2$	$10^4 - 5 \times 10^5$
T_2 Transition	$1/(2\pi T_{2LT})$	$10^4 - 10^5$

Note: $\frac{1}{T_{2LT}^2} = \frac{1}{T_{2lt}^2} - \frac{1}{T_{2ht}^2}$ where lt and ht refer to the low and high temperature sides of the transition.

T_2 and $T_{1\rho}$ are sensitive to approximately the same frequency regime and therefore occur at about the same temperature. Spin-lattice relaxation transitions are sensitive to higher frequency motions and the corresponding minima occur at higher temperatures.

The BPP theory was derived to describe nuclear relaxation in liquids. As alluded to above, the assumptions underlying the theory do not hold for solids. However, the theory has been modified to account for polymeric solids. Typically T_1 and T_2 relaxation times of the original and modified theories for a log-normal function are illustrated in Figure 2.9.¹⁷ The effect on T_2 is minimal but T_1 is broadened and becomes more shallow for the modified theory compared to the original response.

NMR relaxation measurements can yield key insight into both structure and molecular dynamics and are routinely used in the identification of the molecular motions involved in mechanical transitions and energy dissipation processes in bulk polymers. Meaningful correlation frequencies, which generally fall within a range that typically spans 13 decades of frequency ($10^{-4} < \nu_c < 10^9$ Hz.)^{9,10}, may be extracted from NMR, DMTA and DSC experiments, and collated as a plot of $\log \nu_c$ (or τ_c) as a function of temperature, known as a 'transition map'. The data points tend to lie on well-defined loci, indicating that diverse experimental observations are

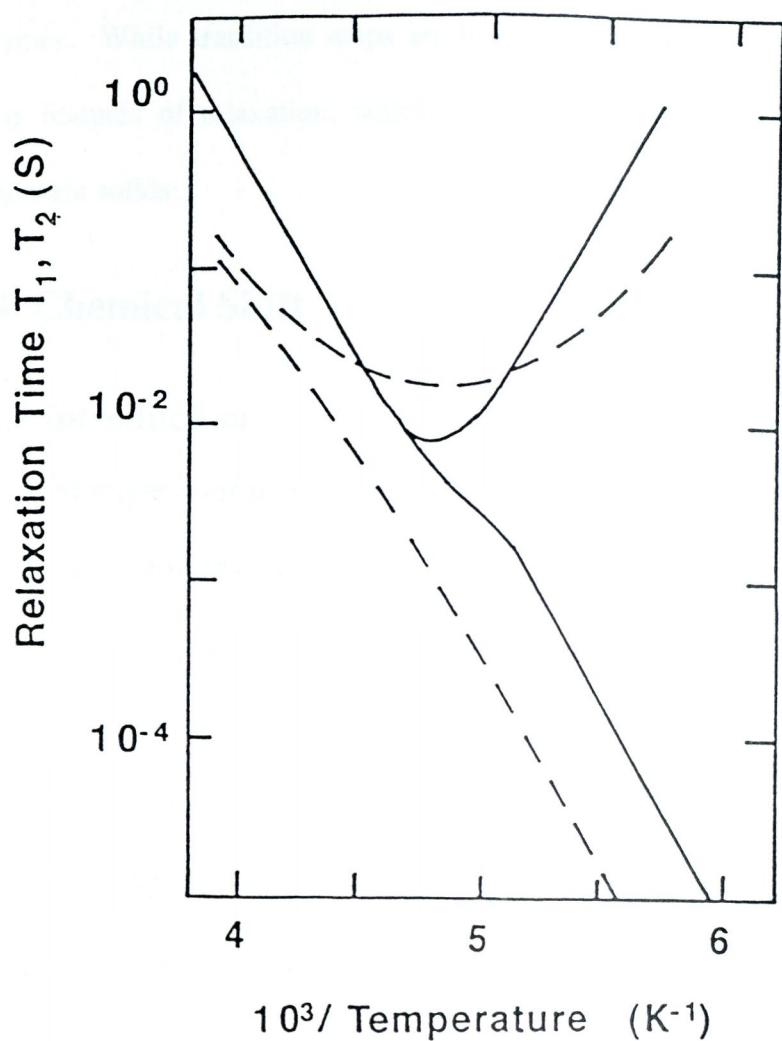


Figure 2.9. T_1 and T_2 relaxation times *versus* inverse temperature for an assumed single correlation time motion (—) and for a broad, log-normal, distribution of correlation times (----).

assignable to specific underlying molecular motions or structural transitions in the polymer. While transition maps are limited in some respects, they do identify the gross features of relaxation, which are important in practical applications of bulk polymeric solids.

2.4 Chemical Shift

2.4.1 Introduction

Multiple resonances are observed in the NMR spectra of liquids and solutions, arising from differences in the electronic environments of the nuclei due to the 'shielding effect' of the electron orbitals. The external field, H_0 , induces orbital currents that produce a small local magnetic field, H_{loc} , which is opposed to H_0 . The nucleus inside the electron cloud experiences an effective field, H_{eff} , that is slightly smaller than H_0 , and therefore resonates at a lower frequency. This is known as electronic shielding. Different resonances for the observed nuclei in a given molecule arise from differences in the shielding effect. The resulting effective field is proportional to the field strength, H_0 . Therefore the shielding field, H_s , is given by

$$H_{eff} = H_0 + H_s = H_0(1 - \sigma) \quad (2.18).$$

where
$$H_s = -\sigma H_0 \quad (2.19).$$

σ is a proportionality factor called the screening constant and is characteristic of the shielding effect caused by the chemical surroundings of the resonant spin.

In the first reported observation of different chemical shifts in the same molecule the 1H NMR spectrum of ethyl alcohol (Figure 2.10) comprised three different lines resulting from the three types of protons, with the ratio of the intensities

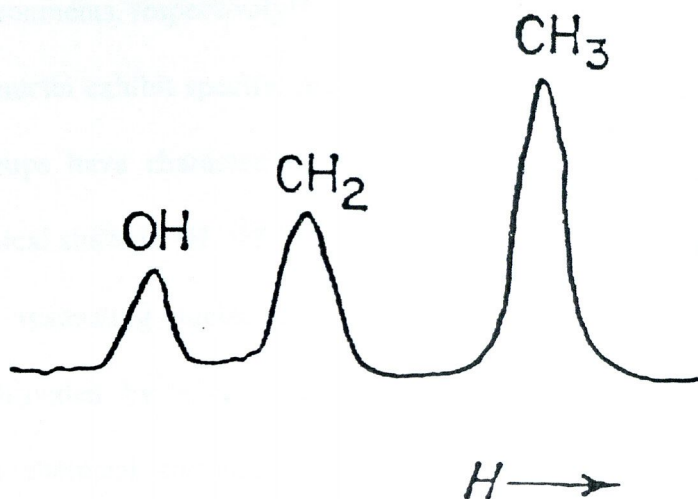


Figure 2.10. The NMR spectrum of ethyl alcohol at low magnetic field, which was the first NMR observation of different chemical shifts in the same molecule.¹⁸

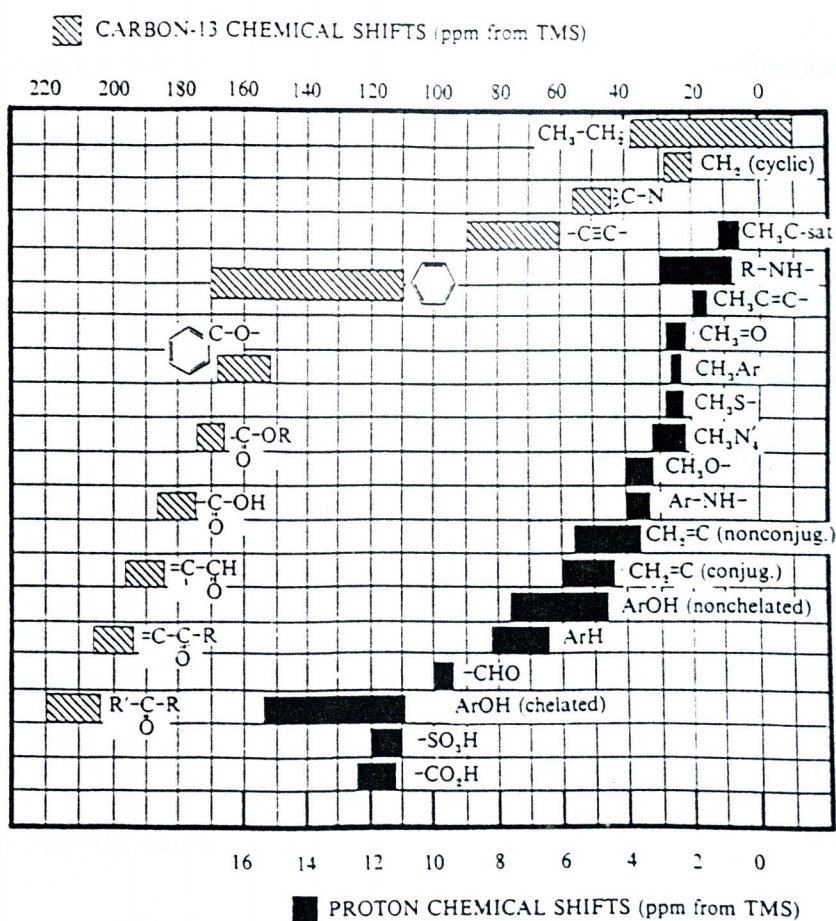


Figure 2.11. Typical ¹H and ¹³C NMR chemical shifts for polymers.⁸

(3:2:1) reflecting the direct relationship to the number of protons in the CH_3 , CH_2 and hydroxyl environments, respectively¹⁸

Since nuclei exhibit specific resonances that depend on their chemical nature, molecular groups have characteristic chemical shifts. Catalogues of correlations between chemical shifts in ^1H , ^{19}F , ^{29}Si and ^{13}C NMR spectroscopy and the chemical nature of the resonating nuclei are widely used, in conjunction with additional information provided by relative spectral peak intensity ratio measurements, to determine the chemical structures of small molecules, monomers and polymers (Figure 2.11).^{8,19-22}

2.4.2 Conventions and Terminology

In order to obtain a point of reference for different effective fields, a standard, generally tetramethylsilane (TMS), is used as an internal reference and a dimensionless number, δ , is defined as a measure of the chemical shift as follows:

$$\delta_{\text{sample}} = (\sigma_{\text{TMS}} - \sigma_{\text{sample}}) \times 10^6 \quad (2.20).$$

The screening constants are found to be approximately 10^{-5} or less, and the factor of 10^6 transforms δ to units of parts per million (ppm). NMR spectra are by convention plotted with increasing wavelength (or decreasing frequency) to the right. Therefore, the more shielded a nucleus is, the lower the frequency of its signal and it appears further towards the right hand side of the spectrum (upfield), with a correspondingly lower chemical shift value. Chemical shift values for ^1H and ^{13}C NMR spectra generally occur over the ranges of 0-20 ppm and 0-200 ppm, respectively, indicating the greater sensitivity and resolution of ^{13}C spectra compared with ^1H spectra.

2.4.3 Other Factors Effecting Chemical Shift

The local field experienced by a nucleus may also be modified by a 'bulk shielding' effect, produced by the surrounding medium,

$$H_{bs} = S_f \chi H_o \quad (2.21).$$

Where χ is the magnetic susceptibility of the medium and S_f is a numerical factor that depends on the orientation and shape of the sample. Since the magnitude of χ is of the order of 10^{-5} for common materials, in principle, its effect cannot be ignored. However, when an internal reference compound is added or is intrinsic to the sample, both experience the same bulk shielding and no corrections for susceptibility effects are necessary. Corrections may be necessary when using external standards.

The magnitude of local diamagnetic shielding effects, as described in *Section 2.4.1.* above, are determined primarily by the local electron density, so factors such as the electronegativity of adjacent atoms are reflected in the magnitude of the observed chemical shifts. Long-range shielding effects, such as ring current shifts from aromatic systems, can also greatly influence chemical shift, though only if the motion of the neighbouring electrons differs according to the orientation of the molecule in the applied field *i.e.* the motion is anisotropic.

The measured value of electronic shielding depends, among other things, on the relative motions of the molecules in the sample. When rapid molecular tumbling occurs, as in non-viscous liquids, the induced secondary field is averaged with respect to the neighbouring nuclei and an isotropic-average chemical shift is observed. When motion is restricted, as with solids, the shielding depends not only on the electronic configuration but also on the orientation of the chemical bonds with respect to the applied field, and the resulting variable chemical shift is said to be anisotropic.

Chemical shift anisotropy also provides a mechanism for spin-spin and spin lattice relaxation.

2.5 Spin-Spin Coupling

At high resolution (high magnetic field) proton resonances split into patterns reflecting the environments of the nuclei. When resonating homonuclear nuclei are in the same molecule, spin-spin interactions via bonding electrons will occur. To the first order, these scalar through-bond interactions are normally observed through three chemical bonds, and are independent of the orientation with the magnetic field and are therefore not averaged to zero by rapid motion in liquids. Information concerning the nuclear spin-states is transmitted through the electron orbitals of the bonds and the result is a splitting of the energy levels to produce new resonances that appear as perturbations of the original energy levels. Figure 2.12 illustrates the various orientations and energy levels of the methyl and methylene protons of ethyl alcohol (*also, see Figure 2.14*) from early ^1H NMR experiments.¹⁸ The splitting patterns observed in the spectra obtained are a direct result of these different energy levels being available to the nuclei and the intensities of the lines are a function of the number of available states for each energy level. The magnitude of the separation of these lines, termed the J coupling constant (Hz), is determined by the strength of the scalar coupling and is specific and characteristic of the chemical nature of the two interacting nuclei. As the number of equivalent nuclei involved in scalar coupling increases, the number of split lines observed in the spectra also increases. In general, the multiplicity of the splitting is given by $2NI_s + 1$, where N is the number of magnetically equivalent nuclei with spin I_s (Figure 2.13). This rule applies to first order scalar interactions, when the chemical shift differences are much greater than

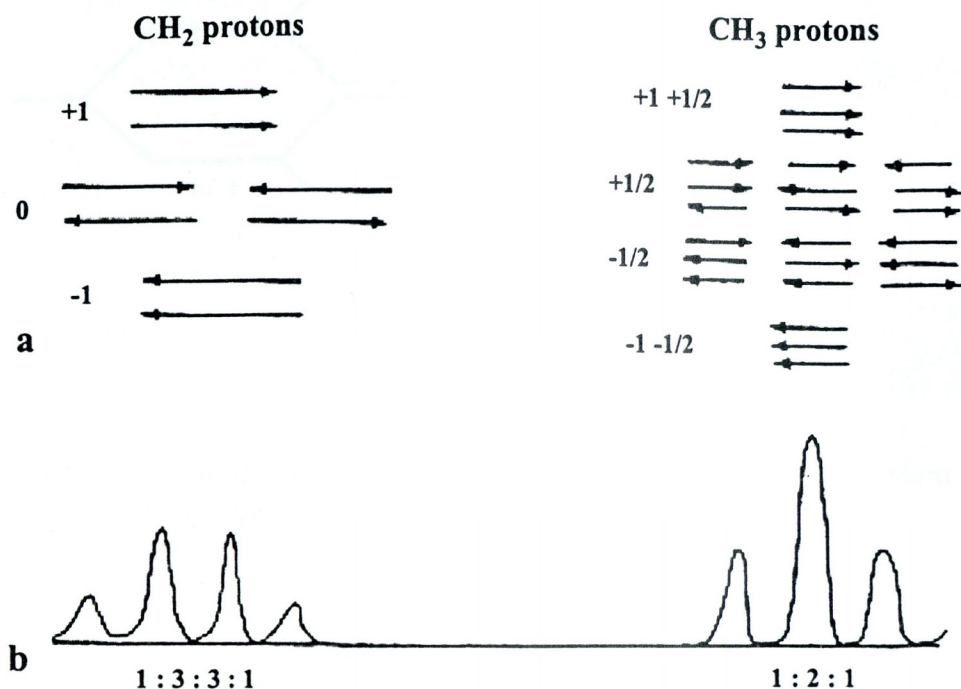


Figure 2.12. Spin-spin coupling diagrams showing a) the possible spin orientations of the methyl and methylene protons of ethyl alcohol and b) the region of the corresponding ^1H NMR spectrum with these functionalities as neighbouring groups.¹⁸

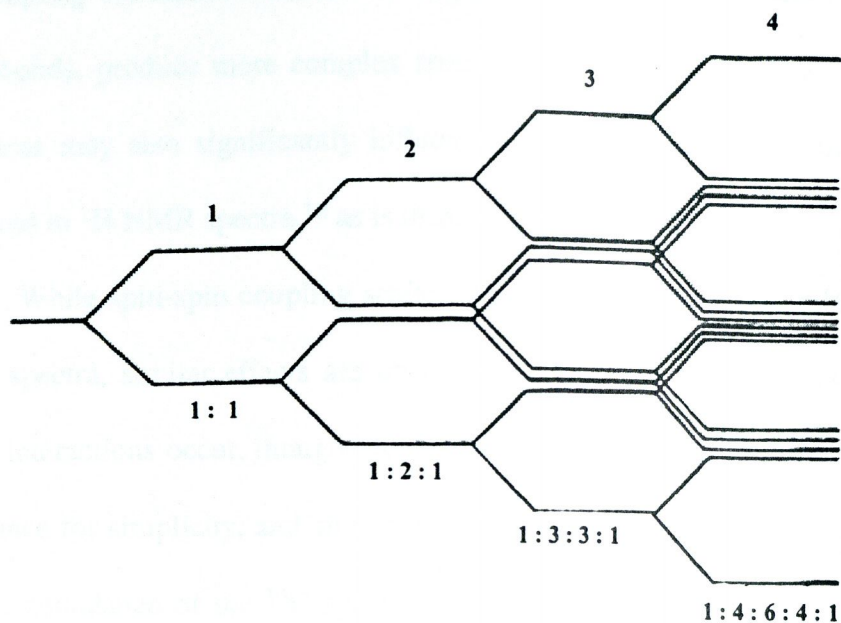


Figure 2.13. The spin-spin coupling effect for increasing numbers of equivalent nuclei showing the number of lines and their relative intensities.

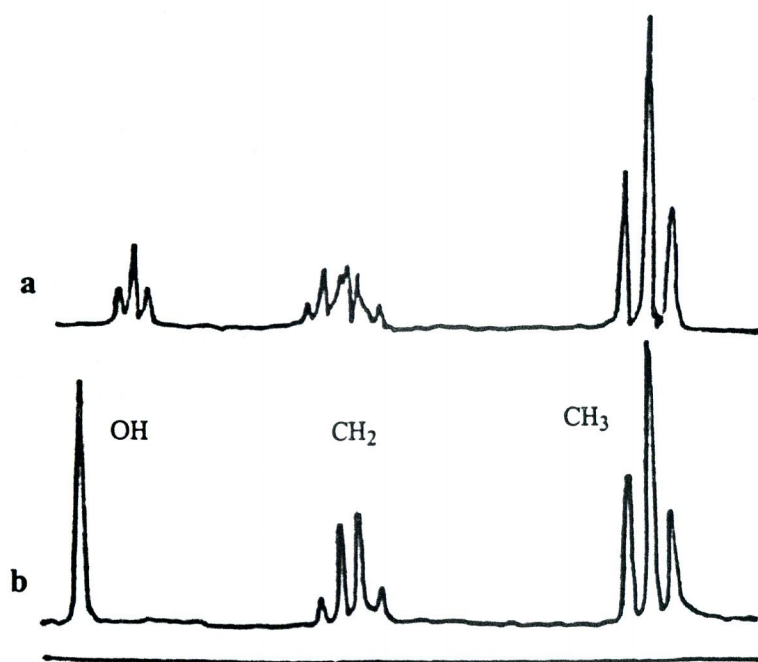


Figure 2.14. ^1H NMR spectra of a) pure dry ethyl alcohol and b) slightly acidic alcohol. The slightly acidic environment causes rapid exchange of the hydroxyl group between neighbouring molecules. This exchange is sufficiently rapid to 'average' the electronic environment.¹⁸

the coupling constants. Second order interactions, which occur through more than three bonds, produce more complex spectral splitting patterns. Chemical exchange processes may also significantly influence the resulting spin-spin splitting patterns observed in ^1H NMR spectra,¹⁸ as is illustrated in Figure 2.14.

While spin-spin coupling scalar interactions have particular relevance for ^1H NMR spectra, similar effects are observed for other nuclei. Heteronuclear ^1H - ^{13}C scalar interactions occur, though they are generally suppressed (decoupled) by double resonance for simplicity, and since the ^{13}C - ^{13}C scalar couplings are weak due to low natural abundance of the ^{13}C species, this ensures the observation single resonance lines in ^{13}C NMR spectra.

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Chapter Three

Experimental Methods

3.1 Introduction

This chapter describes the experimental techniques employed to characterise the curing behaviour of multi-component hydrogel systems and the individual components thereof. While a number of techniques from the fields of thermal analysis and spectroscopy were used to these ends, the efficacy of the various NMR experiments conducted ensured that the technique became the central experimental technique of the entire study. A key feature of the thesis is the development of a new methodology to follow curing of component monomers in a multi-component monomer mixture from initiation to completion.

3.2 Liquid NMR Measurements

The majority of the one- and two-dimensional NMR experiments were conducted using a high resolution Bruker MSL 300 spectrometer¹ operating at a frequency of 300.13 MHz for proton (^1H) and 74.47 MHz for carbon (^{13}C), respectively. The instrument comprises of a superconducting magnet with a field strength of 7.05 tesla and an Aspect 3000 data recording station and console, shown schematically with the remaining elements of the spectrometer in Figure 3.1. Sample temperature control of ± 1 K was achieved with a Bruker BVT-1000 temperature controller unit. A number of modifications were made to a Bruker multinuclear, 5mm CIDNP probe (section 3.2.4.1), which was used in most of the NMR experiments involving *in situ* curing with UV light. Other spectra were collected using a high

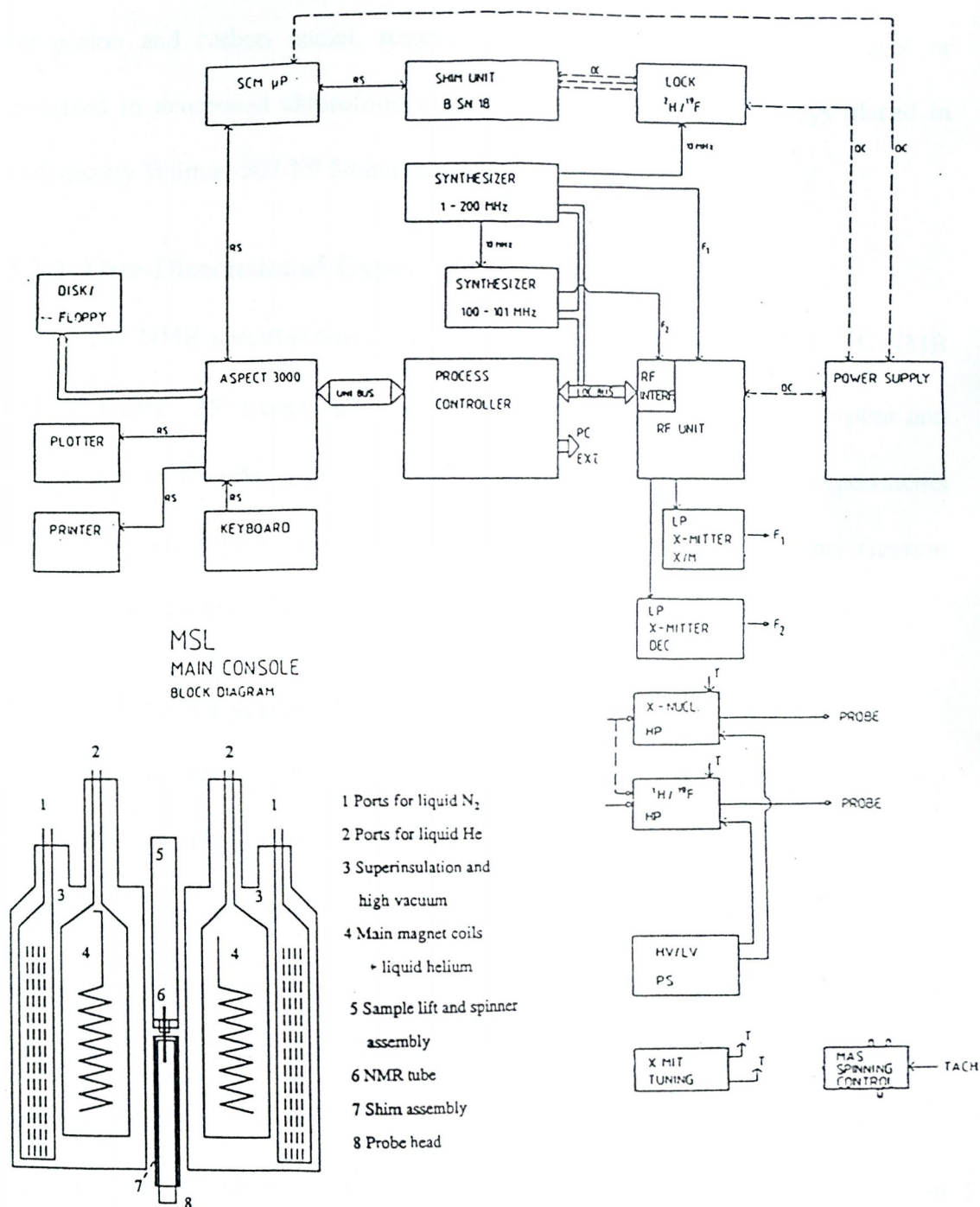


Figure 3.1. Block diagram of the components of the MSL300 NMR spectrometer and the construction of the superconducting magnet.

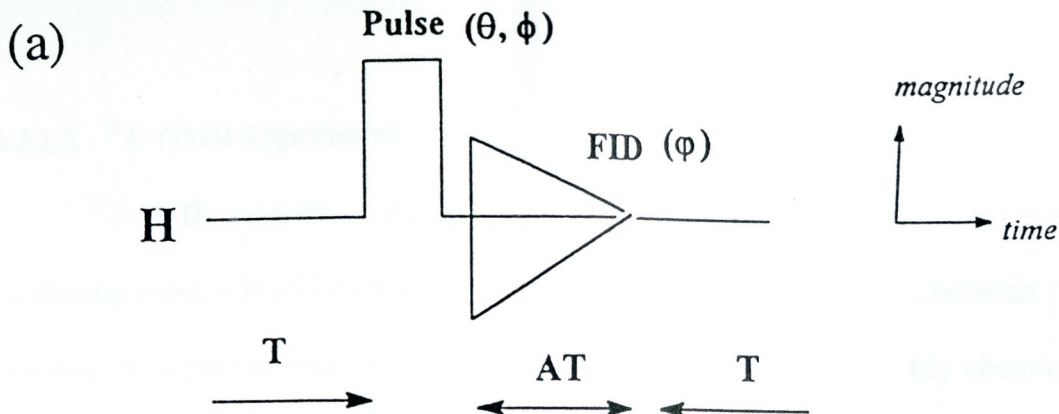
resolution Bruker DPX 400 spectrometer, operating at 400.14 MHz and 100.14 MHz for proton and carbon nuclei, respectively. The liquid samples, either neat or dissolved in deuterated chloroform containing 0.03% TMS, were always placed in high quality Wilmad 507-PP 5mm diameter NMR tubes.

3.2.1 One-Dimensional Experimental Techniques

1-D NMR spectroscopic techniques include the standard ^1H -NMR, ^{13}C -NMR and ^{13}C -DEPT 135° experiments, as described below. In addition, 1-D proton and carbon spin lattice relaxation time (T_1) (section 3.2.3) and liquid NMR experiments probed the cure profile, structure and relaxation of the hydrogel systems (section 3.2.4). Pulse sequences and representative spectra are shown in each case.

3.2.1.1 ^1H -NMR Experiment

The standard ^1H -NMR experiment provides structure-related, site-specific information in the sample *i.e.* chemical shifts, spin-spin couplings and peak intensities.² Figure 3.2(a) shows the pulse sequence and the accompanying table provides the phase cycling routine used to collect ^1H -NMR spectra such as the one shown in Figure 3.2(b). The data collected following the application of a short radio frequency (*r.f.*) pulse (3 μs , 28° tip angle) yields the Free Induction Decay (FID). Quadrature phase detection with phase cycling ensures that the selected observation frequency is in the centre of the spectral range. This sequence routinely used a 5 second recycle delay time and a sample spinning rate of 20 Hz to obtain proton spectra of the liquid monomers (neat and in solution).



- RF Pulse - Pulse width ($\theta : 20-90^\circ$) and phase (ϕ)

Pulse Phase cycle	+X	-Y	-X	+Y
Receiver cycle	+X	-Y	-X	+Y

- Signal response - Acquisition time (AT)

- Delay Time and Recovery of Magnetisation (T) - T_1 dependence
(the delay is usually $5T_1$ i.e. 5 to 60secs depending on θ utilised)

- Frequency and observation range
(e.g. ^1H : 300.13MHz, typical bandwidth 3600Hz or 12ppm)

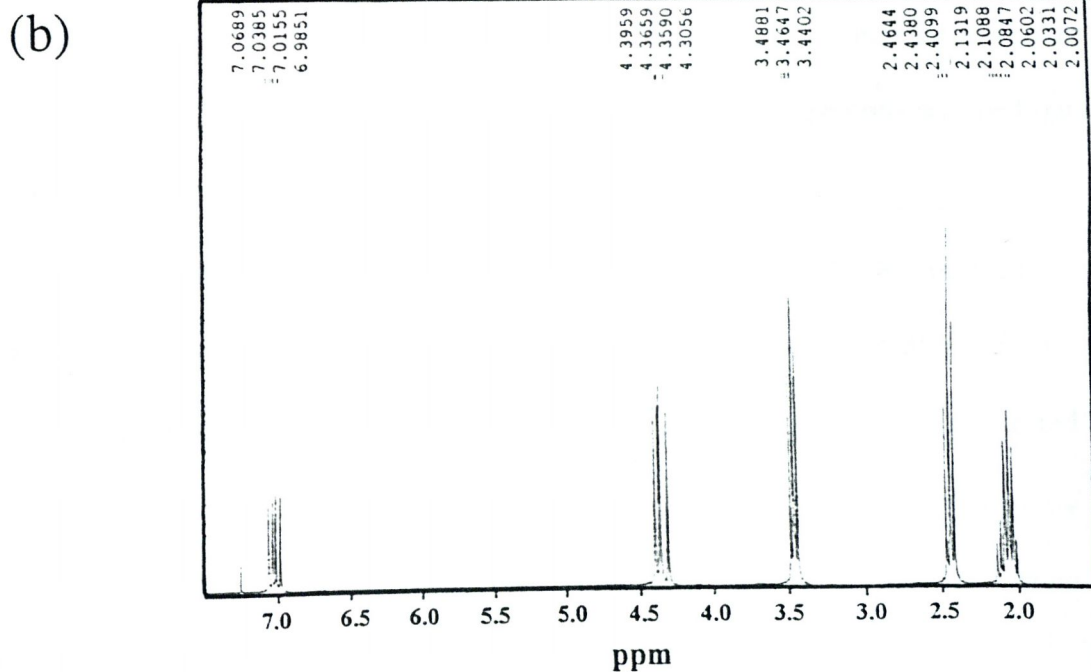


Figure 3.2. The pulse sequence and the phase cycling routine (a) used to collect ^1H -NMR spectra (b) (NVP in CDCl_3).

3.2.1.2 ^{13}C -NMR Experiment

^{13}C -NMR spectra were recorded under proton broadband decoupling conditions using a WALTZ16 phase cycling routine along with data accumulation (to improve the signal to noise ratio). The resulting spectra contained the key chemical shift information.² To achieve proton broadband spin decoupling in ^{13}C -NMR spectra, the irradiation frequency applied on the proton channel is pulse-modulated over a wide range of frequencies in order to disrupt the couplings between proton and carbon spin systems effectively.³ Figure 3.3(a) shows the pulse sequence used to collect ^{13}C -NMR spectra such as the one shown in Figure 3.3(c).

When the ^1H channel is irradiated both during the delay time (T) and the data acquisition time (AT), the relaxation profile of the entire spin system is altered. Cross-relaxation between neighbouring ^1H - ^1H and ^1H - ^{13}C spin systems can occur and a nuclear Overhauser Effect (NOE) is observed. NOE results in an increase in signal strength of up to a factor of 2.9 for carbon systems with multiple protons attached but has no effect on quarternary carbon intensities.

While NOE improves the sensitivity of a standard ^{13}C -NMR spectrum, it complicates interpretation of peak areas in terms the relative concentration of site-specific carbon moieties on the polymer chain. However, use of 'inverse gated decoupling'⁴ through selective irradiation of protons during the acquisition time only (Figure 3.3(b)), produces a decoupled spectrum with no NOE signal for use in more direct quantitative measurements.

3.2.1.3 ^{13}C -DEPT NMR Experiments

Freeman and Morris (1979) devised a pulse sequence called 'Insensitive Nuclei Enhanced by Polarisation Transfer' (INEPT) by which, as the name suggests,

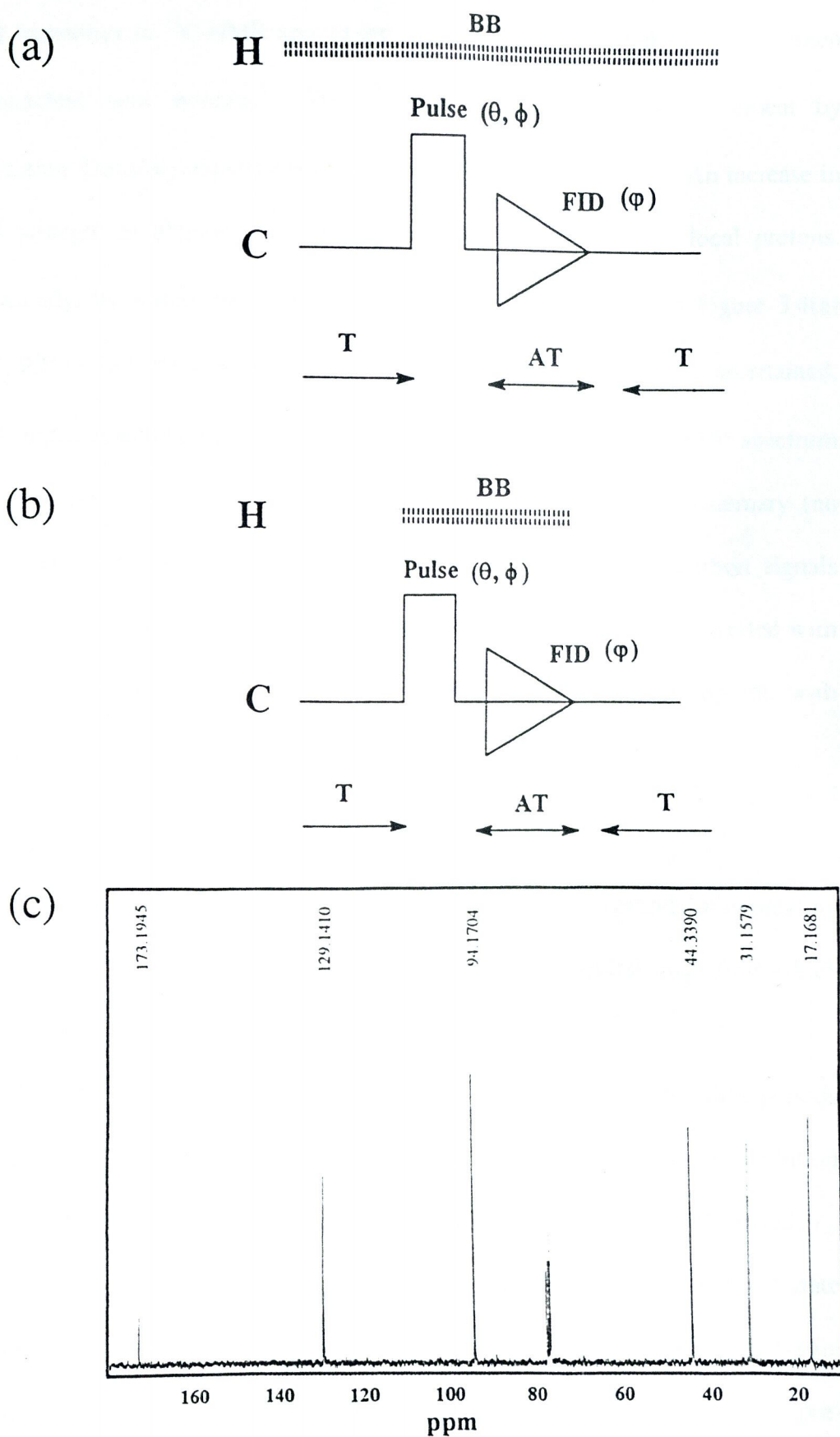


Figure 3.3. The 'standard' pulse sequence (a) used to collect ^{13}C -NMR spectrum (c) (NVP in CDCl_3). (b) the 'inverse gated' pulse sequence used to obtain ^{13}C -NMR spectra with no NOE signal enhancement. BB = broadband.

signal intensities in ^{13}C -NMR spectra are increased by polarisation transfer between heteronuclear spin systems.⁵ The ^{13}C -DEPT (Distortionless Enhancement by Polarisation Transfer) sequence is a modification of this experiment.⁶ An increase in signal strength is observed for carbon resonances spin-coupled to local protons. Additionally, by setting the pulse width (θ) of the third ^1H pulse in Figure 3.4(a) to 45° , 90° or 135° the number of protons attached to each carbon can be ascertained. For example, selecting a pulse width $\theta = 135^\circ$, results in a ^{13}C -DEPT 135° spectrum (Figure 3.4(b)) which provides the following spectral features; (i) quaternary (no protons attached) carbon peaks are suppressed, (ii) methine (CH) carbon signals remain upright and unaltered (iii) methylene (CH_2) carbon signals are inverted with enhanced intensity and (iv) methyl (CH_3) carbon resonances appear upright with enhanced intensity. This greatly facilitates spectral peak assignments.

3.2.2 Two Dimensional Experimental Techniques

Two dimensional (2-D) NMR techniques are powerful methods of expressing chemical shift, relaxation and coupling information in one spectral map, from which structural information can be readily extracted.

In 2-D experiments, raw data are collected as a function of two time periods which follow an initial preparation time period (T): these are termed the evolution period (t_1) (which may also include a mixing period) and the detection period (t_2) (Figure 3.5(a)). The preparation period involves excitation of nuclei to a known state by at least one *r.f.* pulse. In the evolution period the chemical shifts and spin-spin couplings evolve. During the mixing period the spin systems are subjected to a pre-selected interaction (generated by the selected pulse sequence) such as homonuclear or heteronuclear spin coupling, which creates an observable transverse magnetisation.

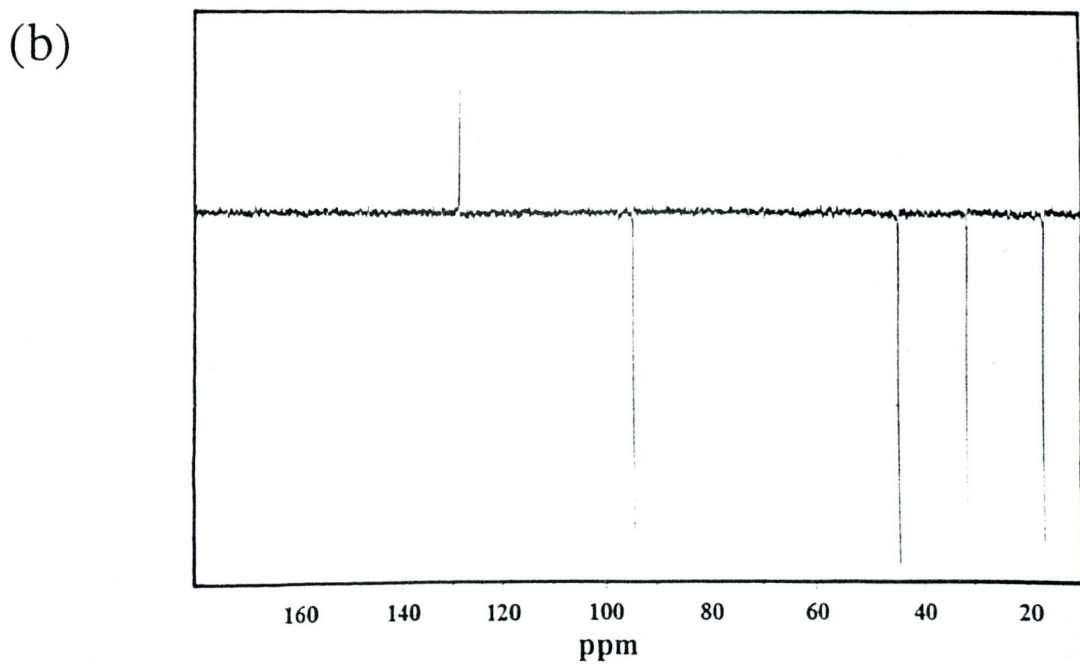
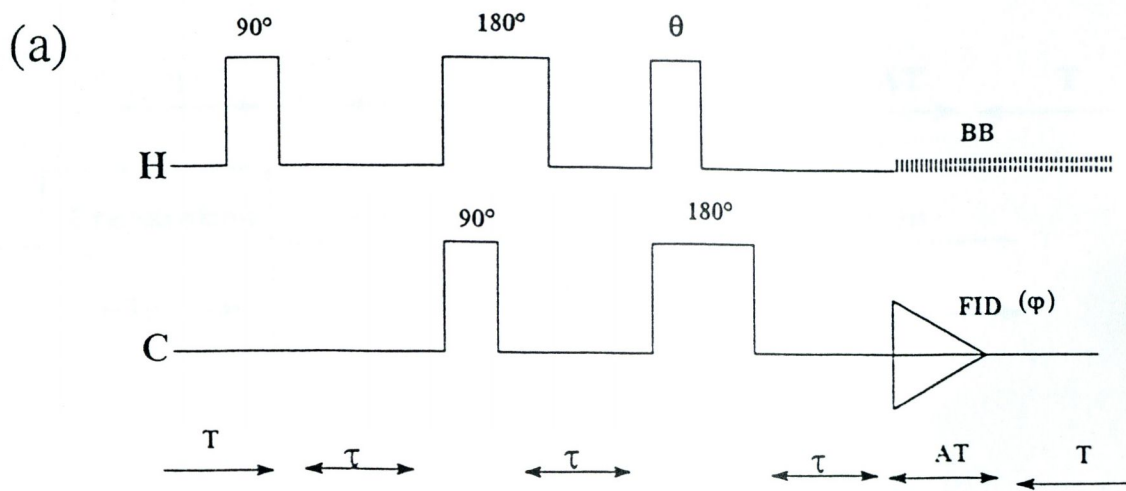


Figure 3.4. The pulse sequence (a) used to collect ^{13}C -DEPT 135° NMR spectra (b) (NVP in CDCl_3). BB = broadband.

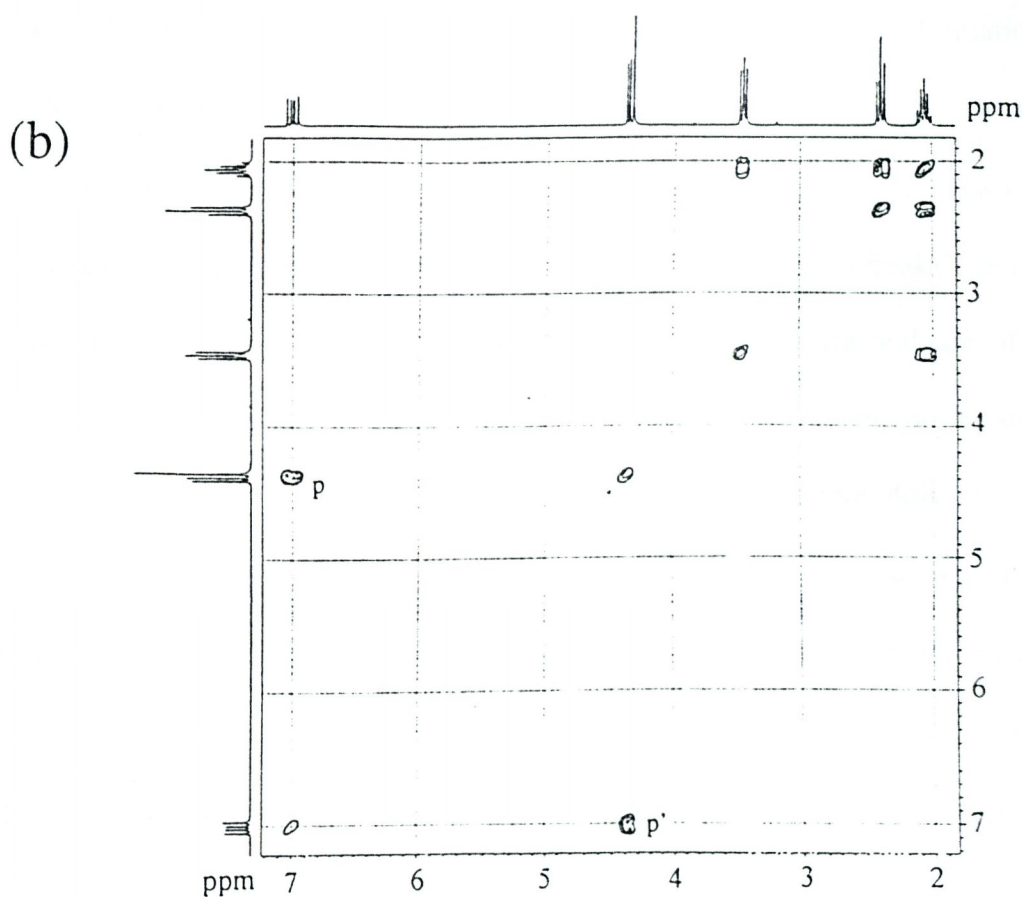
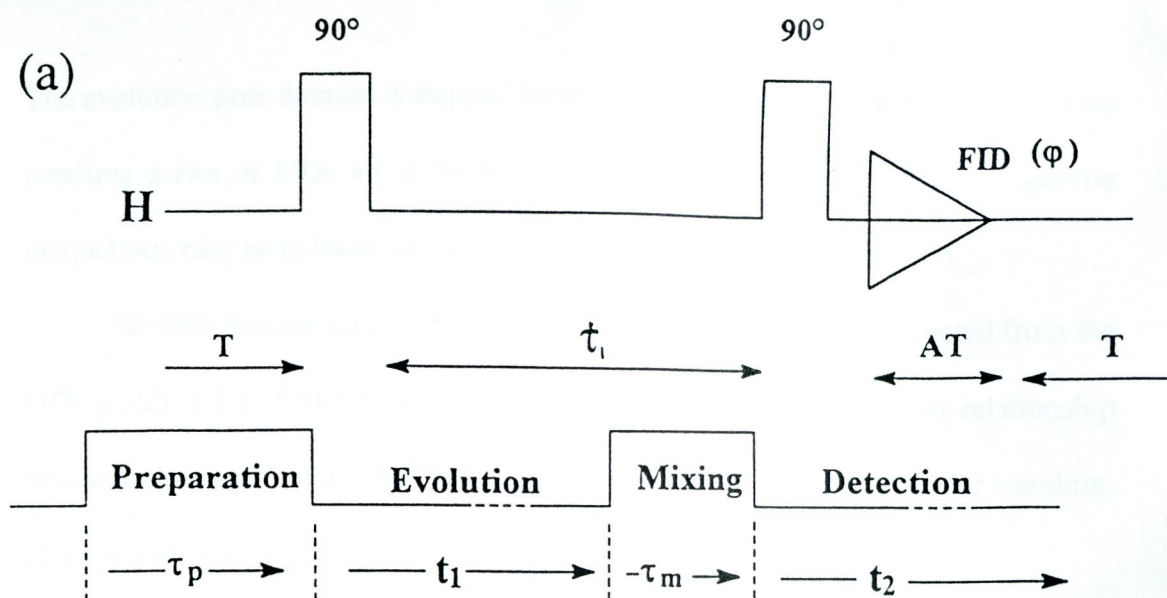


Figure 3.5. The pulse sequence (a), which consists of a preparation time period (T), an evolution and mixing period (t_1) and a detection period (t_2), used to obtain 2-D ^1H - ^1H COSY spectra (b) (NVP in CDCl_3). Cross peaks always appear as pairs in matched positions (p, p') in the spectra.

The evolution time domain is stepped incrementally through a range of values and the resulting series of FIDs are collected during the detection period. Further specific interactions may be induced during the detection time domain, as required.

Double Fourier transformation of matrices of data points constructed from the FIDs yields a 2-D NMR spectrum with two frequency axes. The inter-relationship between the axes is established through homonuclear or heteronuclear scalar coupling, as described in the literature.^{7,8}

3.2.2.1 ^1H - ^1H COSY NMR Experiment

Homonuclear correlation spectroscopy (^1H - ^1H COSY) is the technique most frequently used in 2-D-FT NMR⁹ and the resulting spectra provide information on complex spin-spin coupling systems in the form of a two-dimensional map. Standard 1-D ^1H NMR spectra are shown on both the vertical and horizontal axes. Two types of peak are displayed in the 2-D spectra. The first are the 'diagonal peaks', along the diagonal intersection of both axes; these mimic the 1-D spectra and are of little interest. The second are the 'cross peaks' resulting from communication between protons or groups of protons which are near neighbours in the sample molecule.

2-D ^1H - ^1H COSY spectra therefore provide information about the physical location of protons relative to each other, which further elucidate molecular structure. Cross peaks always appear as a pair in matched positions (p, p') in the spectra (Figure 3.5(b)). The pulse sequence used to obtain a 2-D ^1H - ^1H COSY spectrum is shown in Figure 3.5(a).⁸

3.2.2.2 ^1H - ^{13}C COSY NMR Experiment

In heteronuclear COSY experiments (^1H - ^{13}C COSY)¹⁰, one axis shows the standard ^1H NMR spectrum; the other is the decoupled ^{13}C spectrum. A two dimensional ^1H - ^{13}C correlation experiment of this type yields cross signals for all ^1H and ^{13}C nuclei directly bonded to each other (Figure 3.6(b)). Hence, the assignment of one member of a spin coupled pair leads immediately to the assignment of the other.

The relevant pulse sequence used to obtain a 2-D ^1H - ^{13}C COSY spectrum (Figure 3.6(a)) incorporates broadband proton decoupling while collecting the ^{13}C data.^{8, 10} Hence the ^{13}C component appears as a decoupled spectrum.

3.2.3 Spin Lattice Relaxation Time (T_1) Measurements

^1H and ^{13}C spin lattice relaxation times (T_1) using the inversion recovery technique were recorded for neat liquid samples of both the individual monomers and of the composite mixtures (*Chapter 5*).

Knowledge of the spin lattice relaxation times of these systems was a necessary prerequisite for the subsequent curing studies in order to establish the recycle time in spectral acquisition and accumulation ($\geq 5T_1$). This ensured that the spin systems returned fully to their equilibrium state to avoid spectral distortion.

T_1 values of a liquid monomer mixture were routinely monitored over the course of a photoinitiated polymerisation process (*Chapter 7*).

3.2.3.1 T_1 (^1H): Inversion Recovery Experiment

The inversion recovery sequence¹¹ is commonly used to determine T_1 . The 180° pulse of the $180^\circ - \tau - 90^\circ$ sequence inverts the equilibrium bulk magnetisation M_0 , which then reverts to its equilibrium at a rate characterised by (T_1) (Figure 3.7).

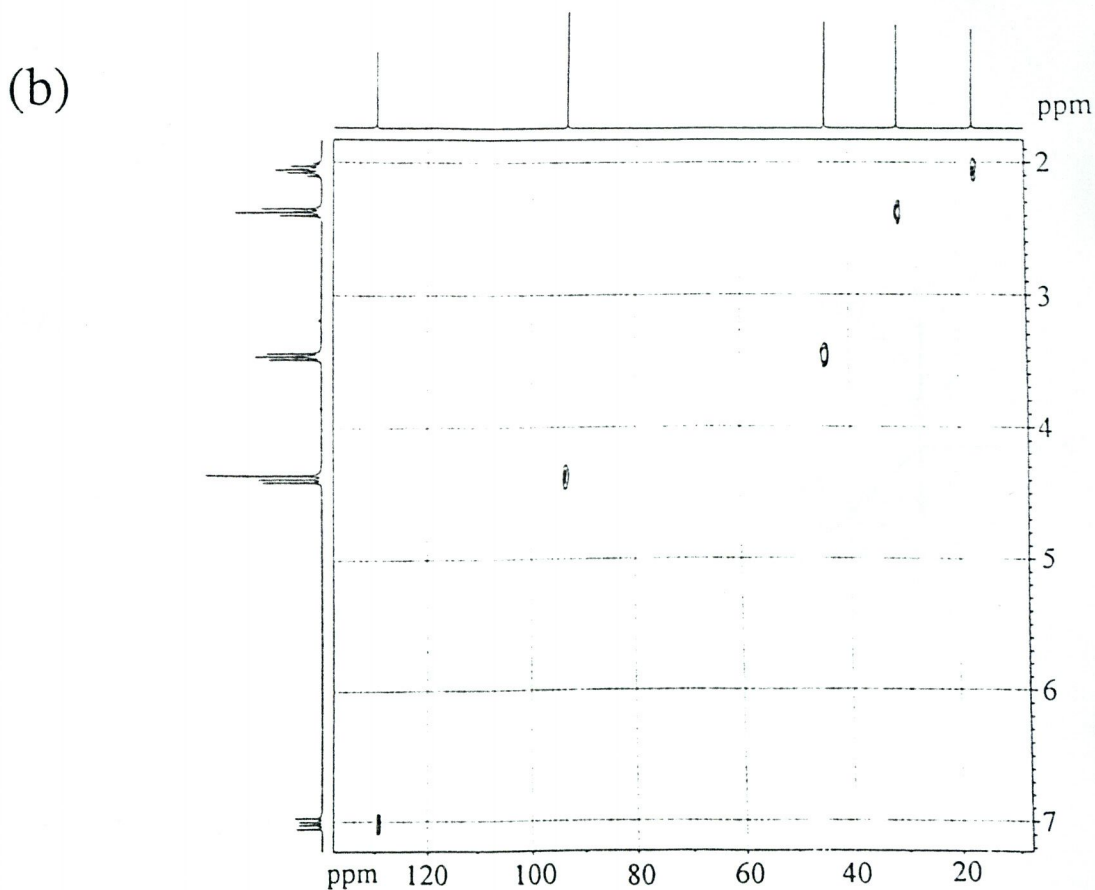
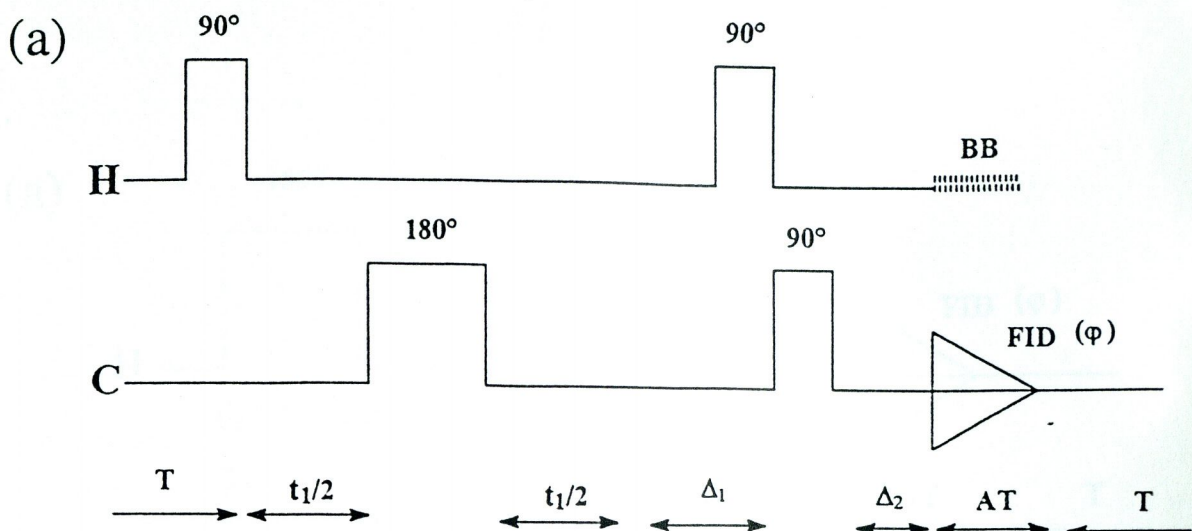


Figure 3.6. The pulse sequence (a) used to obtain 2-D ^1H - ^{13}C COSY spectra (b) (NVP in CDCl_3), which shows cross signals for all directly bonded ^1H and ^{13}C nuclei. BB = broadband.

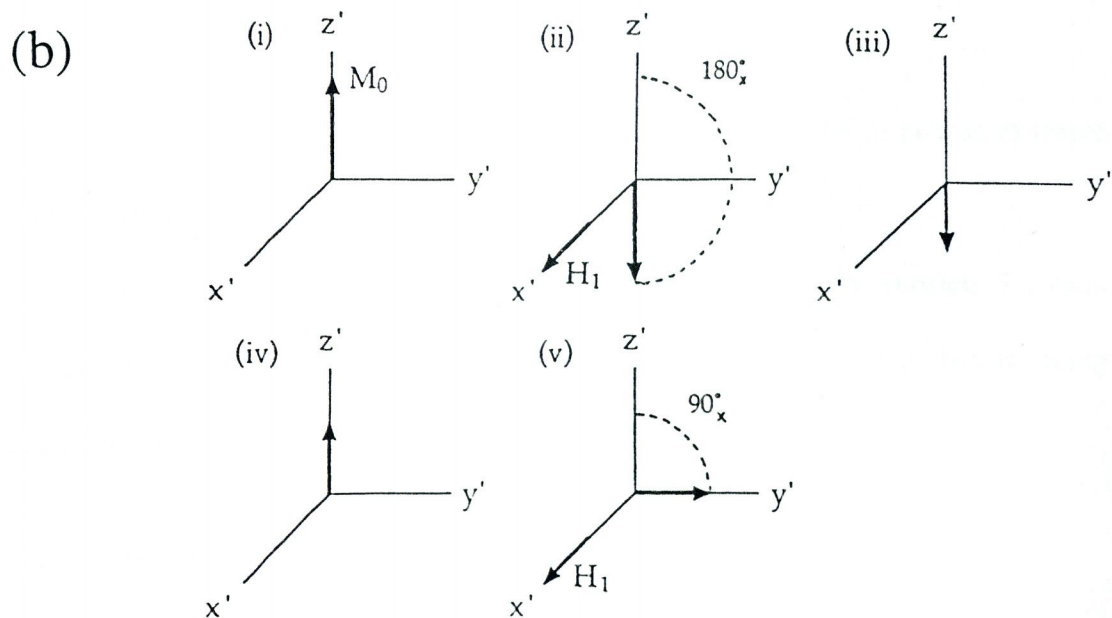
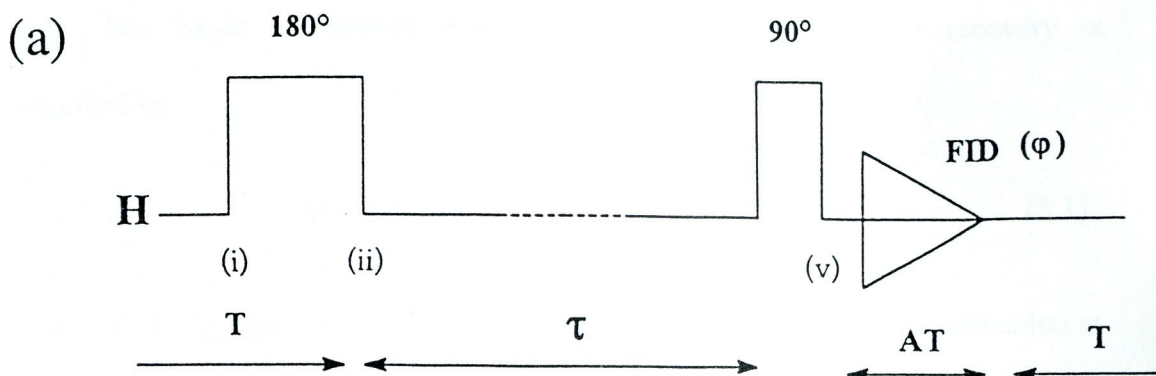


Figure 3.7. The 'inversion recovery' pulse sequence (a) used to obtain $T_1(^1\text{H})$. (b) the behaviour of the net magnetisation in the rotating frame of reference.

The 90° pulse monitors $M(\tau)$ for a range of τ values and the resulting spectra are collected (Figure 3.8(a)).

For single component relaxation decays the magnetisation recovery is described by

$$M(\tau) = M_o \left\{ 1 - 2 \exp\left(\frac{-\tau}{T_1}\right) \right\} \quad (3.1)$$

where, M_o is the equilibrium magnetisation and $M(\tau)$ is the measured magnetisation at time (τ).

T_1 can be determined by plotting

$$\ln \left\{ \frac{M_o - M(\tau)}{2M_o} \right\} \text{ vs. } \tau \quad (3.2)$$

or, in the case of exponential decay, from the null point, *i.e.* where $M(\tau)=0$,

$$\tau_{\text{null}} = T_1 \ln 2. \quad (3.3)$$

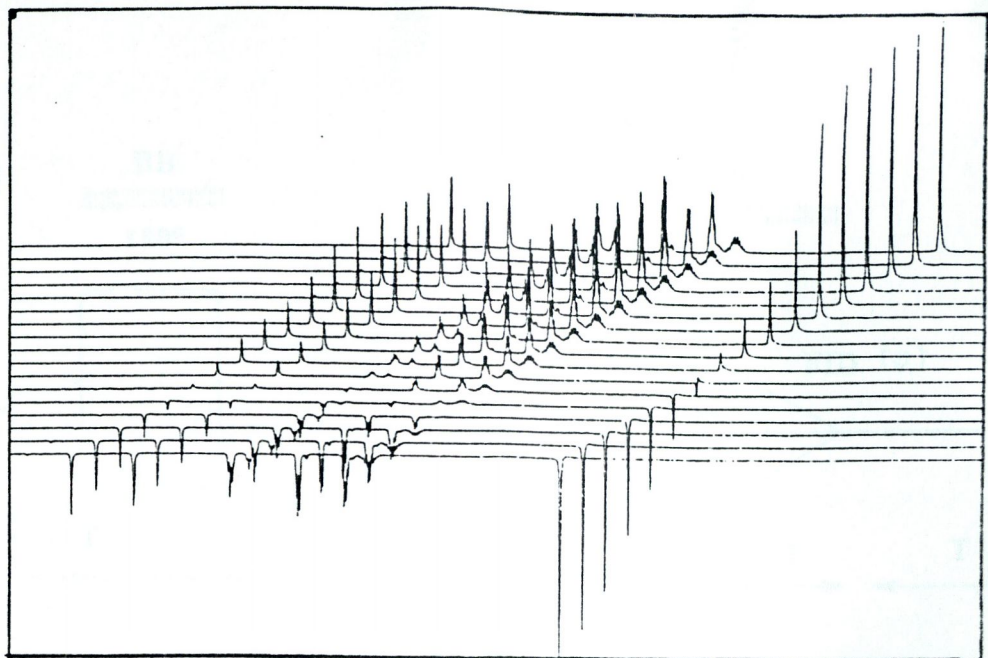
A typical suite of $T_1(^1\text{H})$ spectra is illustrated in Figure 3.8(a) and an example T_1 exponential decay is portrayed in Figure 3.8(b).

Because dissolved paramagnetic oxygen can dramatically shorten T_1 , each sample was degassed by exposure to nitrogen in an atmosphere bag before being sealed in a NMR tube.

3.2.3.2 $T_1(^{13}\text{C})$ Measurement

The pulse sequence in Figure 3.9a was used to determine $T_1(^{13}\text{C})$: as discussed above certain resonances are selectively enhanced due to the NOE effect (*section 3.2.1.2*). 'Inverse gated decoupling' (Figure 3.9(a)) suppressed NOE signal

(a)



(b)

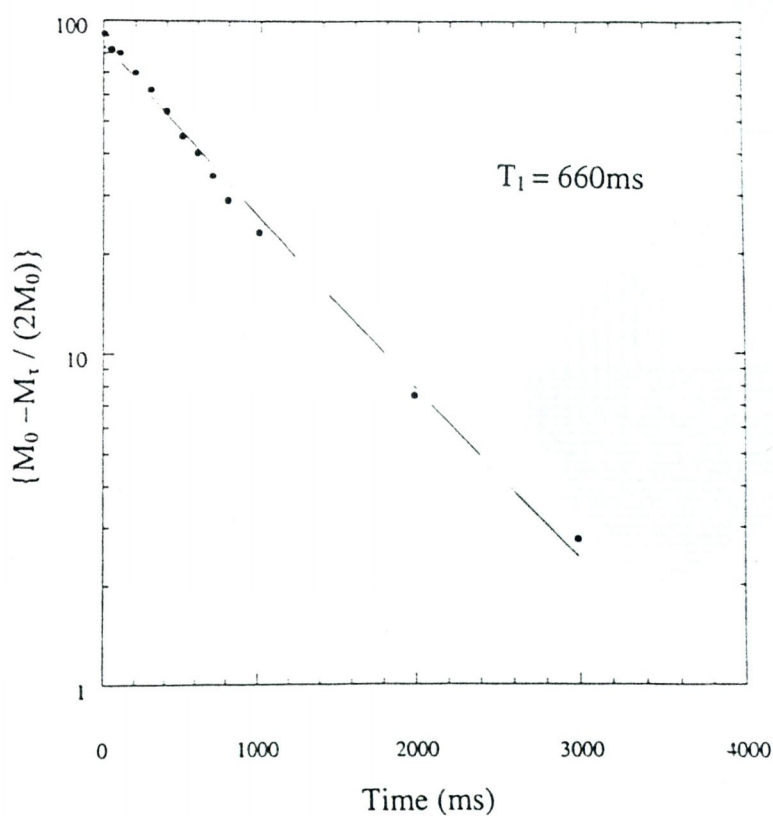


Figure 3.8. A typical suite of $T_1(^1\text{H})$ spectra (a) and the resulting exponential decay plot (b) used to determine the spin-lattice relaxation time, T_1 .

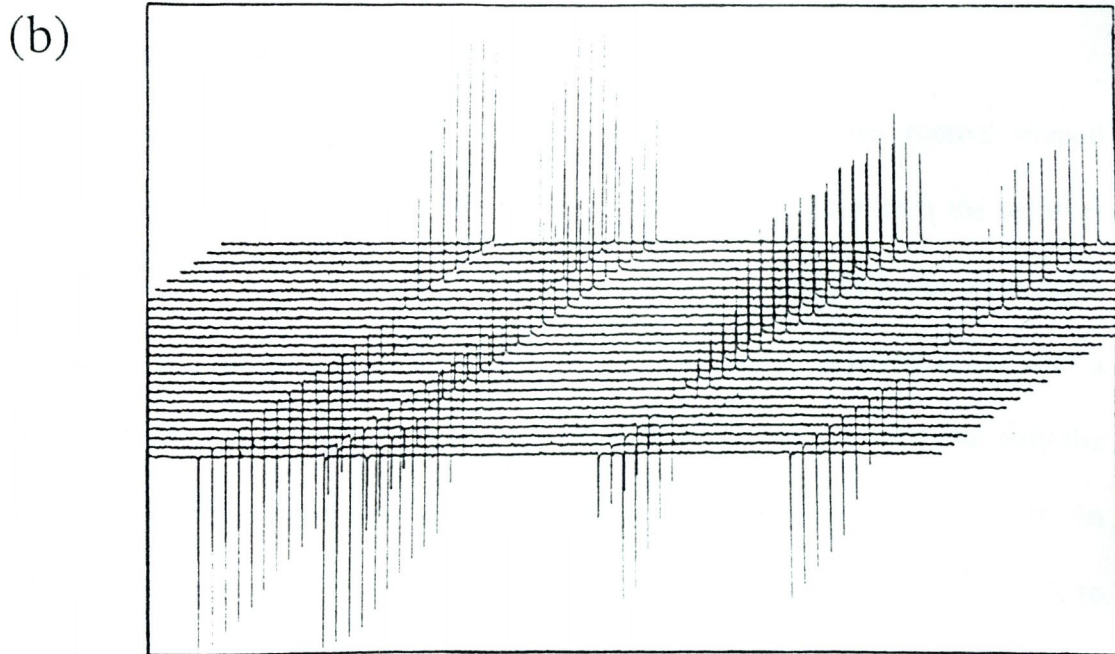
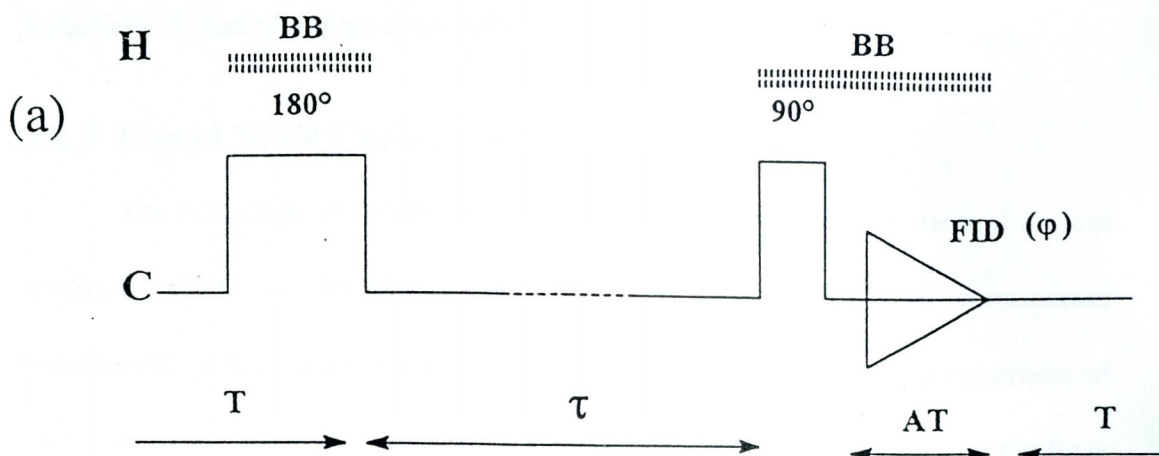


Figure 3.9. Inverse gated decoupling was applied to the ^{13}C inversion recovery pulse sequence (a) to suppress NOE signal enhancement. A typical suite of $T_1(^{13}\text{C})$ spectra (b).

enhancement if required. A typical suite of spectra is shown in Figure 3.9(b). Routinely, all samples were degassed to remove dissolved paramagnetic oxygen.

3.2.4 Liquid NMR Curing Profiles of Hydrogel Systems

The full range of NMR experiments discussed above complemented current literature results in identifying the individual spectral lines of all comonomer constituents. It was further possible to label peaks that were uniquely characteristic of each component in the composite monomer mixture. As the monomers cure, the lines broaden considerably and in an NMR liquids probe, are subsumed into the baseline as described in *Chapter 7*. The conversion of monomer into polymer can therefore be monitored as a function of time as *in situ* curing progresses. The details of the technique will be discussed more fully in *Chapter 7.1.4*.

3.2.4.1 CIDNP Probe Modifications

A standard 5mm CIDNP commercial NMR probe has an internal shaped quartz light rod, which reflects light passed along its vertical axis into the receiver coils area. To effect *in situ* curing a number of modifications to the probe were made in order to provide efficient UV light delivery to the sample. A teflon cover with a small aperture was placed over the top of the quartz rod, which ensured that only the sample area within the receiver coils of the probe was illuminated (Figure 3.10). In addition, the base of the probe was modified to allow a UV grade fibre optic bundle to be coupled securely to the end of the quartz light rod.

A coupling stage was designed and built to facilitate transmission of light pulses produced by a VSL-337 nitrogen laser (Laser Science Inc.) along the fibre optic bundle (3mm core diameter). This was, in turn, connected to the base of the CIDNP

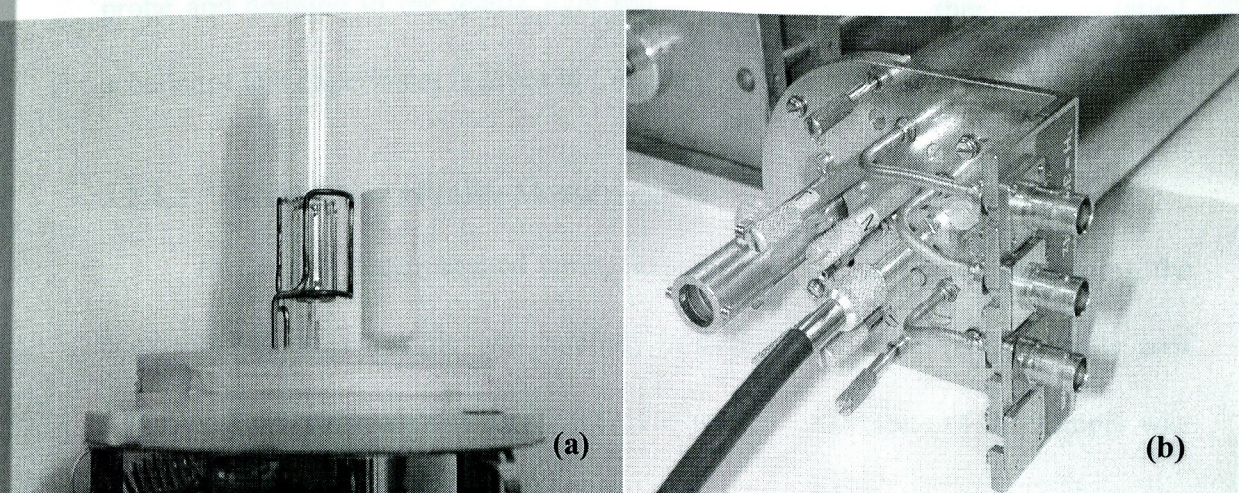


Figure 3.10. (a) A Teflon[®] cover with a small aperture was placed over the end of the quartz light rod, which permitted illumination of the receiver coils area of the modified NMR probe only. (b) The base of the probe was modified to allow a UV grade fibre optic bundle to be coupled to the end of the quartz light rod.

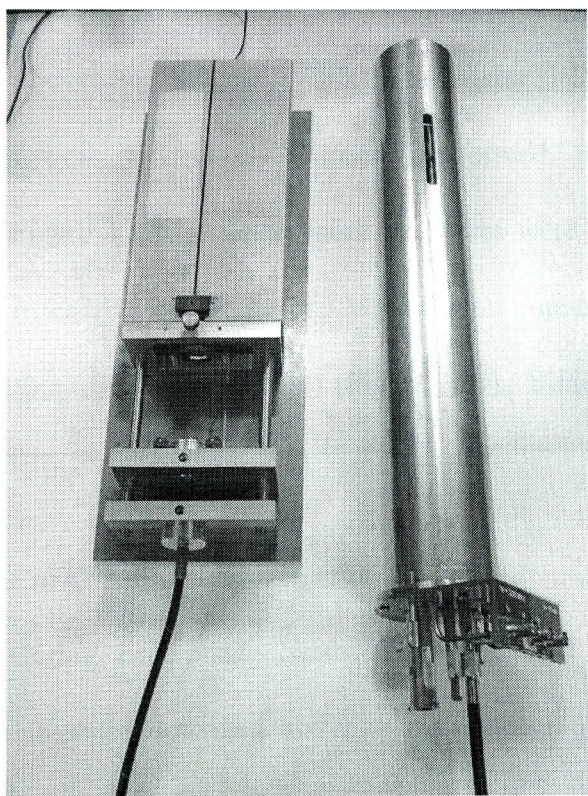


Figure 3.11. The coupling stage allowed light pulses, produced by a VSL-337 nitrogen laser, transmitted *via* a UV grade fibre optic bundle (coupled to the quartz light rod of the CIDNP probe) to illuminate the sample *in situ*.

probe and coupled to the quartz light rod (Figure 3.11). A further, more detailed, account of this experiment is given in *Chapter 7*.

3.2.4.2 ^1H -NMR Cure Profile Measurements

In the UV photoinitiated curing experiments, the NMR tube containing the degassed monomer sample was carefully positioned within the receiver coils area where it was irradiated with UV light. The chosen temperature of the sample was fixed for the duration of curing using the Bruker VT-1000 temperature controller unit.

In these experiments, proton spectra were obtained with the standard pulse sequence (*section 3.2.1.1*) employing quadrature detection, using a pulse length of $3\mu\text{s}$, a 5 second recycle delay, a sample spinning rate of 5Hz, and 8K data points. The FIDs were collected continuously, with 4 or 8 acquisitions per spectrum over the entire duration of the curing process. Using the Bruker 1-D winnmr™ software package, the FIDs were successively Fourier transformed, phase corrected and baseline adjusted (Figure 3.12). Relevant peak intensities were monitored using the same software and recorded as a function of UV irradiation time over the course of the UV-irradiation photoinitiated curing process (Figure 3.13). Similar procedures apply in the case of thermally cured systems.

3.2.4.3 ^{13}C -NMR Cure Profile Measurements

^{13}C -NMR Curing experiments were also conducted using experimental procedures similar to those described above. The inverse gated pulse sequence (*section 3.2.1.2*) suppressed signal enhancement to facilitate accurate peak intensity determinations. The acquisition of meaningful peak intensity versus time data, as opposed to averages over prolonged spectral acquisition times, which is a feature of ^{13}C -NMR, places a severe constraint on the experiment. These experiments are

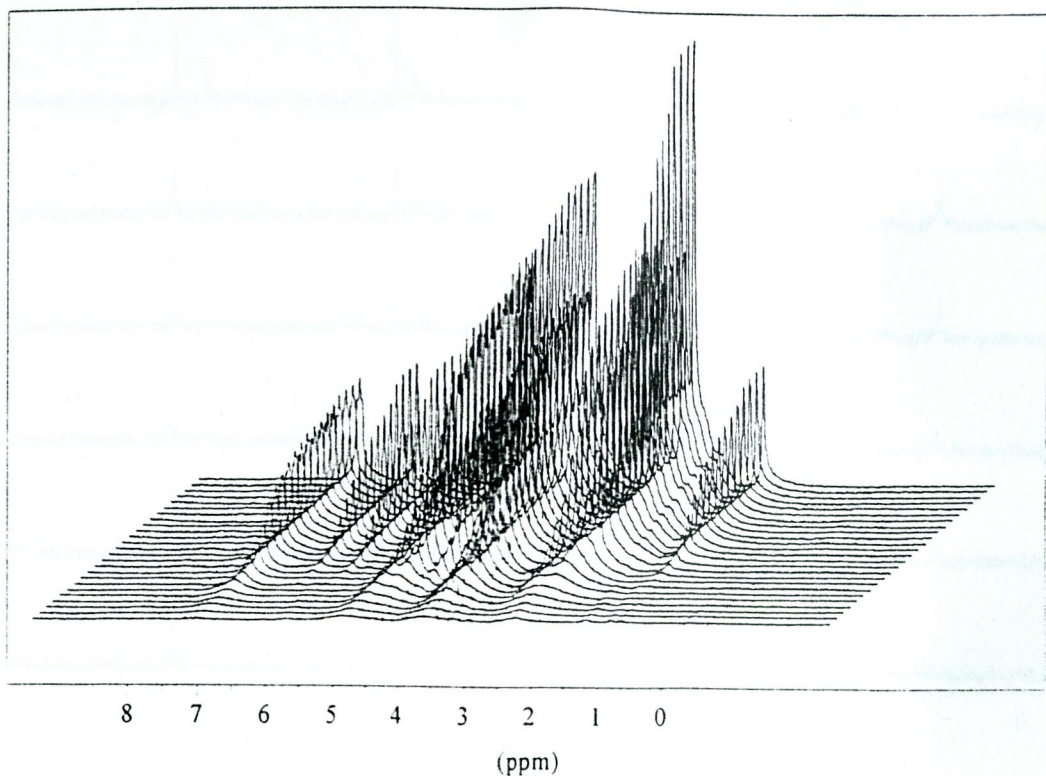


Figure 3.12. A typical suite of ^1H -NMR spectra of a composite monomer mixture, obtained over the course of an *in situ* photoinitiated curing experiment.

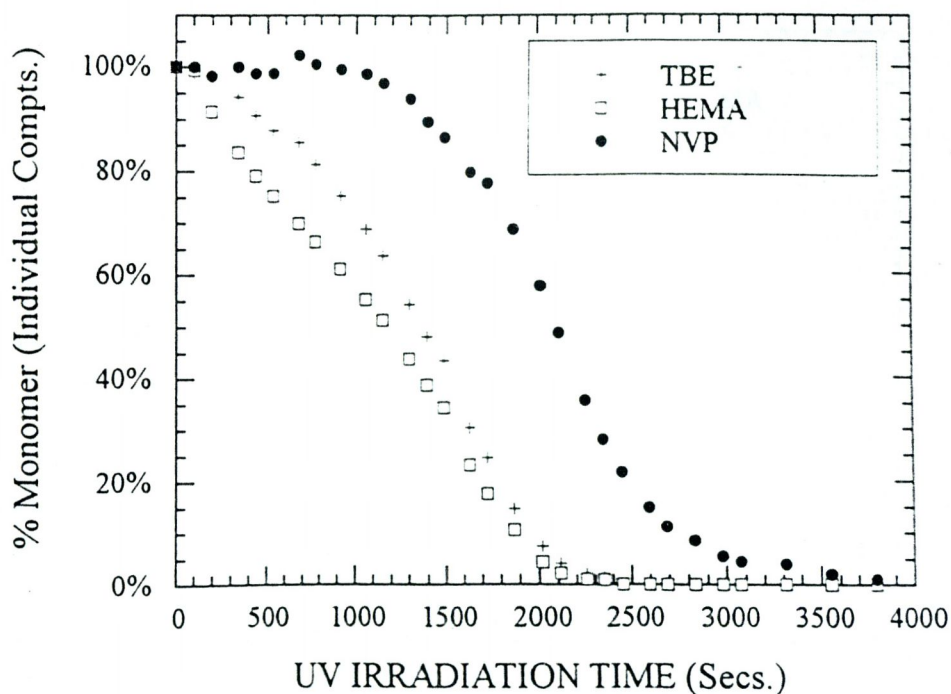


Figure 3.13. A typical plot of the relevant peak intensities as a function of UV irradiation time, measured from the ^1H -NMR spectra above.

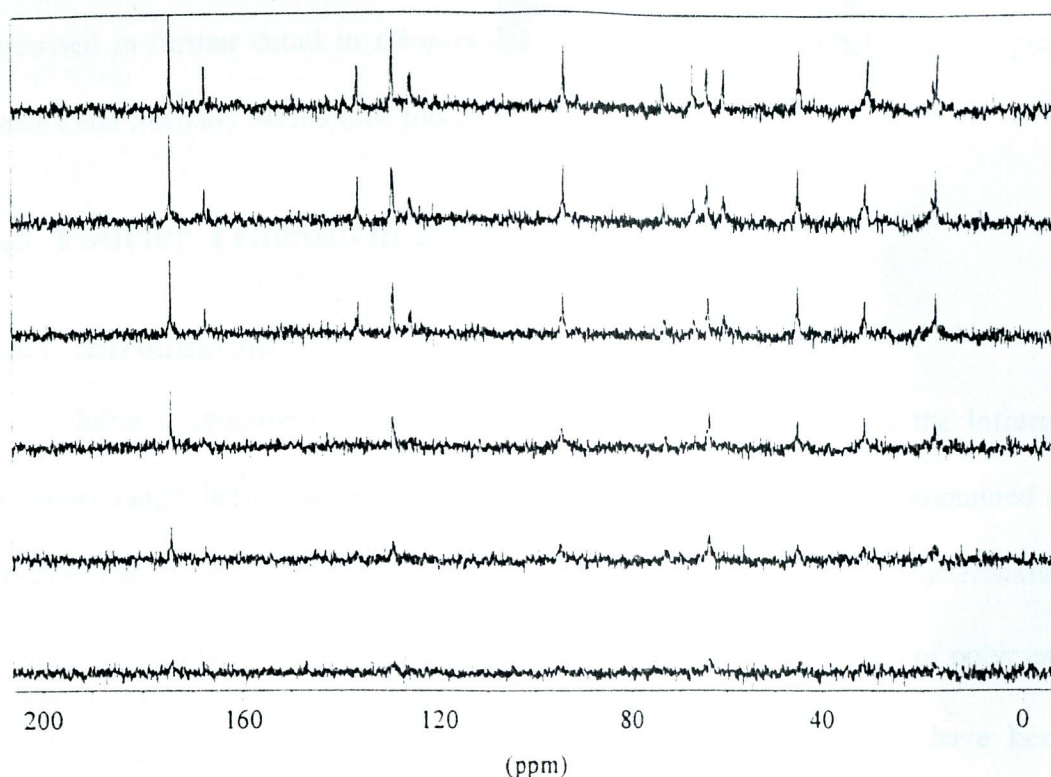


Figure 3.14. A typical suite of ^{13}C -NMR spectra of a composite monomer mixture obtained over the course of an *in situ* photoinitiated curing experiment.

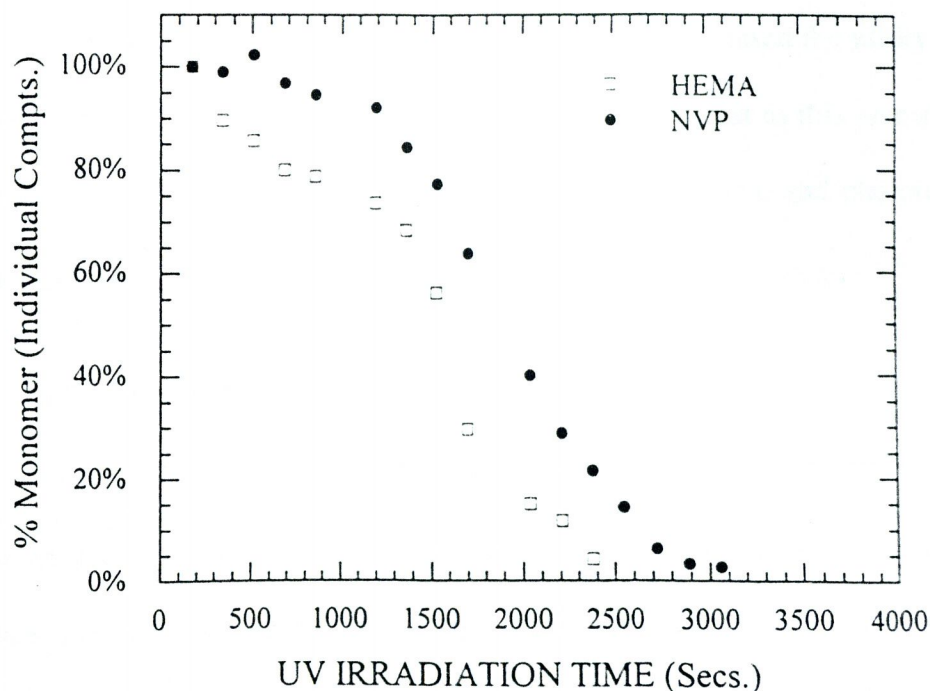


Figure 3.15. A typical plot of the relevant peak intensities as a function of UV irradiation time, measured from the ^{13}C -NMR spectra above.

discussed in further detail in *Chapter 7.3.3.5*. Figures 3.14 and 3.15 show typical spectra and intensity *versus* time plots from such an experiment.

3.3 Fourier Transform Infrared Spectroscopy

3.3.1 Introduction

Infrared spectroscopy, based on the absorption of radiation in the infrared frequency range due to the molecular vibrations of the functional groups contained in a polymer chain, is a long established and powerful technique for the characterisation and study of polymers.¹² The relevant theory of vibrational spectroscopy of polymers has been treated in detail elsewhere.¹³ Older dispersive instruments have been superseded by Fourier Transform Infrared Spectrometers (FT-IR) which incorporate a Michelson Interferometer as the optical device at their core and a dedicated computer to process the digitised interferograms using fast Fourier transform algorithms. Increased acquisition speeds and higher signal-to-noise ratios, combined with increasingly sophisticated data processing techniques, have increased the utility of FT-IR in polymer research quite significantly. It is of central interest to this research that quantitative studies of time-dependent phenomena such as thermal and photoinitiated polymerisation of monomer systems are now possible using this technique^{14,15}.

3.3.2 Instrumentation

Infrared spectra were collected using a Nicolet 510-P FT-IR spectrometer¹⁶ with a spectral resolution of 1 cm^{-1} , between 4800 cm^{-1} and 400 cm^{-1} . Figure 3.16 illustrates the layout of the electronic and optical components of the instrument and shows the light path of the infrared radiation. The broad spectrum of infrared light from the source is collected and focused by a series of mirrors and passed into the

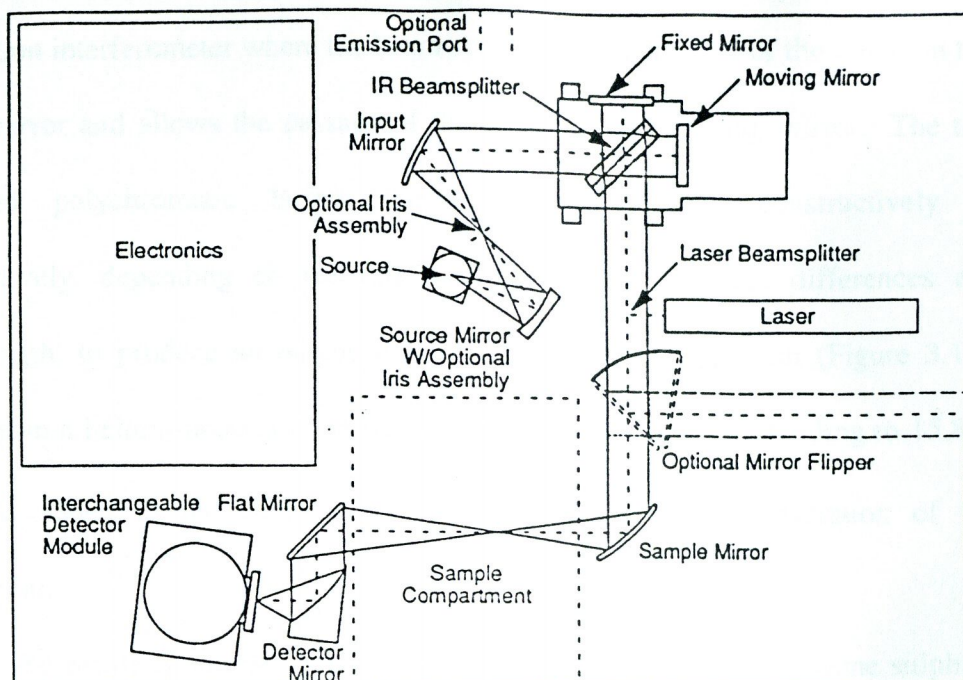


Figure 3.16. The layout of the electronic and optical components of the Nicolet 510-P FT-IR spectrometer.

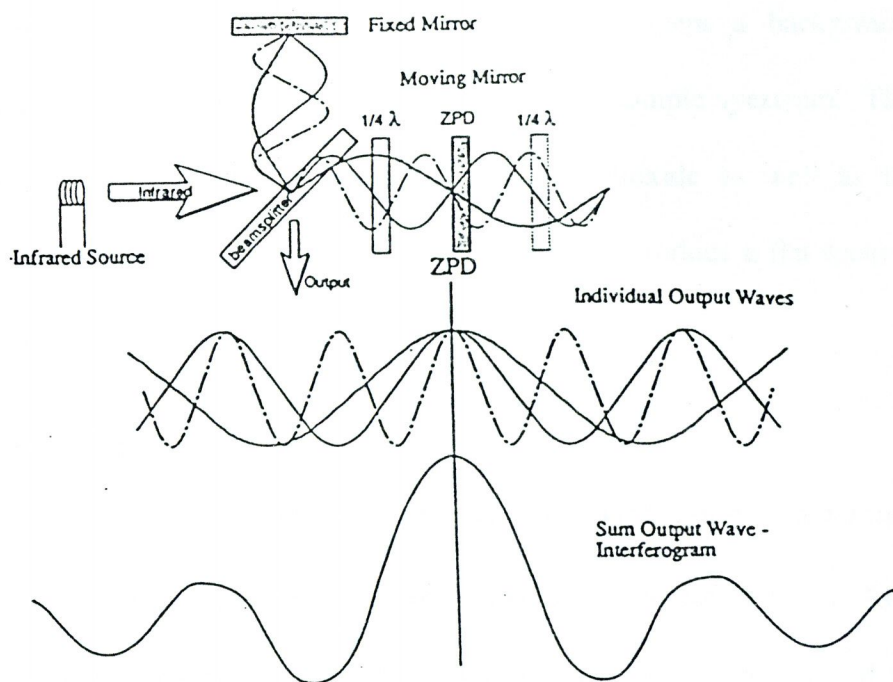


Figure 3.17. The principles of operation of a Michelson interferometer.

Michelson interferometer where the beam splitter reflects one half of the radiation to a fixed mirror and allows the passage of the other half to a moving mirror. The two reflected polychromatic beams recombine and interfere constructively or destructively, depending on the relationship between their path differences and wavelength, to produce an output signal known as an interferogram (Figure 3.17). Light from a helium-neon laser of wavelength of 632.8 nm (corresponding to $15,803\text{ cm}^{-1}$) is added to the beam to provide continuous spectral calibration of the instrument.

The resulting interferogram is captured using a deuterated triglycine sulphate (DTGS) detector. Application of a fast Fourier transformation algorithm to the digitised signal results in a spectral plot of infrared light intensity *versus* frequency. A sample absorbs specific frequencies to yield the characteristic infrared spectrum of the sample (Figure 3.18).

Since the spectrometer is not a double beam instrument a background spectrum was collected and subsequently subtracted from the sample spectrum. This removes bands due to atmospheric moisture and carbon dioxide as well as the characteristic shape of the emission spectrum of the source to produce a flat spectral baseline in the absence of a sample.

3.3.3 Sample Preparation

FT-IR spectra of the liquid monomers were obtained using a horizontal attenuated total reflectance¹⁴ (ATR) sampling accessory (Figure 3.19). After collecting the background spectrum with the crystal in place, a small amount of the sample monomer was pipetted into the sample trough, the base of which consists of a shaped zinc selenide crystal, and the spectrum was recorded. The infrared beam

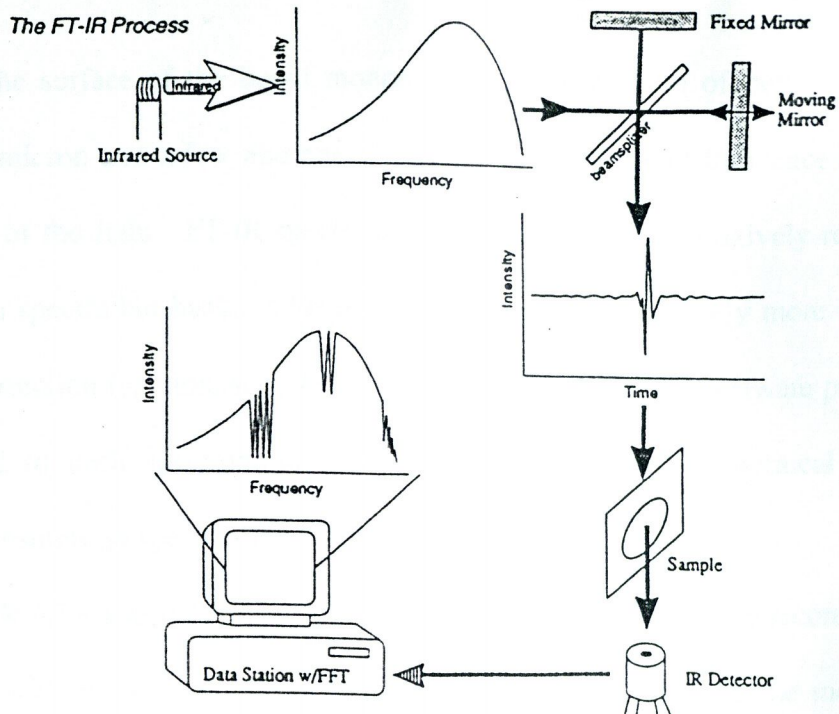


Figure 3.18. The principles of operation of the FT-IR spectrometer.

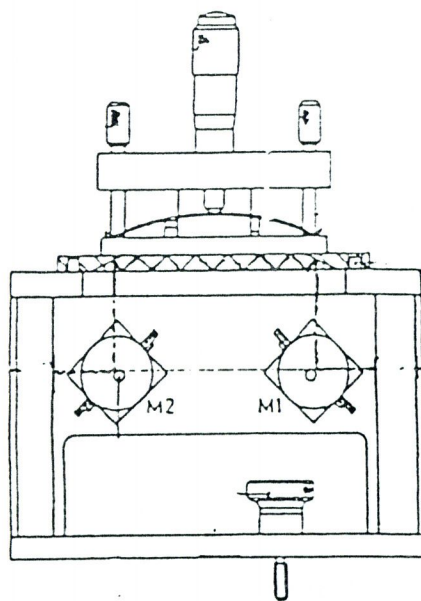


Figure 3.19. FT-IR horizontal attenuated total reflectance (ATR) sampling accessory.

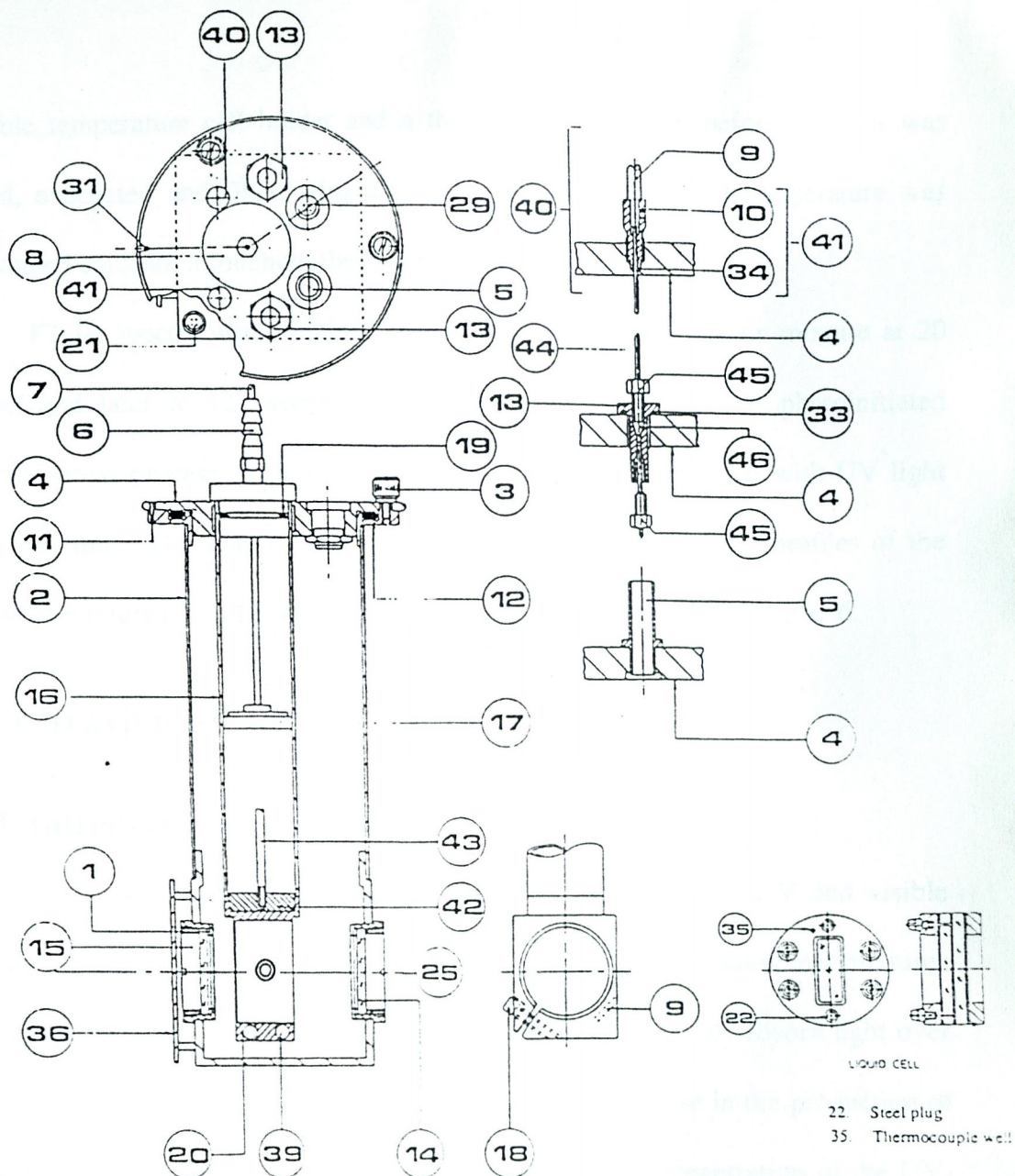
penetrates the surface of the liquid monomer sample to a depth of between a few tenths of a micron and a few microns, depending on the angle of incidence and the wavelength of the light. FT-IR spectra collected in this way qualitatively resemble transmission spectra but bands at longer wavelengths appear relatively more intense. An ATR correction function, supplied as part of the Nicolet PC-IR software package, was applied to each spectrum to produce spectra quantitatively identical to the expected transmission spectra of the same samples.

FT-IR ATR spectra for the full range of monomer mixtures were recorded and interpreted, with the help of spectra previously recorded for each of the monomer constituents (*Chapter 4*). Solid samples, such as the thermal initiator, were incorporated in KBr discs for examination by transmission FT-IR.

3.3.4 Curing studies using FT-IR spectroscopy

Modifications were made to a Variable Temperature Cell (Figure 3.20) manufactured by Specac Ltd., to facilitate UV irradiation of the liquid sample cell. Light pulses from the VSL-337 nitrogen laser were delivered *via* a UV grade fibre optic bundle that was passed through an airtight port built into the sidewall of the temperature cell unit. The apparatus was then evacuated and filled with dry nitrogen gas prior to collecting the background spectrum.

A sample of the monomer mixture under study was degassed by exposure to dry nitrogen in an atmosphere bag for 30 minutes before being injected into a solution cell. The cell consisted of two shaped NaCl plates, the top one containing suitably drilled injection ports and a thermocouple receptacle, separated by a teflon spacer 0.1 mm thick, clamped tightly together in a stainless steel holder. The cell containing the liquid monomer was then removed from the atmosphere bag and placed in the



1. Silicone Elastomer seal
2. Vacuum tight jacket
3. Thumb screws to hold top plate
4. Top plate of cryostat unit
5. Vacuum pump connection
6. Metal venting tube
7. "Mushroom" piston
8. Refrigerant chamber bung
9. Copper-Constantan thermocouple and thermocouple well
10. Screw plug for thermocouple
11. Locating pin for top plate
12. 'O' ring retaining groove of top plate
13. Flow through connector ports
14. Jacket window
15. Screw threaded retaining ring
16. Refrigerant chamber
17. Polyurethane foam layer of "mushroom"

13. Clamp screw of cell holder
19. 'O' ring groove for bung
20. Cell holder
21. Latching socket for window heaters
29. Electrical leads socket for cell heater
31. Pin locating slot on top plate
33. 'O' ring for connector ports
34. Silicone Elastomer seal for thermocouple
36. 3" x 2" mounting plate
39. Heaters for sample holder
40. Thermocouple port for cell holder
41. Extra access port
42. Stainless steel 'drop' disc
43. Stainless steel threaded rod for 'drop' disc
44. Stainless steel rod for plugging flow through connector ports
46. Ferrule seal

*25. Air-tight through port for UV fiberoptic bundle (modification)

Figure 3.20. The modified FT-IR Variable Temperature Cell (Specac Ltd.).

variable temperature cell holder and a thermocouple inserted, before the unit was sealed, evacuated and filled with dry nitrogen gas. The desired temperature was maintained constant throughout the experiment.

FT-IR spectra were obtained for the thin section of monomer mixture at 20 second and later at 120 second intervals, over the course of the photoinitiated polymerisation process while the sample was continuously irradiated with UV light from the laser. The suite of spectra was then used to obtain curing profiles of the monomer mixtures. Further experimental details are documented in *Chapter 6*.

3.4 Ultraviolet-Visible Spectroscopy

3.4.1 Introduction

Ultraviolet-Visible Spectroscopy¹⁷ (UV-Vis) monitored the UV and visible absorption characteristics of the neat monomers, of the composite monomer mixtures and of the polymerised films. The degree to which these materials absorb light over this range of wavelengths not only defines their suitability for use in the production of optically transparent lenses but also determines the depth of penetration of the UV-light used to photoinitiate the free radical polymerisation process by which the lenses are manufactured.

3.4.2 Instrumentation

All measurements were made using a 'Shimadzu UV-1601 PC'¹⁸ double beam, grating spectrophotometer linked to a 486 PC with UVPC spectroscopy software version 3.7,¹⁹ operating within the Microsoft® Windows™ 3.1 protocol. A wavelength range of between 190nm and 1100nm was accessed by means of two separate light sources. A fixed slit width of 2.0nm is used to define the spectral

D_2 : Deuterium Lamp
 $W1$: Halogen lamp
 F : Filter
 G : Grating
 S_1 : Entrance slit
 S_2 : Exit Slit
 W : Windows
 $M_1 \sim M_5$: Mirrors (M_3 is half mirror)
 L : Lens
 Sam : Cell for sample beam
 Ref : Cell for reference Beam
 PD : Photo diode dector

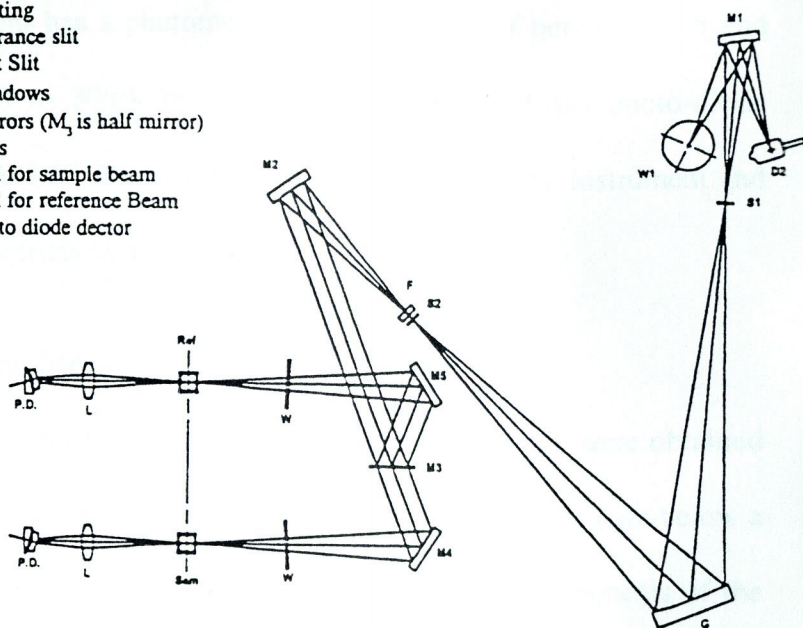


Figure 3.21. The layout of the optical components of the Shimadzu UV-1601 PC UV-Vis spectrometer.

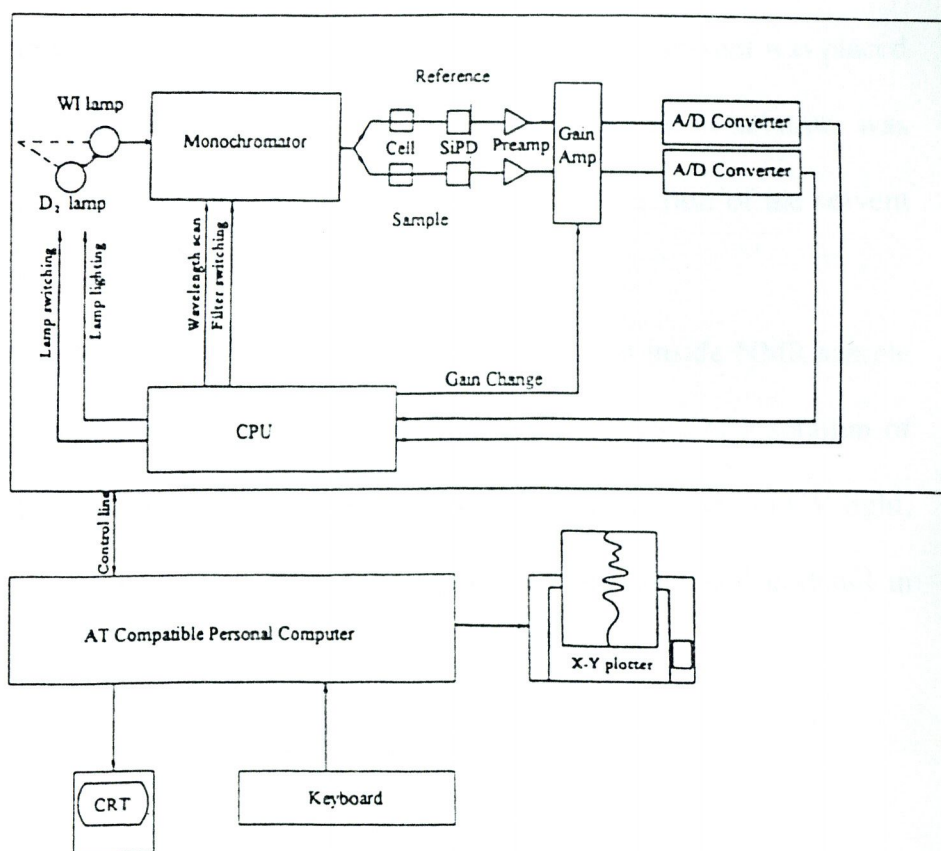


Figure 3.22. A block diagram of the electrical system of the Shimadzu UV-1601 PC UV-Vis spectrometer.

resolution. The instrument has a photometric recording range of between -0.5 and 3.99 absorbance units (0 to 300% transmittance), utilising a silicon photo-diode detector. Figures 3.21 and 3.22 illustrate the optical schematics of the instrument and a block diagram of the electrical system, respectively.

3.4.3 Sample Preparation

UV-Vis spectra of neat liquid monomers and mixtures thereof were obtained using polystyrene 1cm pathlength disposable cuvettes that fully absorbed light below a wavelength of 280nm. UV-Vis spectra of the strongly absorbing components of the monomer mixtures, such as the photoinitiators and the visible tint, were obtained by dissolving a sample in a solvent (ethanol or chloroform) at a low concentration and utilising optically matched quartz cuvettes. Quartz cells of 1mm, 2mm, 5mm and 10mm pathlength were available. One cuvette containing the pure solvent was placed in the reference cell holder while the other, containing the sample in solution, was placed in the sample cell holder. This permitted automatic subtraction of the solvent spectrum from the sample spectrum.

In situ UV-light intensity measurements were made from inside NMR sample tubes utilising Chemical Actinometry by monitoring the absorbance of a solution of 'Aberchrome 540' at a particular wavelength, before and after exposure to UV light, using the UV-Vis spectrophotometer. These experiments are described in detail in Chapter 6.

3.5 Thermogravimetric Analysis

3.5.1 Introduction

In thermogravimetric analysis²⁰ (TGA) changes in sample weight are sensitively monitored as a function of time and/or temperature (293 K - 1273 K) under controlled atmospheric conditions. Results are plotted in the form of a thermograph as in Figure 3.23.

3.5.2 Instrumentation

A Mettler M3 TGA system is a sensitive microbalance, which has a resolution of $\pm 10 \mu\text{g}$, interfaced to an Epson personal computer *via* a Mettler TC11 interface processor (Figure 3.24).²¹ It was used to examine the thermogravimetric behaviour of the liquid monomer mixtures and their constituents as well as the polymerised hydrogel systems. Dry nitrogen or air purged the sample chamber at a controlled flow rate of 200 ml/hour. The controller unit was then programmed to carry out specific thermal cycling, such as dynamic heating over a selected temperature range or isothermal measurements for predetermined time periods. Data were subsequently analysed on the computer at the end of each experiment. Thermographs displaying weight loss or gain as a function of time (minute) or temperature (K) were then analysed and plotted.

3.5.3 Calibration

Calibration was performed periodically over the entire operating temperature range of the instrument (293 K to 1273 K) at a heating rate of 5 K min^{-1} , utilising the Curie temperatures of three metal alloys;

- (i) Isatherm at 417.5 K

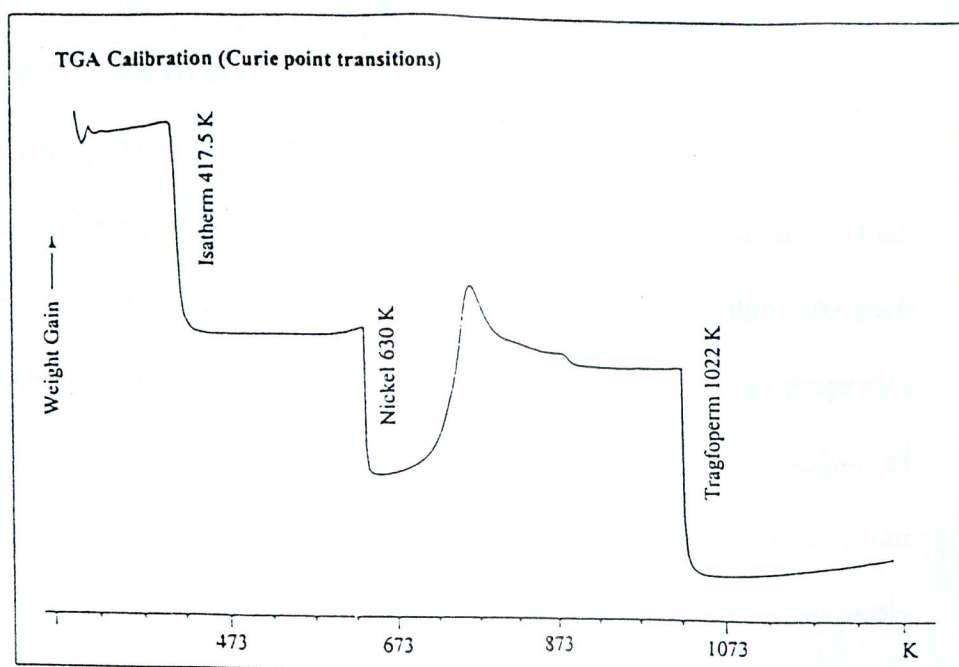


Figure 3.23. A thermograph of the instrument temperature calibration, obtained by comparison to the known Curie points of three magnetic alloy samples.

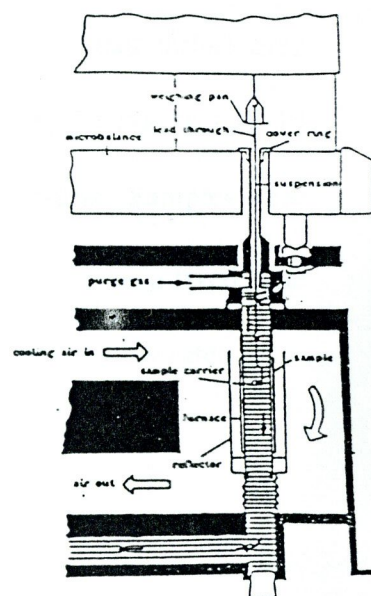
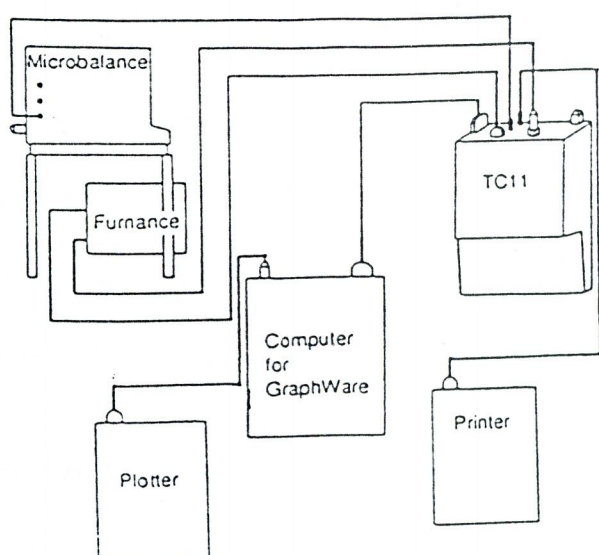


Figure 3.24. The Mettler Thermogravimetric Analysis (TGA) system and a schematic diagram of the M3 microbalance and furnace (right).

(ii) Nickel at 630 K

(iii) Tragferm at 1022 K.

An external magnet was fitted to the outside casing of the furnace, which induced an apparent weight increase in the magnetic alloy samples within. As each characteristic Curie temperature of the alloys was traversed its magnetic properties were destroyed and an abrupt weight loss ensued (Figure 3.23). Automatic analysis of the thermograph provided the instrument controller unit with an accurate three-point calibration curve, which facilitated an automatic correction to the thermocouple response function, thereby ensuring accurate temperature determination.

3.5.4 Sample Preparation

Modified aluminium DSC pans were used to hold liquid monomer samples while porous aluminium oxide crucibles were used to hold solids. The step configuration of the specially pressed aluminium sample pans (shown later in Figure 3.27) was used to minimise meniscus formation and to provide a constant surface area of the viscous liquid monomers. Samples of similar mass (6-8 mg for liquids / 10-14 mg for solids) facilitate intercomparisons and reproducibility of results. Samples were usually heated at a controlled rate ($1-5 \text{ K min}^{-1}$) or held isothermally for a fixed time period, under a selected atmosphere (dry nitrogen or air) at a fixed gas flow rate.

3.6 Differential Scanning Calorimetry

3.6.1 Introduction

Differential Scanning Calorimetry²⁰ (DSC) experiments were conducted on a Perkin-Elmer DSC-4 calorimeter interfaced to a Perkin-Elmer thermal analysis data station (TSDS). A block diagram detailing the principles of operation of the

instrument is shown in Figure 3.25 and a complete description of the apparatus is available in reference 22. The differential scanning calorimeter records the amount of heat required to induce an endothermic event, or the amount of heat liberated by an exothermic event, in a material as a function of temperature and time, relative to a thermally stable standard sample *i.e.* an aluminium reference pan and lid. DSC is sensitive to phase changes within a sample, such as that which occurs when a visco-elastic polymer is heated through its glass transition temperature (T_g); specifically, changes in specific heat capacity are monitored. Schematic representations of a glass transition and of endothermic and exothermic events are shown in Figure 3.26. Samples were examined under temperature cycling regimes at rates that varied from 0 K min^{-1} (isothermal scan at a fixed temperature for a selected time) up to a maximum of 320 K min^{-1} . Most commonly, a temperature ramp rate of 10 K min^{-1} was employed.

3.6.2 Data Acquisition

The DSC sample “head” consists of two platinum chambers, a sample and reference cell mounted in a solid aluminium block that extends into a coolant reservoir below. Samples placed in shaped aluminium pans (Figure 3.27) were carefully located into the left chamber (the sample holder) while a second aluminium pan of similar weight and shape was placed in the right chamber, designated the reference holder. The Perkin-Elmer DSC is a power compensating calorimeter so each chamber has its own individual heater and thermocouple. This type of instrument records the differential amount of current that is supplied to the two heaters, in order to maintain the pans in each chamber at the same temperature during any thermal event that may occur in a sample over the course of an applied thermal

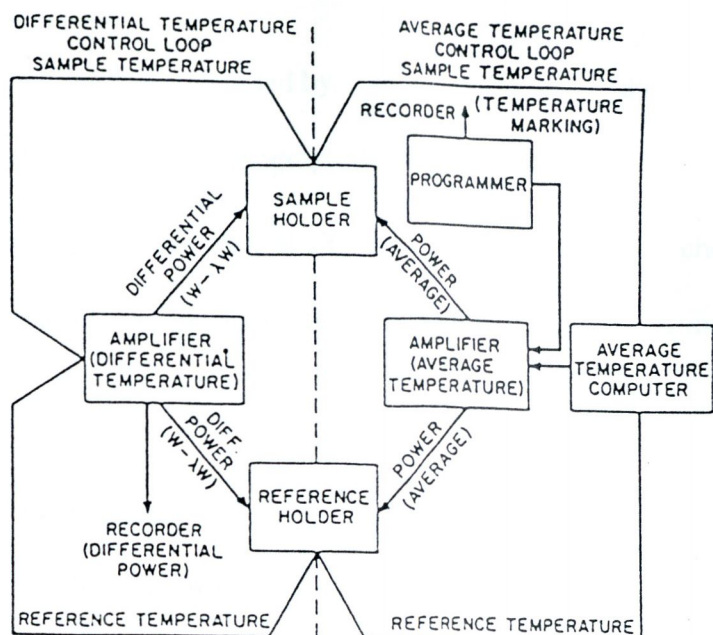


Figure 3.25. A block diagram detailing the principles of operation of the Differential Scanning Calorimeter (DSC4).

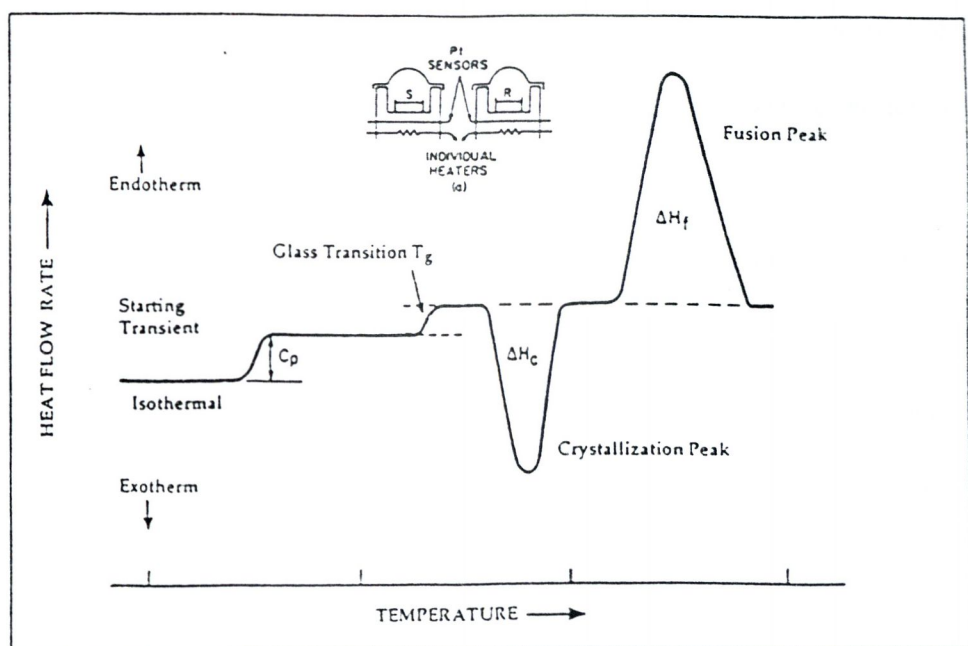


Figure 3.26. A schematic thermograph illustrating typical thermal events as measured by DSC. Inset: sample and reference chambers of the PE-DSC4.

cycle. Thermal transitions were recorded by scanning through a temperature regime at a fixed scanning rate. A DSC thermograph displays the differential power supplied (mcal sec^{-1}) against temperature (K), at the selected scan rate. (The choice of the calorie unit as opposed to the Joule reflects accepted convention in the DSC literature).

3.6.3 Modes of Operation

The DSC-4 instrument was capable of recording data over the temperature range from 153 K to 573 K, in two different operational modes:

- (i) Sub-ambient mode (temperatures from 153 K to 303 K) and
- (ii) Ambient mode (temperatures from 293 K to 573 K)

Liquid nitrogen is decanted into a reservoir below the DSC head to act as the coolant in sub-ambient mode. In this mode it is necessary to use helium, delivered through a standard head cover at a pressure of 1.5 bar, to avoid liquefaction of the purge gas. Only experiments using the instrument in ambient mode were conducted in this research.

In ambient mode, oxygen-free nitrogen, previously routed through a cylinder containing desiccant gel in order to remove water vapour, was used as the purge gas. This was then passed through a “flow-through” head to facilitate the removal of any water vapour and evolved gases or volatiles from the sample and reference chambers. Ice and water were placed in the reservoir below the head to act as the coolant mixture. A glove box attachment, fitted over the top of the DSC head and purged with dry nitrogen gas at a flow rate of $450 \text{ cm}^3 \text{ min}^{-1}$, was used to ensure a dry atmosphere, thereby avoiding condensation on the instrument head.

3.6.4 Calibration

The instrument was calibrated using pure indium metal as a reference sample, for which the enthalpy of fusion is known (6.8 cal g^{-1}) and for which the onset temperature of the fusion peak occurs at precisely 429.6 K (Figure 3.28). Pure water is generally used as a calibrant in the sub-ambient mode where the high transition temperature of indium is inappropriate.

3.6.5 Sample Preparation

A DSC pan sealing press was modified so that it could be used to reshape existing aluminium pans to allow them to effectively hold the viscous monomers. The stepped configuration of these specially pressed pans (Figure 3.27) minimised meniscus formation and produced a constant liquid surface of the monomers, typically 15 to 25 mg in weight. Thermal polymerisation was effected by either applying a ramped temperature regime or by isothermally heating a sample, generally at a higher fixed temperature for a predetermined period of time. These experiments were usually followed by the application of a further temperature cycle to ensure completion of cure of the monomer mixtures.

3.7 References

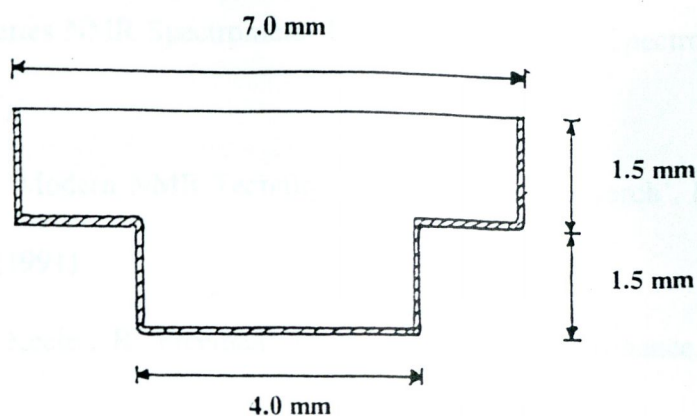


Figure 3.27. Specially pressed DSC pans of stepped configuration minimised meniscus formation and produced a constant liquid surface .

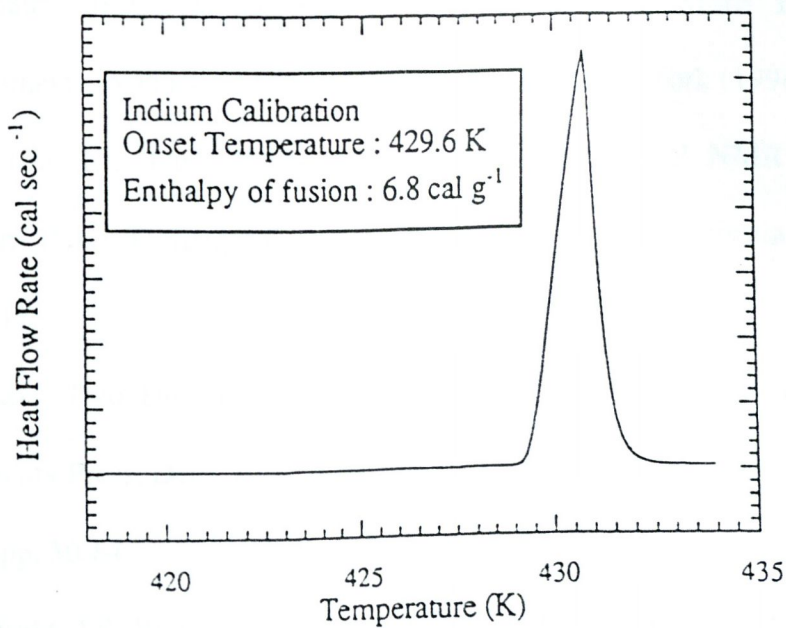


Figure 3.28. DSC instrument calibration using the fusion peak of pure indium metal.

3.7 References

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Chapter Four

Characterisation of Monomer Mixtures

4.1 Introduction

In this chapter the chemical composition, role and spectroscopic response of each of the components of five composite monomer mixtures of commercial relevance are examined. An initial detailed spectroscopic characterisation of the individual components was an essential prerequisite to the full elucidation of the quite complex spectra of the formulations.

The central objective was to identify features in these spectra that could be used to monitor the progression of liquid monomer mixture to cross-linked solid hydrophilic gel, in terms of both the differential rates of co-polymerisation of the individual components and of the overall curing dynamics of the composite system. High resolution 1D and 2D ^1H and ^{13}C Liquid NMR techniques were employed to characterise the individual components initially in solution, then as neat composite liquids and ultimately in the viscous composite monomer formulations.

Using the same procedure, each of the components were studied independently by Fourier Transform Infrared Spectroscopy to facilitate band assignments in the spectra of the composite mixtures. The components and mixtures were also examined using Ultraviolet-Visible Absorption Spectroscopy and particular attention was paid to the effect of the addition of the visible tint and the UV photoinitiators to the spectral response of the final formulations.

For conciseness only a suitably representative selection of the large amount of spectral data required for this comprehensive characterisation study are presented.

4.2 Sample Description

4.2.1 Classes of Hydrogel Components

In general, a hydrogel lens formulation consists of the following range of components^{1,2,3}:

1) Hydrophilic Monomers

- the final water content, which influences oxygen permeability of a hydrogel lens, depends on the hydrophilicity of the monomers employed.⁴ Often more than one hydrophilic monomer is used in a lens formulation to obtain the desired final water content without compromising other physical properties.

2) Cross-linkers

- the monomers are cured with specially tailored cross-linkers to provide dimensional stability and to achieve some key mechanical properties such as modulus and tear strength.^{5,6} Cross-linkers may also adversely affect the final water content if used excessively.

3) Polymerisation Initiators⁷

- the initiator may be thermal or UV-photo activated and it initiates the polymerisation and curing reactions in the mixture.

The following components may also be added as an aid to the manufacturing process or to achieve certain desirable properties in the finished product:

4) Bulky Hydrophilic Monomers

- the addition of relatively bulky hydrophilic monomers, specially formulated so that phase separation does not occur during polymerisation of the mixture, have been found to improve the mechanical properties of the hydrogel material by imparting rigidity to the polymer network formed.⁸

5) Hydrophobic Monomers

- the physical and mechanical properties of the lens may be modified by the addition of a hydrophobic monomer. This will also have an effect on the final water content of the finished hydrogel lens.⁹

6) Non-reactive Solvent or Diluent

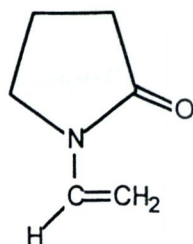
- a non-reactive solvent may be added to effect processing and to allow a high degree of cure to be attained.¹⁰ The solvent is ultimately extracted from the hydrogel along with any unpolymerised monomer, usually in hot distilled water.

7) Visible Tint

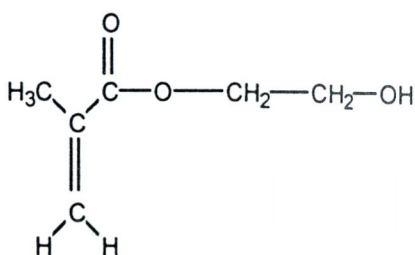
- tint is usually added for a) visibility *i.e.* to make the lens more visible when out of the eye and hence easier to locate and handle or b) for cosmetic reasons *i.e.* to modify or change the eye colour of the wearer. A dye molecule with methacrylate groups attached can be polymerised directly into the lens matrix during manufacture.¹¹

4.2.2 Hydrogel Components

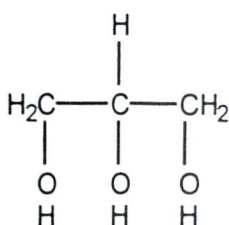
Most of the reagents and materials used in this study were purchased by Bausch & Lomb, Waterford, from Aldrich Chemical and then further purified using a low-pressure distillation technique where necessary. Three exceptions were HEMA-VC and TBE, both of which were synthesised by Bausch & Lomb Inc., Rochester, New York^{6,8}; and Darocur 1173, which was purchased from Ciba-Geigy. Bausch & Lomb, Waterford, provided the purified individual components and the complete composite formulations along with precise details of their compositions for examination.



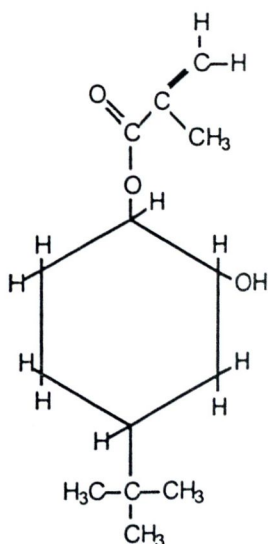
NVP N-vinyl-2 pyrrolidone, $MW=111.144 \text{ g.mol}^{-1}$, (hydrophilic monomer unit)



HEMA 2-hydroxyethyl methacrylate, $MW=130.144 \text{ g.mol}^{-1}$, (hydrophilic monomer unit)



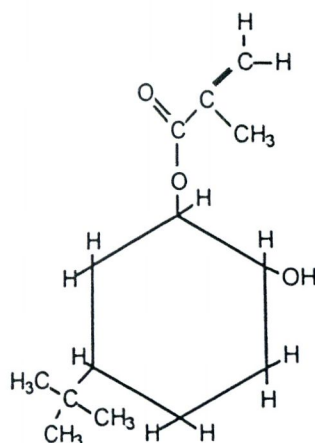
Glycerol, $MW=92.095 \text{ g.mol}^{-1}$, (non-reactive solvent and polymerisation aid)



TBE (isomer 1)

(4-tert-butyl-2-hydroxy cyclohexyl methacrylate)

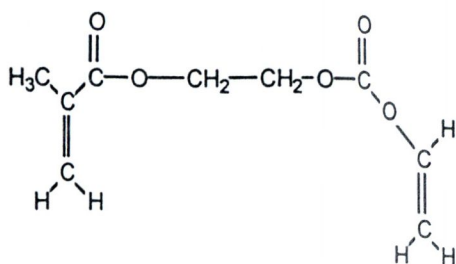
$MW=239.336 \text{ g.mol}^{-1}$, (bulky hydrophilic monomer and modulus modifier)



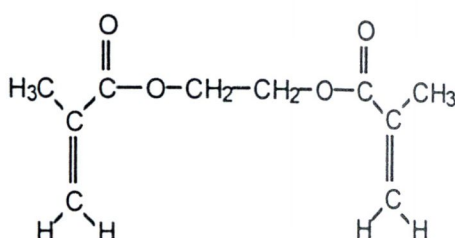
TBE (isomer 2)

(5-tert-butyl-2-hydroxy cyclohexyl methacrylate)

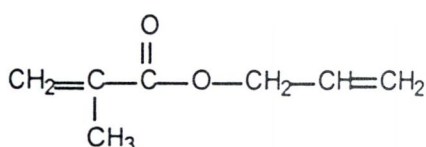
Figure 4.1. Structural formulae of the constituents of composite Mixtures A, B, H, I and J. The compositions of the formulations are described in Table 4.1.



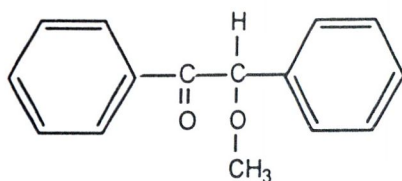
HEMA VC hydroxyethyl methacrylate vinyl carbonate, $MW=200.192 \text{ g.mol}^{-1}$, (crosslinker)



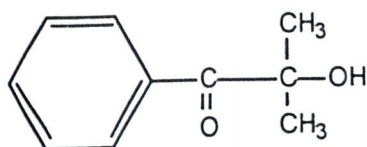
EGDMA ethylene glycol dimethacrylate, $MW=198.220 \text{ g.mol}^{-1}$, (crosslinker)



AMA allyl methacrylate, $MW=126.156 \text{ g.mol}^{-1}$, (crosslinker)

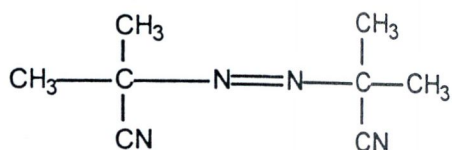


BME benzoin methyl ether, $MW=226.276 \text{ g.mol}^{-1}$, (photo and thermal initiator)

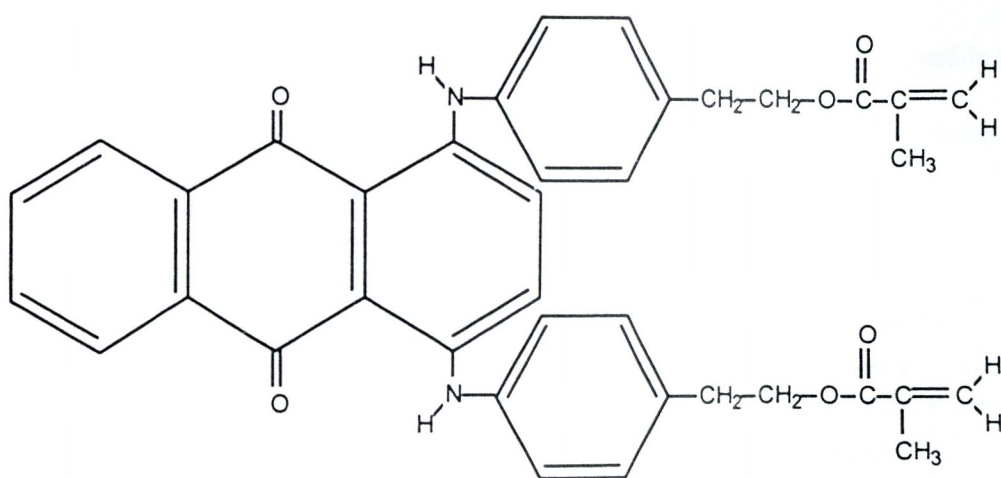


Darocur 1173 α,α-dimethyl α hydroxy acetophenone, $MW=164.205 \text{ g.mol}^{-1}$ (photo initiator)

Figure 4.1 cont. Structural formulae of the constituents of composite Mixtures A, B, H, I and J. The compositions of the formulations are described in Table 4.1.



AIBN 2,2 azobisisobutyronitrile, MW=164.211 g.mol⁻¹, (thermal initiator)



IMVT (1,4-Bis- [4-(2-methacryloxyethyl)phenylamino]anthraquinone)
MW=614.700 g.mol⁻¹, (In Monomer Visible Tint)

Figure 4.1 cont. Structural formulae of the constituents of composite Mixtures A, B, H, I and J. The compositions of the formulations are described in Table 4.1.

The various constituents of the composite mixtures are described in Figure 4.1. and Table 4.1.

4.2.3 Formulations of the Monomer Mixtures.

Five commercially utilised composite monomer mixtures were studied (Table 4.1). Mixture A and Mixture B contain BME and Darocur 1173 photoinitiators respectively and are cured with ultraviolet light. Mixtures H, I and J contain the thermal initiator AIBN and are thermally cured.

The curing behaviour of each of the five systems was examined to varying degrees. However, the UV-photoinitiated differential co-polymerisation profiles of the three hydrophilic monomers in Mixture B were of special interest and therefore this composite was examined in much greater detail.

Table 4.1. Formulations of the composite monomer mixtures.

		UV Photoinitiated Cure		Thermally Initiated Cure		
		Mixture A	Mixture B	Mixture H	Mixture I	Mixture J
Mixture Component	Mol. Wt. (g.mol ⁻¹)	% Weight	% Weight	% Weight	% Weight	% Weight
NVP	111.144	-----	44.637	44.910	46.704	42.003
HEMA	130.144	84.595	31.748	44.910	52.591	47.323
Glycerol	92.095	14.899	14.849	-----	-----	10.025
TBE	239.336	-----	7.950	9.980	-----	-----
HEMA VC	200.192	-----	0.500	-----	-----	-----
EGDMA	198.220	0.333	0.110	-----	-----	-----
AMA	126.156	-----	-----	-----	0.499	0.449
BME	226.276	0.167	-----	-----	-----	-----
Darocur 1173	164.205	-----	0.200	-----	-----	-----
AIBN	164.211	-----	-----	0.200	0.200	0.200
I.M.V.T.	612.684	0.006	0.006	-----	0.006	-----

4.3 Spectroscopic Characterisation

Each of the three spectroscopic techniques used to examine and characterise the composite monomer mixtures (i.e. NMR, FT-IR, UV-Vis) provided unique and complementary information.¹² However, high resolution liquid NMR was alone in its ability to produce spectra containing features well enough resolved to permit independent monitoring in real time of the curing behaviour of three major components in the complex systems.¹³ The spectral information underpinning the characterisation of the components and mixtures is now described.

4.3.1 Liquid Nuclear Magnetic Resonance Spectroscopy

4.3.1.1 NMR Spectral Acquisition and Analysis

One- and two-dimensional spectra were recorded at 293±1K on high resolution Bruker MSL 300 and DPX 400 spectrometers operating at 300.13 MHz and 75.47 MHz and 400.14 MHz and 100.14 MHz for protons and carbons, respectively. In a first series of measurements, each component was dissolved in deuterated chloroform, CDCl₃, (25mg/g or 50mg/g) which also served as the lock signal.¹⁴ The pulse sequences detailed in *Chapter 3.2* were conventionally used to obtain high resolution spectra in which characteristic peaks could be identified. Spectra were subsequently recorded for the neat liquid monomers using the experimental conditions established in the first series of runs. A third series included measurements on the five composite monomer mixtures, initially in CDCl₃ + 0.03 v/v TMS (tetramethylsilane) solution and then as the neat viscous liquid mixtures. These measurements were used to establish the precise chemical shifts of the spectral lines relative to TMS and to confirm that there was negligible drift in peak positions in the second and third sets of spectra recorded in the unlocked mode.

1-D Spectroscopy: Proton spectra with 16K data points zero-filled to 32K points were obtained with a standard pulse sequence, employing quadrature detection, a pulse length of 3 μ s, a 5s delay between data acquisition cycles and a sample spinning rate of the order of 20Hz for solutions and 5Hz for the neat viscous monomer mixtures.¹⁴ Carbon ^{13}C spectra were off-resonance proton-decoupled and recorded using a WALTZ16 pulse sequence.^{15,16} The ^{13}C DEPT 135° (Distortionless Enhancement by Polarisation Transfer) spectral editing sequence permitted discrimination of methyl, methylene, methine and quaternary carbon resonances respectively.^{17,18,19}

2-D Spectroscopy: Two dimensional analyses are presented in the form of contour maps for both homonuclear^{14,20,21} and heteronuclear COSY (Correlation Spectroscopy) spectra.^{22,23} These spectra provide a graphic representation of the spin coupling of specific ^1H - ^1H and ^1H and ^{13}C nuclei in the sample, respectively. Recall that in ^1H - ^1H COSY spectra, the diagonal peaks are a superposition of the 1-D spectra whereas off-diagonal peaks indicate coupling between different resonant nuclei.

4.3.1.2 NMR Results and Discussion

Detailed NMR analyses were carried out on the five mixtures and on each component thereof. Where possible, assignments were validated using published data.^{24,25,26} Spectra are reported in some detail for NVP as a representative example of the approach adopted and to illustrate the type of information provided: in the interest of conciseness, peak assignments for the remaining samples, recorded and analysed using the same methodology, are in most cases simply displayed on their respective ^1H and ^{13}C spectra.

The ^1H spectrum (a), ^{13}C (b) and ^{13}C DEPT 135 $^\circ$ (c) spectra, and 2-D ^1H - ^1H (a) and ^1H - ^{13}C COSY (b) spectra for NVP in CDCl_3 (50mg/gm) are furnished in Figures 4.2 and 4.3, respectively. Figure 4.4 presents ^1H (a) and ^{13}C (b) spectra for neat NVP monomer along with peak assignments, which could be made in confidence based on information deduced from the preceding spectra. In correlating spectra for HEMA in CDCl_3 solution and for the neat monomer (Figures 4.5 and 4.6), account was taken of the dependence of the proton OH peak position (chemical shift) on concentration of the monomer in the solvent: in ^1H spectra, the peak shifts down field as the concentration in CDCl_3 increases, as observed in Table 4.1 below.

Table 4.1. Concentration effect on HEMA -OH ^1H chemical shift position.

Concentration of HEMA in CDCl_3 (mg/g)	-OH ^1H Chemical Shift Position (ppm)
neat monomer	4.916
120.2	3.103
50.0	2.342
20.1	2.120
7.1	1.636

Spectra for TBE in CDCl_3 (50mg/g) are furnished in Figure 4.7. Two isomers of TBE monomer were identified in the sample provided and peak assignment in the resulting complex spectra was only possible utilising detailed information contained in the spectral maps produced by the powerful 2D NMR techniques (Figure 4.8). Based on the ratio of the integrated areas of the I.v and II.v peaks in the ^1H spectrum (Figure 4.7a) it was possible to determine that the ratio of isomer I to isomer II in the TBE sample was 40:60 ± 2 . The t-butyl peak (p) in the ^1H spectrum of TBE is intense

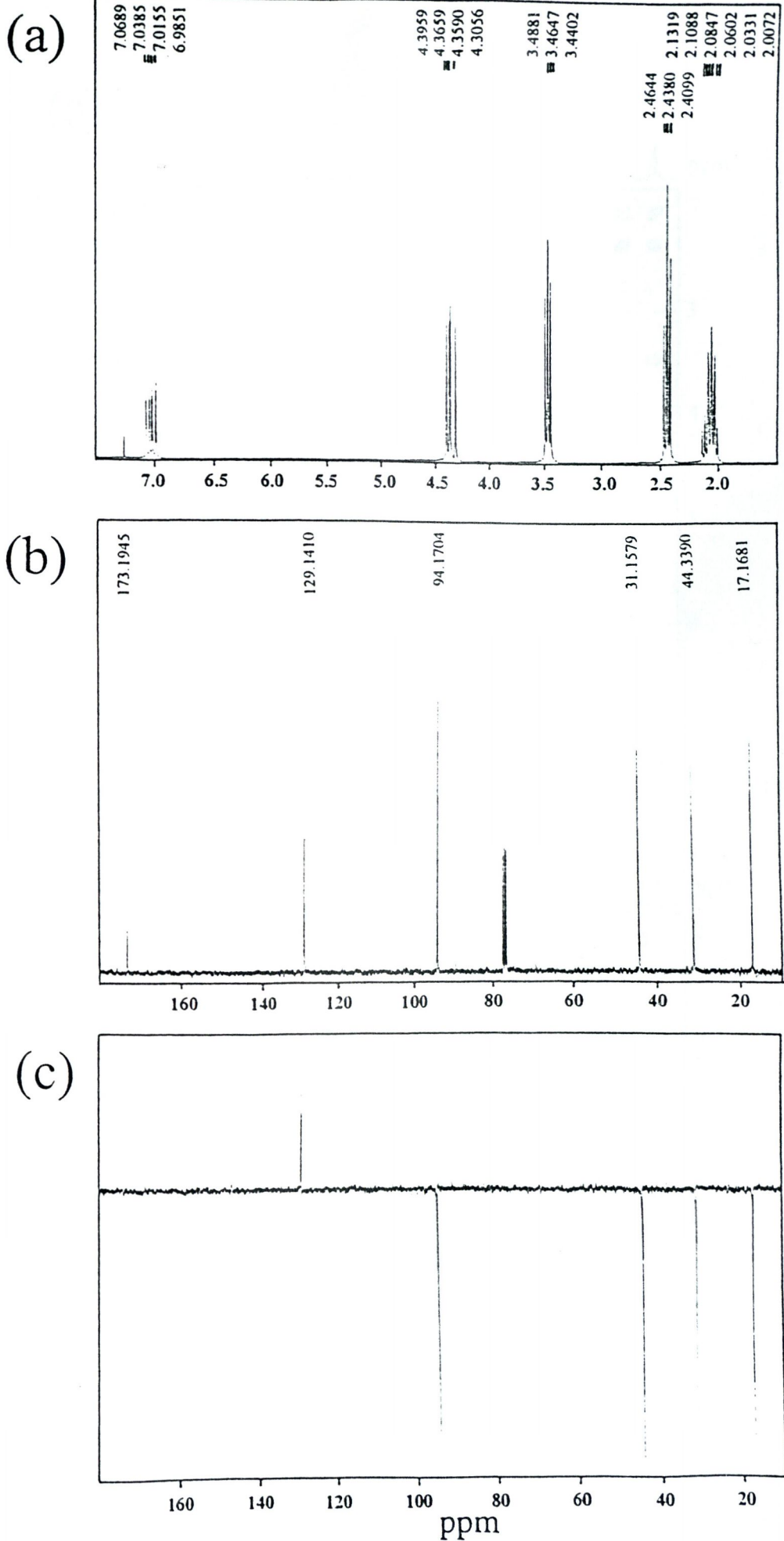
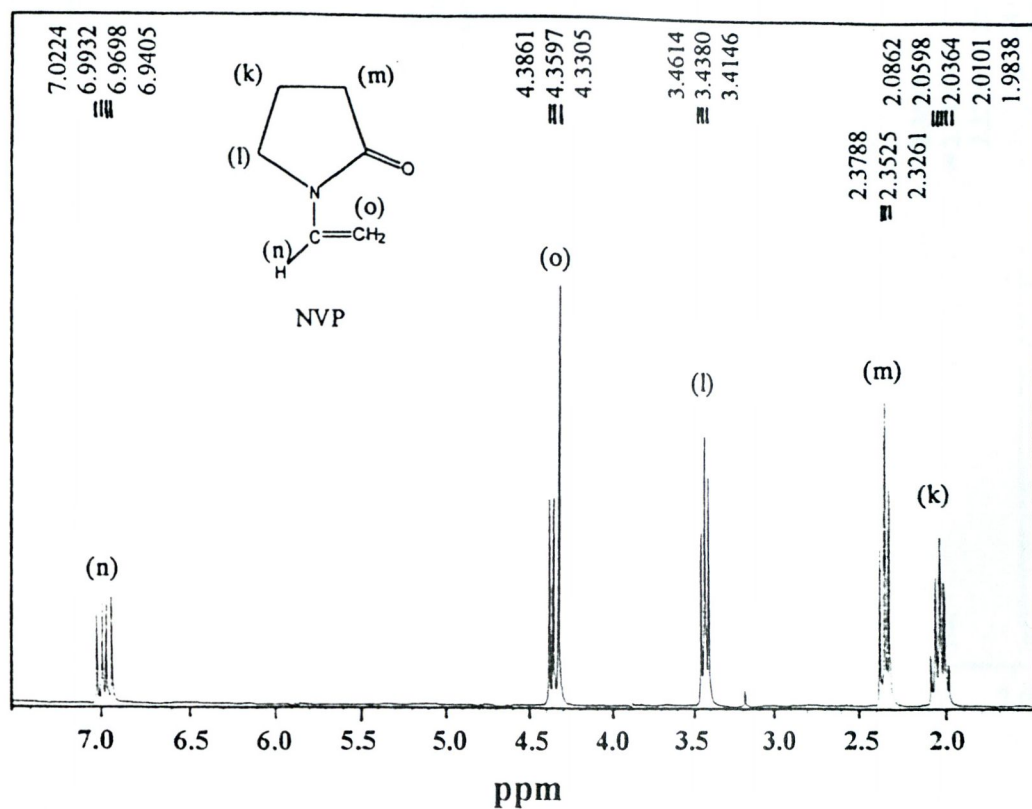


Figure 4.2. ^1H NMR (a), ^{13}C NMR (b) and ^{13}C DEPT 135° (c) spectra of NVI in CDCl_3 (50 mg/g).

(a)



(b)

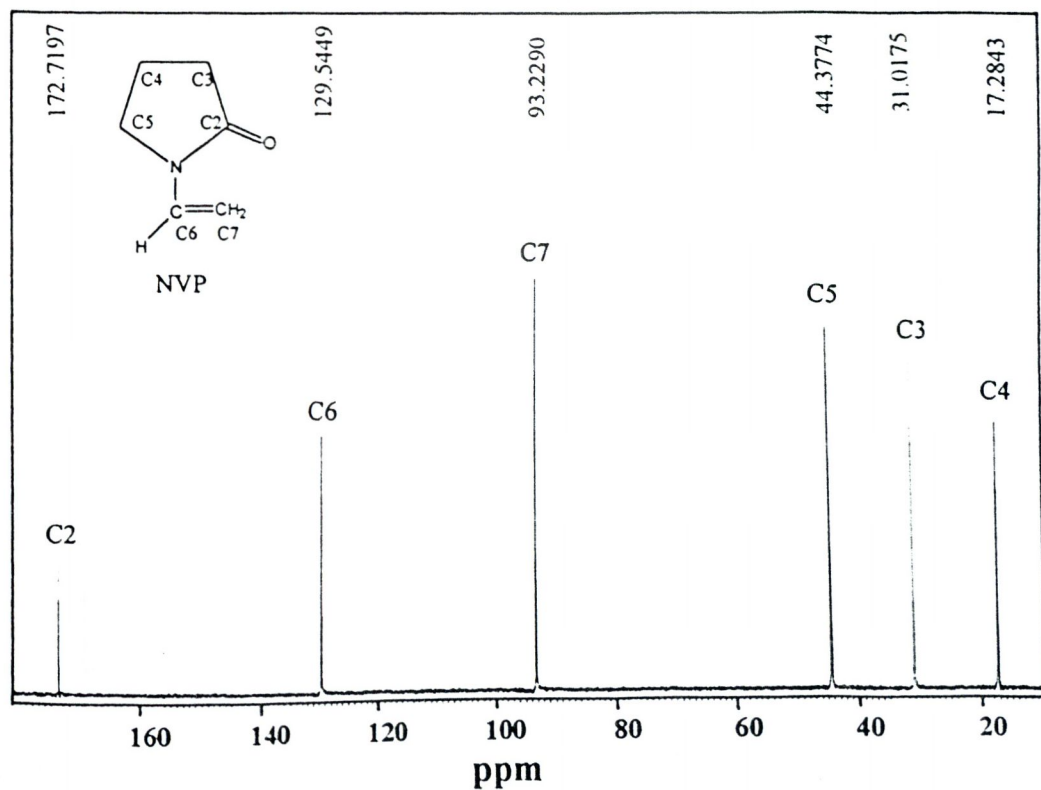
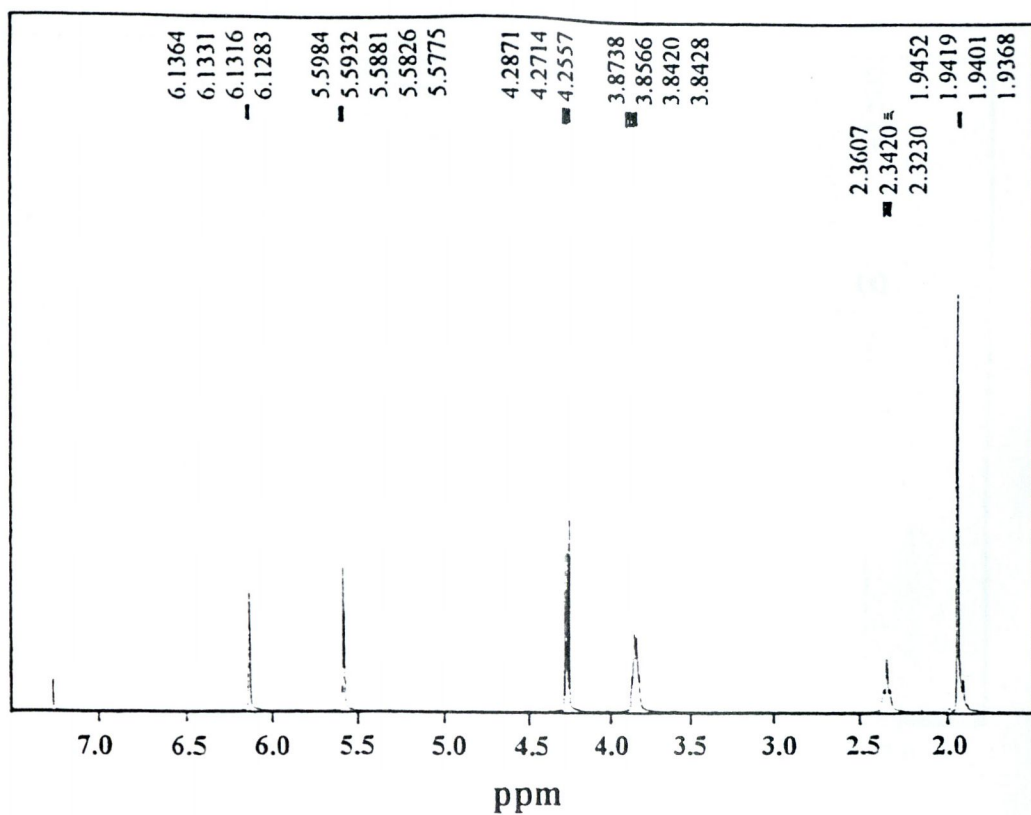


Figure 4.4. ¹H NMR (a) and ¹³C NMR (b) spectra of neat NVP monomer with peak assignments shown on the structural representations (inset).

(a)



(b)

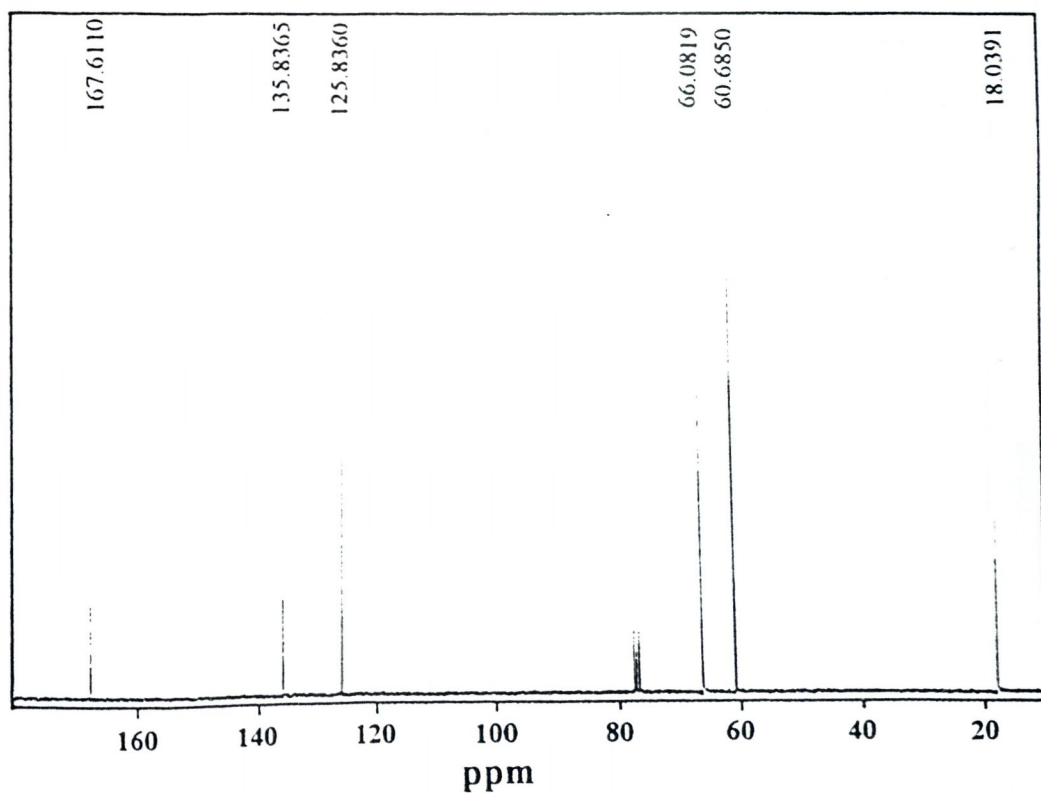
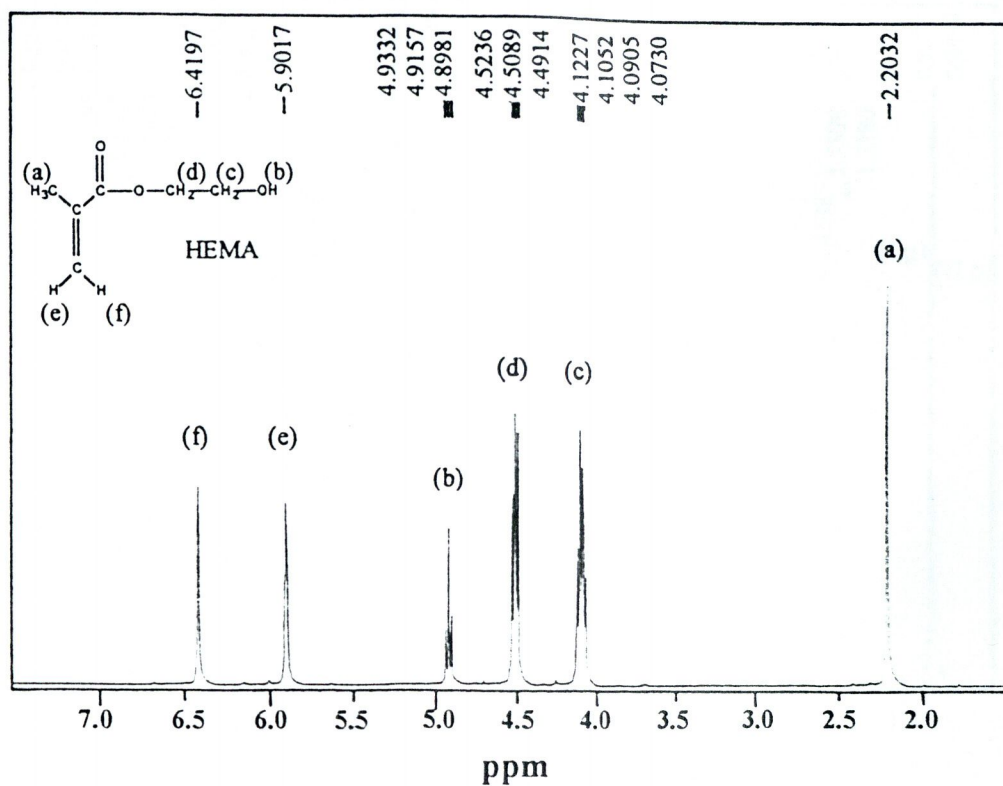


Figure 4.5. ^1H NMR (a) and ^{13}C NMR (b) spectra of HEMA in CDCl_3 (50 mg/g).

(a)



(b)

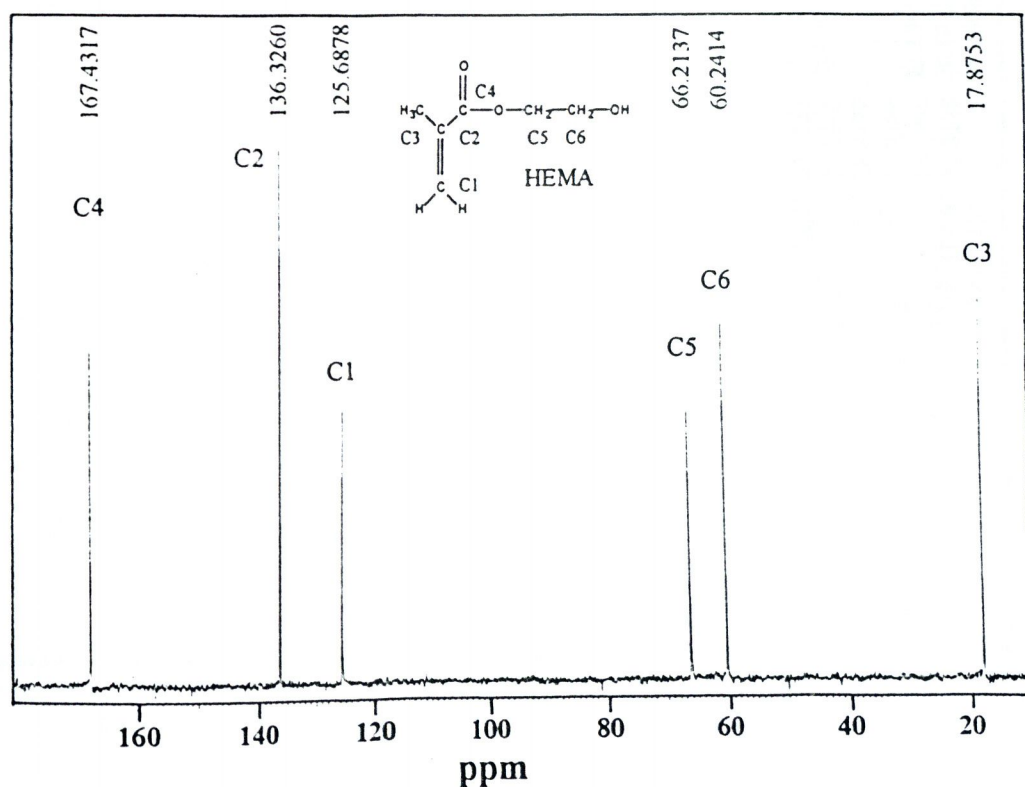
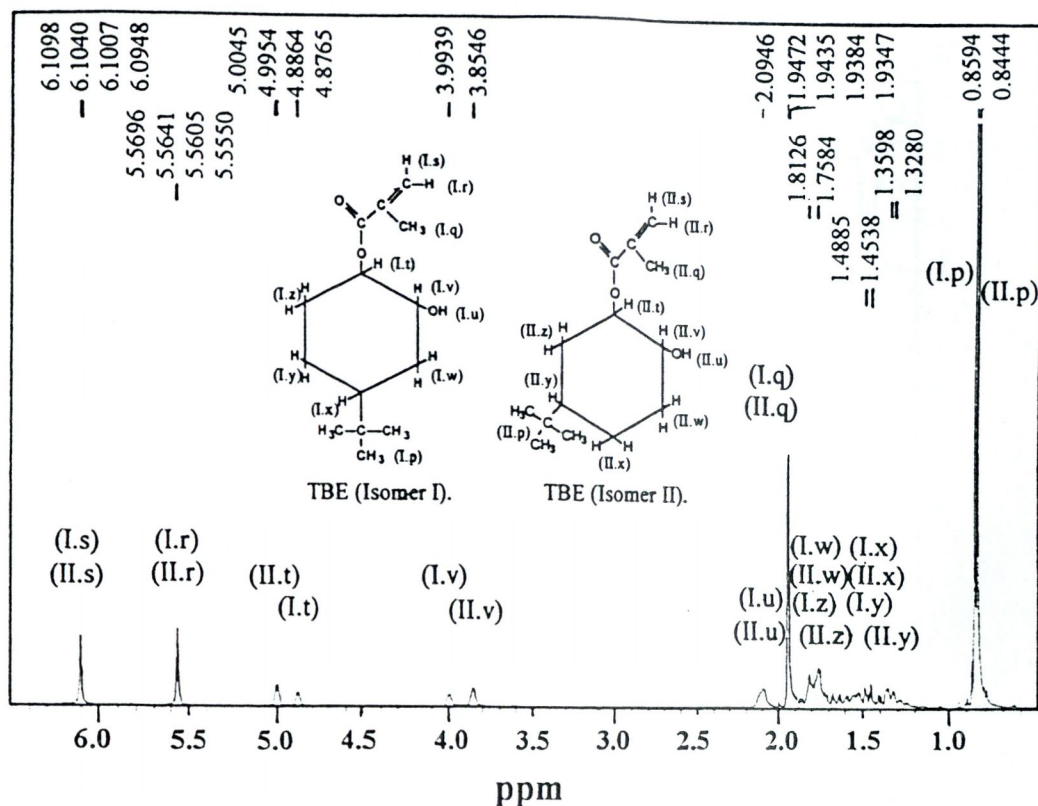


Figure 4.6. ^1H NMR (a) and ^{13}C NMR (b) spectra of neat HEMA monomer with peak assignments shown on the structural representations (inset).

(a)



(b)

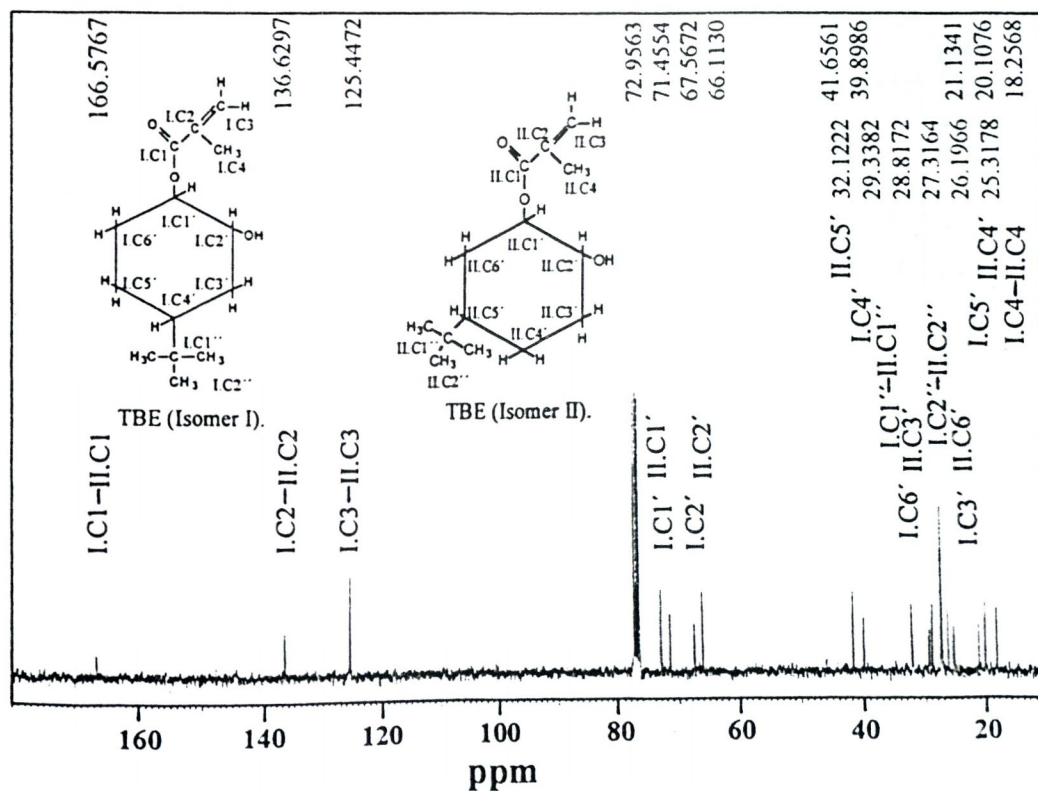


Figure 4.7. ^1H NMR (a) and ^{13}C NMR (b) spectra of TBE in CDCl_3 (50 mg/g) with peak assignments shown on the structural representations (inset).

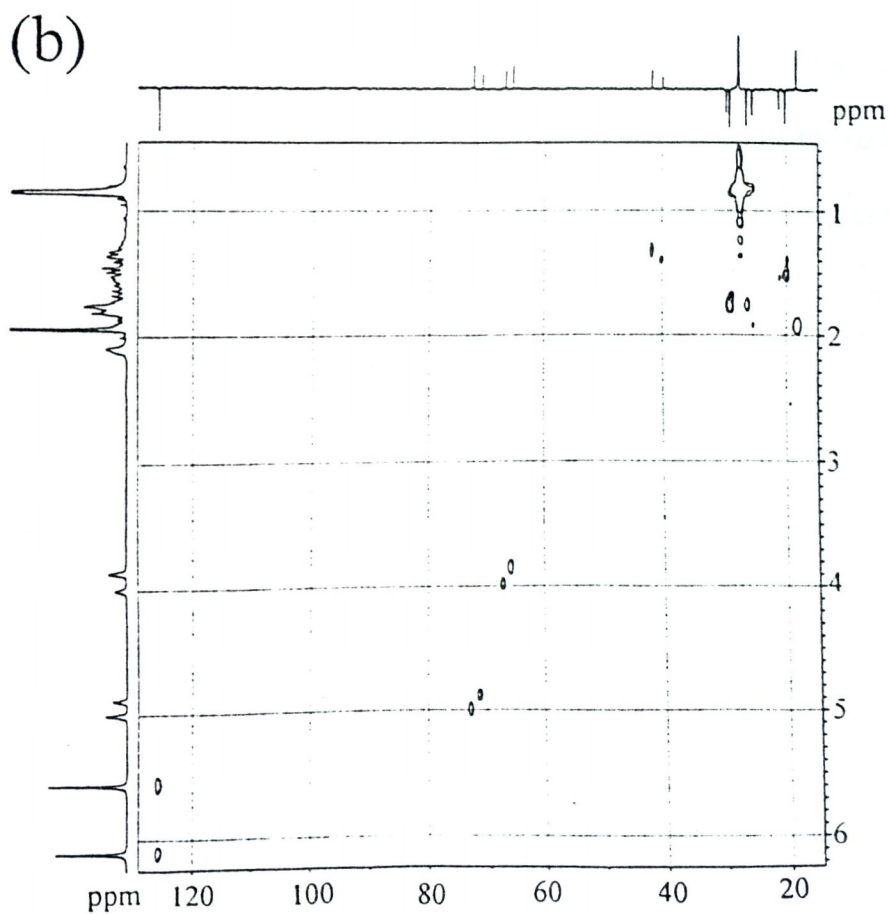
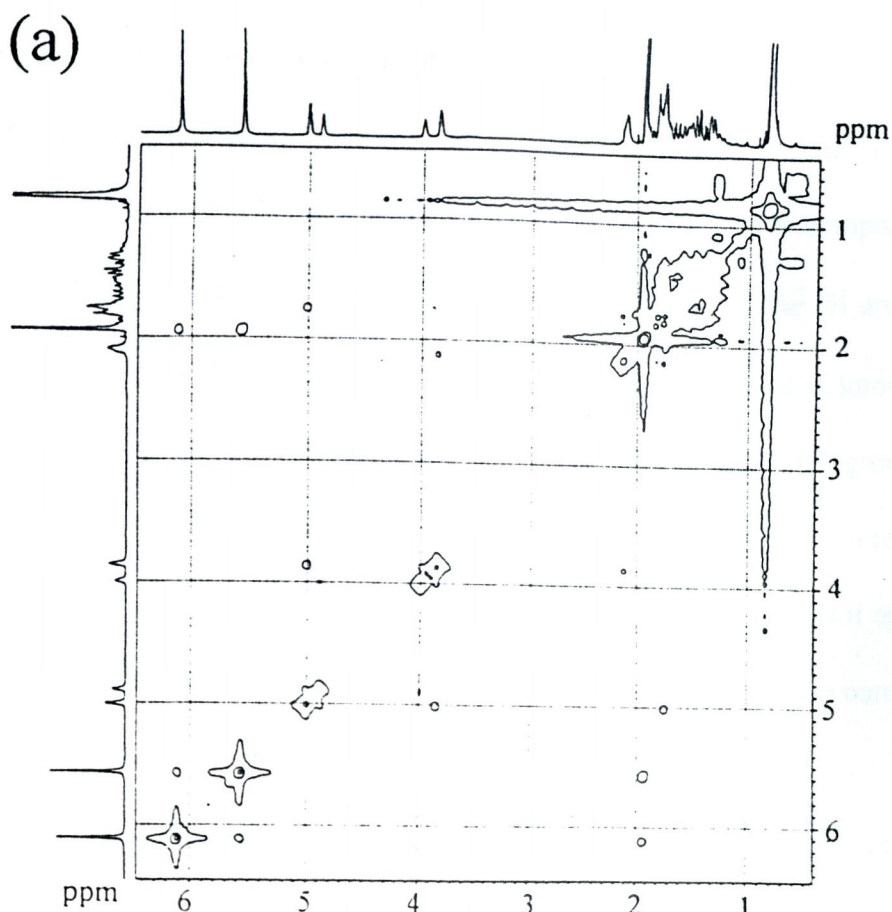


Figure 4.8. 2D ^1H - ^1H COSY (a) and ^1H - ^{13}C DEPT 135° COSY (b) spectra of TBE in CDCl_3 (50 mg/g).

since it involves contributions from nine protons. As a result this peak is apparent in the spectra of the mixtures, even though TBE is present at relatively low concentration, and it can be used as a monitor of the curing profile of this component.

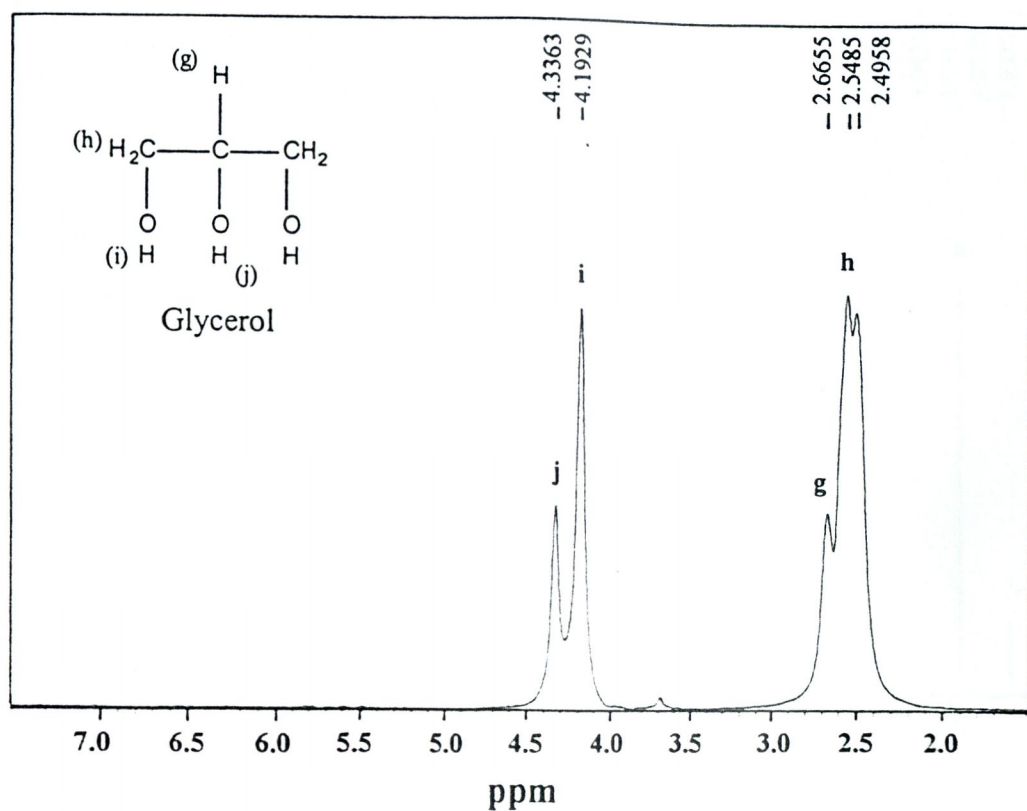
Glycerol was found to be only partially soluble in CDCl_3 and the ^1H and ^{13}C spectra shown in Figure 4.9 are therefore of the neat diluent. Glycerol is known to interact strongly between its pendant hydroxyl groups and the carbonyl group of HEMA via intermolecular hydrogen bonding in a manner known as the template effect.¹⁰ This effect may explain why the chemical shift positions of glycerol appear at higher ppm values in the spectra of the mixtures i.e. due to the deshielding nature of the electronegative carbonyl groups of adjacent HEMA molecules.

Although only the previous four components were present at high enough concentrations to permit their routine detection in the ^1H and ^{13}C spectra of the composite monomer mixtures, a full spectral characterisation of every species used in the composite formulations is included for completeness. Figures 4.10 through 4.16 show ^1H and ^{13}C spectra with peak assignments for the crosslinkers HEMA VC, EGDMA and AMA, the initiators BME, Darocur 1173 and AIBN and the in-monomer visible tint additive IMVT, respectively.

With the information on the assignments of individual peaks in the spectra of the constituent materials at hand, it was reasonably straightforward to interpret the complex spectra of the composite monomer mixtures with confidence.¹³

^{13}C (a) and ^1H (b) spectral peaks for neat Monomer Mixture A are assigned in Figure 4.17. The ^1H spectrum of a neat Monomer Mixture A sample obtained prior to UV-photocuring is also shown (c). Note the reduced spectral resolution compared with spectra of the same sample either in solvent or under more suitable acquisition

(a)



(b)

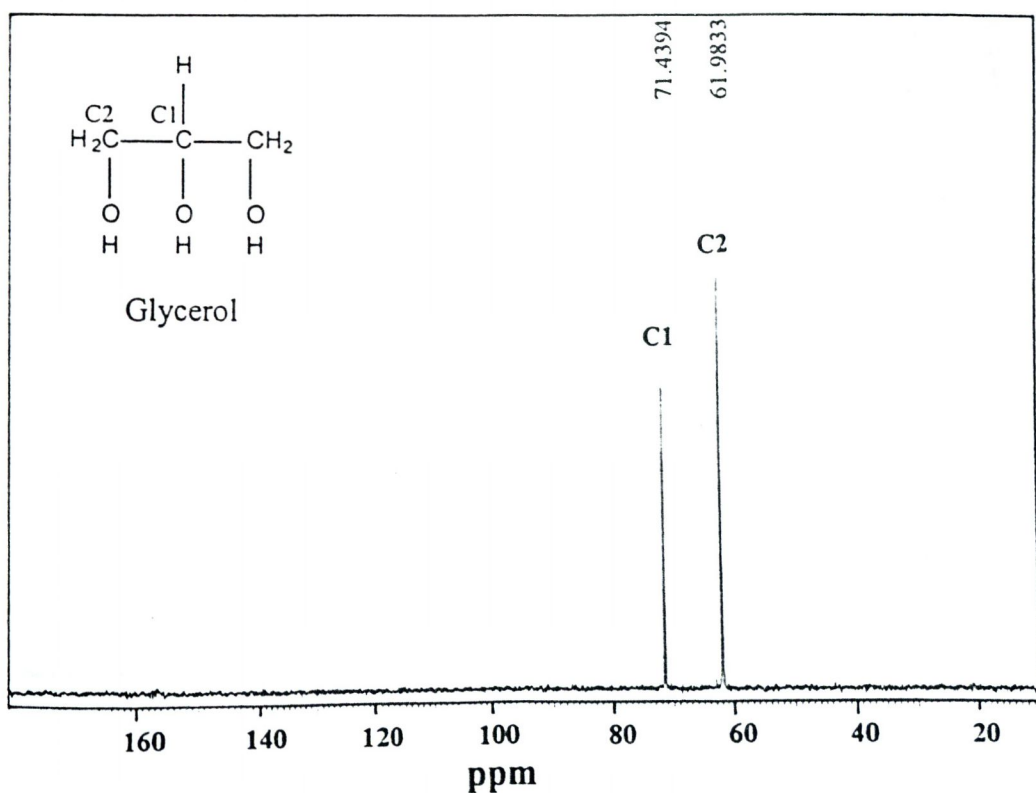
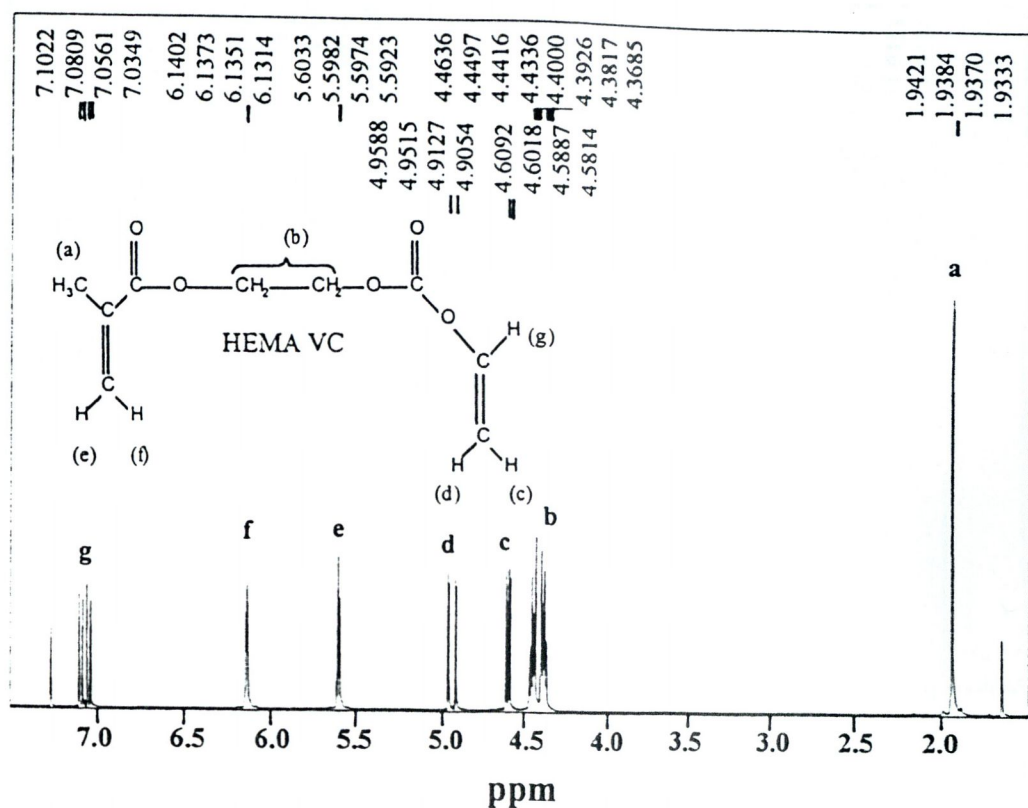


Figure 4.9. ¹H NMR (a) and ¹³C NMR (b) spectra of neat glycerol with peak assignments shown on the structural representations (inset).

(a)



(b)

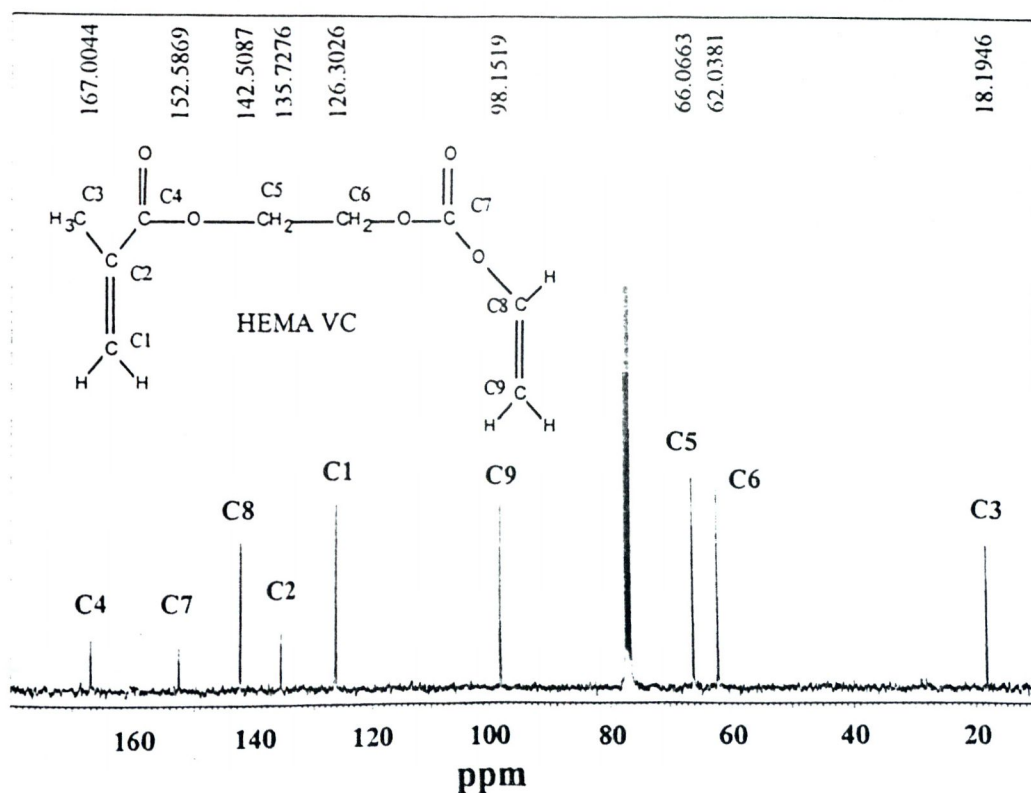
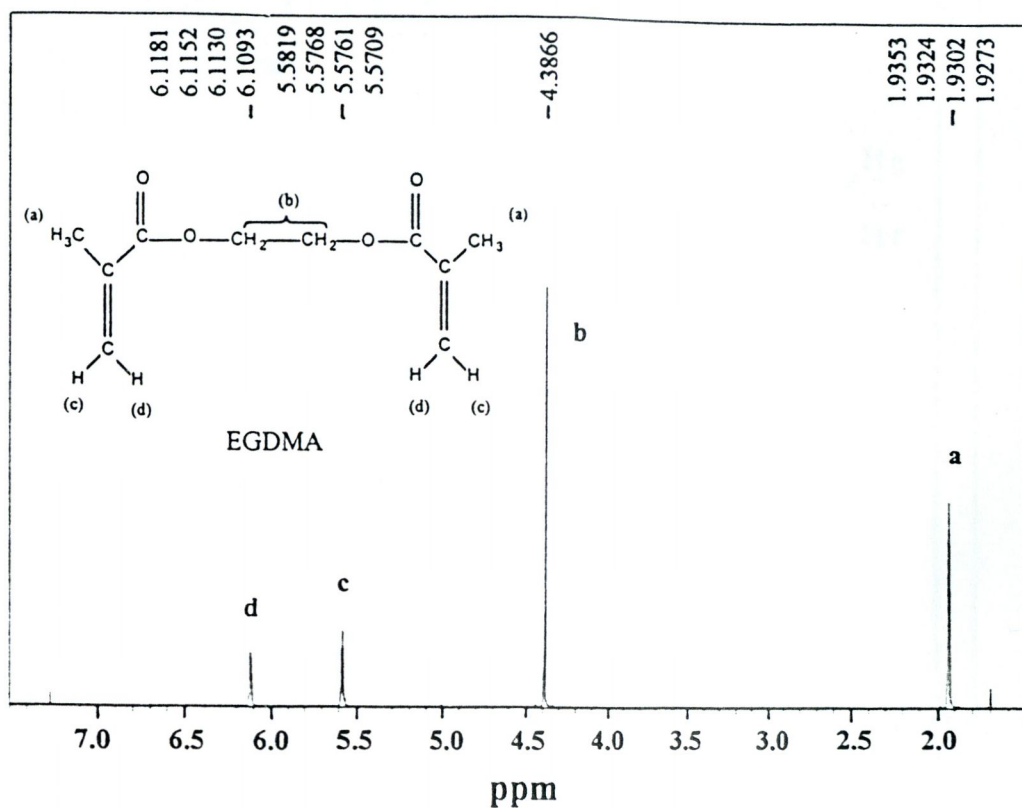


Figure 4.10. ¹H NMR (a) and ¹³C NMR (b) spectra of HEMA VC in CDCl₃ (25 mg/g) with peak assignments shown on the structural representations (inset).

(a)



(b)

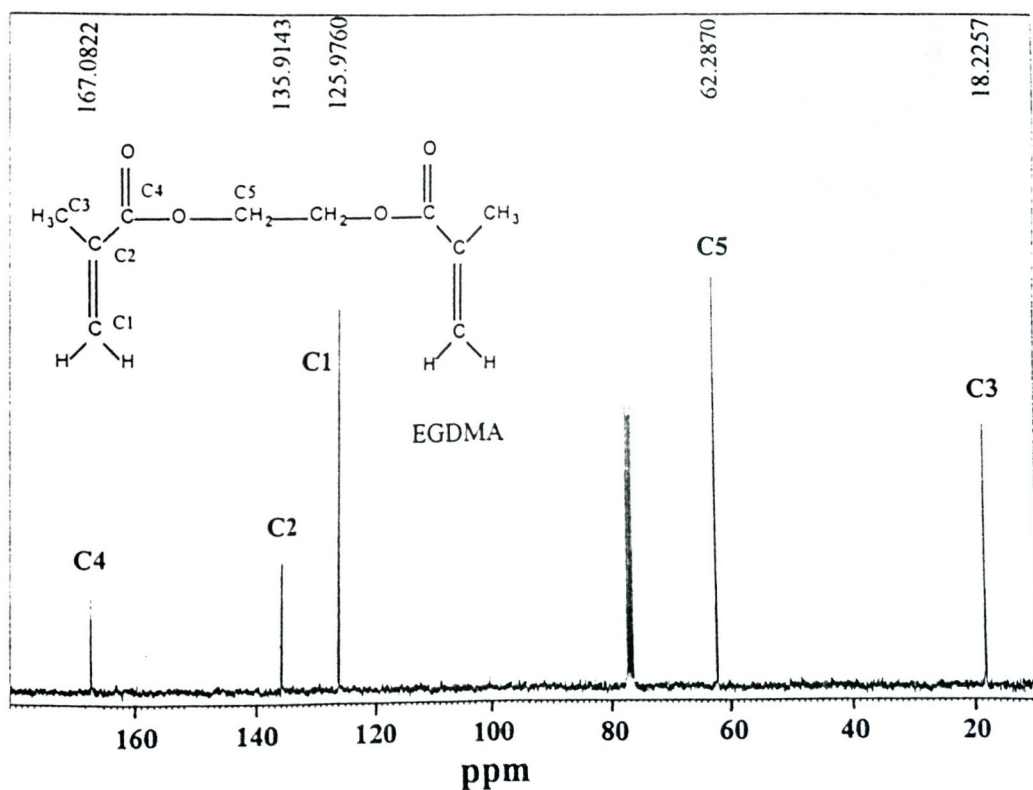
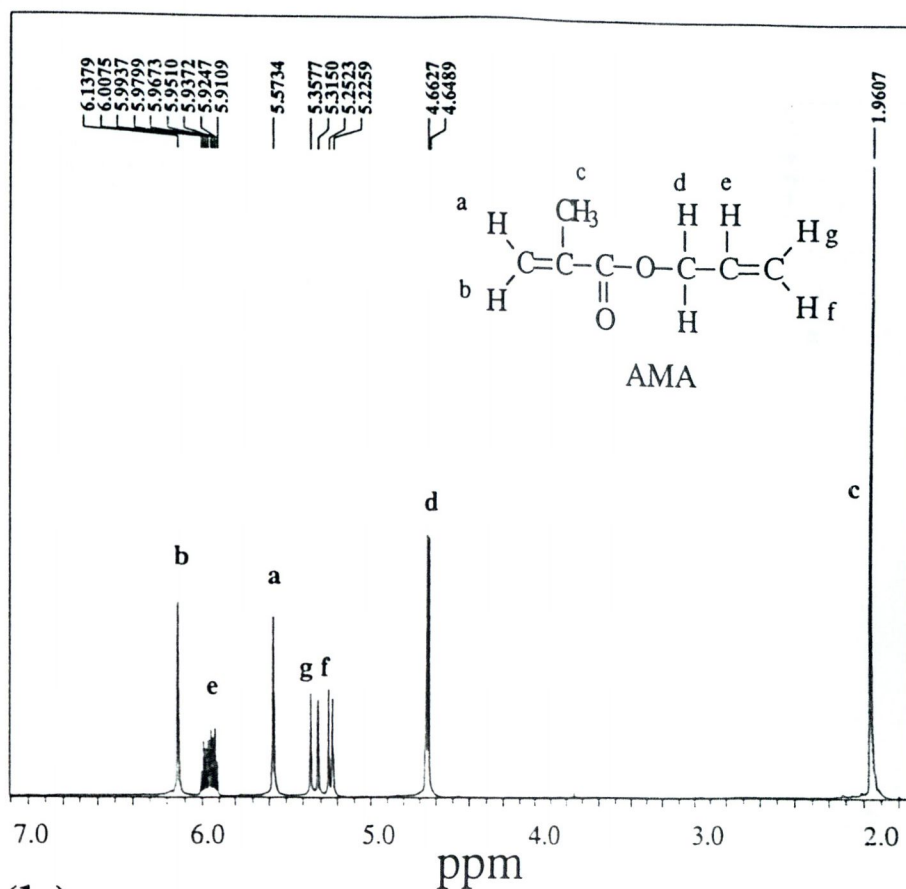


Figure 4.11. ^1H NMR (a) and ^{13}C NMR (b) spectra of EGDMA in CDCl_3 (50 mg/g) with peak assignments shown on the structural representations (inset).

(a)



(b)

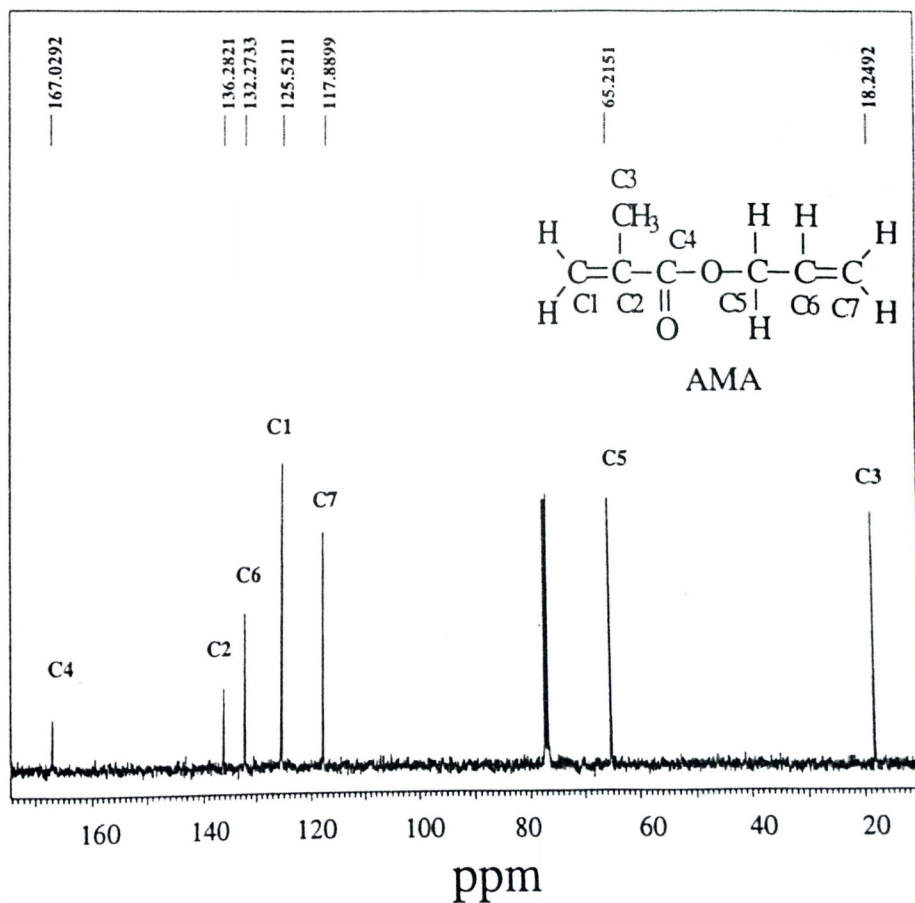
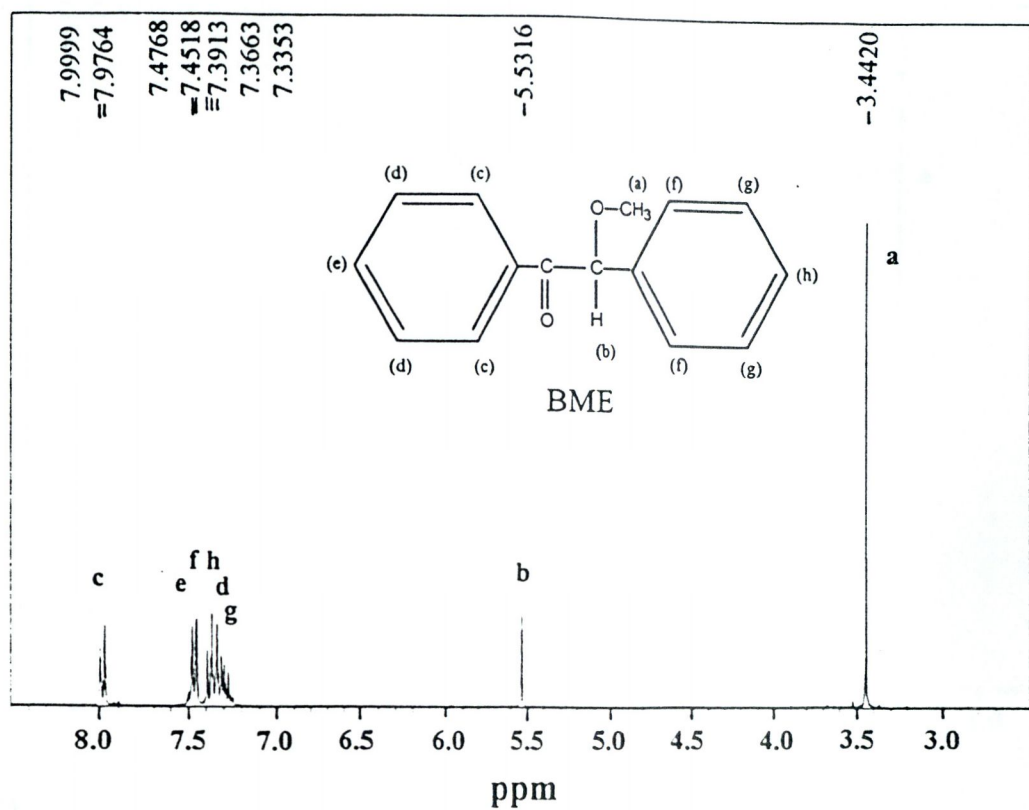


Figure 4.12. ¹H NMR (a) and ¹³C NMR (b) spectra of AMA in CDCl₃ (50 mg/g) with peak assignments shown on the structural representations (inset).

(a)



(b)

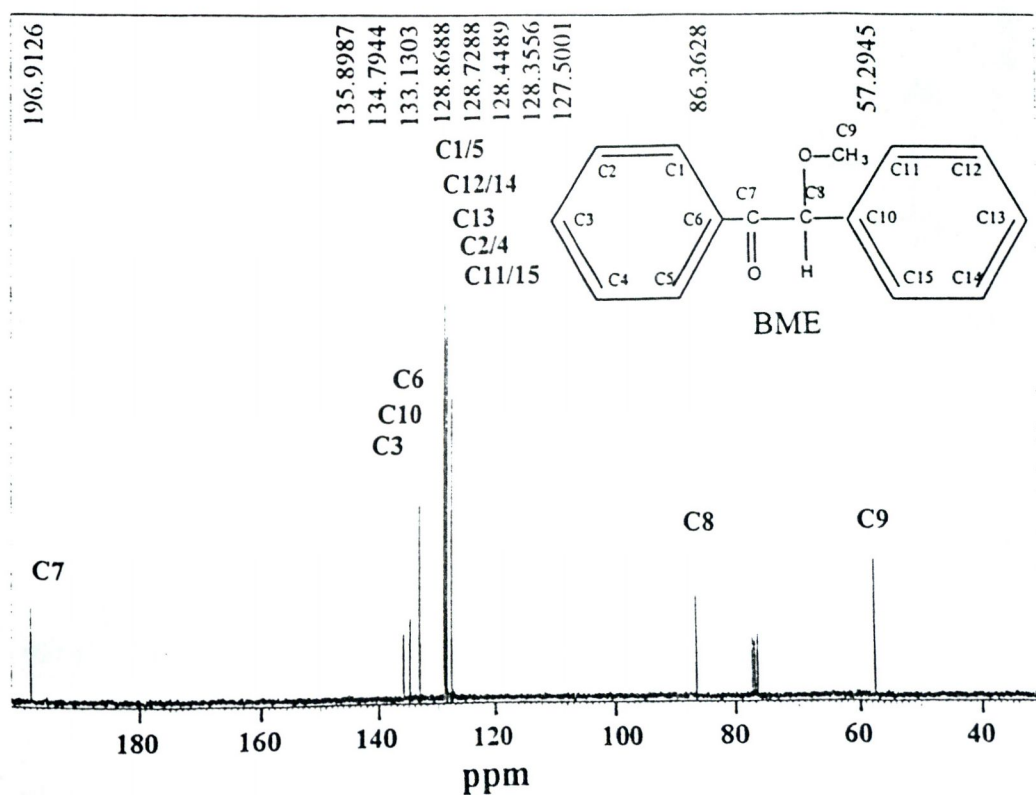
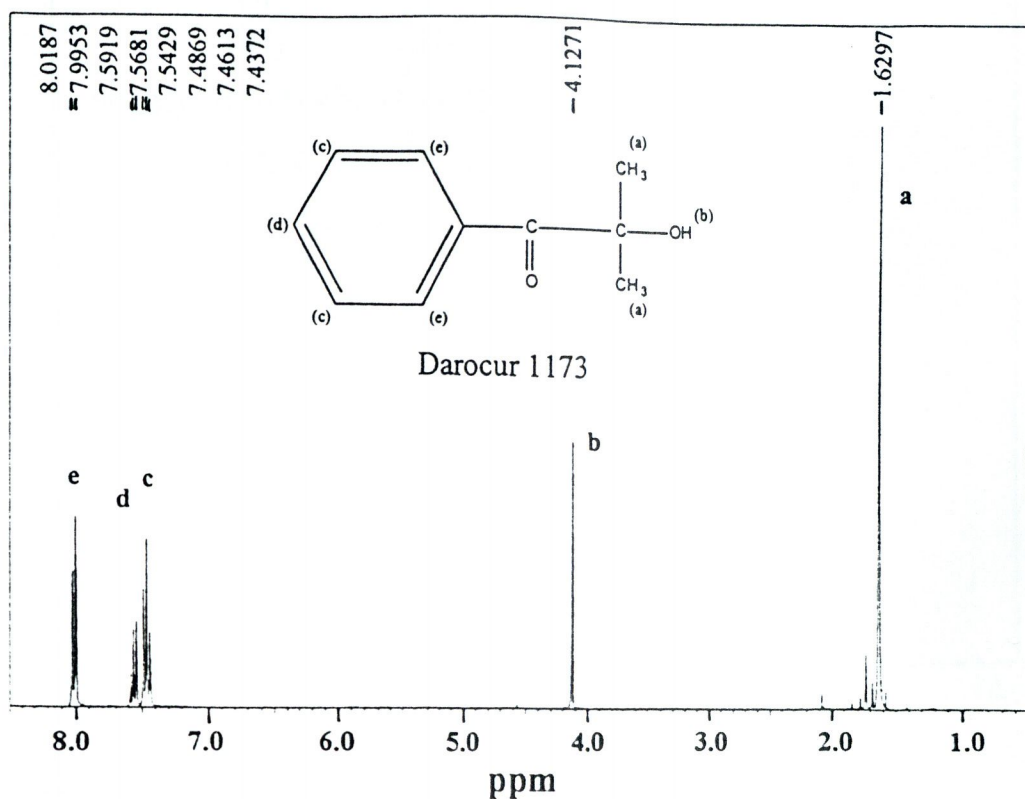


Figure 4.13. ^1H NMR (a) and ^{13}C NMR (b) spectra of BME in CDCl_3 (50 mg/g) with peak assignments shown on the structural representations (inset).

(a)



(b)

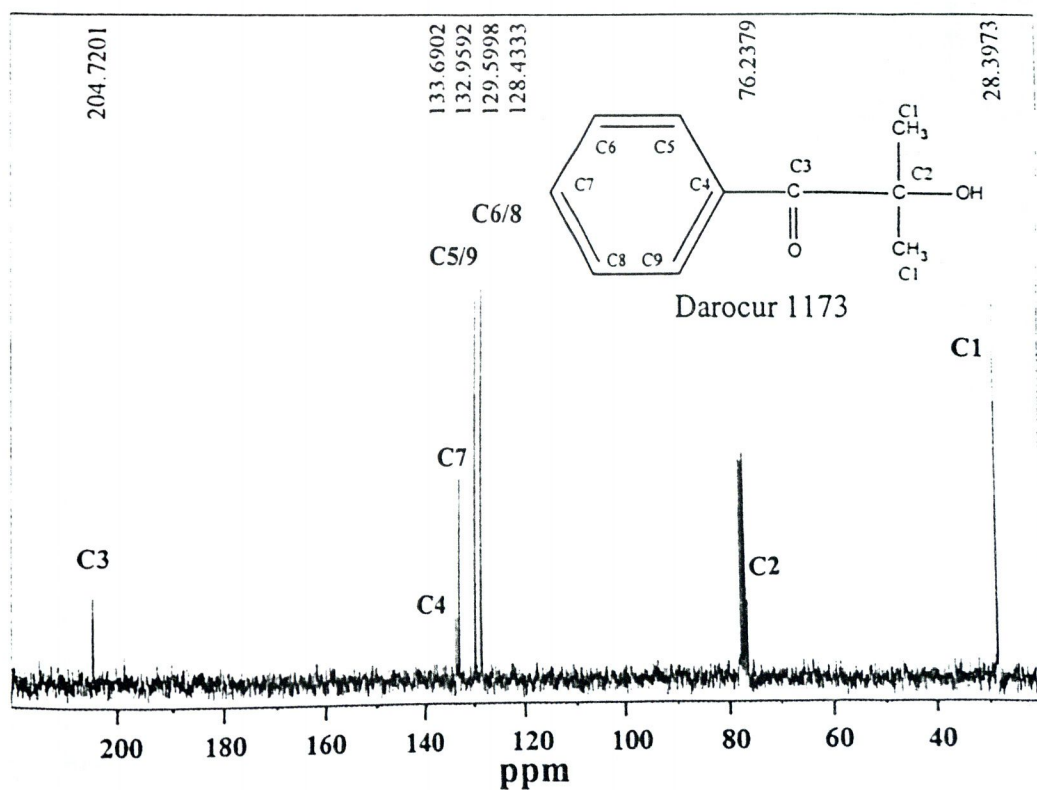
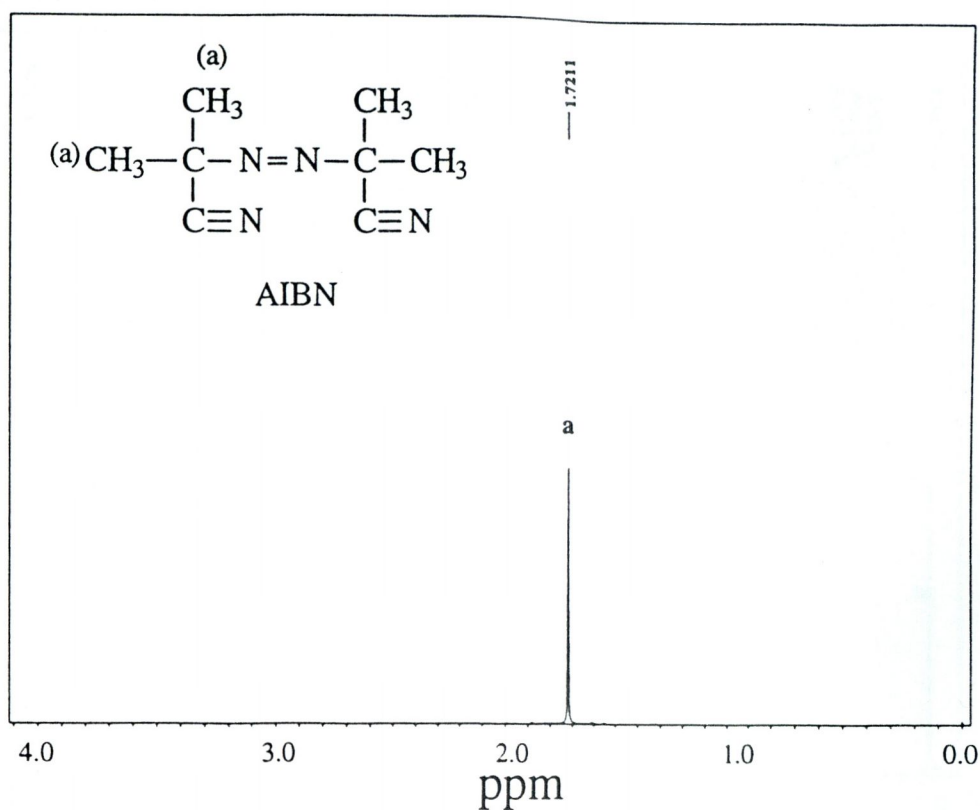


Figure 4.14. ¹H NMR (a) and ¹³C NMR (b) spectra of Darocur 1173 in CDCl₃ (50 mg/g) with peak assignments shown on the structural representations (inset).

(a)



(b)

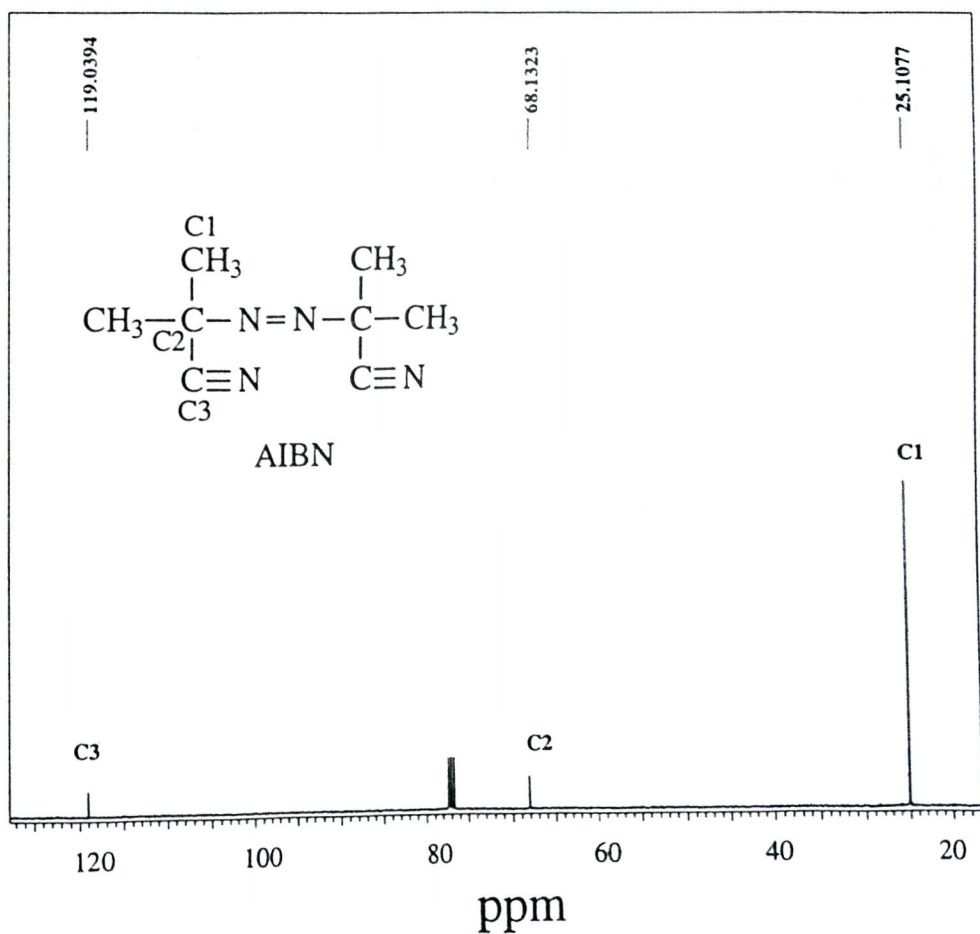
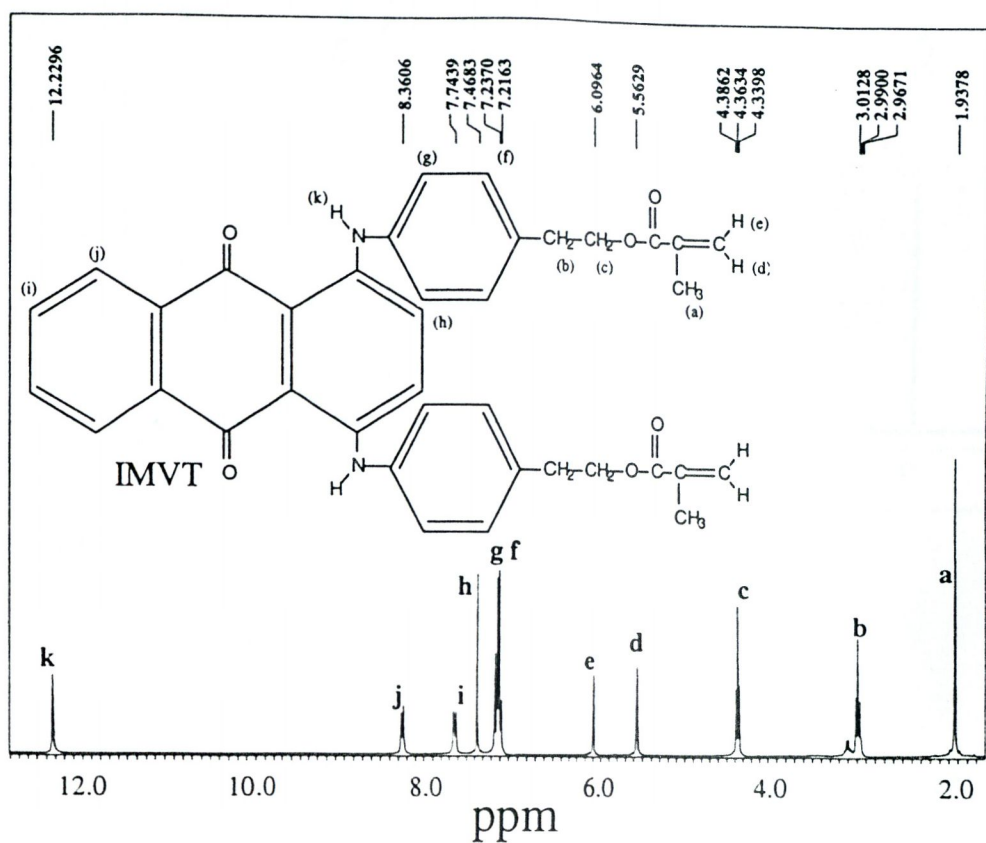


Figure 4.15. ^1H NMR (a) and ^{13}C NMR (b) spectra of AIBN in CDCl_3 (50 mg/g) with peak assignments shown on the structural representations (inset).

(a)



(b)

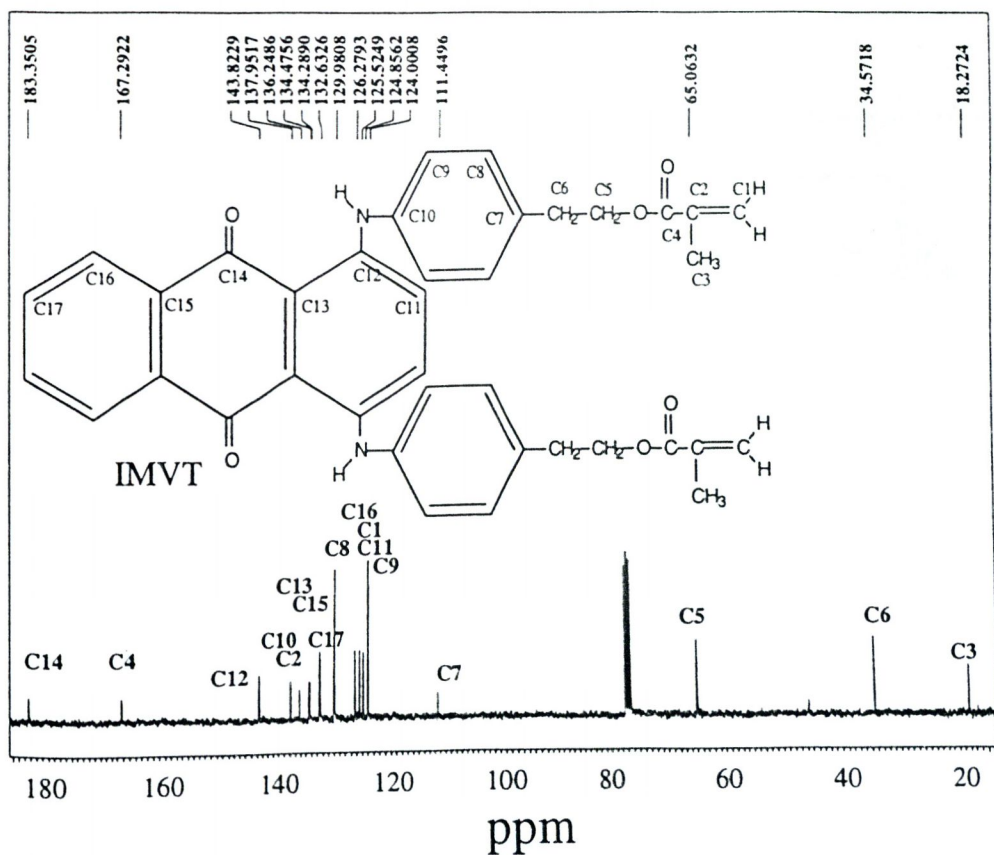


Figure 4.16. ¹H NMR (a) and ¹³C NMR (b) spectra of IMVT in CDCl₃ (25 mg/g) with peak assignments shown on the structural representations (inset).

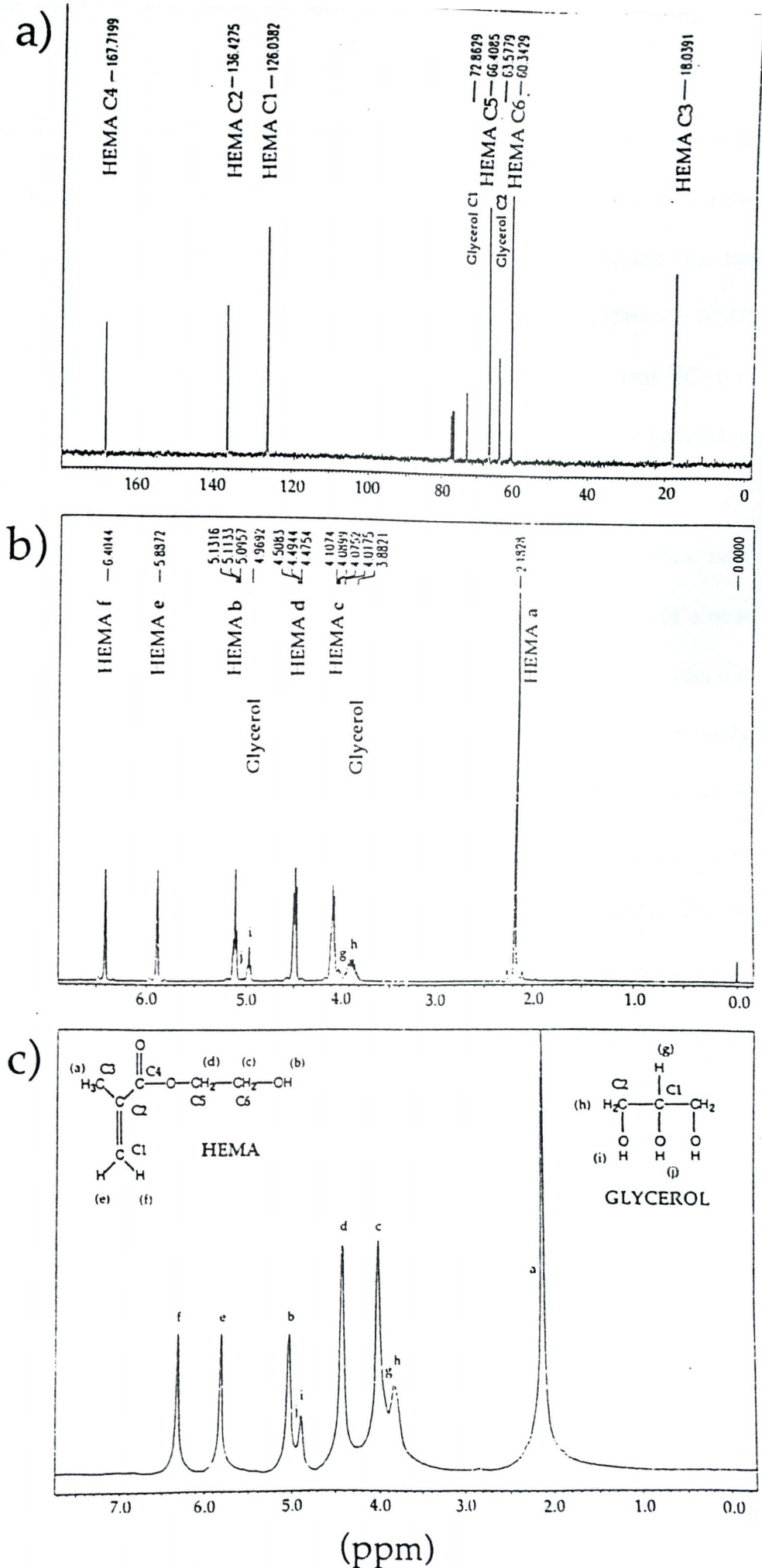


Figure 4.17. ^{13}C NMR (a) and ^1H NMR (b) spectra of neat Monomer Mixture A with peak assignments and ^1H NMR (c) spectrum of neat Monomer Mixture A obtained prior to a UV-photocuring experiment (20 °C).

conditions. This reduction in resolution results from the experimental requirements of (i) shorter spectral acquisition times, (ii) a slower spinning rate of 5Hz to prevent the curing mixture from creeping up the sides of the NMR sample tube, and (iii) the smaller sample volume used to ensure that all of the sample resided within the NMR probe coils and was illuminated uniformly. Note that the ^1H (e, f) peaks and ^{13}C (C1) peak characterise the vinylidene environment in HEMA monomer and may be used to monitor the curing behaviour of HEMA in this mixture.

Similarly, ^{13}C (a) and ^1H (b) spectral peaks for the more complex neat Monomer Mixture B are assigned in Figure 4.18, along with a ^1H spectrum of a neat sample (c) obtained prior to UV-photocuring, with the expected reduced spectral resolution. Note that the proton NVP(n) peaks and carbon NVP(C7) peak uniquely characterise the NVP monomer: C7 is chosen because, as part of the vinyl group, it reflects direct participation in the polymerising process whereas C2 does not. Furthermore C2 has a significantly longer T_1 relaxation time (*see Chapter 5*). The ^1H (e, f) peaks and ^{13}C (C1) peak again characterise HEMA. As TBE is present at lower concentration, the ^1H (p) and ^{13}C TBE peak arising from the tertiary butyl group are the only signals intense enough to be readily detected in the spectra of the mixtures; they are used to monitor the curing behaviour of the TBE component.^{13,27}

^{13}C (a) and ^1H (b) spectral peaks for Monomer Mixture H in solution are assigned in Figure 4.19, along with a ^1H spectrum of a neat sample (c) obtained prior to thermal curing at 343 K. A larger sample volume could be used for thermal curing measurements and the spectral resolution is less adversely affected by the other experimental acquisition requirements. This improved resolution is also evident in the ^1H spectra of the neat, thermally cured Monomer Mixtures I (a) and J (b) (Figure

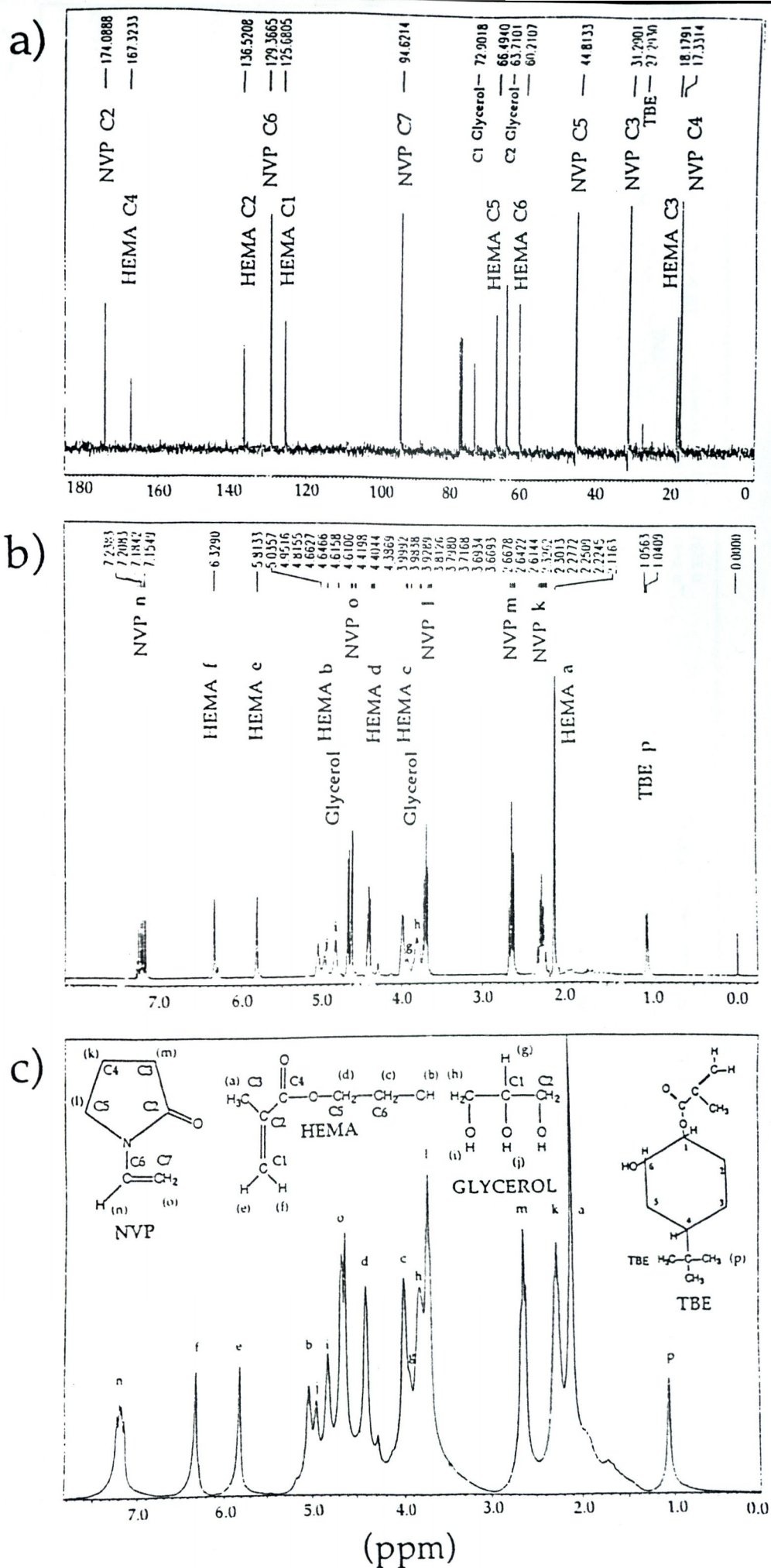


Figure 4.18. ^{13}C NMR (a) and ^1H NMR (b) spectra of neat Monomer Mixture B with peak assignments and ^1H NMR (c) spectrum of neat Monomer Mixture B obtained prior to a UV-photocuring experiment (20 °C).

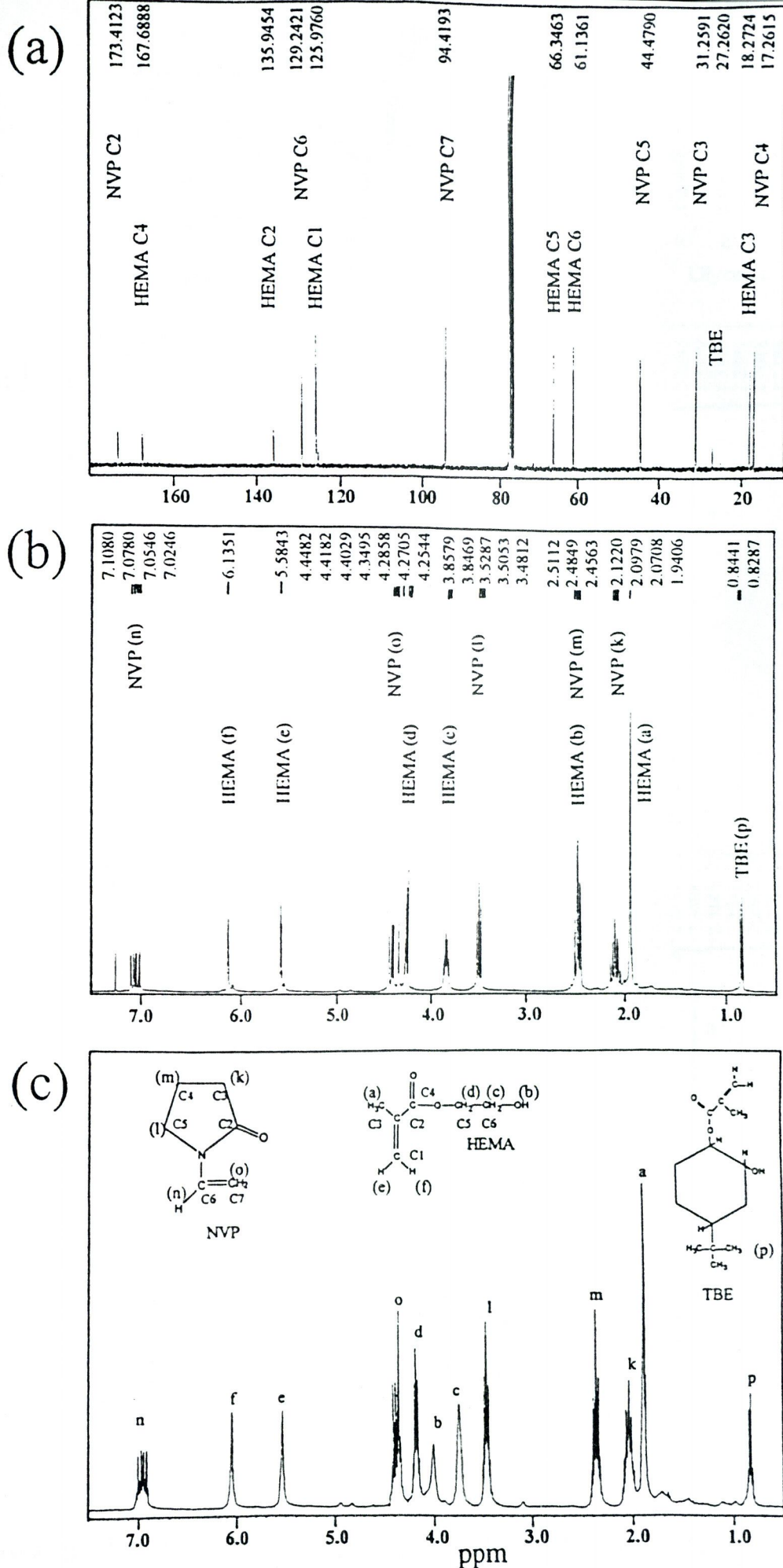
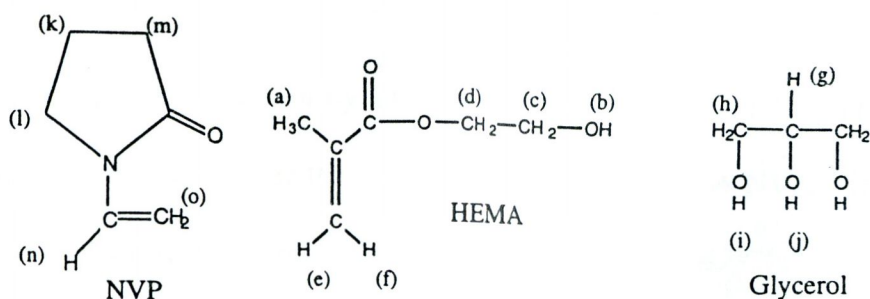
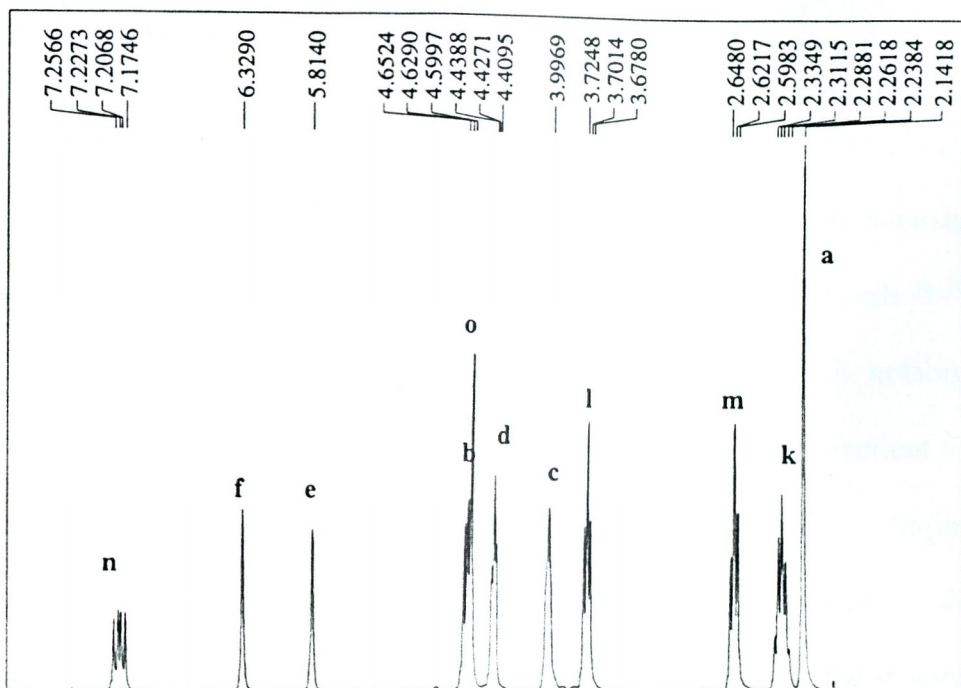


Figure 4.19. ¹³C NMR (a) and ¹H NMR (b) spectra of Monomer Mixture H in CDCl₃ (50 mg/g) with peak assignments and ¹H NMR (c) spectrum of neat Monomer Mixture H obtained prior to a thermal curing experiment (70 °C).



(a)



(b)

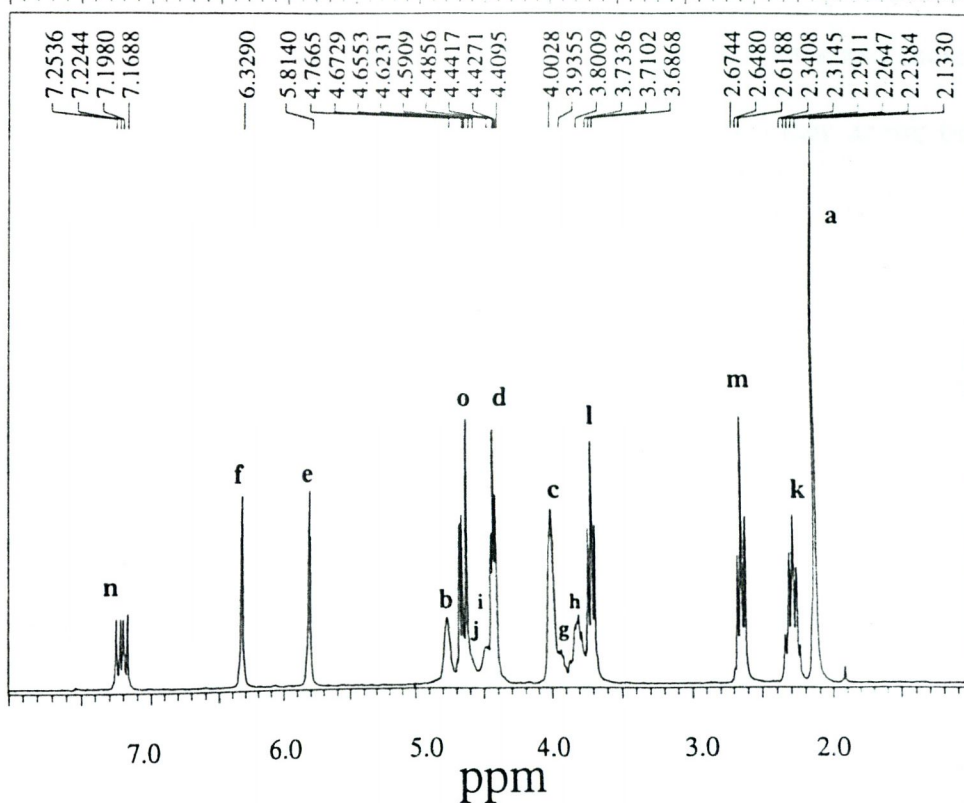


Figure 4.20. ^1H NMR spectra of neat Monomer Mixture I (a) and of neat Monomer Mixture J (b) with peak assignments obtained prior to thermal curing experiments (70°C).

4.20). The same peaks as previously identified for Mixture B can be used to characterise and ultimately monitor the thermal curing profiles of the NVP, HEMA and TBE components, where present, in these three composite systems.¹³

4.3.2 Fourier Transform Infrared Spectroscopy

4.3.2.1 Introduction

Infrared spectroscopy has been used successfully in the past to continuously monitor the degree of polymerisation of monomer composites as curing proceeds.^{28,29} The technique has a number of difficulties and limitations associated with it, notably (i) the poor resolution of overlapping bands in the spectra, and (ii) the requirement to monitor internal reference bands, in order to obviate effects due to changes in sample thickness which can occur as a result of shrinkage or thermal expansion.³⁰ A prerequisite to any such experiments is the characterisation of the bands in the spectra *i.e.* the identification of those that respond to the polymerisation process and those that can satisfactorily be used as internal reference bands. This can again be problematic, for reasons of poor resolution.

4.3.2.2 FT-IR Results and Discussion

Table 4.3 presents as detailed and as accurate a characterisation of the bands in the spectra of the main components, and complete composite mixtures as is viable, given the breadth of the bands recorded and the range of wavenumbers over which a specific band may occur.^{24,26,31,32} The spectra of the four major components in the formulations (and the only components present at high enough concentration to be detected in the spectra of the mixtures) are shown in Figure 4.21. The bands which monitor the cure of the monomers, such as the vinylidene ($R'R''-C=C-H_2$) symmetric

Table 4.3. FT-IR spectral band assignments of the major components of the mixtures and the positions of bands detected in the spectra of the composite formulations.

Bond Vibration Type strength	HEMA (cm ⁻¹)	Bond Vibration Type strength	NVP (cm ⁻¹)	Bond Vibration Type strength	Glycerol (cm ⁻¹)	Bond Vibration Type strength	TBE (cm ⁻¹)	MIX A (cm ⁻¹)	MIX B (cm ⁻¹)	MIX H (cm ⁻¹)	MIX I (cm ⁻¹)	MIX J (cm ⁻¹)
R-H ₂ C-O-H <i>Vs</i> s/br	3428	H-O-H <i>Vs</i> s/br	3565	C-O-H <i>Vs</i> s/br	3306	RR-CH-O-H <i>Vs</i> s/br	3436	3412	3410	3419	3418	3410
R-C-H ₃ <i>Va</i> s		C=C-H ₂ <i>Va</i> w	3080			C=C-H ₂ <i>Va/Vs</i> m/w						
C=C-H ₂ <i>Va/Vs</i> m	2957	C=C-H ₂ <i>Vs</i> w	3045			R-C-H ₃ <i>Va/Vs</i> s						
R'-C-H ₂ -R'' <i>Va</i> s	2935	cyclic -C-H ₂ - <i>Va</i> s	2976			cyclic -C-H ₂ - <i>Va</i> s	2953	2955	2951	2954	2955	2953
R'-C-H ₂ -R'' <i>Vs</i> s	2905			-C-H ₂ -OH <i>Va</i> s	2936							
R'-C-H ₂ -OH <i>Vs</i> m		cyclic -C-H ₂ - <i>Vs</i> s	2887	R'-C-H ₂ -OH <i>Vs</i> m		cyclic -C-H ₂ - <i>Vs</i> s	2868	2882	2885	2890	2889	2886
R-C-H ₃ <i>Vs</i> s				RR-C-H-OH <i>Vs</i> m	2860	RR-C-H-OH <i>Vs</i> m						
R'-C=OO-R'' <i>Vs</i> vs	1717	cyclic amide				R'-C=OO-R'' <i>Vs</i> vs	1716	1716	1710	1710	1707	1707
		-C=O <i>Vs</i> vs	1690									
R'R''-C=CH ₂ <i>Vs</i> s	1638					R'R''-C=CH ₂ <i>Vs</i> s	1638	1638	1638	1638	1638	1638
		RH-C=CH ₂ <i>Vs</i> s	1630					1638	1628	1629	1628	1629
R-C-H ₃ $\delta\alpha$ m	1455	-N-C-H ₂ -R- δsc m	1487			R-C-H ₃ $\delta\alpha$ m	1479		1489	1488	1489	1488
R'-C-H ₂ -OH $\delta\alpha$ m	1440	-R-C-H ₂ -R- δsc m	1460	R'-C-H ₂ -OH $\delta\alpha$ m	1430	-R-C-H ₂ -R- δsc m	1452	1456	1460	1460	1460	1456
-C=C-H ₂ δsc ρ m		-CO-C-H ₂ -R- δsc m	1422			-C=C-H ₂ δsc ρ m	1437	1440	1423	1424	1423	1423
C-O-H δ m	1404			C-O-H δ m	1416	C-O-H δ m	1402	1404				
R-C-H ₃ δs s		-N-C-H ₂ -R- ω m	1383	-C-H-OH ω m		R-C-H ₃ δs s	1394		1390	1390	1388	1390
R'-C-H ₂ -OH ω m	1379			-C-H-OH $\delta\alpha$ m	1350	-C-H-OH $\omega/\delta\alpha$ m	1365	1378				
R'-C-H ₂ -R'' ω/τ m	1319	-R-C-H ₂ -R- ω m	1331			-R-C-H ₂ -R- ω m	1332	1319	1329	1322	1323	1322
R'-C-H ₂ -OH τ m	1296	-CO-C-H ₂ -R- ω m	1307			C-(CH ₃) ₃ <i>sk</i> s	1292	1298				
		-C-N- <i>Vs</i> s	1275						1286	1287	1286	1288
		cyclic-C-N- <i>Vs</i> m	1171	R'-C-H ₂ -OH τ m	1213							
R'-CO-O-R'' <i>Vs</i> s	1163					R'-CO-O-R'' <i>Vs</i> s	1161	1165	1167	1165	1163	1166
R-C-H ₃ ρ m	1078	-N-C-H ₂ -R- τ w	1074	RR-HC-O-H <i>Vs</i> s	1109	RR-HC-O-H <i>Vs</i> s	1103	1080	1080	1082	1082	1080
C-O-H <i>Vs</i> s		-R-C-H ₂ -R- τ m	1043			-R-C-H ₂ -R- τ m	1047		1043	1031	1032	1034
C-C-O <i>Vs</i> m/w	1030	-CO-C-H ₂ -R- τ w	1005	R-H ₂ C-O-H <i>Vs</i> s	1028	C-C-O <i>Vs</i> m/w	1020	1036				
		RH-C=C-H ₂ γ s	981			C-O-C <i>Vs</i> m/w	980		980	980	982	980
C=C-H ₂ ρ m	945	C=C-H ₂ ρ m	932			C=C-H ₂ ρ m	939	949	950	945	947	948
C=C-H ₂ ω m	903			RR-C-H-OH ρ w	922	RR-C-H-OH ρ w	916	904	901	900	900	901
R'-C-H ₂ -R'' ρ w	870			R'-C-H ₂ -OH ρ w	852			868				
		-C-C- <i>sk</i> s	843			-C-C- <i>sk</i> s	852		850	851	851	853
R'R''-C=CH ₂ <i>Vs</i> m Ov	816					R'R''-C=CH ₂ <i>Vs</i> m Ov	814	815	816	816	816	816
		cyclic-C-H ₂ - ρ m	746			cyclic-C-H ₂ - ρ m	740		750	750	750	748
		cyclic-C-H ₂ - ρ w	700			cyclic-C-H ₂ - ρ w	700			700	700	700
R-H ₂ C-O-H γ m/br	652	H-O-H γ m/br	648	R-H ₂ C-O-H γ m/br	661	RR-HC-O-H γ m/br	650	650	650	650	648	650

Vibration Type :*Va* antisymmetric stretch*Vs* symmetric stretch $\delta\alpha$ antisymmetric deformation $\delta s/\delta sc$ symmetric deformation/scissoring γ out-of-plane deformation ω wagging vibration ρ rocking vibration τ twisting vibration*sk* skeletal stretchStrength :

vs very strong

s strong

m moderate

w weak

br broad

Bands of interest :☒ vinyl or vinylidene bands that monitor cure☐ bands used as internal reference

stretch overtone (V_s O_v) band of HEMA at 816cm^{-1} and the vinyl ($\text{RH-C}=\text{C-H}_2$) out-of-plane deformation (γ) band of NVP at 981cm^{-1} are highlighted both in Table 4.3 and in the spectra shown in Figures 4.21 through 4.24. Highlighted in a lighter tone in the same table and figures are the bands used as internal reference bands, such as the $\text{R}'\text{-CO-O-R}''$ symmetric stretch (V_s) band in HEMA at 1163cm^{-1} and the -C-C- skeletal stretch (sk) in NVP at 843cm^{-1} .

Figure 4.22 shows the FT-IR spectrum of a sample of Monomer Mixture A, obtained at the start of a UV-photoinitiated polymerisation experiment (*see Chapter 6*), with the relevant bands used to monitor the cure behaviour of HEMA highlighted. In this composite system the bands of interest are reasonably well resolved and the application of the FT-IR experiment to monitor the cure behaviour of the single monomer proved successful.

Figure 4.23 shows the FT-IR spectrum of a sample of Monomer Mixture B, again recorded at the start of a UV-photoinitiated polymerisation experiment; the relevant bands used to monitor the cure behaviour of both HEMA and NVP monomers are highlighted. Unlike NMR, it was not possible to follow the cure behaviour of TBE since no representative bands for this monomer were adequately resolved. The TBE bands of interest overlap with those of both NVP and HEMA thereby reducing the overall accuracy of the experiment, as discussed further in *Chapter 6*. The FT-IR spectra of Monomer Mixtures B, H, I and J are compared in Figure 4.24 and are found to be essentially similar in behaviour.

Although the remaining components in the composites remained undetected their FT-IR spectra are included for completeness. Figure 4.25 presents the FT-IR spectra of the three crosslinkers, obtained using the ATR horizontal trough attachment. Figure 4.26 shows spectra of the three initiators and of the visible tint

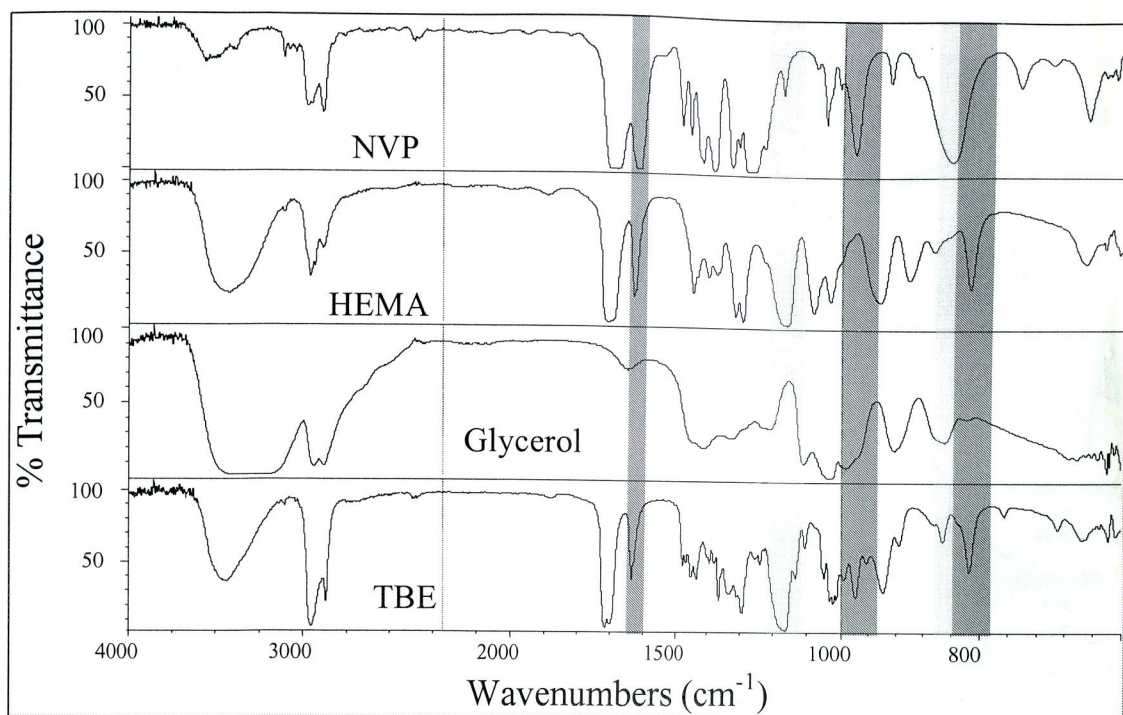


Figure 4.21. FTIR spectra of the four major components of the monomer mixtures with the bands used to monitor cure (■) and as internal reference (□) highlighted (see Table 4.3).

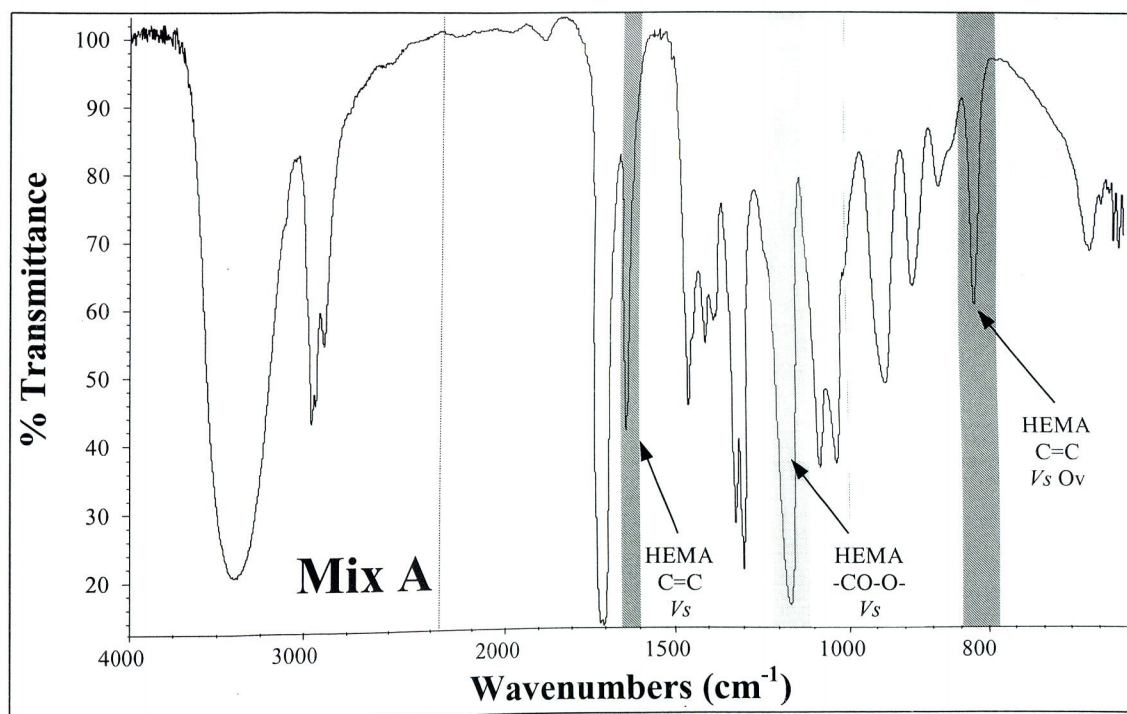


Figure 4.22. A FTIR spectrum of monomer mixture A with the bands used to monitor cure (■) and as internal reference (□) highlighted (see Table 4.3).

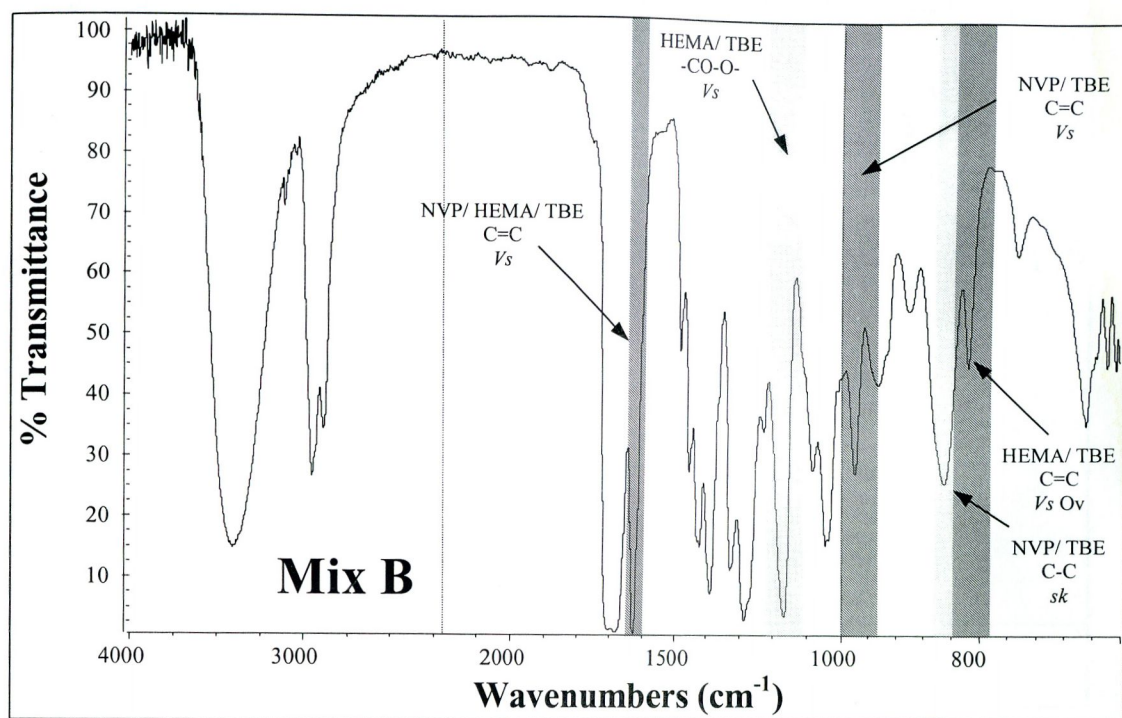


Figure 4.23. A FTIR spectrum of monomer mixture B with the bands used to monitor cure (■) and as internal reference (□) highlighted (see Table 4.3).

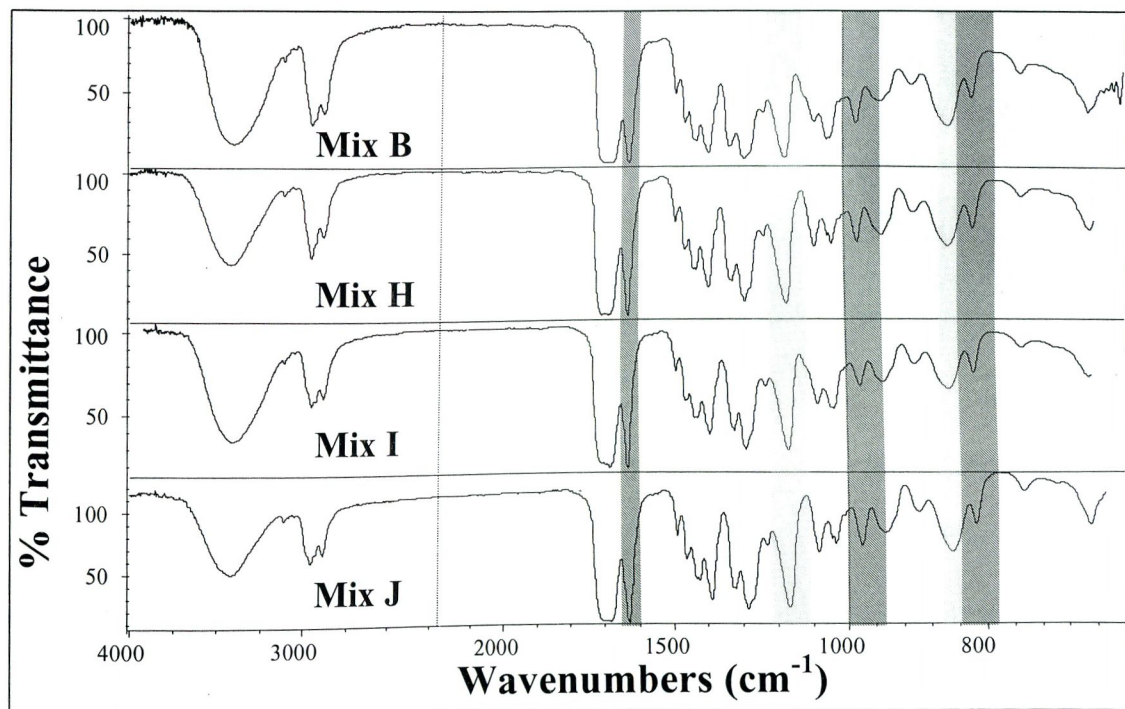


Figure 4.24. FTIR spectra of monomer mixtures B, H, I and J with the bands used to monitor cure (■) and as internal reference (□) highlighted (see Table 4.3).

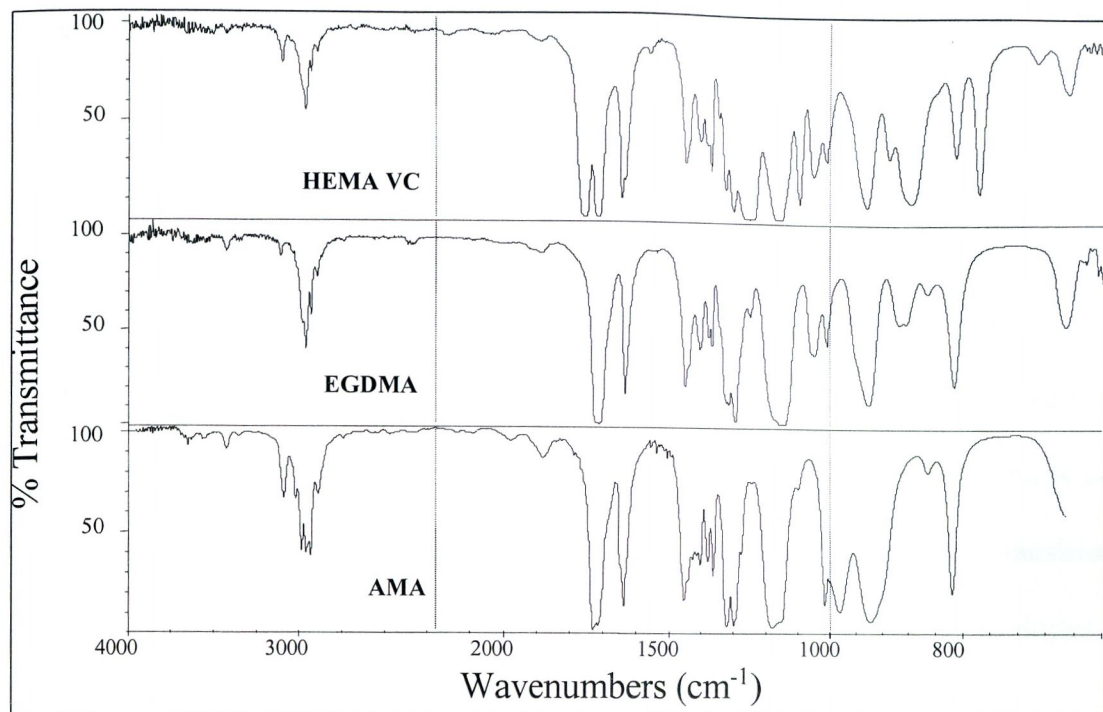


Figure 4.25. FTIR spectra of the crosslinkers present in the monomer mixtures (see Table 4.1).

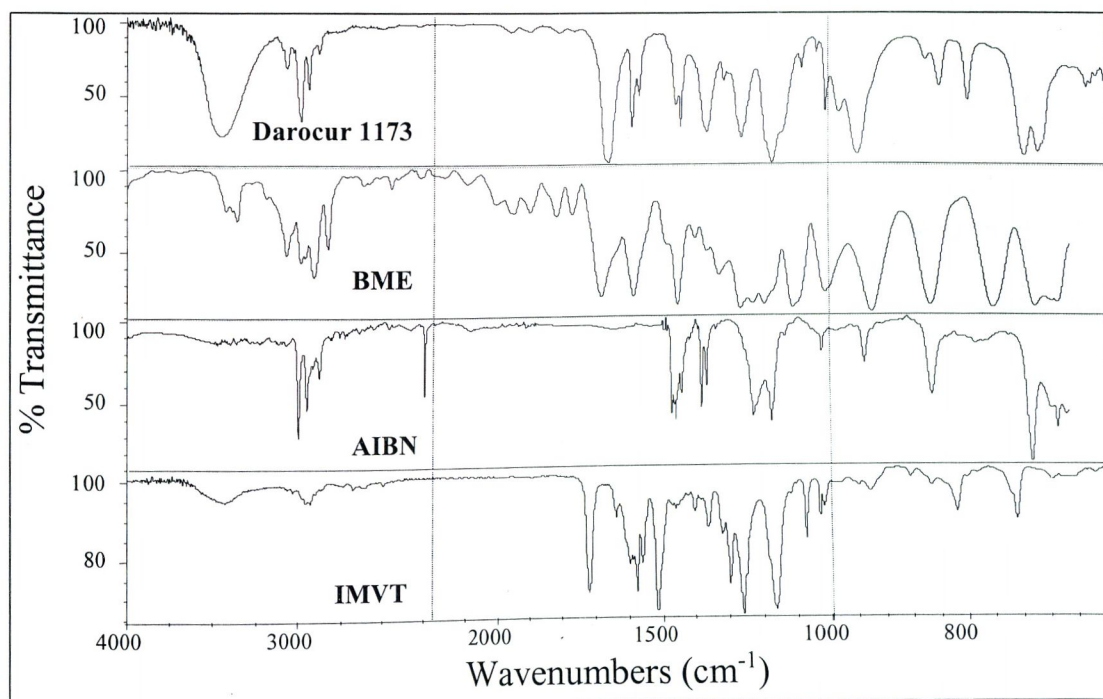


Figure 4.26. FTIR spectra of the photo and thermal initiators and of the visible tint present in the monomer mixtures (see Table 4.1).

component. These last three components were solid powders and their spectra were obtained from KBr disks containing 2% by weight of sample.

4.3.3 Ultraviolet-Visible Absorption Spectroscopy

4.3.3.1 Spectral Features

The absorption of ultraviolet-visible radiation by a polyatomic molecule leads to multiple transitions among its electronic energy levels. Samples in the gaseous phase yield electronic spectra that are generally complex. In spectra of liquids and solids rotational and vibrational effects are superimposed on the electronic transitions and the fine structure disappears, to be replaced with broad absorbance envelopes or bands.^{24,26,33}

Here we are concerned only with the absorption of UV and visible wavelengths. Experimental details of the acquisition of the spectra were provided in *section 3.4*.

4.3.3.2 UV-Vis Results and Discussion

The Ultraviolet-Visible absorbance spectra of the three neat hydrophilic monomers, the diluent, and the three crosslinkers are shown in Figure 4.27. As is expected, these materials show minimal absorption over the visible wavelengths (800nm to 400nm). Only NVP and HEMA VC absorb above 320nm in the UV range, possibly attenuating the available UV intensity for the photoinitiator species in the lower strata of thick samples. However, this is not likely to be a limiting factor in the photocuring process of thin contact lenses. Also shown in Figure 4.27 is an absorbance spectrum of IMVT as a dilute solution in ethanol. There is the expected absorbance bands in the visible region which provide the blue tint. Significantly, the spectrum shows a decrease in absorbance in the UV range between 400nm and 320

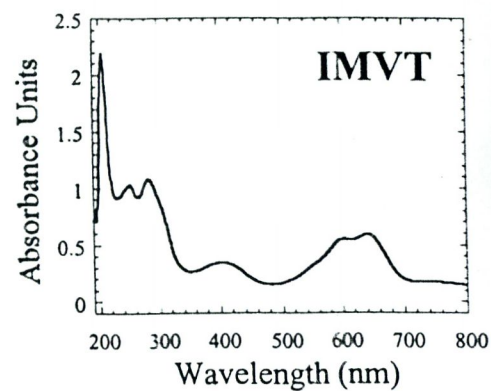
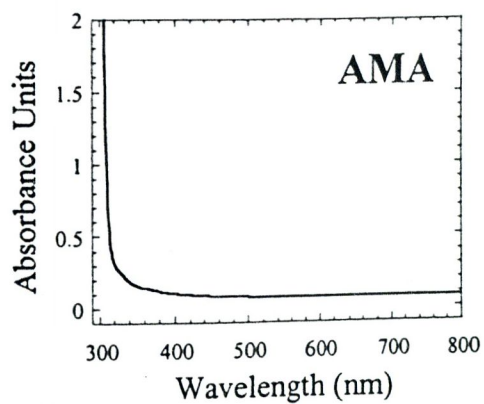
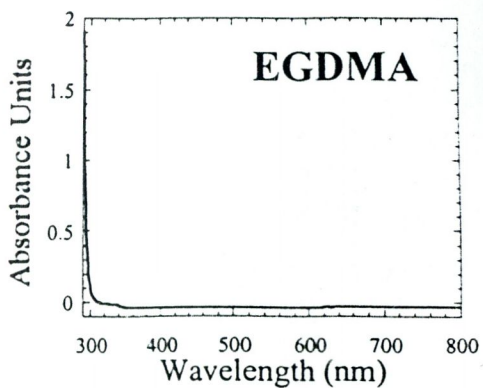
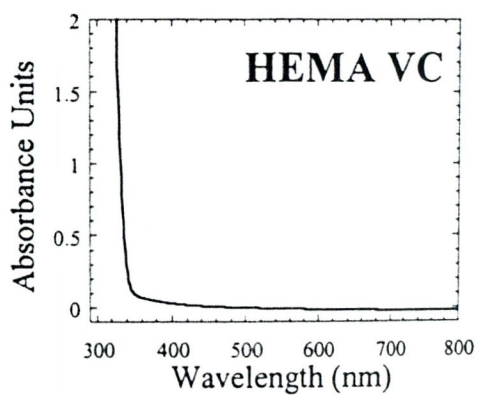
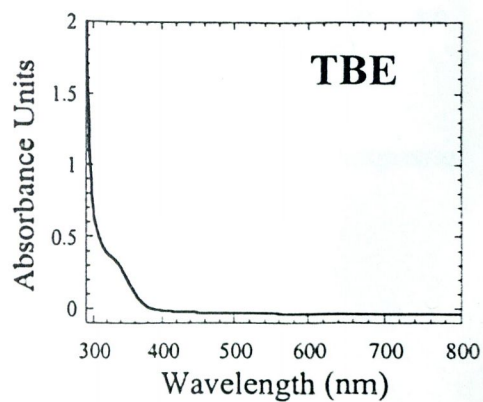
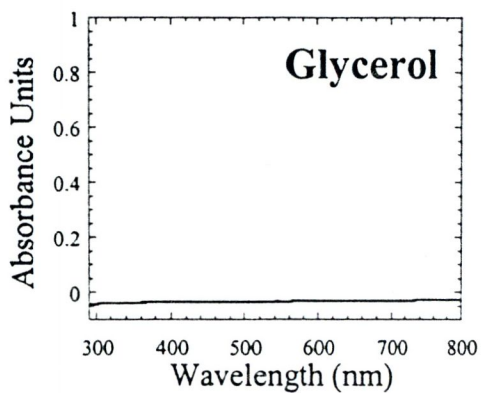
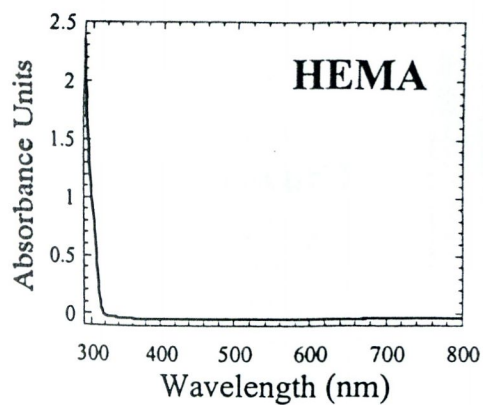
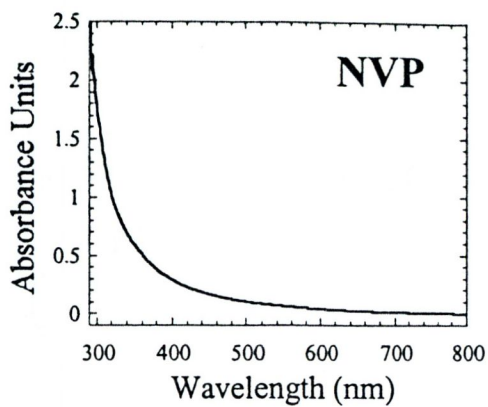


Figure 4.27. UV-Vis spectra of the components of the composite monomer mixtures.

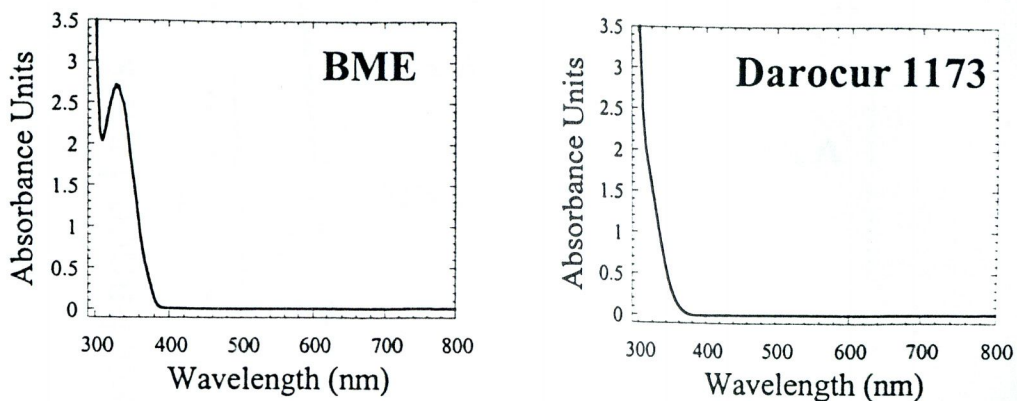


Figure 4.28. UV-Vis spectra of the two UV-photoinitiators used in the composite monomer mixtures.

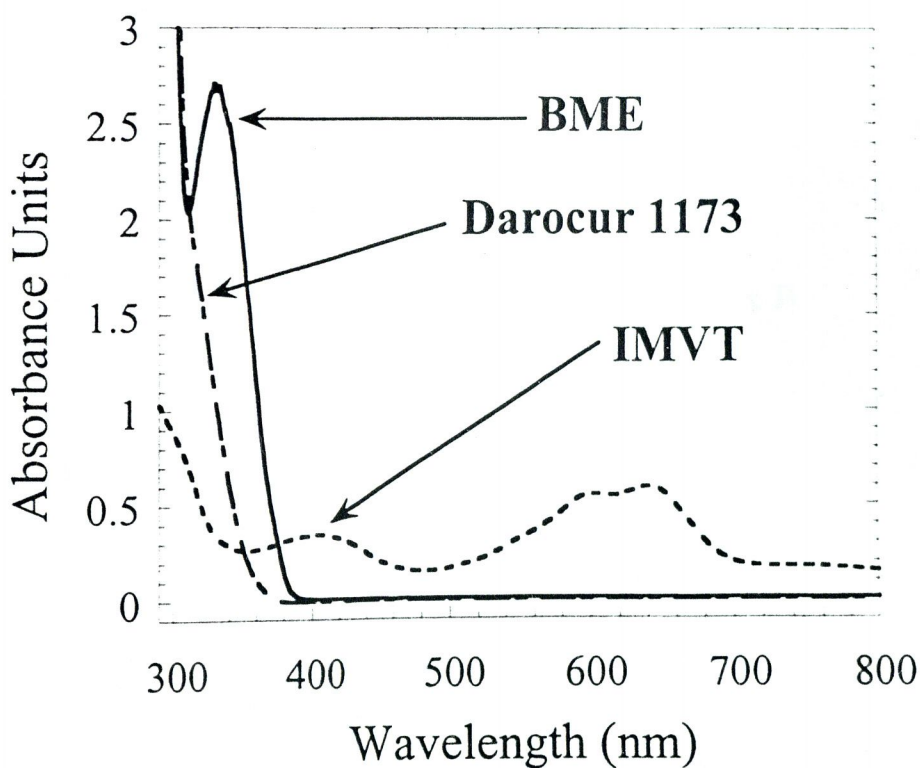


Figure 4.29. UV-Vis spectra of dilute solutions of the two UV-photoinitiators and of the visible tint used in the composite monomer mixtures.

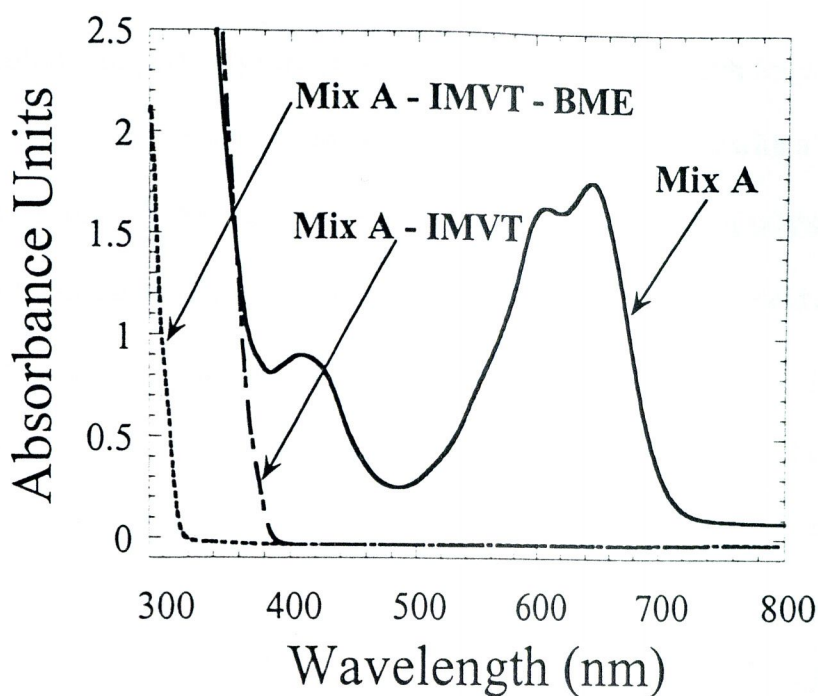


Figure 4.30. UV-Vis spectra of neat monomer mixture A, mixture A minus the visible tint and mixture A minus both the tint and the UV-photoinitiator.

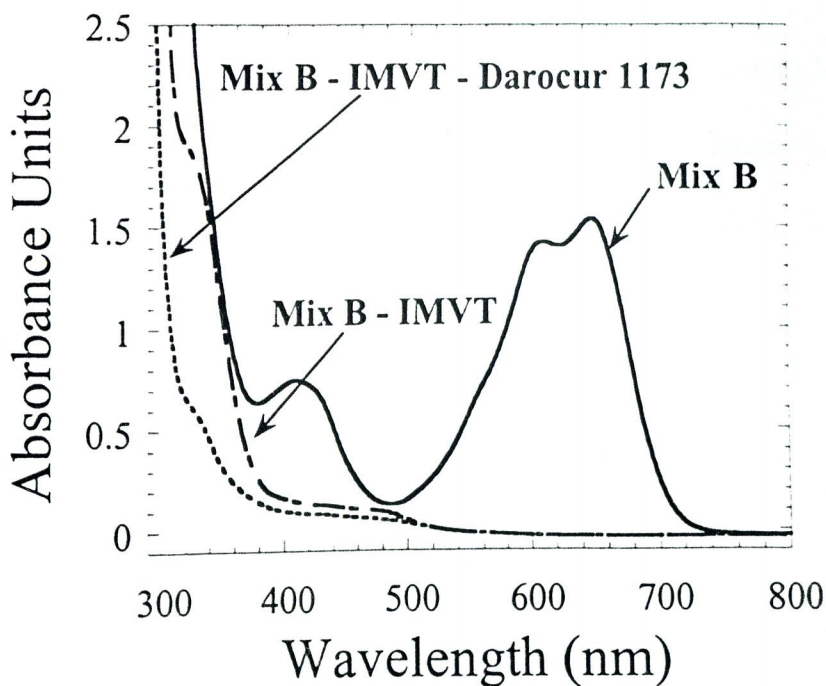


Figure 4.31. UV-Vis spectra of neat monomer mixture B, mixture B minus the visible tint and mixture B minus both the tint and the UV-photoinitiator.

nm. The spectra of the UV-photoinitiators BME and Darocur 1173 (0.16% and 0.2% w/w in chloroform, respectively) are presented in Figure 4.28. Through fragmentation BME forms radicals at a maximum absorbance wavelength of 230nm with a quantum yield of almost unity.³⁴ Similarly, Darocur 1173 forms radicals at a slightly lower maximum absorbance wavelength of 220nm, also with a high quantum yield and with the added advantage of the absence of any yellow or toxic by-products.³³ Figure 4.29 illustrates the comparative absorbance behaviour of the photoinitiators and the tint.

To illustrate further the influence of the photoinitiators and visible tint on the absorbance behaviour of the composite mixtures, Figure 4.30 presents first the spectrum of Mixture A (without BME or IMVT), exhibiting the onset of absorbance at lower than 320nm; with the addition of BME to the mixture the system now absorbs strongly up to 400nm; the further addition of IMVT shows absorbance over the visible wavelengths in the complete tinted formulation. Figure 4.31 shows similar behaviour in Mixture B, with and without Darocur 1173 and IMVT. Since Monomer Mixtures H, I and J undergo polymerisation *via* thermal rather than UV-photoinitiated free radical processes, their light absorbance characteristics are irrelevant.

4.4 Conclusions

As an aid to understanding the curing dynamics of complex composite monomer systems, component materials and five monomer mixtures of interest have been characterised by techniques including high resolution ¹H and ¹³C NMR spectroscopy, FT-IR spectroscopy and UV-Vis absorbance spectroscopy. Characteristic features in the NMR and FTIR spectra permit the identification of the main components in the composite monomers. This site specific information is the key to monitoring the curing dynamics of the various components in real time.

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Chapter Five

Spin-Lattice Relaxation in Monomers and Composite Mixtures

5.1 Introduction

This chapter reports NMR ^1H and ^{13}C spin-lattice (T_1) relaxation in neat liquid samples of the individual primary monomers, the diluent and ultimately of the two main composite mixtures. The methodology for recording and analysing T_1 data is described in Chapter 3.2.3.^{1,2,3} Spin-lattice relaxation (T_1) determines the appropriate experimental recycle time in spectral acquisition and accumulation ($>5T_{1\text{max}}$) in subsequent curing studies. A delay time of this magnitude in the pulse sequences was necessary to ensure that the nuclear spin systems had adequate time to return to their equilibrium state, in order to avoid spectral distortions leading to reduced accuracy of quantitative peak area measurements.

$T_1(^1\text{H})$ for the neat liquid monomers were obtained over a range of temperatures to illustrate the inherent sensitivity to changes in liquid viscosity and temperature. The necessity of 'degassing' the liquid systems in order to remove dissolved paramagnetic oxygen, which can shorten the intrinsic T_1 values, was also demonstrated. $T_1(^1\text{H})$ times of the residual liquid components of a composite system recorded over the course of a UV-photoinitiated cure reaction are presented and discussed in *Chapter 7*.

5.2 Inversion Recovery Experiments: Experimental Considerations

The inversion recovery sequence commonly used to determine ^1H and ^{13}C T_1 magnitudes (see Chapter 3.2.3.) may be written as $-(\text{PD} - 180^\circ - \tau - 90^\circ - \text{AQ})_n$; τ is the variable time, PD ($>5T_{1\text{max}}$) is the pulse delay time between successively repeating pulse sequences, AQ denotes signal acquisition.⁴ To achieve accurate 90° and 180° pulses the standard pulse sequences (with inverse gated decoupling applied in the ^{13}C experiment to remove NOE peak enhancements) were modified to include a variable delay list, which was programmed to contain a suitable series of pulse times of increasing duration.⁵ These experiments produced suites of spectra with varying peak intensities, from which the relationship between the applied pulse duration and the resulting tip angle could be determined.⁶ ^1H NMR spectra of a standard sample of chloroform (10% w/w) in acetone- d_6 (+0.03% TMS) shown in Figure 5.1 are typical. Each ^1H NMR spectrum exhibits peaks arising from TMS at 0.00 ppm, from residual protons in the solvent at 2.04 ppm and from chloroform at 7.94 ppm. Identical phase corrections were applied to each spectrum in the series. Figure 5.2 shows a plot of the measured relative peak intensities of the TMS signal versus the applied r.f. pulse durations in microseconds (μs). These data showed that $\tau_{90^\circ} = 9\mu\text{s}$ and $\tau_{180^\circ} = 18\mu\text{s}$, respectively.

^{13}C NMR spectra of the same standard sample of chloroform (10% w/w) in acetone- d_6 (+0.03% TMS) contain peaks arising from the carbons in the methyl groups of the solvent at 29.8 ppm, from chloroform at 77.0 ppm and from the carbonyl group in the solvent at 206.5 ppm (Figure 5.3). Here again, identical phase corrections were applied to each spectrum in the series. In similar fashion, Figure 5.4

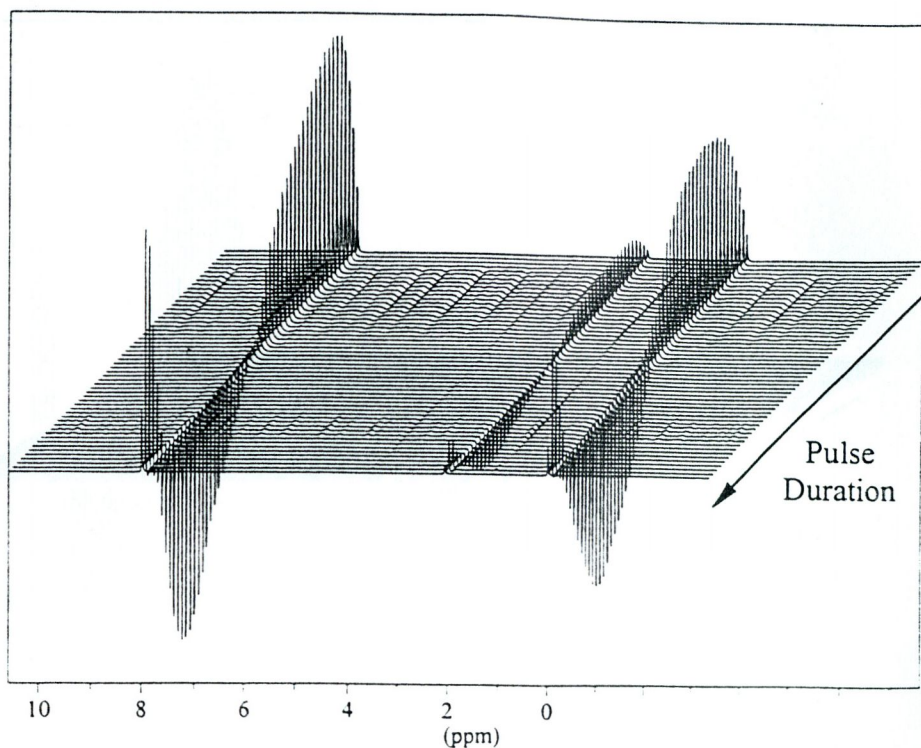


Figure 5.1. ^1H NMR experiments to determine the pulse durations required to induce bulk magnetisation tip angles of exactly 90° and 180° .

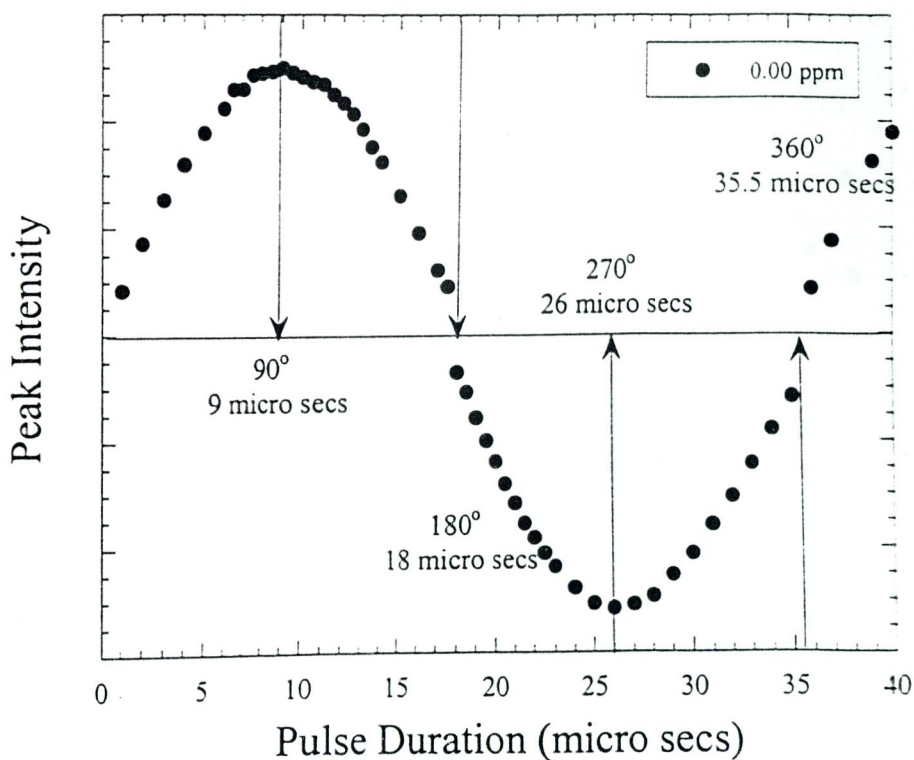


Figure 5.2. ^1H peak intensity *versus* applied pulse duration data for the TMS peak indicating the pulse durations that induce bulk magnetisation tip angles of exactly 90° and 180° .

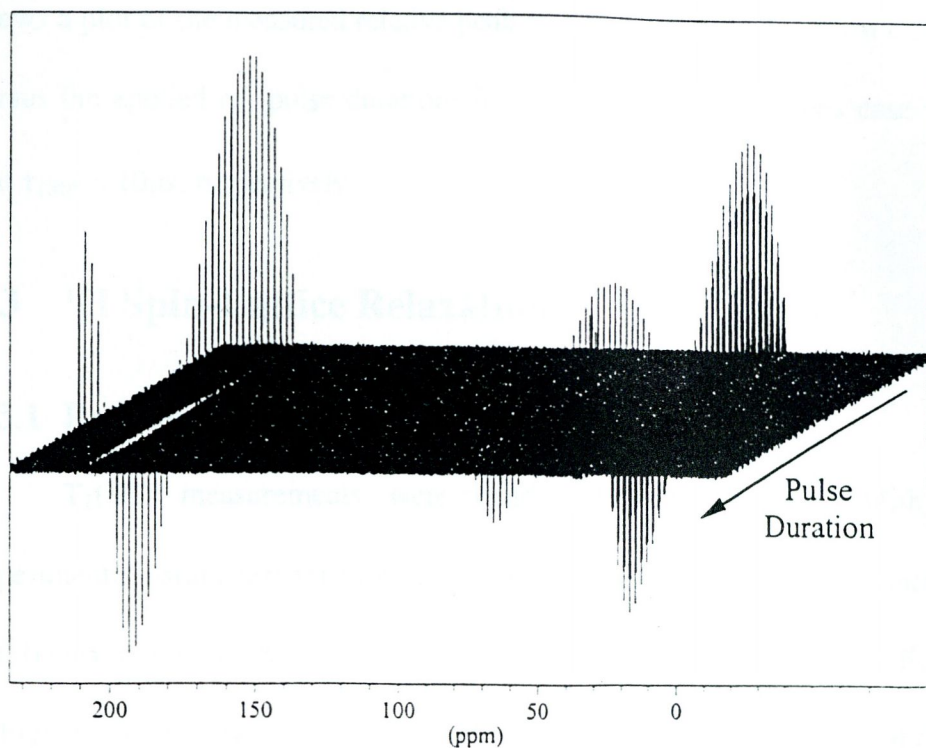


Figure 5.3. ^{13}C NMR experiments to determine the pulse duration required to induce bulk magnetisation tip angles of exactly 90° and 180° for chloroform in acetone (*see text*).

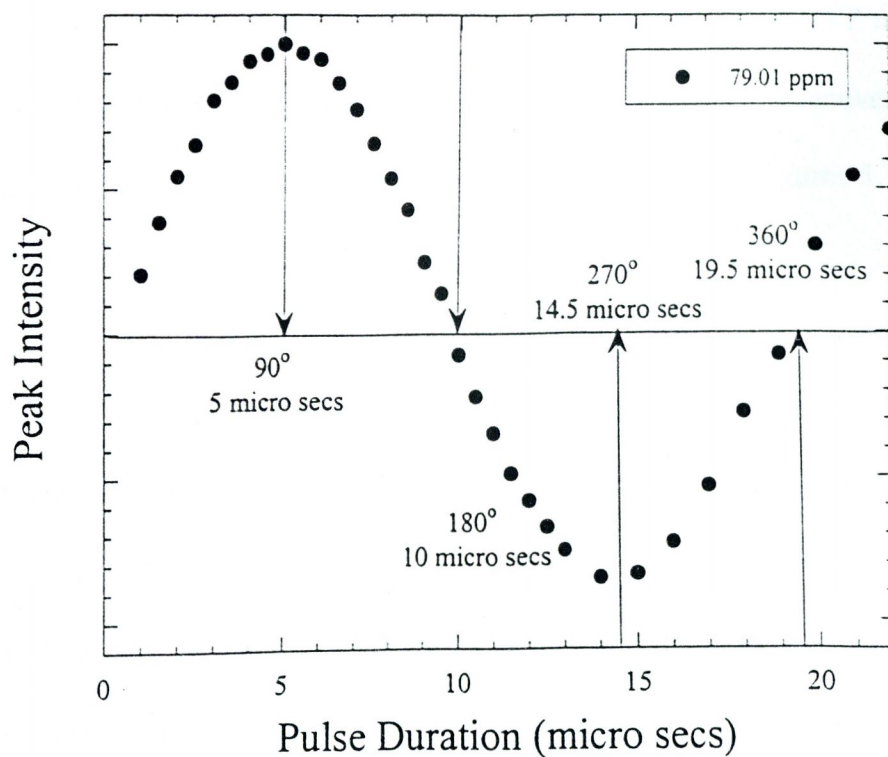


Figure 5.4. ^{13}C peak intensity *versus* applied pulse duration data for the chloroform peak indicating the pulse durations that induce bulk magnetisation tip angles of exactly 90° and 180° .

shows a plot of the measured relative peak intensities of the chloroform carbon signal versus the applied r.f. pulse durations in microseconds (μs). In this case $\tau_{90^\circ} = 5\mu\text{s}$ and $\tau_{180^\circ} = 10\mu\text{s}$, respectively.

5.3 ^1H Spin-Lattice Relaxation

5.3.1 Results of $T_1(^1\text{H})$ Measurements

$T_1(^1\text{H})$ measurements were conducted primarily to establish suitable experimental parameters for subsequent quantitative curing studies. A typical suite of $T_1(^1\text{H})$ inversion recovery spectra, for neat liquid HEMA monomer at 293K, is shown in Figure 5.5 along with proton peak assignments. As discussed in *Section 3.2.3.1*, T_1 can readily be determined from the null point when decay is exponential, as shown in Figure 5.6 for the methyl (a) group in HEMA monomer.⁷

$T_1(^1\text{H})$ data for degassed liquid samples of neat HEMA and NVP monomers and of glycerol diluent (293K) are presented in Table 5.1. Inversion recovery spectra for degassed composite monomer mixtures A and B are shown in Figures 5.7 and 5.8, respectively. The extracted $T_1(^1\text{H})$ magnitudes are listed in Table 5.1.

Relaxation time measurements obtained from relative signal intensities are subject to greater experimental uncertainty than frequency measurements.⁸ Even with careful selection of recycle delay times and co-addition of multiple phase cycled pulses to improve signal-to-noise ratios, experimental accuracy of better than $\pm 10\%$ for $T_1(^1\text{H})$ and $\pm 20\%$ for $T_1(^{13}\text{C})$ can not be assured without multiple repeated measurements.⁹ These results are adequate to ensure that spectral distortion, and therefore errors in relative spectral peak area measurements in the real-time curing experiments, is avoided. Peak intensity measurements under these conditions are

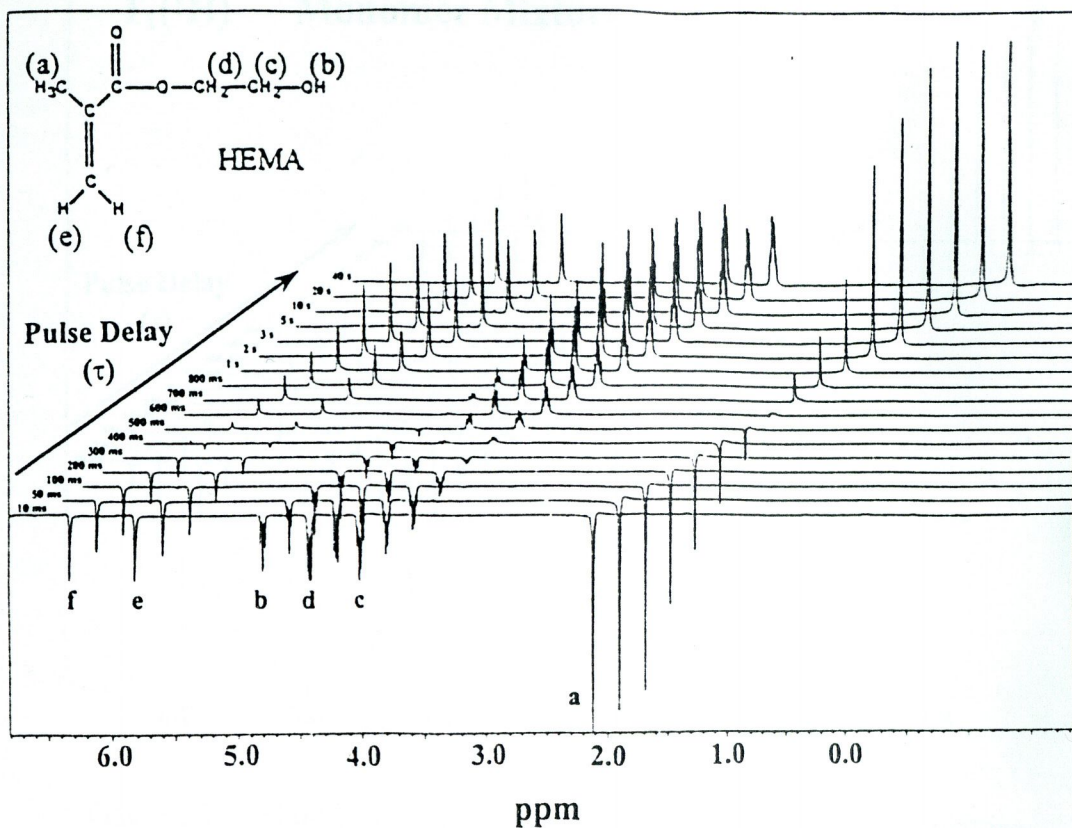


Figure 5.5. ^1H inversion recovery spectra used to determine $T_1(^1\text{H})$ for neat HEMA monomer (293K).

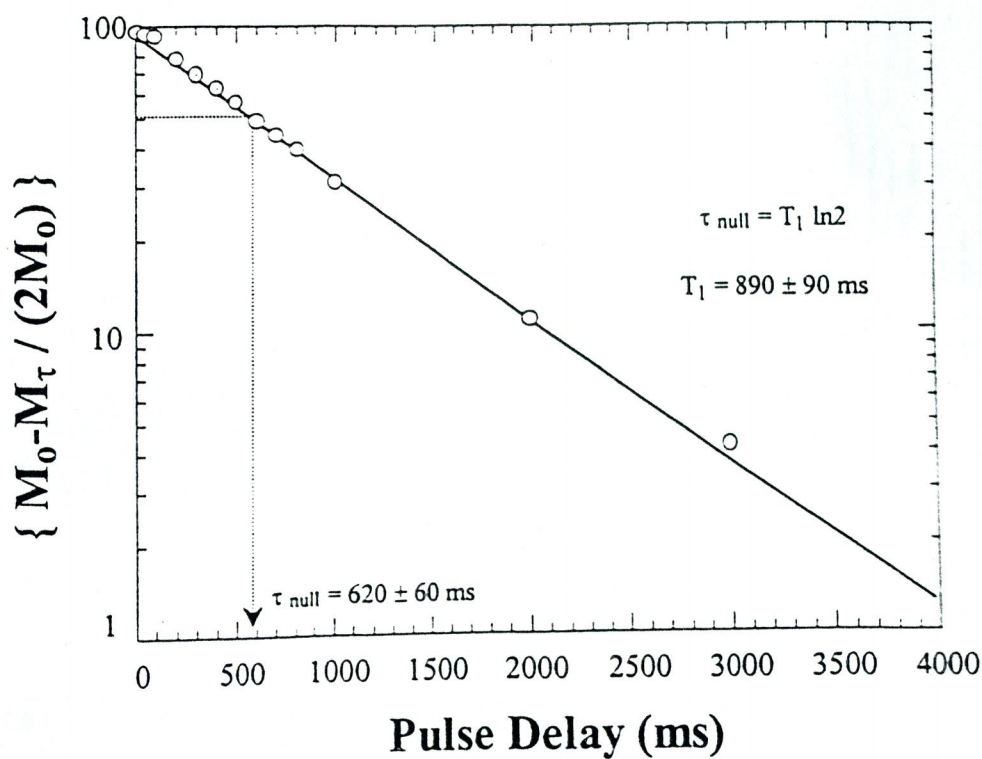


Figure 5.6. The ^1H spin-lattice relaxation of the methyl group in neat HEMA monomer.

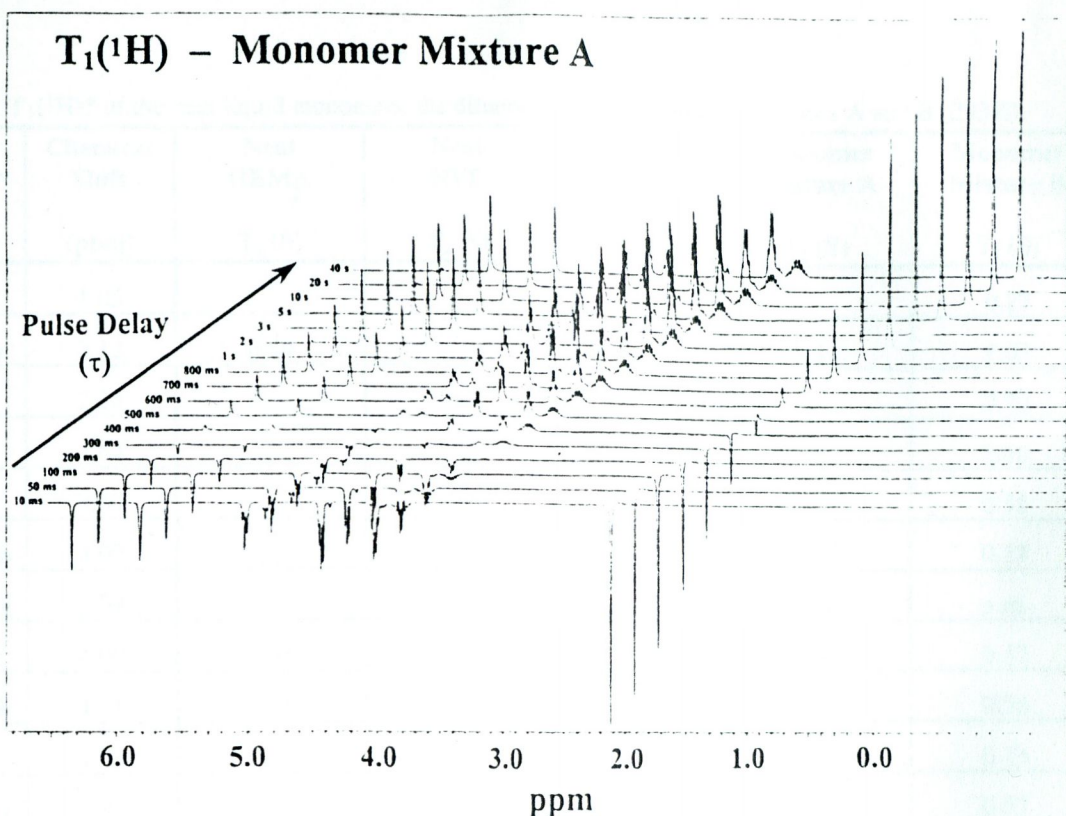


Figure 5.7. ^1H inversion recovery spectra used to determine the spin-lattice relaxation times of the components of Monomer Mixture A (293K).

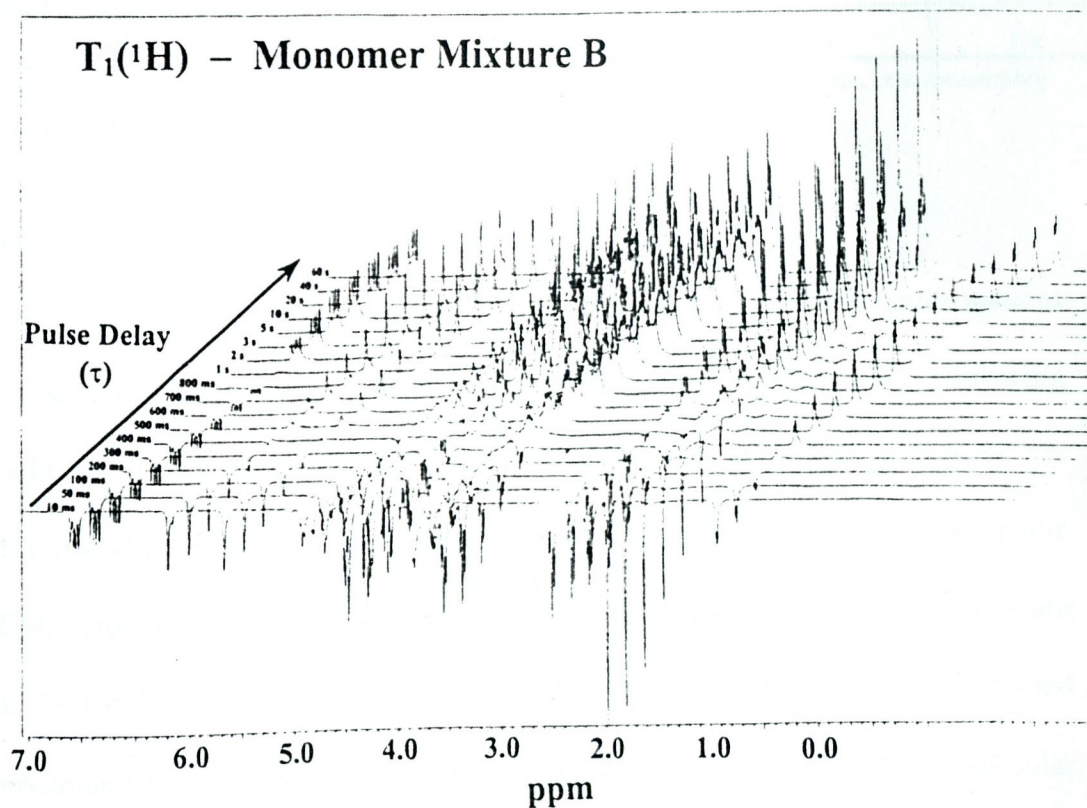


Figure 5.8. ^1H inversion recovery spectra used to determine the spin-lattice relaxation times of the components of Monomer Mixture B (293K).

Table 5.1. $T_1(^1\text{H})^*$ of the neat liquid monomers, the diluent and of the composite mixtures A and B (293K).

Proton Position**	Chemical Shift (ppm)	Neat HEMA T_1 (S)	Neat NVP T_1 (S)	Neat Glycerol T_1 (S)	Monomer Mixture A T_1 (S)	Monomer Mixture B T_1 (S)
TBE p	1.05					0.27
HEMA a	2.12	0.89			0.82	1.02
NVP k	2.28		1.88			0.70
NVP m	2.64		2.09			0.66
NVP l	3.69		1.66			0.58
Glycerol h	3.90			0.31	0.33	0.37
Glycerol g	3.99			0.32	n.m.	n.m.
HEMA c	4.00	0.46			0.46	0.52
HEMA d	4.41	0.56			0.50	0.56
NVP o	4.65		1.82			0.73
Glycerol i	4.83			0.34	0.59	0.57
Glycerol j	4.95			0.33	n.m.	0.55
HEMA b	5.06	0.65			0.64	0.64
HEMA e	5.81	0.65			0.55	0.60
HEMA f	6.33	0.64			0.56	0.67
NVP n	7.18		3.97			1.58
PD :		10 s	20s	5s	10s	10s

* all T_1 values quoted have an experimental accuracy of the order of $\pm 10\%$. n.m., not measurable.

** peak assignments are furnished in Figures 4.17 and 4.18.

accurate to within plus or minus a few percent.

Some general observations on the molecular dynamics of the liquid systems can be drawn from the relaxation data. As expected, under extreme narrowing conditions (rapid motion) changes in the viscosity due to mixing influences the relaxation characteristics of the constituents when mixed together.¹⁰ When the fluidic HEMA monomer is mixed with the viscous glycerol diluent (as in Monomer Mixture A), T_1 for HEMA decreases (*i.e.* increased viscosity / less mobility / decreased correlation time / increased relaxation rate) because of the overall shift of molecular motions to lower correlation frequencies, while T_1 for glycerol increases. Similarly,

in Monomer Mixture B T_1 of NVP decreases while T_1 of glycerol again increases. The relaxation behaviour of HEMA in this mixture is less clear from the $T_1(^1\text{H})$ data for the composite: T_1 of HEMA either remained unchanged within experimental error or increased slightly. Spin diffusion may be operative, albeit weakly, in the high correlation frequency regime (long T_2).¹¹

5.3.2 Temperature Effects

Since the cure dynamics of both the UV-photoinitiated and thermally initiated composite monomer systems were to be examined over a range of temperatures as part of this study, clarification of the effect of temperature on $T_1(^1\text{H})$ was a necessary prerequisite. The data from these experiments are presented in Table 5.2 below and in Figures 5.9 and 5.10.

Table 5.2. $T_1(^1\text{H})^*$ of neat liquid HEMA monomer (293K to 333K).

Proton Position**	Chemical Shift (ppm)	Neat HEMA 293K T_1 (S)	Neat HEMA 303K T_1 (S)	Neat HEMA 313K T_1 (S)	Neat HEMA 323K T_1 (S)	Neat HEMA 333K T_1 (S)
HEMA a	2.12	0.89	1.34	1.75	2.24	2.39
HEMA c	4.00	0.46	0.77	1.13	1.54	1.91
HEMA d	4.41	0.56	0.84	1.19	n.m.	1.66
HEMA b (293K) (303K) (313K) (323K) (333K)	4.80 4.69 4.55 4.42 4.34	0.65	1.31	1.90	n.m.	1.90
HEMA e	5.81	0.65	1.13	1.54	1.76	2.05
HEMA f	6.33	0.64	0.98	1.39	1.83	2.01
PD :		10 s	10s	10s	10s	10s

* all T_1 values quoted have an experimental accuracy of the order of $\pm 10\%$. n.m., not measurable.

** Ref. Figure 5.9.

Figure 5.9 shows the superimposed spectra of neat HEMA monomer over a range of temperatures, 293K to 333K. It was found that the hydroxyl (b) peak exhibited an upfield migration in chemical shift position with increasing temperature (*i.e.* from 4.80ppm at 293K to 4.34ppm at 333K - *see inset*). This was due to a decrease in intermolecular hydrogen bonding between hydroxyl groups with increasing temperature, with the corresponding reduction in the deshielding effect on the hydroxyl proton thus manifesting itself in a chemical shift migration towards lower ppm values. A similar decrease in the deshielding effect by disruption of hydrogen bonding resulted from dilution of the monomer in solvent (*Section 4.3.1.2*). This induced significantly larger changes in chemical shift position for the hydroxyl proton.

The plot of $T_1(^1\text{H})$ in neat HEMA monomer over a temperature range of 293K to 333K in Figure 5.10 is as expected for a liquid in the extreme narrowing regime.¹⁰ This increase in T_1 relaxation times at higher temperatures has obvious significance when selecting pulse cycle delay times when monitoring the curing dynamics of the composite liquid systems as a function of temperature (*Chapter 7*).

5.3.3 Effect of Cure on $T_1(^1\text{H})$

This behaviour described above for the monomer need not reflect the situation in the composite monomer as curing proceeds. An experiment which monitored $T_1(^1\text{H})$ of the residual liquid components of sample B during the course of UV curing, showed that T_1 decreased with increasing viscosity as curing proceeded. These results are presented and discussed further in *Chapter 7*.

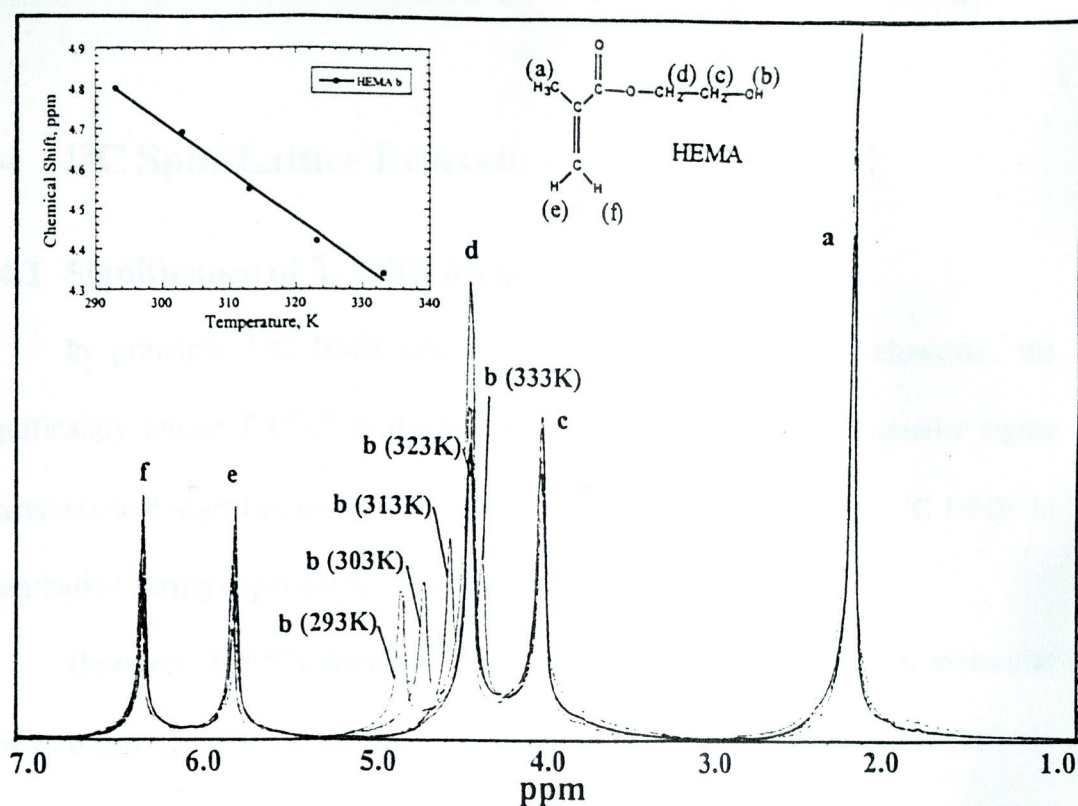


Figure 5.9. ^1H NMR spectra of HEMA (293K to 333K) exhibiting an upfield migration in chemical shift position of the hydroxyl (b) peak with increasing temperature (see inset).

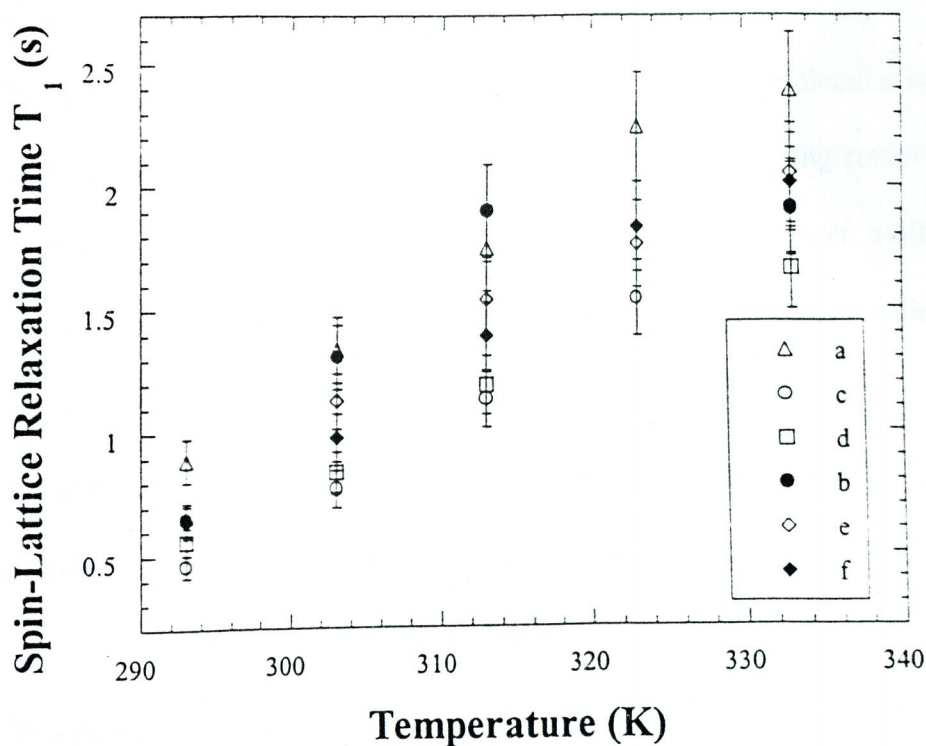


Figure 5.10. The observed increase in $T_1(^1\text{H})$ of neat HEMA monomer with increasing temperature (293K to 333K).

5.4 ^{13}C Spin-Lattice Relaxation

5.4.1 Significance of $T_1(^{13}\text{C})$ Measurements

In principle ^{13}C NMR can be used to monitor curing. However, the significantly longer $T_1(^{13}\text{C})$ relaxation times together with the much smaller signal intensities and signal-to-noise ratios, severely limits the usefulness of ^{13}C NMR in quantitative curing experiments (*Chapter 7*).

However, $T_1(^{13}\text{C})$ does provide more site-specific information on molecular structure and dynamics in the liquid systems than $T_1(^1\text{H})$ data.^{12,13} For the relatively small monomer molecules in a neat liquid system, $T_1(^{13}\text{C})$ data reflect variations in molecular motion due mainly to the effect of changes in viscosity of the liquids as a result of mixing and, subsequently, curing.

$T_1(^{13}\text{C})$ is markedly affected by two factors:

- 1). The vigour of molecular movement :

In liquid systems with molecules of less than a few hundred molecular weight units, undergoing very rapid motion (*i.e.* under extreme narrowing conditions), it may be assumed that shorter $T_1(^{13}\text{C})$'s correspond to slower molecular movement and conversely, longer $T_1(^{13}\text{C})$'s reflect faster molecular movement.

- 2). The number of protons attached to each carbon nucleus influence $T_1(^{13}\text{C})$ relaxation behaviour according to the following scheme^{14,15} :

$$T_1(\text{CH}_2) < T_1(\text{CH}) \ll T_1(\text{C}).$$

This pattern may be overridden by molecular characteristics. For this reason, it is usually the case that $T_1(\text{CH}_3) > T_1(\text{CH}_2)$ despite the greater number of

attached protons due to the terminal position of a methyl group and its easily activated rapid free rotation.

5.4.2 Results of $T_1(^{13}\text{C})$ Measurements

As discussed in *section 3.2.3.2*, an inversion recovery pulse sequence with inverse gated decoupling (to suppress NOE signal enhancement) was used to determine the $T_1(^{13}\text{C})$ data for the systems of interest.¹⁶ Typical inversion recovery $T_1(^{13}\text{C})$ spectra, for a sample of neat liquid HEMA monomer at 293K, are shown in Figure 5.11 along with peak assignments. Corresponding relaxation data for individual carbon nuclei are shown in Figure 5.12. The number of attached protons can be determined in each case. Although this technique successfully distinguishes between quaternary, tertiary and secondary carbons in the same molecule on the basis of their T_1 relaxation, the method is too time consuming to be practical compared with techniques such as off-resonance measurements or the DEPT approach.¹⁷ The structural information obtained from the subsequent $T_1(^{13}\text{C})$ relaxation experiments was in every instance consistent with the conclusions of the spectroscopic molecular characterisation studies of the component materials described in *Chapter 4*.

^{13}C NMR inversion recovery spectra were recorded for degassed samples of neat liquid HEMA and NVP monomers, the glycerol diluent, as well as the composite monomer mixtures A and B (293K). Representative data are shown in Figures 5.13 and 5.14. Figure 5.13 shows a suite of $T_1(^{13}\text{C})$ spectra of a sample of neat monomer mixture A (293K), while Figure 5.14 shows the more complex suite of spectra obtained during a similar experiment on a sample of neat composite monomer mixture B. Table 5.2 contains the consolidated set of results.

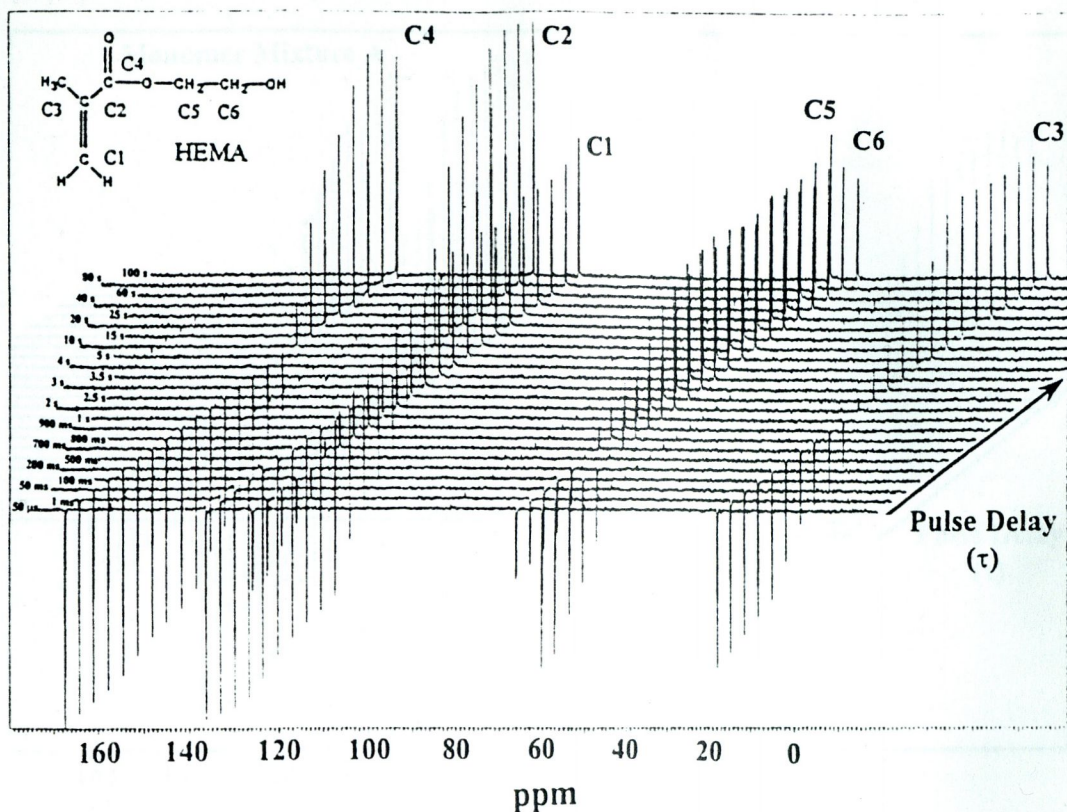


Figure 5.11. ^{13}C inversion recovery spectra used to determine $T_1(^{13}\text{C})$ for neat HEMA monomer (293K).

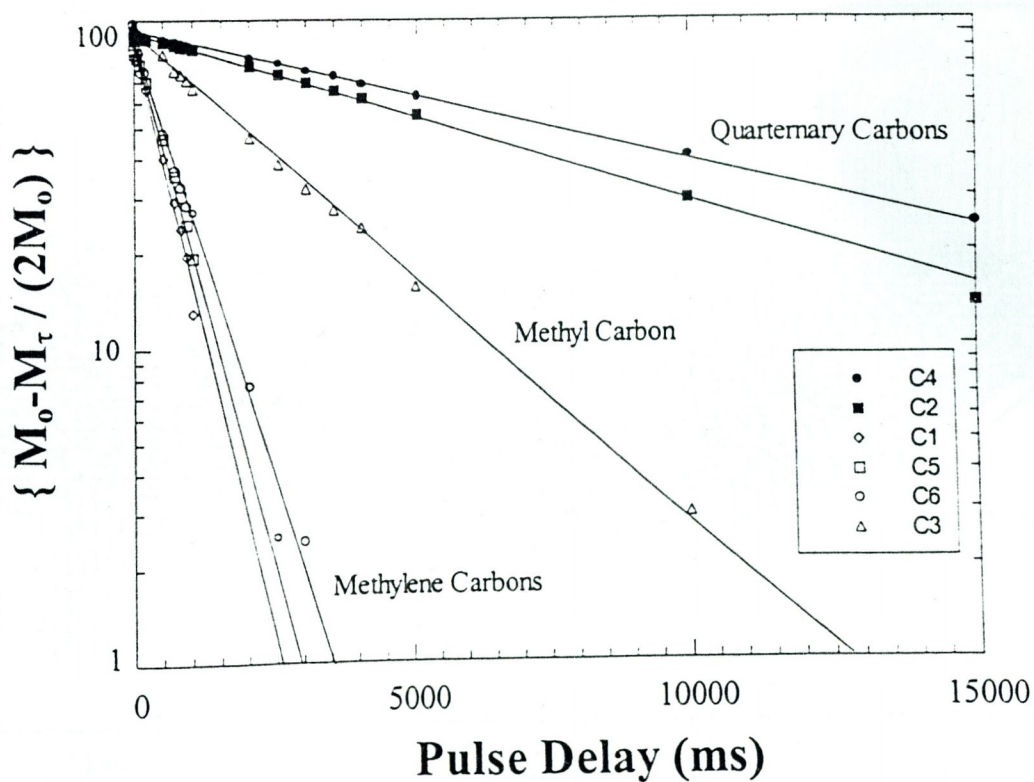


Figure 5.12. Methylene, methyl and quarternary $T_1(^{13}\text{C})$ relaxation in neat HEMA monomer (293K).

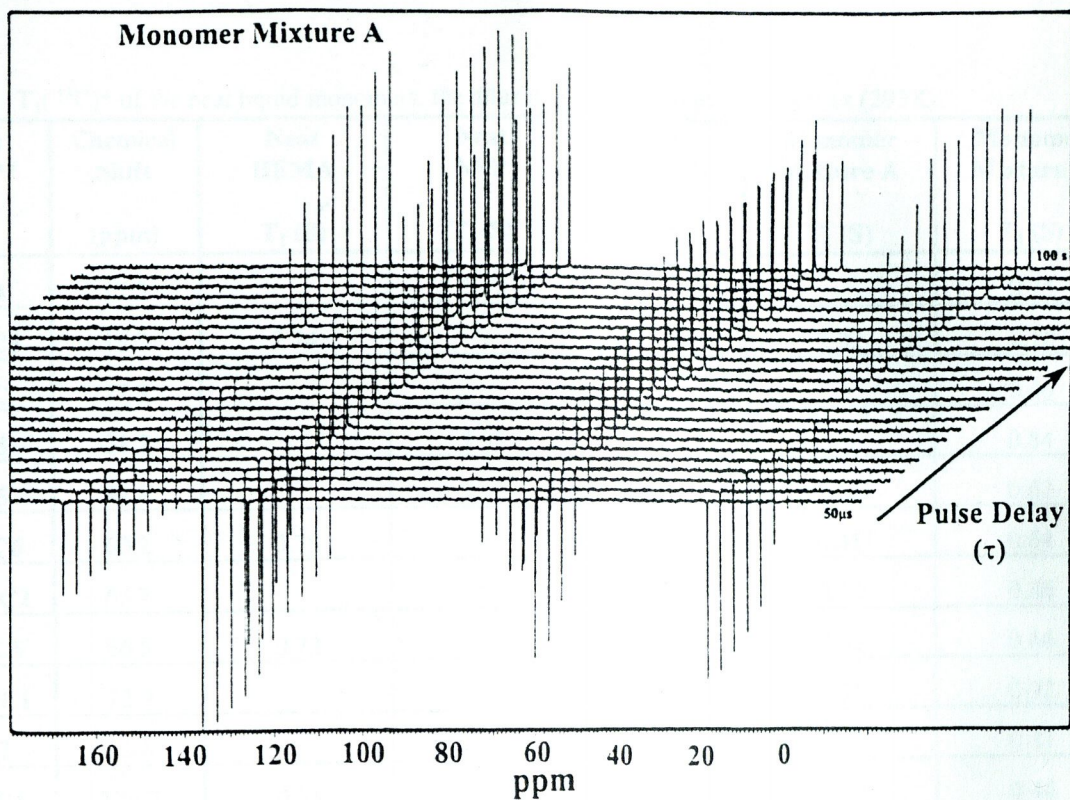


Figure 5.13. ^{13}C inversion recovery spectra used to determine $T_1(^{13}\text{C})$ of the components of Monomer Mixture A (293K).

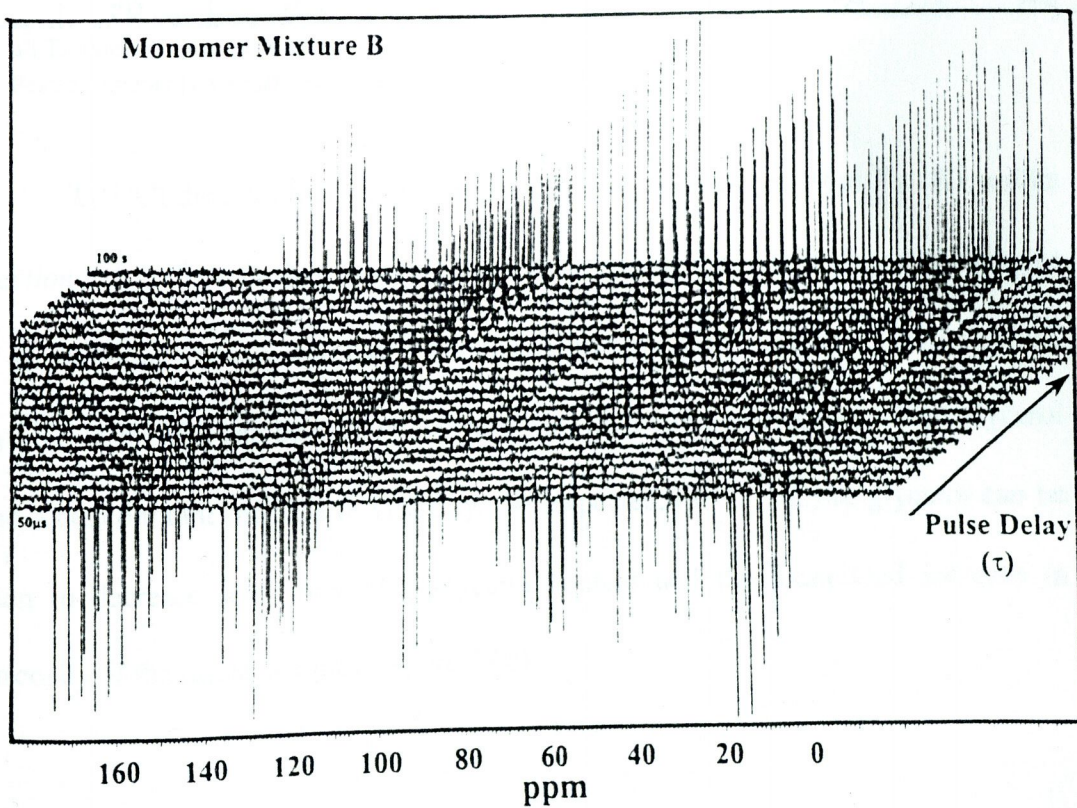


Figure 5.14. ^{13}C inversion recovery spectra used to determine $T_1(^{13}\text{C})$ of the components of Monomer Mixture B (293K).

Table 5.2. $T_1(^{13}\text{C})^*$ of the neat liquid monomers, the diluent and of the composite mixtures (293K).

Carbon Position**	Chemical Shift (ppm)	Neat HEMA T_1 (S)	Neat NVP T_1 (S)	Neat Glycerol T_1 (S)	Monomer Mixture A T_1 (S)	Monomer Mixture B T_1 (S)
NVP C4	17.3		3.17			0.75
HEMA C3	18.2	2.74			2.02	2.16
TBE TC	27.3					0.46
NVP C3	31.3		2.88			0.84
NVP C5	44.8		2.12			0.62
HEMA C6	60.2	0.75			0.45	0.64
Glycerol C2	63.7			0.09	0.33	0.46
HEMA C5	66.5	0.72			0.52	0.66
Glycerol C1	72.9			0.20	0.55	0.92
NVP C7	94.6		2.45			0.81
HEMA C1	125.7	0.56			0.40	0.46
NVP C6	129.4		3.82			0.97
HEMA C2	136.5	8.37			5.50	5.77
HEMA C4	167.3	12.26			9.52	6.92
NVP C2	174.1		22.36			8.08
	PD :	40 s	150s	2s	40s	60s

* all T_1 values quoted have an experimental accuracy of the order of $\pm 20\%$.

** Peak assignments are furnished in Figures 4.17 and 4.18.

$T_1(^{13}\text{C})$ data confirm the molecular dynamics as deduced from $T_1(^1\text{H})$ results (section 5.3.1).¹⁸ In further support of these conclusions, $T_1(^{13}\text{C})$ of degassed samples of mixtures at various ratios of HEMA and glycerol were recorded (Figure 5.15). $T_1(^{13}\text{C})$ in HEMA can be seen to decrease with increasing amounts of added glycerol and a concomitant increase in viscosity. As expected, the $T_1(^{13}\text{C})$ in glycerol can be seen to decrease with increasing glycerol content and the associated increase in viscosity of the liquid samples (Figure 5.16).

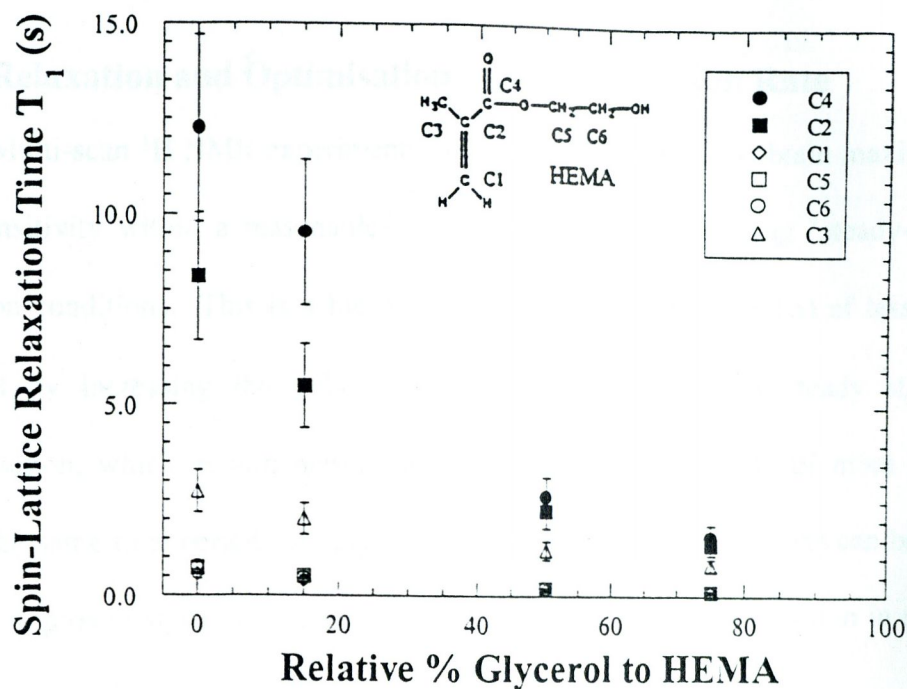


Figure 5.15. ^{13}C spin-lattice relaxation (T_1) times of HEMA, in mixtures of HEMA monomer as a function of Glycerol content (293K).

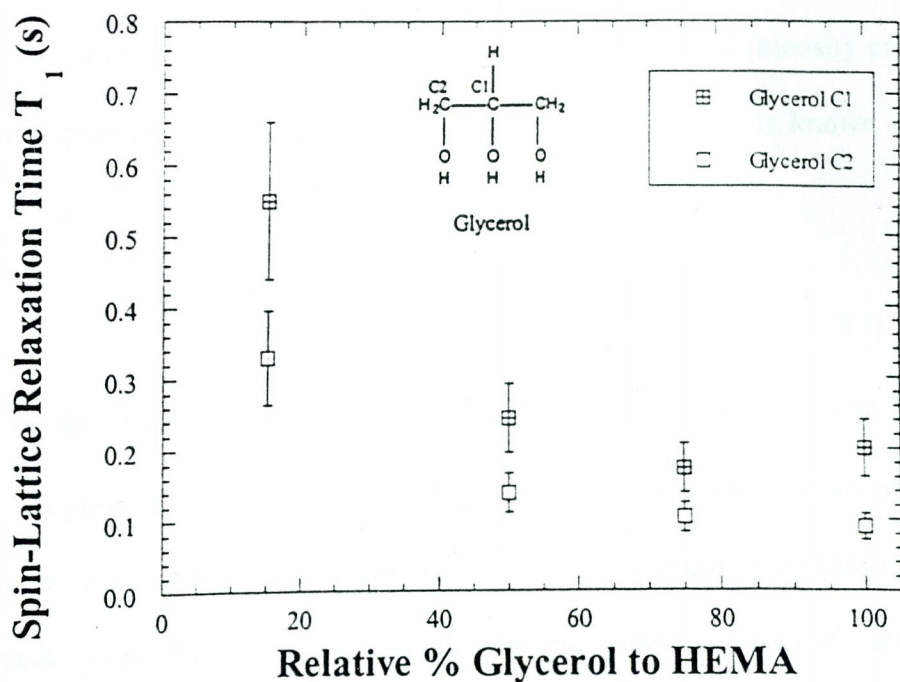


Figure 5.16. ^{13}C spin-lattice relaxation (T_1) times of Glycerol, in mixtures of HEMA monomer as a function of Glycerol content (293K).

5.5 Quantitative Intensity Measurements

5.5.1 Relaxation and Optimisation of Pulse Repetition Rate

Multi-scan ^1H NMR experiments are routinely optimised to obtain maximised peak sensitivity within a reasonable experimental time period using 'steady-state' relaxation conditions. This is achieved by employing a pulse angle (α) of less than 90° and by increasing the pulse repetition rate to establish a steady state z magnetisation, which in turn permits the collection and co-addition of more scans within the same time period. A spectrum obtained under such conditions can benefit from an improved signal-to-noise ratio at the cost of only a slight reduction in signal intensity.

When using repetitive signal averaging techniques to improve sensitivity in this way, it is often most efficient to select a pulse repetition rate equal to the acquisition time, which in turn is determined by the required resolution, and then to select a pulse angle (α) so as to maximise the 'steady state' signal intensity created. An average optimum value for pulse angle in these circumstances is known as the Ernst angle (α_E), which has been defined as

$$\cos \alpha_E = e^{-\frac{T_r}{T_1}} \quad (5.1)$$

where T_r is the time delay between pulses and T_1 is the longest T_1 time in the sample.²² In practice though, a smaller pulse angle than the calculated Ernst angle is generally selected in order to produce an improvement in the quantitative nature of the spectral peak areas. This is done to ensure that integration can provide accurate enough determinations of the relative numbers of contributing protons to each spectral peak for use in routine assignments and characterisation studies.

5.4.3 Effect of Dissolved Paramagnetic Oxygen on T_1 Measurements

Dissolved paramagnetic oxygen can dramatically shorten T_1 times, particularly in the case of proton relaxation studies.¹⁹ Such is the case in HEMA monomer. $T_1(^{13}\text{C})$ data were recorded for two samples of HEMA monomer, one of which was degassed, that is, paramagnetic oxygen removed (Table 5.3). $T_1(^{13}\text{C})$ in the sample that had not been degassed was indeed shorter due to the presence of dissolved paramagnetic oxygen.

Table 5.3. $T_1(^{13}\text{C})^*$ of neat liquid HEMA monomer, degassed and not degassed (293K).

Carbon Position**	Chemical Shift (ppm)	HEMA (Degassed) 293K T_1 (S)	HEMA (Not Degassed) 293K T_1 (S)
HEMA C3	18.2	2.74	2.73
HEMA C6	60.2	0.75	0.57
HEMA C5	66.5	0.72	0.61
HEMA C1	125.7	0.56	0.49
HEMA C2	136.5	8.37	7.49
HEMA C4	167.3	12.26	10.30
PD :		60 s	60s

* all T_1 values quoted have an experimental accuracy of the order of $\pm 20\%$.

** Peak assignments are furnished in Figure 4.6.

Therefore, all samples were degassed by exposure to nitrogen (deoxygenation by displacement) in an atmosphere bag before being sealed in a NMR tube, prior to all NMR experiments.²⁰ Removal of dissolved oxygen was also necessary to prevent the anticipated oxygen inhibition effects in the free radical polymerisation reactions during curing dynamics measurements (*Chapter 7*).²¹

5.5.2 Ensuring the Quantitative Nature of Spectral Peak Areas

Obtaining ^1H NMR spectra under the 'steady state' conditions described above easily produces a quantitative accuracy of the order of 10% - 15%, which is adequate for comparison of contributing proton counts by spectral peak integration. However, for true quantitative applications where accuracy of the order of 1% or 2% is required it is essential that spectral acquisitions be conducted under 'equilibrium' conditions to avoid inaccuracies due to signal saturation. The steady state z magnetisation (M_z) is described by

$$M_z = M_0 \left(\frac{1 - e^{-T_r/T_1}}{1 - e^{-T_r/T_1} \cos \alpha} \right) \quad (5.2)$$

where T_r is the time delay between pulses, T_1 is the longest relaxation time in the sample, and α is the pulse flip angle.⁹ When the pulse flip angle α is set to $\pi/2$, equation 5.2 simplifies to

$$M_z = M_0 \left(1 - e^{-T_r/T_1} \right) \quad (5.3)$$

For quantitative measurements M_z should not deviate from M_0 by more than 1% or 2% (*i.e.* $M_z \geq 0.99M_0$), therefore the time between pulses (T_r) needs to be set to a value about 5 times greater than the longest T_1 time in the sample to meet this condition.

By reducing the pulse flip angle (α) to 30° it becomes possible to establish the necessary equilibrium conditions for quantitative measurements using a much shorter pulse recycle delay time (T_r) *i.e.* of the order of 2.5 times T_1 . Although doubling the permissible spectral acquisition rate in this way reduces the overall signal intensity, in curing studies where non-dilute solutions or neat monomer mixtures are used, the high

sample concentrations ensure ample proton signal response.

5.6 Conclusions

$T_1(^1\text{H})$ and $T_1(^{13}\text{C})$ were measured in neat samples of the individual primary monomers, the diluent and in the two main composite mixtures. These parameters were important in defining the correct spectral acquisition parameters. Additional information on molecular structure and dynamics of the various liquid monomers in the composite mixtures was also forthcoming. The equilibrium relaxation conditions for truly quantitative NMR spectral peak area integration measurements were discussed. Spectral acquisition parameters permitting reduced pulse recycle delay times within these limitations were also defined.

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Chapter Six

UV-Light Measurements, Chemical Actinometry and UV Cure Behaviour Monitored by FTIR Spectroscopy

6.1 Introduction

This chapter discusses the way in which Fourier transform infrared spectroscopy (FTIR) has been used to probe the *in situ* UV-photoinitiated curing profiles of composite monomer mixtures. The limitations inherent in the technique when used to monitor complex, multi-component monomer systems are explained.¹ A novel, alternative and appreciably more informative approach that exploits the site-specific information provided by high resolution NMR is presented and discussed in detail in Chapter 7.^{2,3} In both the FTIR and NMR studies, a pulsed UV laser was employed to deliver precisely defined light energy within specified time periods to the samples, thereby permitting controlled experiments in a way that was not possible heretofore with the more traditional UV lamps.⁴ The ability to accurately measure the intensity of the incident UV irradiation was therefore an important aspect of these experiments.⁵

6.2 UV Light Source and Intensity Measurements

6.2.1 VSL-337 Nitrogen UV Laser

The light source used in this study was a VSL-337 UV laser, by Laser Science Inc., which is a class 3B laser, rated as having a maximum power output of 3 mW at a wavelength of 337nm (near UV-A region). It produces pulses of 3 ns in duration and has a variable pulse frequency of 1-20 Hz.⁷ A coupling stage was designed and built

which facilitated the transmission of light pulses from the laser along a 3 mm core diameter UV-grade fibre optic bundle, which in turn could be connected to either the FTIR or NMR experimental apparatus, permitting the *in situ* irradiation and cure of monomer mixture samples (see Chapter 3.2.4.1 and Figure 3.11). The suitability of UV laser sources for effectively initiating photo-curing reactions in contact lens monomer mixtures had been previously demonstrated and formed the basis of a patent describing industrial applications of the technique.⁴

6.2.2 UV Light Intensity Measurements – Joulemeter Detector

A Gentec ED100A fast response Joulemeter, which is a pyroelectric detector designed to measure energy emitted by pulsed light sources such as UV lasers, connected to a Tektronix 2230 100Mhz digital storage oscilloscope (Figure 6.1), was used for radiometry measurements. The detector head (Figure 6.2) is composed of a pyroelectric ceramic, a heatsink and an optical absorptive coating that has a uniform light adsorptivity from 200 nm (UV) to 40,000 nm (far infrared). Light pulses incident on the coating were transformed into heat that flowed to the heatsink through the ceramic, which produced a voltage proportional to pulse energy. The optical energy was then calculated by multiplying the peak voltage response, measured using the oscilloscope, by a calibration factor unique to the detector (8.525 $\mu\text{J}/\text{mV}$). The results of UV light intensity measurements made using the Joulemeter device, *i.e.* of the laser output, of the light emerging from UV-grade fibre optic bundle and illuminating the sample location in the receiver coil area of the NMR CIDNP probe, are presented in Table 6.1. These measurements detail the typical sample irradiation conditions used for *in-situ* UV-photoinitiated FTIR and NMR monitored curing experiments, which are described fully in Chapters 6 and 7.

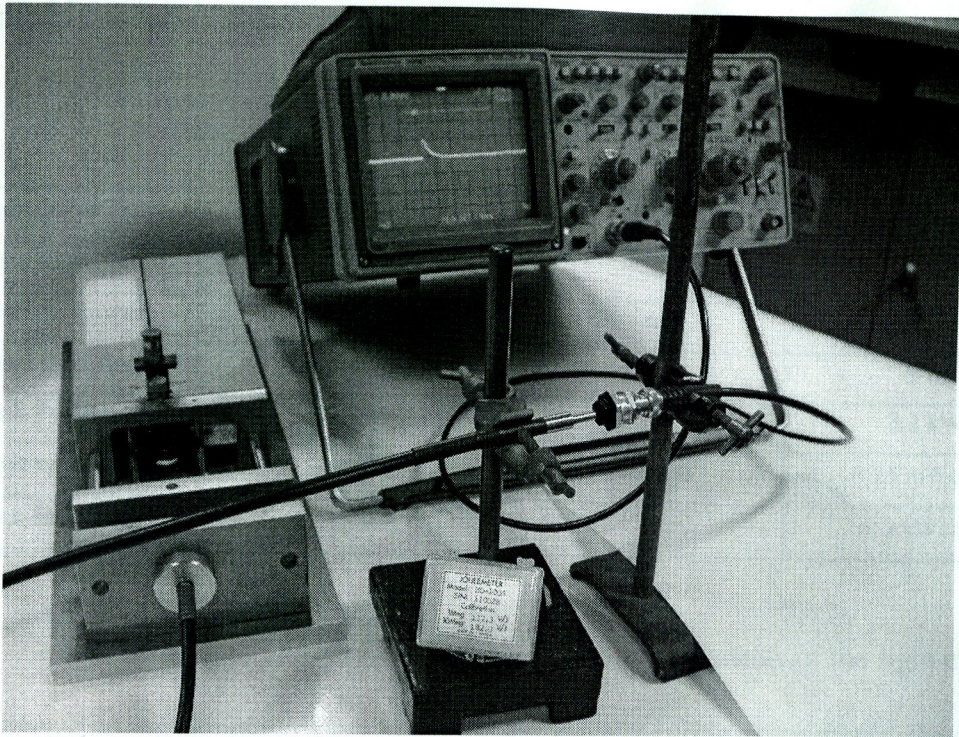


Figure 6.1. UV Light intensity measurements were made using a Gentec ED100A joulemeter connected to a Tektronix 2230 100MHz digital storage oscilloscope.

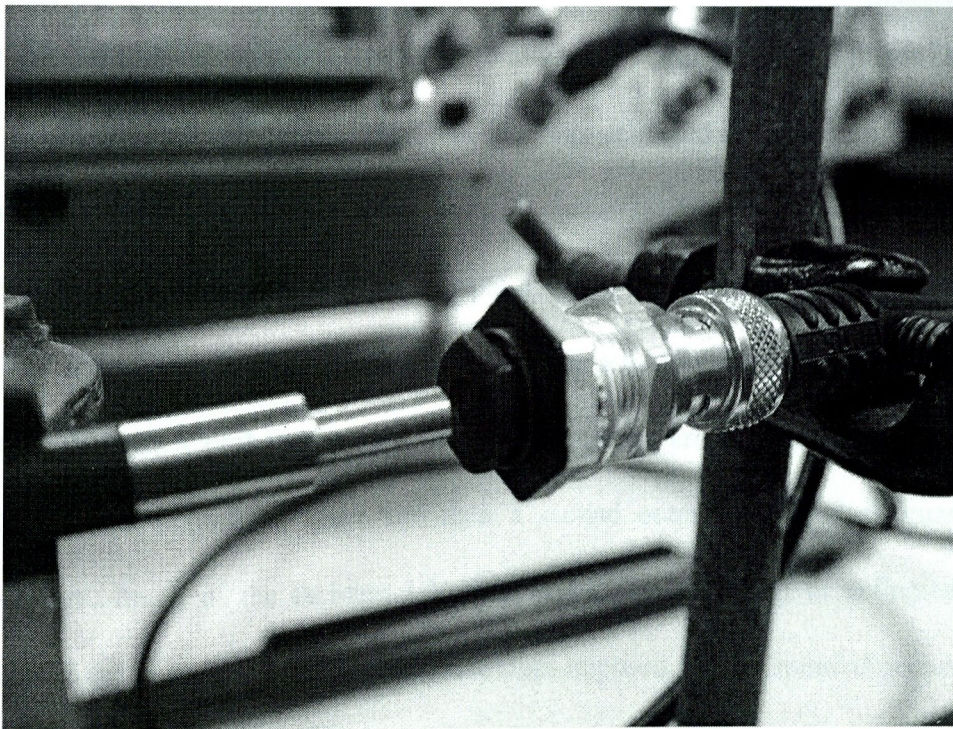


Figure 6.2. The Gentec ED100A joulemeter used to measure the light intensity output from a VSL-337 UV laser delivered *via* a UV-grade fibre optic bundle.

Table 6.1. UV light Intensity Measurements made using a Gentec ED100A Joulemeter.

	UV Light Output from VSL-337 UV Laser	UV Light Output from Fibre Optic Bundle	UV Light Measured at the Sample Area of the CIDNP NMR Probe
Energy Per Pulse	132 μJ	48 μJ	9.5 μJ
Repetition Rate	20 Hz	20 Hz	20 Hz
Average Power	2.64 mW	0.96 mW	0.19 mW
Pulse Duration	3 ns	3 ns	3 ns
Peak Power	44 kW	16 kW	3.2 kW
Average Intensity	11.0 mWcm^{-2}	13.6 mWcm^{-2}	0.25 mWcm^{-2}
Peak Intensity	183 kWcm^{-2}	226 kWcm^{-2}	4.3 kWcm^{-2}

While these radiometry values are accurate measurements of the light energies delivered to the sample holders in the FTIR and NMR curing experiments, they do not represent the actual light energies incident on the liquid monomer mixture samples themselves. For example, in the *in situ* FTIR curing experiments, liquid monomer samples were sandwiched in a heated cell arrangement between NaCl plates separated by a 100 μm Teflon[®] gasket. The UV light was delivered *via* the fibre optic bundle ‘thin-side-on’ to the sample in the cell (so as not to swamp the IR detector) and therefore it did not illuminate the sample directly, *i.e.* only the fraction of the total light that was scattered or reflected to the sample actually ‘cured’ the mixture. Inside the CIDNP NMR probe, the liquid monomer samples were contained in a glass NMR tube, located behind an inner and then a second outer, quartz glass guard tube. Therefore, much of the incident UV light was either absorbed or reflected before reaching the sample. Due to size constraints imposed by the inner diameter of the NMR sample tube (4 mm), the only type of detection system that could be practically used to determine the actual UV light energy reaching the sample *in situ* in the CIDNP probe, was a liquid phase chemical actinometer.

6.2.3 Liquid Phase Chemical Actinometry

Fluid actinometers have been widely used in the past by photochemists for measuring radiation fluxes in photochemical reactors.^{5,8,9} They have one main advantage over physical detection methods in that the liquid system can be irradiated *in situ* in place of the sample, under identical experimental conditions. The actinometer traditionally used for UV light measurements is the potassium ferrioxalate system, but its use is demanding, requiring the careful preparation of standard solutions and the construction of a calibration graph before measurements can be made.¹⁰ A more recent, commercially available actinometry system, Aberchrome™ 540, was selected for use in this study on the basis that it purported to be well suited for UV light measurements and was considerably easier to use.¹¹

6.2.4 Aberchrome™ 540 UV Chemical Actinometer System

Aberchrome™ 540 is a thermally stable, reversible and fatigue resistant, photochromic fulgide system, synthesised and sold by Aberchromics Ltd., University of Wales. The chemical structures of the two forms of the compound and their UV spectra are shown in Figure 6.3. Form 1 undergoes a major reversible colour change on irradiation with UV light to quantitatively form the more highly coloured visible form 2. An approximately 1×10^{-2} molar solution of Aberchrome 540 in toluene was prepared and the absorbance at 494 nm was measured. UV absorption data were recorded on a Shimadzu UV-1601 PC® double beam spectrophotometer (*see Chapter 3.4*). A stirred sample of the solution was then irradiated with UV laser light (*i.e.* 337 nm) for a measured period of time and the absorbance at 494 nm was again measured. The quantum yield for colouring (ϕ_c) is reported to be temperature independent.¹²

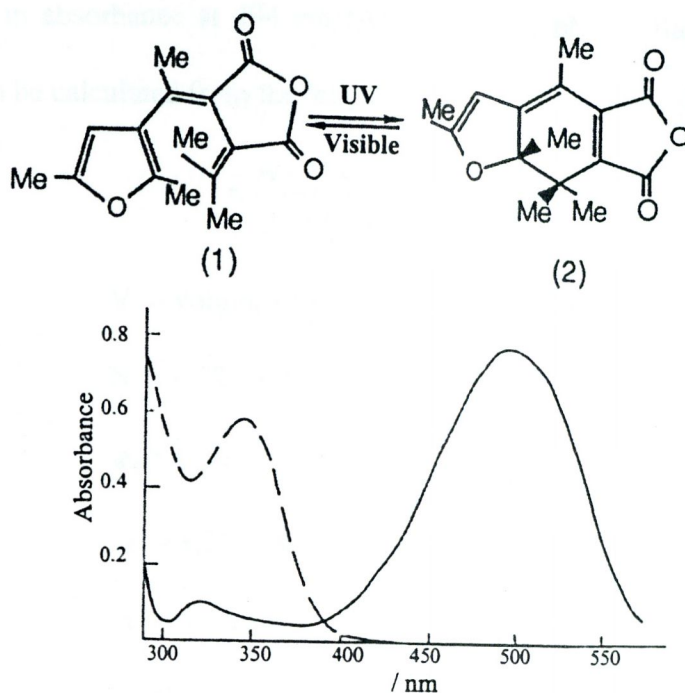


Figure 6.3. The UV-Vis spectra of a solution of (1) Aberchrome™ 540 in toluene (---) and (2) after conversion in to the coloured form by incident UV light (—).¹²

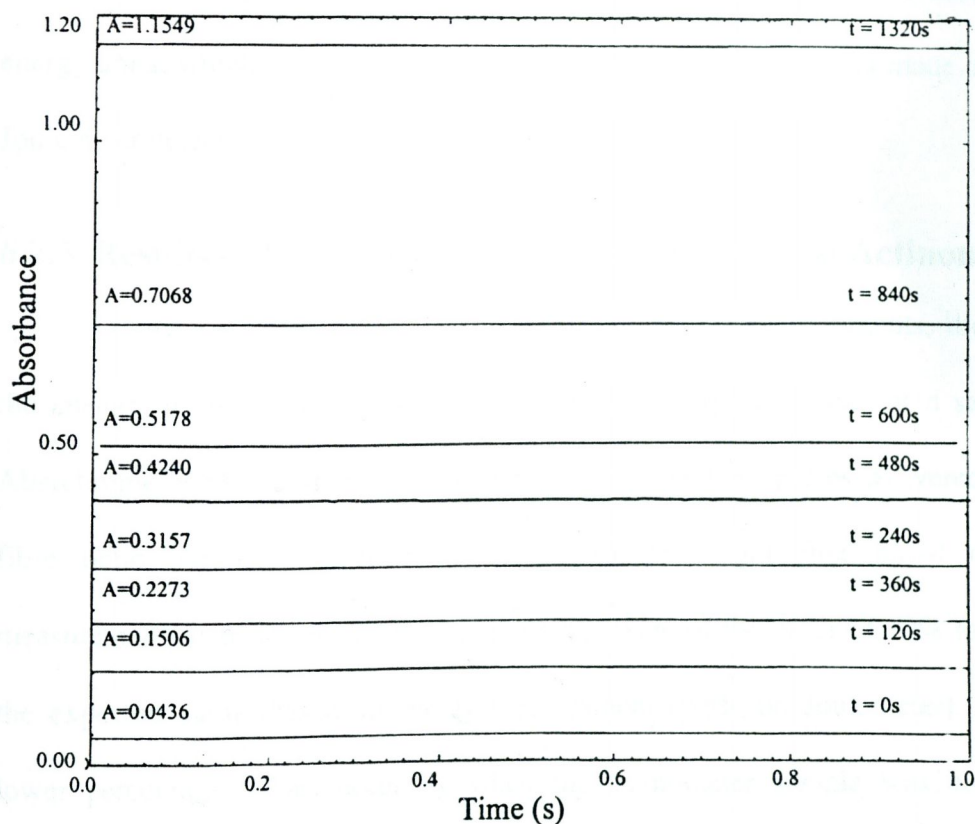


Figure 6.4. UV-Vis spectra of a solution of Aberchrome™ 540 in a quartz cuvette, having been exposed to UV light from the laser delivered via a UV-grade fibre optic bundle for the time periods indicated.

The increase in absorbance at 494 nm (A) enabled the photon flux (I), in units of photons s⁻¹, to be calculated from the following equation

$$I = \frac{A \times V \times N}{\phi_c \times \epsilon \times \tau} \quad (6.1)$$

where V = volume of solution irradiated (dm³)

$N = 6.023 \times 10^{23} \text{ mol}^{-1}$

$\phi_c = 0.20$ (from 310 – 370 nm)

$\epsilon = 8,200 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ at 494 nm

τ = time (s)

The energy of a photon of UV light at 337 nm was calculated, using the equation $E = h\nu/c$, to be $5.895 \times 10^{-19} \text{ J.photon}^{-1}$. Multiplying the liquid phase actinometry UV light flux measurements by this value yields light measurements in energy units, which could then be compared to similar measurements made using the Joulemeter detector.

6.2.5 Results of UV Light Measurements by Chemical Actinometry

Figure 6.4 shows typical UV-Visible spectroscopy measurements, illustrating the change in absorbance (494 nm) with increasing exposure time, of a sample of Aberchrome™ 540 solution to irradiation by UV laser light pulses delivered *via* the fibre optic bundle. Calculations of the incident light flux based on such measurements consistently yielded energies that were of the order of 10% to 20% of the expected value (based on energy measurements with the Joulemeter), with the lower percentage values occurring when the actinometer sample was not stirred efficiently or if the light beam was focused to a fine point. Precautions such as increasing the concentration of the actinometer solution, more vigorous stirring and

increasing the light path length did not improve the accuracy of the measurements. The cause of the inability of the actinometer to accurately measure the pulsed UV laser light flux is not understood, but Aberchromics Ltd. have suggested that may be to some extent due to the very short light pulse duration (3 ns).

The average light power delivered to sample area in the CIDNP probe was measured using the Joulemeter to be 0.19 mW (see Table 6.1). This value corresponds to a photon flux of 3.22×10^{14} photons.s⁻¹. The UV photon flux detected *in situ* in an NMR sample tube, based on measurements using the liquid actinometer system, was 3.79×10^{12} photons.s⁻¹. Assuming, since it was not possible to stir the actinometer solution during the measurement, that only 10% of the actual light flux was detected, then the photon flux irradiating a sample *in situ* during an NMR photocuring experiment was *ca.* 3.8×10^{13} photons.s⁻¹, which corresponds to an average power of *ca.* 22 μ W and an average intensity of *ca.* 30 μ Wcm⁻². This value is only *ca.* 12% of the incident light energy, which implies that 88% of the incident UV light was absorbed by, or reflected from the polished surfaces of the two cylindrical quartz guard tubes and the glass NMR sample tube surrounding the sample.

This average UV light intensity value is *ca.* 1% of that used in industrial contact lens manufacture. Since the rate of cure is known to be proportional to the square root of the absorbed average light intensity,¹³ this would imply that these samples should take roughly 10 times longer to cure than in lens manufacture processes. However, the monochromatic laser source used in these experiments is considerably more efficient at producing free radicals from the photoinitiators present in the mixtures than the polychromatic fluorescent lamps used in the industrial process and the resulting polymerisation rates are accordingly higher.

By the same principle, since identical monomer mixture samples cured approximately 1.25 more quickly in the *in situ* FTIR experiments than in the *in situ* NMR experiments (293K), and the average light intensity incident on the NMR sample has been estimated as *ca.* $30 \mu\text{Wcm}^{-2}$, then the average light intensity incident on the FTIR sample, *i.e.* indirect illumination from reflected and scattered UV light, can be estimated to be *ca.* 1.6 times this value, or *ca.* $48 \mu\text{Wcm}^{-2}$.

6.3 UV Cure Behaviour Monitored by FTIR Spectroscopy

6.3.1 Introduction

The recent advent of FTIR spectrometers with improved spectral acquisition speeds and signal-to-noise ratios, superior IR light sources, and increasingly sophisticated data processing techniques, permits quantitative studies of photoinitiated or thermally induced polymerisation *in real time*.^{4,14,15} Specialised rapid-scan spectrophotometers have been developed that are capable of collecting and storing spectra every 10 ms and these have been used in studies of the kinetics of fast curing coating formulations.¹⁶ A standard FTIR spectrometer was employed in this study, which was more than adequate for more modest spectral acquisition rates (*ca.* 4s acquisitions recorded at 20s intervals). In this approach curing profiles are constructed from the diminishing intensity of specific absorbance bands that are sensitive to polymerisation. Problems can arise, however, from poor resolution owing to overlapping bands in the spectrum and the need to monitor internal reference bands to obviate the further complications due to changes in sample thickness due to shrinkage or thermal expansion.

This section presents an account of the way in which the *in situ* FTIR technique has been used to probe the UV photoinitiated curing dynamics of two

composite monomer systems, Mixture A and Mixture B (*see Table 4.1*). Specifically the curing experiments involving Mixture B form part of a systematic investigation of the curing behaviour of hydrogels with N-vinyl-2-pyrrolidone (NVP), hydroxy ethyl methacrylate (HEMA) and the modulus modifier 4- or 5-*t*-butyl-2-hydroxy cyclohexyl methacrylate (TBE) as principal components.^{2,17,18} The measured *in situ* FTIR curing profile of Mixture B is compared with similar *in situ* ¹H NMR curing results in *Chapter 7*, and the types of information provided by each technique is discussed in detail therein.

6.3.2 Experimental Procedure

Characteristic infrared spectra of the composite monomer mixtures and their individual constituents were recorded between 4800 cm⁻¹ and 400 cm⁻¹ on a Nicolet 510-P FTIR spectrometer with a spectral resolution of 1 cm⁻¹ using a horizontal attenuated total reflectance (ATR) sampling accessory (*Chapter 3.3*). A detailed assignment of the functional groups responsible for each absorbance in the spectra identified those bands that were sensitive to the progression of polymerisation and those that could be used as internal references (*see Chapter 4.3.2 and Table 4.3*). To effect UV irradiation in the *in situ* FTIR curing experiments, a Specac[®] Variable Temperature Cell unit was modified by inserting an airtight port into the side wall of the cell to support a UV grade fiber optic bundle carrying light pulses from a UV VSL-337[®] nitrogen laser operating at 337 nm. A photograph of the experimental arrangement is shown in Figure 6.5. The sample holder was in the form of two shaped NaCl plates separated by a Teflon[®] spacer 0.1 mm thick. In all curing experiments, the liquid monomer was thoroughly degassed for a period of 30 minutes before being introduced into the cell *via* injection ports in the top plate, which also

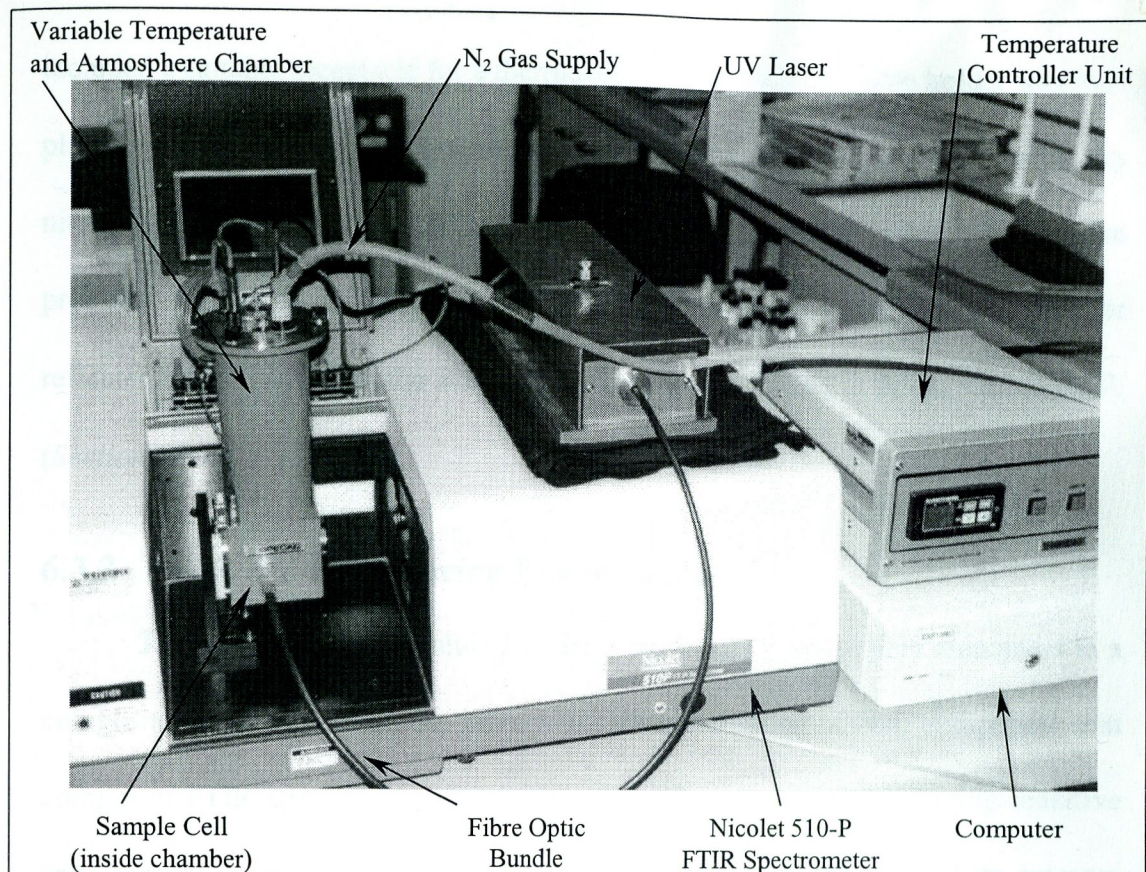


Figure 6.5. FTIR spectroscopy instrumentation used to control the temperature and atmosphere conditions, while recording the *in situ* UV-curing profiles of the composite monomer mixtures.

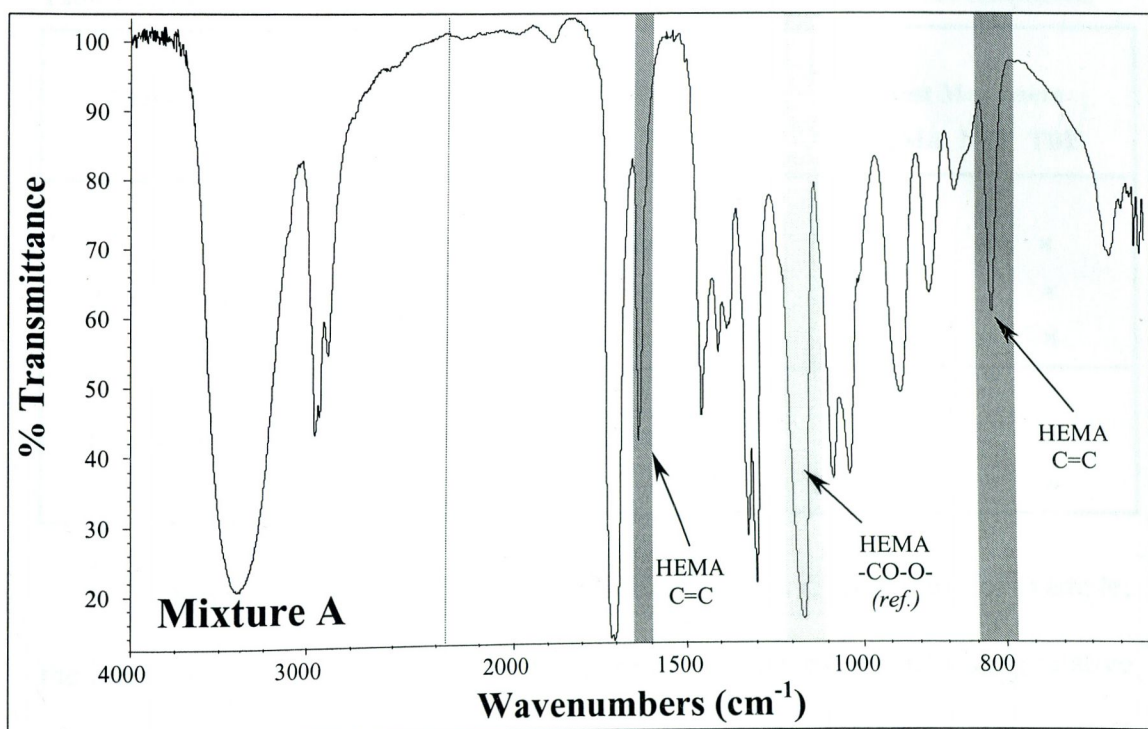


Figure 6.6. FTIR spectrum of monomer Mixture A with the bands used to monitor cure (■) and as internal reference (□) highlighted (see Table 4.3).

included a suitable receptacle for a thermocouple. The loaded sample holder was then placed in the variable temperature cell and maintained in an atmosphere of dry nitrogen gas. The average UV light intensity incident on the sample, having been produced by the laser, delivered *via* the fibre optic bundle and then scattered or reflected to the sample in the cell arrangement, was estimated to be *ca.* 48 μWcm^{-2} . (Section 6.2.4).

6.3.3 FTIR UV-Photocuring Experiments

The use of FTIR to monitor the curing profile of the constituent monomers in a composite sample relies on the prerequisite characterisation of both component and composite FTIR spectra, in particular, the identification of suitable curing-sensitive and internal reference bands. Data for Mixtures A and B and their primary constituents are summarised in Table 6.2.

Table 6.2: Relevant FTIR curing-sensitive and internal reference bands in the monomer composites.

Type of Band	Band	Position (cm^{-1})	Host Monomers		
			HEMA	NVP	TBE
Curing-sensitive	C=C	<i>ca.</i> 1638	×	×	×
		<i>ca.</i> 815	×		×
		<i>ca.</i> 981		×	×
Internal reference	-CO-O-	<i>ca.</i> 1163	×		×
	-C-C-	<i>ca.</i> 850		×	×

In hydroxyethyl methacrylate (HEMA) in Mixture A (Figure 6.6), for example, the intensity of the C=C band at 815 cm^{-1} preferentially decreases with curing relative to a control CO-O band at 1163 cm^{-1} . In effect, the degree of cure is determined *via* the fractional conversion of carbon-carbon double bonds as curing proceeds, as is

illustrated by a composite plot of overlaid absorption spectra of Mixture A, as shown in Figure 6.7. From these data, it is evident that this approach can be used to construct the curing profile of HEMA in Sample A, since bands that are sensitive to the curing process are reasonably well resolved; one such plot is shown in Figure 6.8.

This is not the case however with Sample B since the TBE bands of interest overlap those of HEMA and NVP, as is shown in Figures 6.9 and 6.10 and indicated in Table 6.2, with two consequences: First, access to the curing profile of TBE is precluded because of poor band resolution and because of its low concentration. Second, the concomitantly minor contribution of TBE to the overlapping HEMA and NVP bands implies that a reasonably good approximation of the curing profile for HEMA and NVP can be constructed. Figure 6.11 shows a composite plot of overlaid absorption spectra of Mixture B, and Figure 6.12 presents data for Sample B in the form of plots of remnant NVP and HEMA monomer as a function of curing time, which confirm the very different curing dynamics of the two major constituents. The curing rate of NVP, which is low over the first *ca.*1000 s, then increases quite markedly up to 2500s before decreasing again in an asymptotic approach towards completion. Note, however, that complete cure is not achieved in this and subsequent curing profiles measured; extractables amounting to no more than a few percent remain. The more rapid curing profile of HEMA exhibits inflection points at *ca.*400s and 700s and the final low rate of cure sets in at *ca.*1500s, no doubt reflecting the complex curing dynamics of the multi-component system with the added dimension of diffusion controlled effects.

At first sight, the C=C band at 1638 cm^{-1} in Sample B offers a route to the curing profile of the composite as a whole: unfortunately, this strong band is readily saturated, even for very thin monomer specimens. Additionally, poor resolution

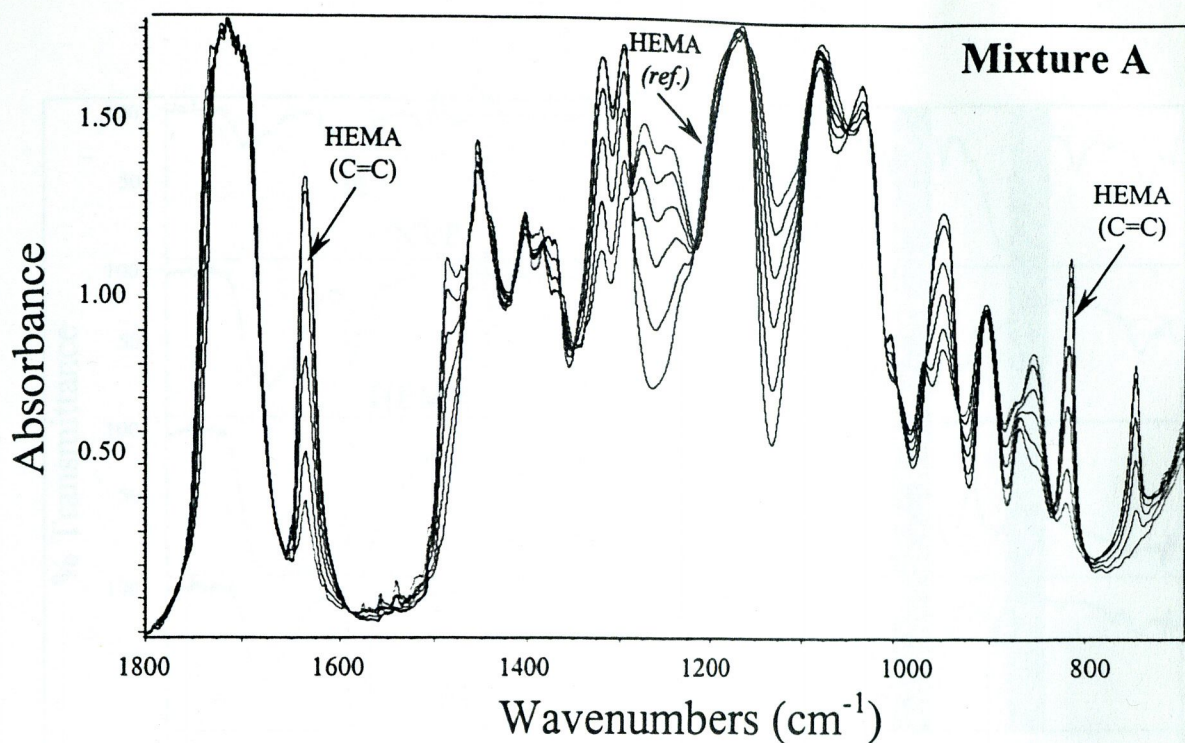


Figure 6.7. FTIR spectra recorded to monitor the *in situ* UV cure profile of HEMA in monomer Mixture A (293 K).

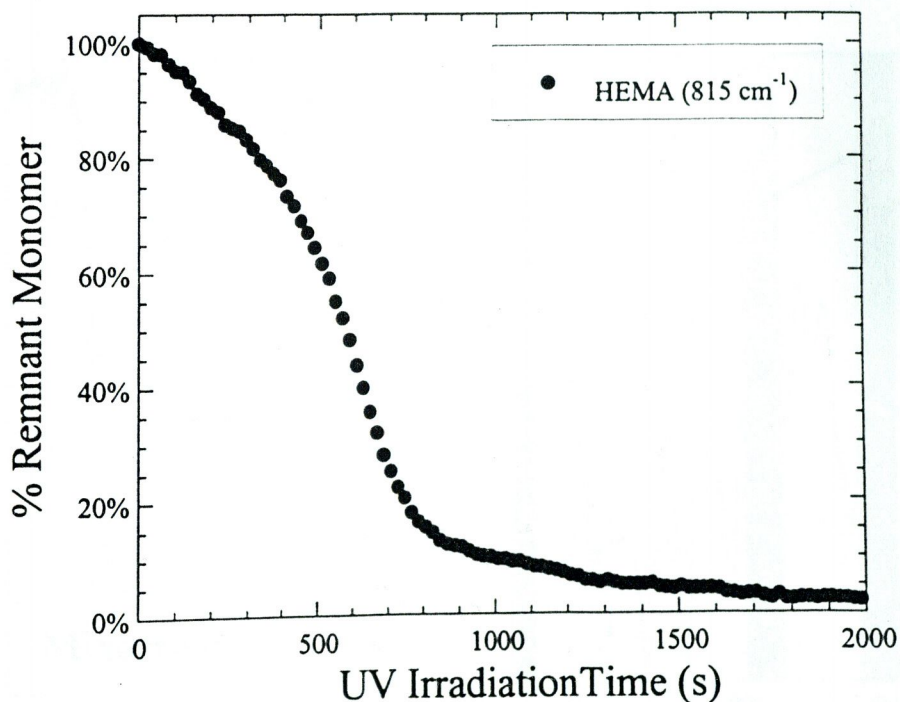


Figure 6.8. UV curing profile of HEMA in monomer Mixture A (293 K) as measured by FTIR spectroscopy.

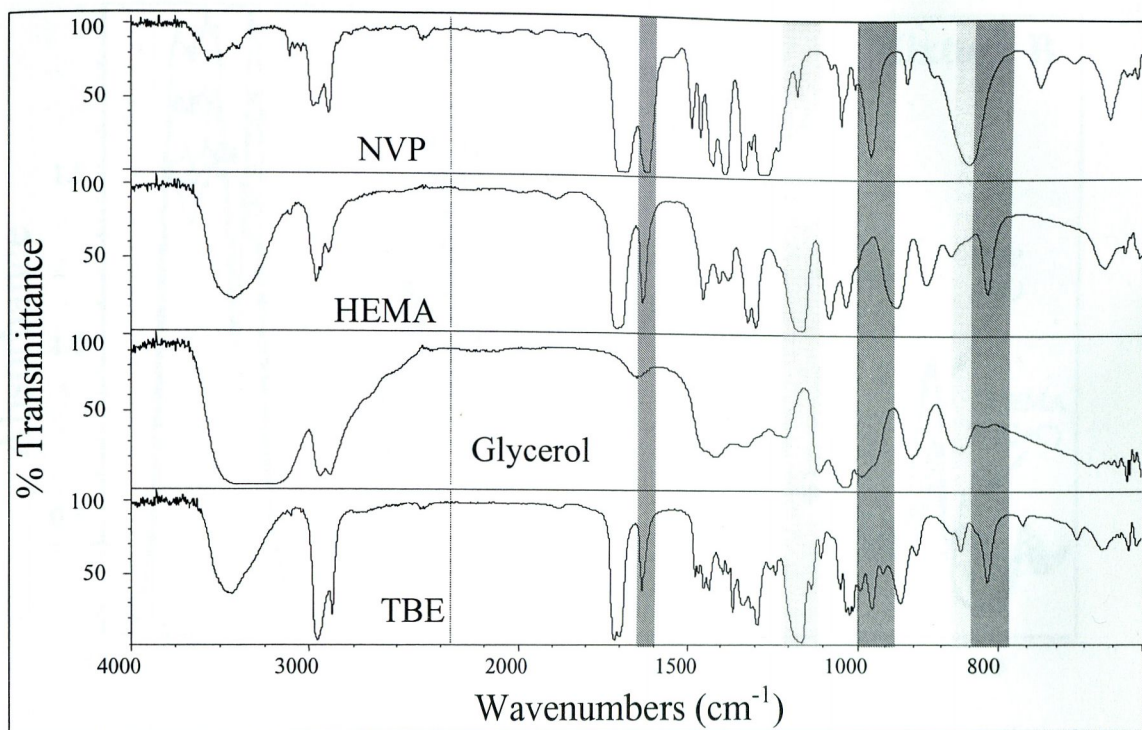


Figure 6.9. FTIR spectra of the four major components of monomer Mixture B with the bands used to monitor cure (■) and as internal reference (□) highlighted.

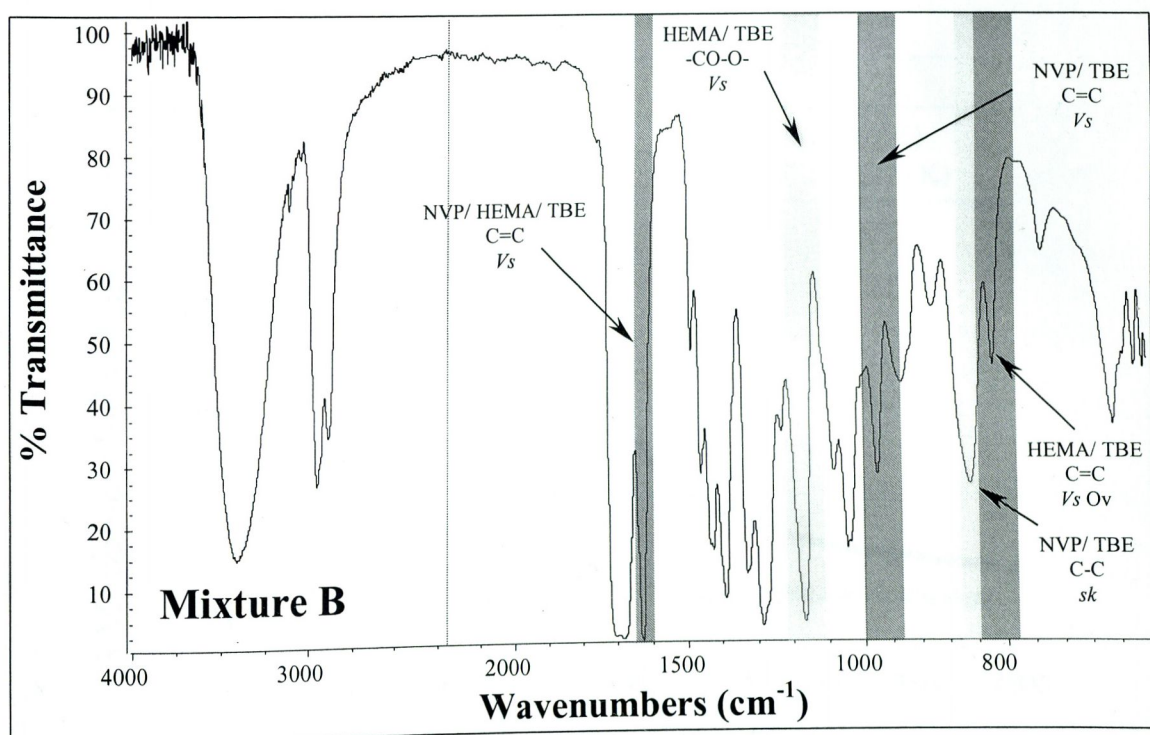


Figure 6.10. FTIR spectrum of monomer Mixture B with the bands used to monitor cure (■) and as internal reference (□) highlighted (see Table 4.3).

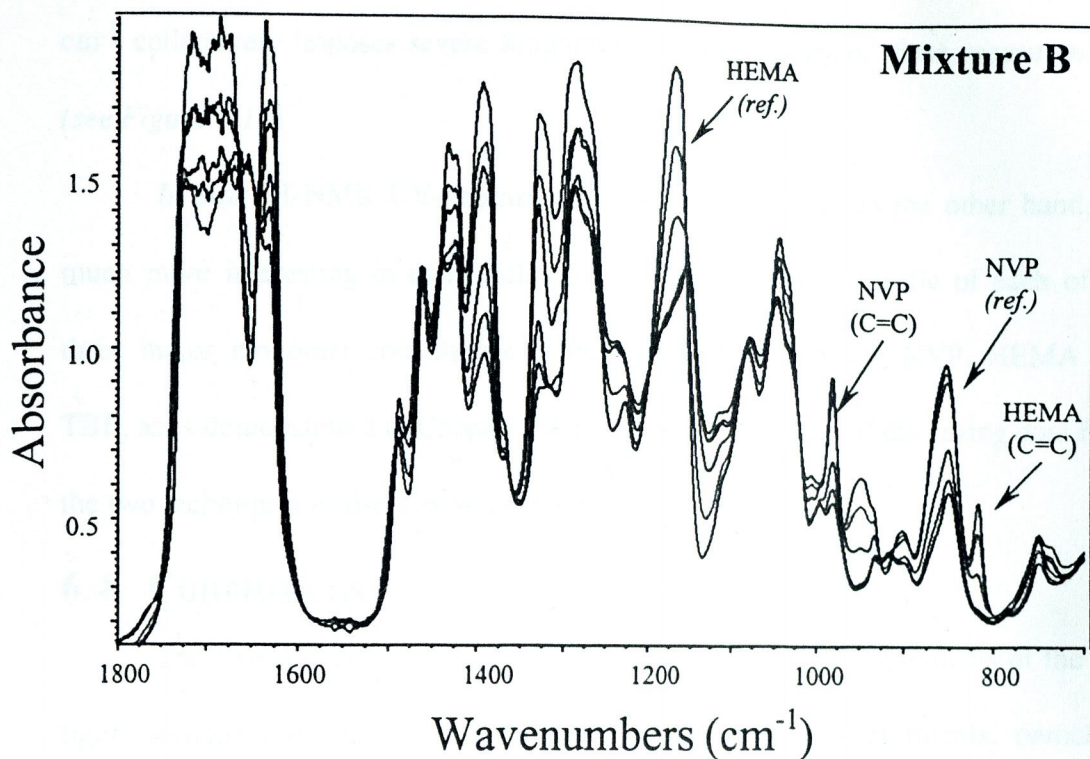


Figure 6.11. FTIR spectra recorded to monitor the *in situ* UV cure profiles of NVP and HEMA in monomer Mixture B (293 K).

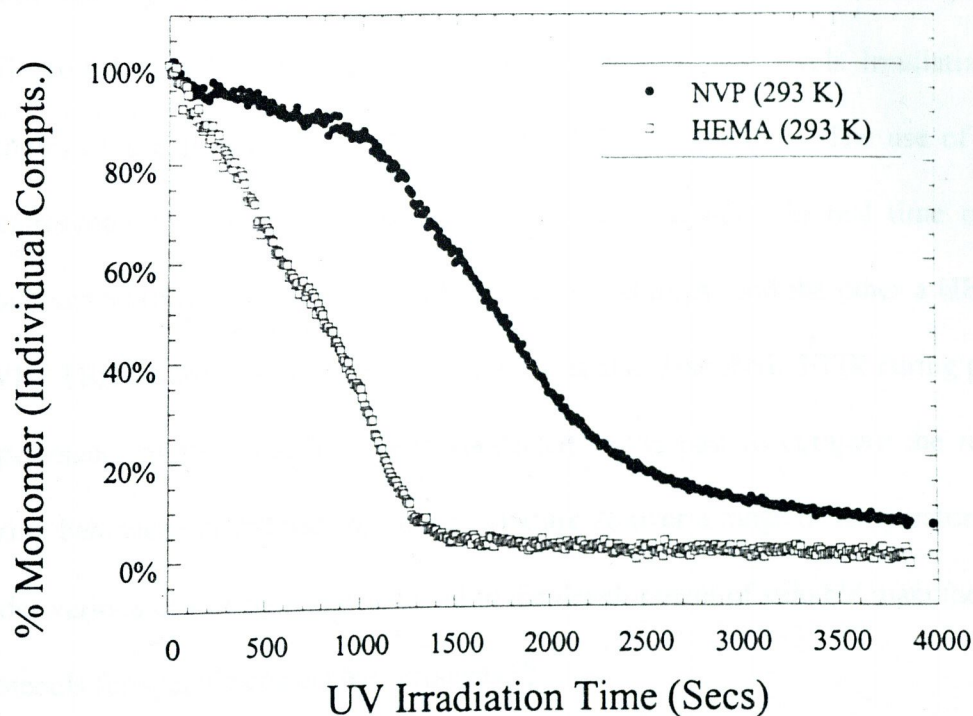


Figure 6.12. UV curing profiles of NVP and HEMA in monomer Mixture B (293 K) as measured by FTIR spectroscopy.

between this band and the even stronger and broader neighbouring C=O band at 1717 cm^{-1} collectively imposes severe limitations on the accuracy of these measurements (see Figure 6.11).

In situ ^1H NMR UV-photocuring data for Sample B, on the other hand, are much more interesting in their ability to delineate the curing profile of each of the three major monomer constituents in the composite system *i.e.* NVP, HEMA and TBE, as is demonstrated in Chapter 7.3.3, where a comparison of the curing data from the two techniques is also discussed in detail.

6.4 Conclusions

The two different methods used to make radiometry measurements of the UV light intensities employed in subsequent UV-photocuring experiments, namely a pyroelectric Joulemeter detector system and a liquid phase chemical actinometer system, were described and the measured light values were reported. The chemical actinometry system did not measure the incident UV light flux values correctly, but it still proved useful in the estimation of the actual UV light levels irradiating the samples *in situ* in the NMR probe and in the FTIR sample cell. The use of FTIR spectroscopy to profile the *in situ* UV-photocuring dynamics in real time of two monomer mixtures, one predominantly HEMA (Mixture A) and the other a HEMA / NVP / TBE comonomer system (Mixture B), was also described. FTIR curing profile experiments of this kind have been conducted in the past to compare the relative curing behaviour of different batches of Mixture A, over a range of temperatures and under various degassing regimes, to aid in the development of suitable manufacturing protocols for specific contact lens products.¹⁹

6.5 References

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Chapter Seven

Thermal and UV-Photoinitiated Cure Behaviour Monitored by Liquid NMR Spectroscopy and Thermal Analysis Techniques

7.1 Liquid NMR Spectroscopy

This chapter discusses the way in which liquid NMR techniques have been used to probe the *in situ* curing of monomers and composite monomer mixtures. The information obtained from these experiments is the first step in understanding the overall curing dynamics and helps to clarify the complex relationship between structure and properties in these systems. This study also facilitates the tailoring of new composite polymers to meet specific applications and is of considerable benefit in providing important guidance in establishing suitable protocols in manufacturing processes.

7.1.1 Introduction

While infrared spectroscopy has been used in the past for continuously monitoring the degree of polymerisation of a monomer composite, the application and sensitivity of the technique is often limited by poor resolution of the broad characteristic spectral features (*see Chapter 6*). An alternative and appreciably more informative approach exploits the site-specific information provided by high resolution nuclear magnetic resonance (NMR) spectroscopy to monitor the behaviour of those chemical moieties which specifically label the individual monomer constituents in multi-component monomer systems as curing proceeds.¹ The

intensity, shape and position (chemical shift) of such labelled peaks in the NMR spectra provide valuable site-specific information on molecular motion and chemical environment.² By following changes in these parameters in the NMR spectra, the curing profiles of the individual components in a composite monomer mixture can be monitored continuously as curing proceeds from the liquid state *via* a gel phase towards the fully cured solid polymer. The data obtained may be subsequently analysed using established procedures.³

7.1.2 Experimental Approach

The experimental basis of the NMR technique is as follows. Progression from the liquid to the solid phase is accompanied by a decrease in the correlation frequency, ν_c , which characterises the molecular motion of the polymerising molecules.² Recall that ν_c is typically 10^8 Hz or higher in a liquid monomer undergoing pseudo-Brownian motion whereas ν_c approaches 0 Hz in the limit of rigid polymer formation. NMR linewidths concomitantly broaden from *ca.* 10 Hz to 50 kHz. The bandwidth used in the acquisition of liquid ^1H -NMR spectra is purposely narrow, of the order of 3 - 4 kHz, to achieve a point resolution of less than 0.2 Hz. As a result, during curing, only the liquid-like signal is detected while the signal from the cured solid polymer, with the possible exception of very short oligomers, is subsumed into the baseline. Conversion of monomer into polymer is therefore reflected in a decrease in intensity of the corresponding lines in the ^1H -NMR liquid spectra recorded during *in situ* thermal or UV curing. Interim gel formation between the extremes of mobile monomer and solid polymer would result in a somewhat broadened line in the liquid spectrum (*see for example References 4 through 7*). Such broadening is indeed observed - of the order of 50 Hz to 150 Hz - just prior to the disappearance of the

liquid-like signal as curing on the NMR-sensitive time scale ($ca. 5 \times 10^{-5}$ s for line width changes) approaches completion (see Section 7.3.3.2).

In effect, important temporal information on the curing dynamics of component monomers in the composite is encoded in the diminishing intensity of the corresponding spectral peaks as curing proceeds. Lineshape and chemical shift information provide further perspective on the molecular environment at intervening stages of cure. Furthermore, the sensitivity of the spectral lines to the presence of unpaired electrons permits at least cursory examination of free radical activity in the monomer system as it gradually transforms into the solid polymer.

In order to identify those peaks that specifically label individual monomer components, it is first necessary to characterise the complex spectra of the composite monomer mixes. Assignments of individual peaks in the constituent materials were first carried out and, with this information at hand, it was reasonably straightforward to interpret the spectral details of the composite monomer mixtures with confidence. The complete assignment of all the peaks detected in the liquid NMR spectra of the complex mixtures was presented in *Chapter 4*.

7.1.3 Cure Initiation Mechanisms

In these experiments curing proceeds *via* free radical addition copolymerisation type reactions, which rely on the supply of free radicals from either the thermal decomposition (thermolysis) or UV photo-activated decomposition (photolysis) of the added initiator reagents. The azo compound AIBN (2, 2-azobisisobutyronitrile) was employed in all of the thermally initiated reactions, which effectively produces radicals by thermolysis in the temperature range of 320 K to 420 K.⁸ UV-photoinitiated cure reactions used either BME (benzoin methyl ether) or

Darocur 1173 (α,α -dimethyl α -hydroxy acetophenone) as photoinitiator in the composite mixtures. Benzoin ethers, including BME, are the most extensively used and studied class of photoinitiators.⁹ Photolysis of BME by an α -cleavage process can be induced by UV-light over a broad wavelength range (230nm to 400nm) resulting in a high quantum yield of primary radicals.¹⁰ Darocur 1173 offers additional advantages over BME, such as low toxicity and no yellow by-products, which makes it particularly suitable for use, for example, in contact lens applications.¹¹

Both the FTIR and NMR *in situ* UV-photo curing experiments conducted during this study relied on the availability of pulsed UV lasers that could deliver precisely defined light energy within specified time periods, thereby permitting controlled experiments in a way that was not possible heretofore with the more traditional UV lamps. Experiments of this nature have, for example, allowed the optimisation of curing conditions by establishing appropriate wavelengths, intensities and duration of UV light energy to be delivered to the sample monomer. Moreover, access to pulsed UV irradiation whereby the cured fraction of monomer can be monitored while the laser is pulsed on and off for selected periods of time provides an alternative route to information on curing dynamics (*see Section 7.3.3.6*).¹²

7.1.4 Experimental Procedure

7.1.4.1 Sample Preparation

The source and spectral characterisation of the various reagents used are detailed in *Chapter 4* and the complete formulations of the five composite mixtures studied are presented in Table 4.1. In all curing experiments, the liquid monomer mixtures, having been previously stored in a refrigerator in darkness, were thoroughly

degassed by displacement of dissolved oxygen¹³ in a dry nitrogen atmosphere for a period of 30 minutes. A specified amount (0.24 ± 0.01 g) of sample was then transferred to a NMR tube, which was sealed under the same dry N₂ atmosphere conditions prior to data acquisition. This amount of mixture was used in each case so that the entire sample volume resided within the NMR probe coils and therefore wholly contributed to the detected signal while being uniformly illuminated with incident UV light. Great care was taken at the outset of every experiment to ensure that each NMR tube was mounted at the same height in the Teflon spinner, so that, upon loading, each sample was located in an identical position within the probe transmitter/receiver coils, residing centrally at the core of the cyromagnet of the NMR spectrometer.

In situ UV curing was achieved with laser light delivered to the sample in a suitably modified CIDNP probe (see Chapter 3, Section 3.2.4.1; Figures 3.10 and 3.11 for details). A focusing and alignment stage was built and attached to the front of the UV laser, so that the pulses of radiation it produced could be delivered to the sample via a UV grade fibre-optic bundle (3mm in diameter) connected to the base of the modified probe. A coupling device then interfaced the fibre-optic bundle to a quartz rod located alongside and parallel to the sample tube in the probe. The top face of the rod was angled at 45° to the vertical in order to direct light towards the sample through a vertical collimator slit in a teflon® sheath encasing the top of the rod. About *ca.*0.8% of the total laser output, corresponding to an average intensity of *ca.* 30 μWcm^{-2} , was ultimately delivered to the sample (see Chapter 6). The required sample temperature was maintained using a Bruker VT-1000 temperature controller unit, which powered and regulated a heating element attachment in the probe with an

accuracy of ± 1.0 K. This facility was primarily used for achieving the higher temperatures required for initiation of *in situ* thermal curing when required.

7.1.4.2 Acquisition Parameters for NMR Curing Experiments

High resolution liquid spectra of the monomer mixtures and their constituents were recorded on a Bruker MSL 300 spectrometer operating at 300.13 MHz and 75.47 MHz for protons and carbons, respectively, using the modified CIDNP NMR probe and employing the pulse routines detailed in *Chapter 3*. In real-time curing experiments ^1H spectra with 16 K data points zero-filled to 32 K points were compiled with a standard pulse sequence, employing quadrature detection, a pulse length of 3 μs , a 5 s delay between data acquisition cycles and a sample spinning rate of the order of 5 Hz.^{2,14} These parameters (particularly the pulse length and pulse recycle delay times) were selected so that the spectral information obtained was truly quantitative in nature (*see Chapter 5, Section 5.5*). This was possible based the knowledge of the spin-lattice relaxation (T_1) times of the nuclei in the liquid systems, as determined from the series of inversion-recovery experiments described in *Chapter 5*. Using these acquisition conditions, proton Free Induction Decays (FIDs) were stored approximately every 30 s throughout the curing cycle, from which selected spectra were Fourier transformed, phase-corrected and baseline-adjusted. Component peak intensities, peak areas, peak linewidths and chemical shift positions were then recorded as a function of curing time.

Performing real-time curing experiments using ^{13}C NMR, to benefit from the improved spectral resolution the technique offers, proved problematic due to a combination of factors, including lower signal intensities, the requirement for significantly longer spectral acquisition times and the necessity to remove selective

NOE signal enhancement in order to ensure quantitative measurements. However, some experiments of this nature were attempted, by employing inverse-gated proton decoupling combined with the WALTZ16 pulse sequence (*see Chapter 3.2.1.2*).^{15,16}

7.1.5 Theoretical Simulation of Curing Dynamics

7.1.5.1 Introduction

A significant body of data has been compiled on polymerisation kinetics by assessing the amount of polymer formed in a series of sequential experiments whereby the curing process, usually for monomers in dilute solution, is arrested after specified periods of time.^{3,17} The real-time curing experiments conducted as part of this study and the resulting dynamic polymerisation profiles obtained have two clear advantages over such techniques: firstly, data was obtained over a single uninterrupted curing cycle and secondly, the composite mixtures were cured in neat form, rather than in dilute solutions, which better reflects actual industrial application conditions. Standard kinetic equations with reactivity ratios of pairs of monomers or, equivalently, $Q-e$ values, as disposable parameters were used to extrapolate curing behaviour over the complete curing cycle.¹⁷⁻¹⁹

A computer programme has been developed which performs the calculations necessary for the theoretical simulation of oligomer concentrations throughout the course of polymerisation of an N -component monomer composite ($N=2,3,4,\dots$) for subsequent comparison with experimental observation.²⁰ The novelty of this simulation is the recognition that the kinetic equations, as usually expressed, can with modest algebra be converted to a form that is dealt with by a standard, commercially available, numerical package. Note, of course, that the simulation does not describe

the time dependence of the curing process *per se*, merely its dependence on the degree of conversion.^{19,21}

7.1.5.2 Computer Programme for Simulation of Curing Dynamics.

Alfrey and Price²² initiated the numerical simulation of the radical copolymerisation process with the development of an accurate general form for the representation of the relative kinetic parameters obtained experimentally, and the astute observation that the elimination of time as a variable from the chemical kinetic equations provides differentials of monomer concentration solely as a function of monomer concentrations. Incorporation of the assumption that radical concentrations are in a steady state throughout the entire copolymerisation process gives a system of coupled differential forms which, when solved, provides the concentrations of monomer components during polymerisation. Readily available numerical routines for solution of differential equations assume that the input system of equations has the form of first order differentials with respect to an independent variable. In the problem at hand the true independent variable, in an experimental sense, has been eliminated and so must be replaced by something else in order to use the standard numerical packages. The degree of polymerisation, θ , is a logical choice as the replacement. However, since θ depends on concentrations, it may not be considered independent unless one monomer concentration is eliminated from the kinetic equations. This elimination is readily carried out algebraically by the use of the definition of the degree of polymerisation, $\theta = 1 - \sum_{i=1}^n [C_i]$, where concentrations are expressed as mole fractions, or by supplementing the numerical calculations with this relation; Douglass adopted the algebraic elimination approach.²⁰ The curing profiles or, if required, the instantaneous composition of the cured polymer at any given

degree of conversion, have been calculated for composites with up to six monomer components on a 33MHz NCR® PC with an Intel® 486 processor using a PowerBasic® compiler.²³ No instabilities were reported and calculation, storage and display of results generally required less than one second.²⁰

7.1.5.3 Parameters used in the Simulation of Curing Dynamics

The computer programme for the theoretical simulation of the cure dynamics of the multi-component monomer systems required the input of certain parameters to perform each calculation, namely the ratios of the individual reactive monomers in the mixture in terms of their relative 'Mole Fractions' and also their associated Q - e values. These parameters are presented in Table 7.1 for each of the five mixtures of interest. Values for Q and e for NVP and HEMA were available in the literature but none were reported for TBE, so values identical to those of ethylene glycol dimethacrylate were selected and successfully used in their stead.²⁴

Table 7.1. Q - e values and mole fractions of the monomer constituents of the composite mixtures as used in the theoretical simulations of the cure dynamics.

		UV Photoinitiated Cure		Thermally Initiated Cure		
		Mixture A	Mixture B	Mixture H	Mixture I	Mixture J
Mixture Component	Q and e values: Q / e	Mole Fraction	Mole Fraction	Mole Fraction	Mole Fraction	Mole Fraction
NVP	0.14 / -1.14	0.00	0.59	0.51	0.51	0.51
HEMA	0.80 / 0.20	1.00	0.36	0.44	0.49	0.49
TBE	0.88 / 0.24	0.00	0.05	0.05	0.00	0.00

7.2 Thermal Analysis Techniques: TGA and DSC

A brief description of some of the findings of Thermogravimetric Analysis (TGA) of the volatility of the liquid monomer mixtures when exposed to a continuous flow of dry nitrogen gas (*i.e.* similar to industrial processing conditions) is relevant to the study. The principles of the technique and the use of specially pressed aluminium pans to hold the liquid samples have been described in *Chapter 3.5*. The technique is also routinely used to determine of the water contents of the hydrated forms of these 'soft' hydrogel-type composite materials.²⁵

Some key results from Differential Scanning Calorimetry (DSC) studies of the thermal cure behaviour of two of the systems (Mixtures I and J) are presented to support and validate the findings of the high temperature NMR curing experiments. DSC measurements explore the cured polymers for evidence of exothermic heats of polymerisation from residual uncured monomer.²⁵ Knowledge of the extent of cure in these systems is critical since the monomers themselves are toxic to varying degrees, which can be a problem in biocompatible materials.²⁶ The principles of this thermal analysis technique have been detailed previously (*Chapter 3.6*).

7.3 Experimental Results: UV Photopolymerisation Experiments

The composite monomer systems examined in this study have been divided into two distinct groups, *i.e.* those cured using UV light (Mixtures A and B) and those thermally cured at elevated temperatures (Mixtures H, I and J) (*see Table 7.1*). The results of NMR experiments to examine the UV-curing behaviour of the two main individual monomers, and that of Mixtures A and B are now presented.

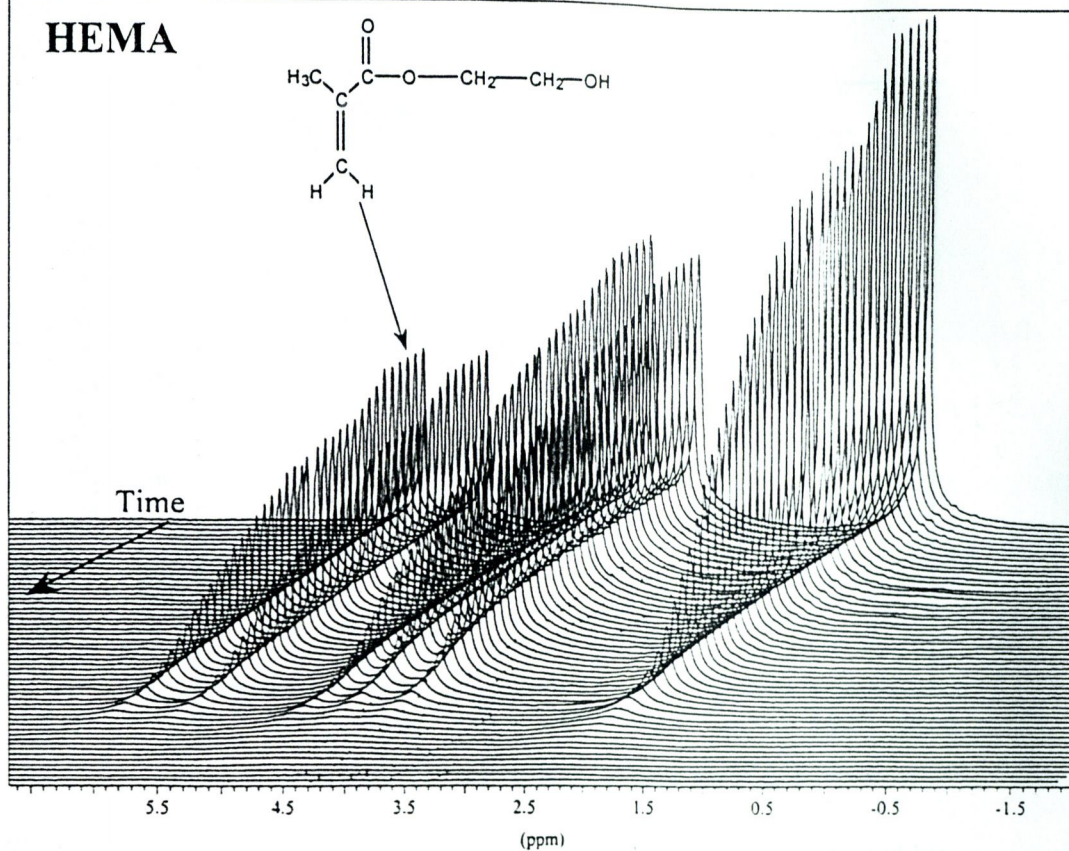
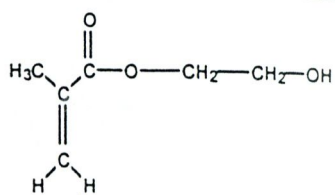
7.3.1 Cure Profiles of HEMA and NVP Monomers

Liquid ^1H NMR spectroscopy, as has been previously described, was used to examine the *in situ* UV-photoinitiated curing profiles of individual degassed samples of the two main monomers present in the mixtures, namely HEMA and NVP, containing equi-molar amounts of Darocur 1173 photoinitiator (approximately 0.2%w/w). Representative selections of the multiple NMR spectra recorded during these experiments, offset to better visually demonstrate the observed decrease in spectral peak intensities with the progression of cure, are presented in Figures 7.1a and 7.1b for HEMA and NVP monomers, respectively. The chemical structures of the monomer units are shown and the locations of protons responsible for the cure-sensitive spectral peaks are indicated. These peaks were selected on the basis that they uniquely characterise the vinylidene and vinyl environments in HEMA and NVP monomers, respectively, and as such, probe direct participation in the polymerising process (*see Chapter 4*). The selected peaks also remain well resolved in the complex spectra of the composite mixtures and accordingly are amenable to analysis by peak height and integration measurements.

Figure 7.2 shows the UV-curing profiles of HEMA and NVP monomers, plotted in the form of the measured characteristic peak intensities (*i.e.* peak heights, ratioed to 100% at time $t = 0$) versus exposure time to incident UV irradiation. This plot illustrates the importance of understanding the fact that in such measurements, the concentrations of the liquid monomer species are more accurately reflected in the peak areas, rather than in simply the peak heights. Peak linewidth changes, which occur over the course of the cure process (*Section 7.3.3.2*), give rise to the clearly anomalous increase in measured peak heights to values in excess of 100%. This feature of the data will be explored elsewhere. Figure 7.3 shows the results of same

a)

HEMA



b)

NVP

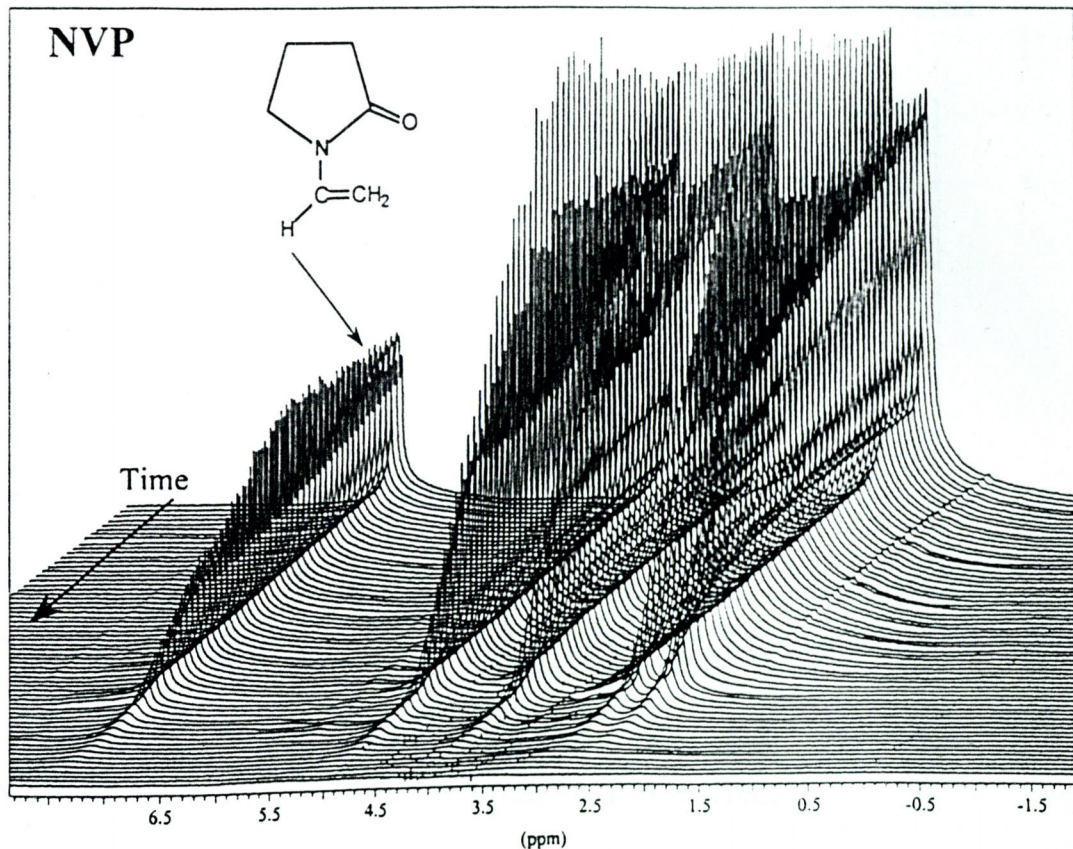
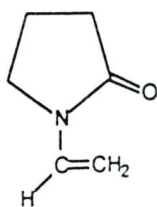


Figure 7.1. ^1H NMR curing profiles of the *in situ* UV-photoinitiated polymerisation of
 a) HEMA and b) NVP monomers (+ 0.2% w/w Darocur 1173 initiator).

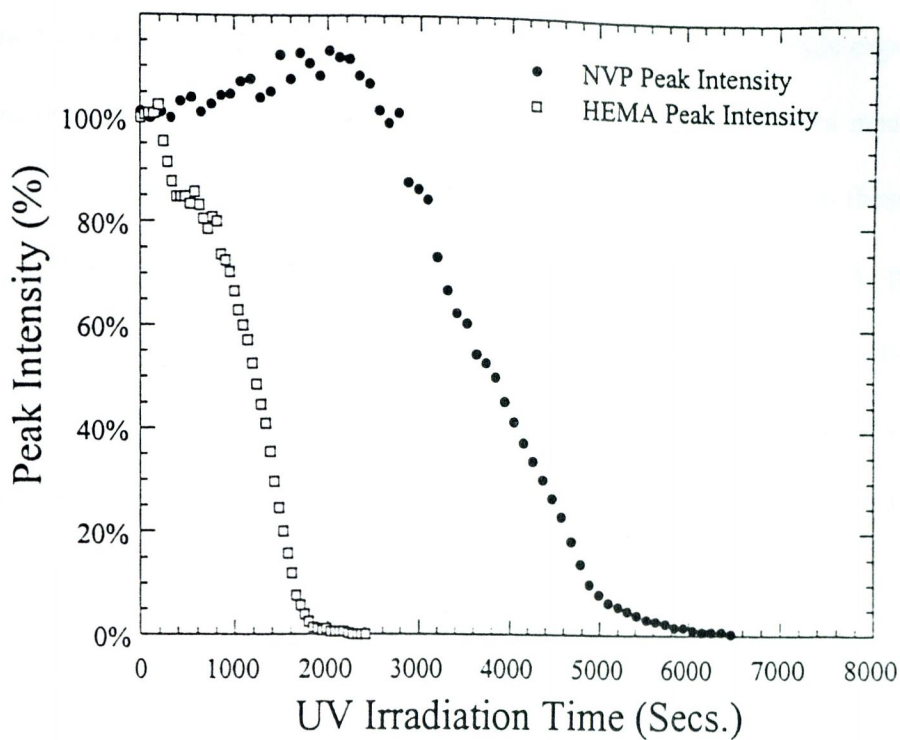


Figure 7.2. UV-curing profiles of HEMA and NVP monomers obtained by measurement of selected peak intensities in the ^1H NMR Spectra.

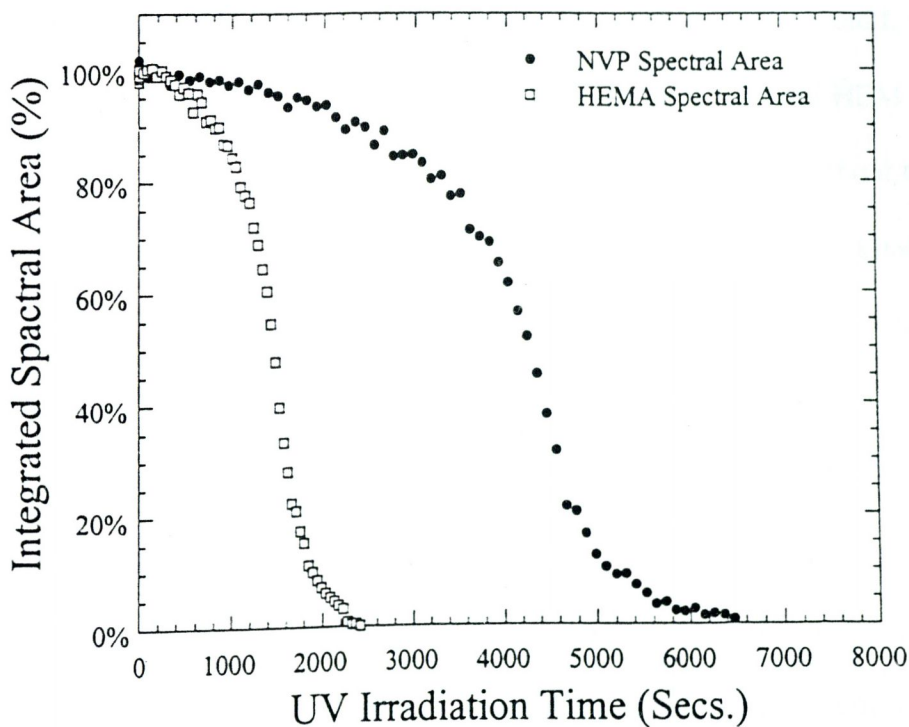


Figure 7.3. UV-curing profiles of HEMA and NVP monomers obtained by measurement of the total integrated peak areas in the ^1H NMR spectra.

UV-curing experiments for HEMA and NVP monomers, plotted this time in the form of the total measured peak areas (ratioed to 100% at time $t = 0$) versus exposure time to incident UV irradiation. UV-curing profiles plotted from peak area measurements are therefore more representative of the dynamics of polymerisation in these systems. Figure 7.3 also illustrates the large time difference required to homopolymerise HEMA and NVP monomers independently under identical conditions, as observed earlier.²⁴ These differences in polymerisation rates have implications for their copolymerisation behaviour, as may be observed in the experimental results for the composite mixtures (Section 7.3.3).

7.3.2 Monomer Mixture A

7.3.2.1 Cure Profile of Monomer Mixture A

Proton liquid NMR spectra for Mixture A over the curing cycle are shown in Figure 7.4 in the form of a stacked plot. Either of the peaks labelled e and f, identified earlier,^{1,21} is a suitable candidate for probing the progressive curing of HEMA. Recall that spectra were recorded and stored approximately every 30 s throughout the curing cycle from which peak intensities were computed as a function of irradiation time. Figure 7.5a shows the UV-curing profile of Mixture A, plotted as % remnant (liquid) monomer (from peak height measurements) *versus* UV-irradiation time. It is evident that HEMA cures more quickly in this mixture than it does as neat monomer (see Figure 7.2). This is partly due to the increased mobility in the system resulting from the addition of the glycerol diluent component. It has been suggested by Lai²⁵ that the increased rates of polymerisation observed are due also to a 'template effect', whereby hydrogen bonding between adjacent -OH groups in glycerol and C=O groups in HEMA better aligns neighbouring monomer units, facilitating free radical attack on

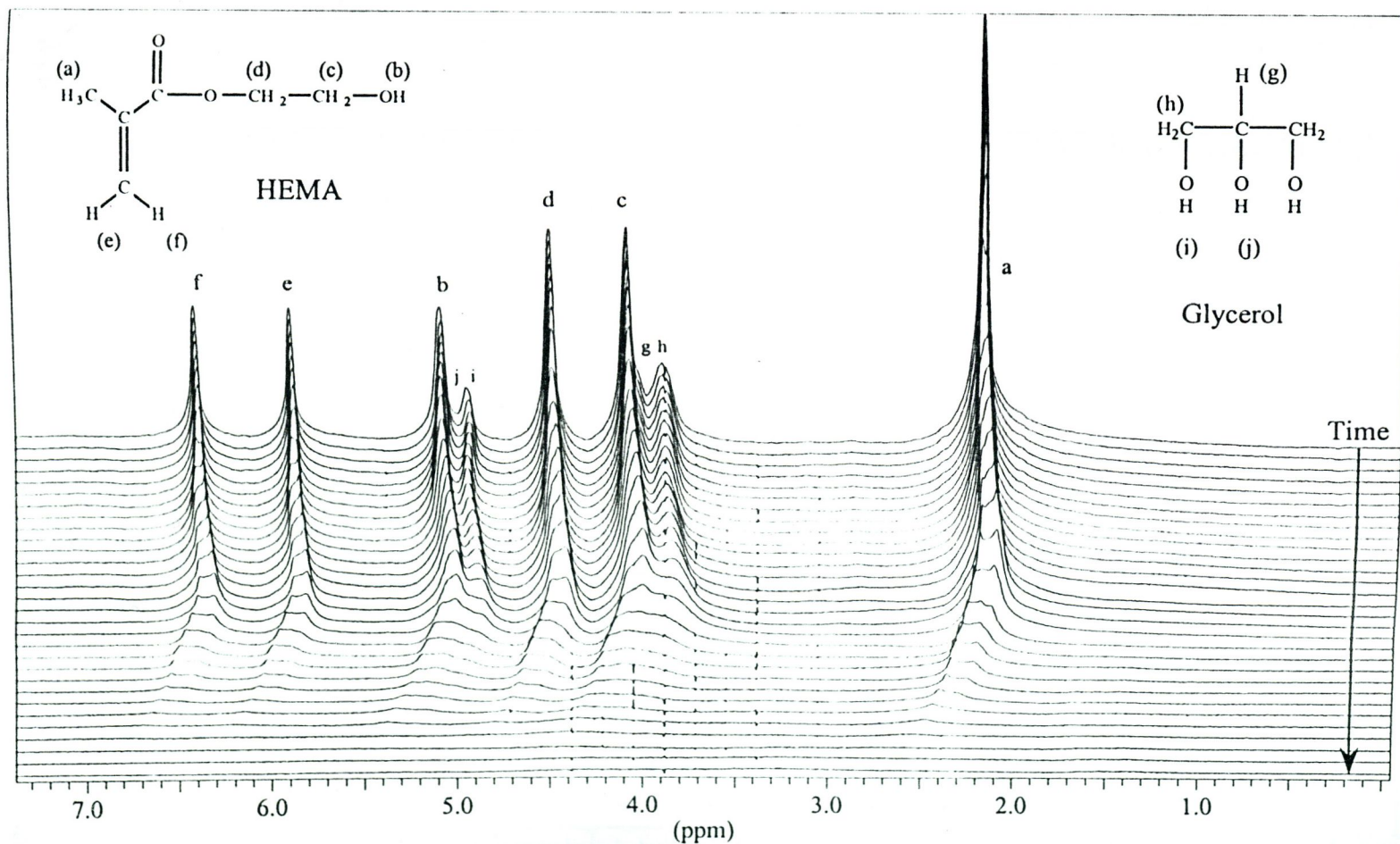
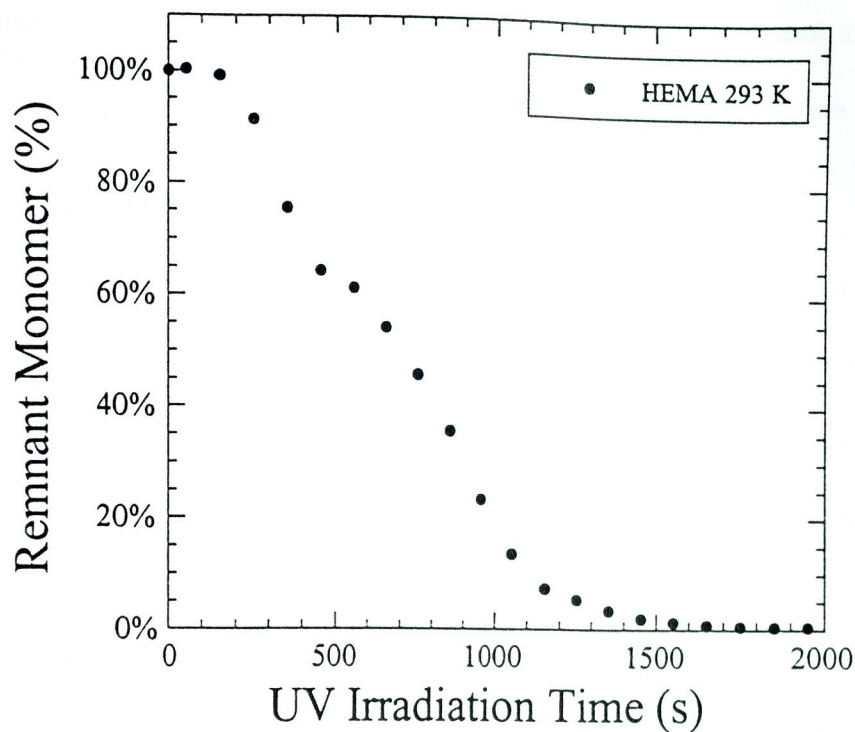


Figure 7.4. Overlaid ^1H NMR liquid spectra (293 K) from the UV-photoinitiated cure of Mixture A. Spectra were stored approximately every 30s during the curing cycle.

a)



b)

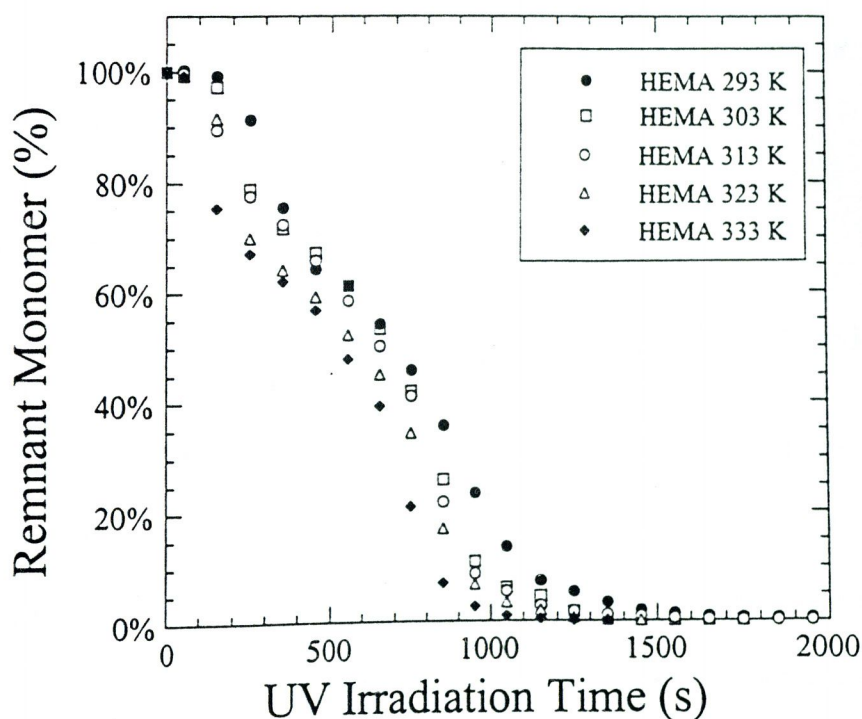


Figure 7.5. a) UV curing profiles of Mixture A in the form of remnant monomer as a function of curing time, as determined from peak intensity measurements in the ^1H NMR spectra. b) Data were recorded for the range of temperatures indicated.

the double bonds, and therefore speeding up the propagation step in the polymerisation process. The positive effect of the addition of glycerol in increasing the curing rates in these composite mixtures is further discussed in *Section 7.4*.

7.3.2.2 Cure Profile of Monomer Mixture A *versus* Temperature

Curing profiles constructed from these intensity data, in this case with temperature as an additional disposable parameter, are shown in Figure 7.5b. As expected, the curing rate progressively increases with increase in temperature from 293K to 333K. While it is recognised that it is possible to derive kinetic values for the rates of polymerisation from an appropriate treatment of the data from the first derivatives of these cure profile curves,³ the focus here is directed towards a study of the dynamics of cure of multi-component composite mixtures. Data for Mixture A, which is a single monomer component system, would only be of passing interest but for the fact that they validate the methodology and instil confidence in the overall reliability of the NMR approach.

7.3.3 Monomer Mixture B

7.3.3.1 Copolymerisation Reaction Profile of Monomer Mixture B and Comparison with Theoretical Simulation Results

NMR data for Mixture B are much more interesting in their ability to delineate the curing profile of each of the three monomer constituents in the composite system. Both the offset plot and the stacked plot of the multiple ¹H NMR spectra, recorded over a curing time of 4000 s and shown in Figures 7.6 and 7.7, respectively, clearly illustrate the progressive decay of peaks representative of NVP, HEMA and TBE as curing proceeds (293 K). The corresponding curing profiles (constructed from peak area measurements normalised to 100% at $t = 0$) are furnished in Figure 7.8. The

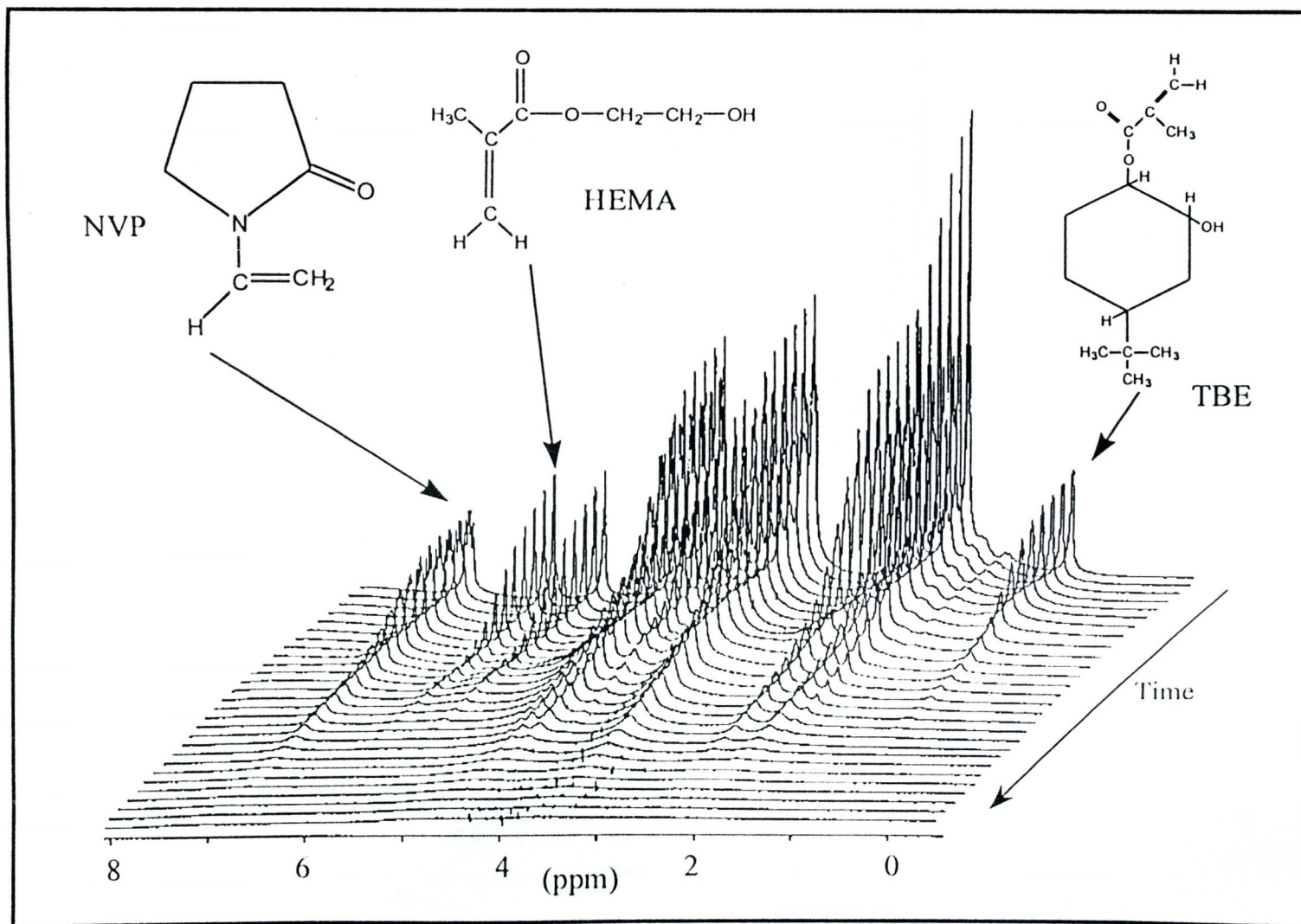


Figure 7.6. ^1H NMR liquid spectra from the UV-photoinitiated cure of monomer Mixture B (293 K).

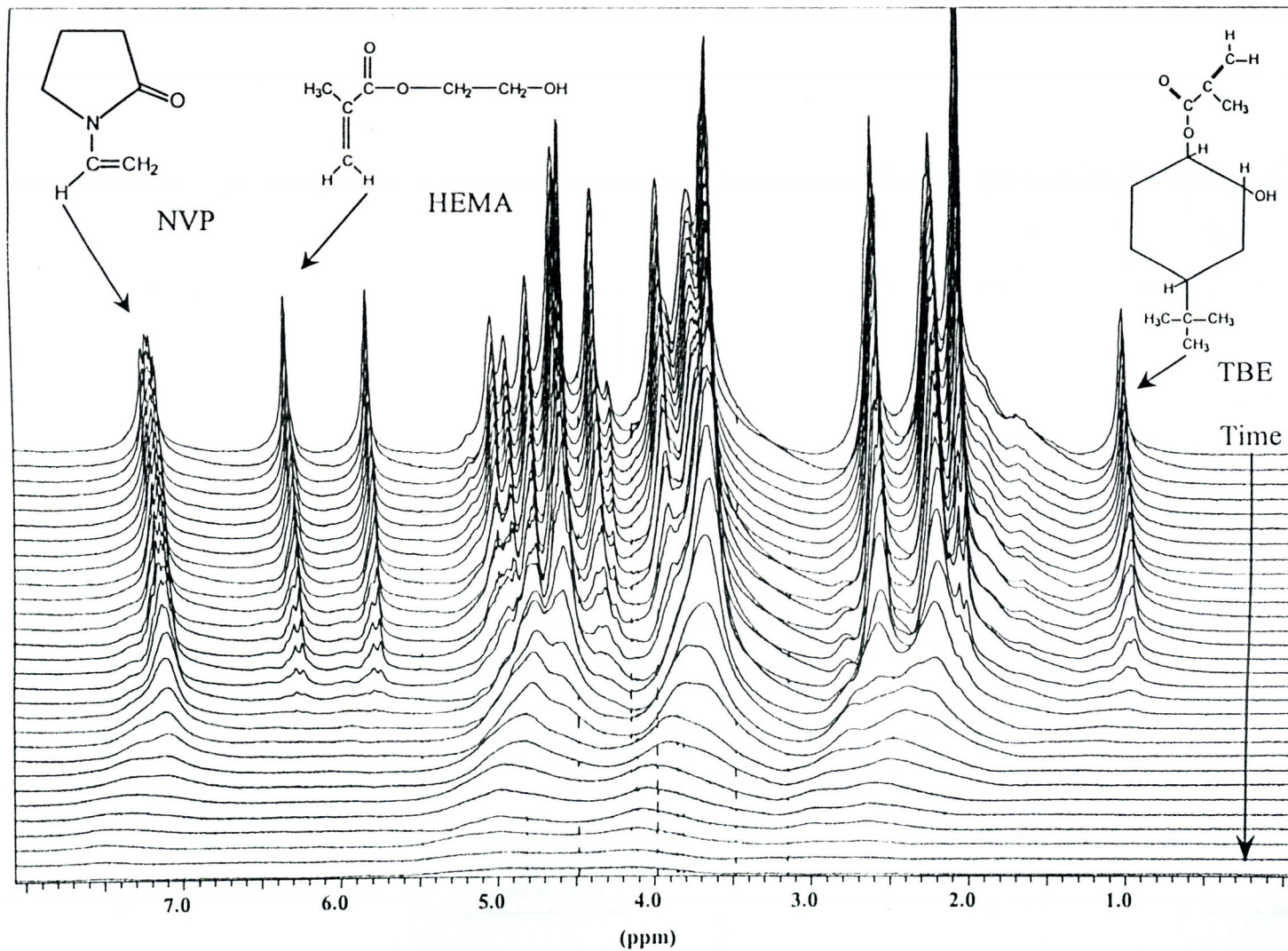


Figure 7.7. Overlaid ^1H NMR liquid spectra from the UV-photoinitiated cure of monomer Mixture B (293 K). Spectra were stored approximately every 30s during the curing cycle.

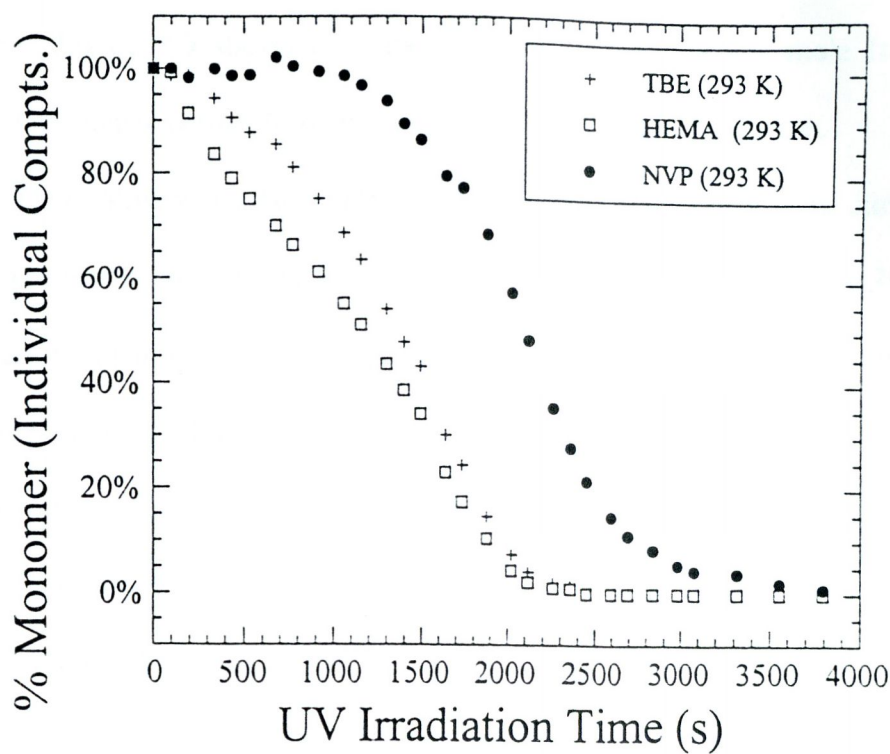


Figure 7.8. Curing profiles of the three constituent monomers in Mixture B as a function of UV-curing time (293 K).

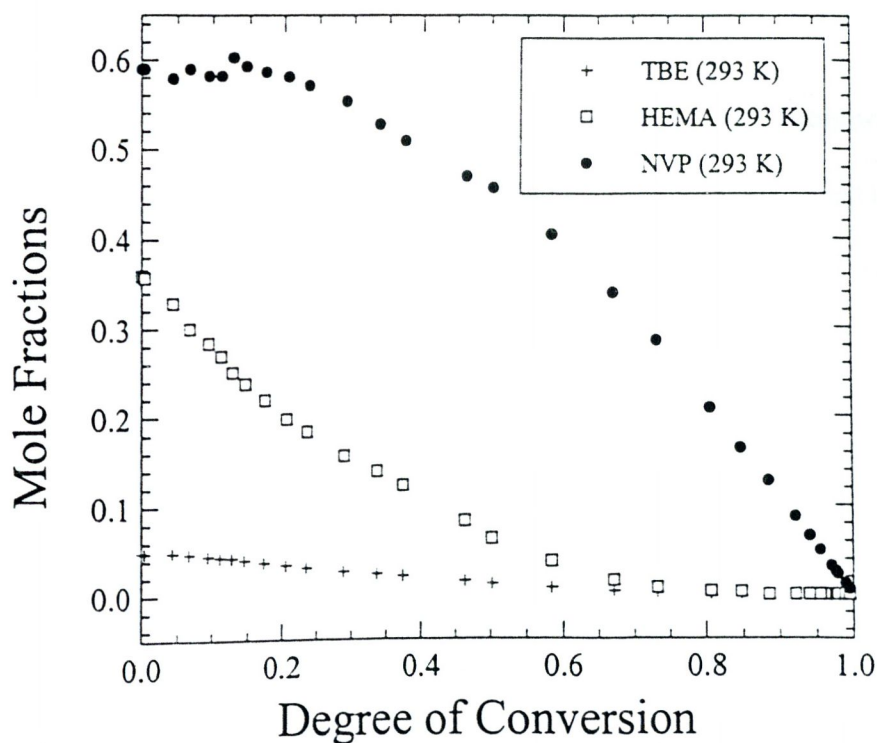


Figure 7.9. Mole fractions of the constituent monomers in composite Mixture B as a function of the instantaneous degree of conversion to copolymer.

differential rates of cure of the three monomers in this copolymerising system are evident. Figure 7.9 shows the data expressed in terms of the mole fractions of residual monomer *versus* the degree of conversion in the curing system.

Qualitatively, the data confirm earlier findings indicating that the curing rate in NVP accelerates once curing in HEMA and TBE approaches completion.²⁴ Though not readily apparent in either Figure 7.8 or 7.9, persistent oscillatory behaviour is observed in the profile of NVP over the initial *ca.* 700 s of UV irradiation. This parallels the initial rapid decay in the HEMA and TBE profiles within this initial time frame. Simulated profiles, calculated using the computer programme and based on the parameters listed in Table 7.2, are furnished in Figure 7.10a, to which the experimental data is compared in Figure 7.10b. A number of preliminary conclusions can be drawn from these results:

- Model calculations are in agreement with earlier two- and three-component simulations reported in the literature.²⁴
- The model predicts about 5% greater conversion of NVP monomer than is experimentally detected over the first half of the curing cycle. This can be due to a number of factors; an overestimate of NMR spectral peak areas, an under estimate of the amount of NVP monomer in the composite; or inaccurate *Q-e* values; Differences may also be technique-related in view of the significantly better agreement achieved between the model simulations and the FTIR data (*see Section 7.3.3.3*).
- In Figure 7.10b, a better fit with the experimental data could be achieved with a downward shift in HEMA monomer content which is in accord with the speculated increase in NVP content proposed above.

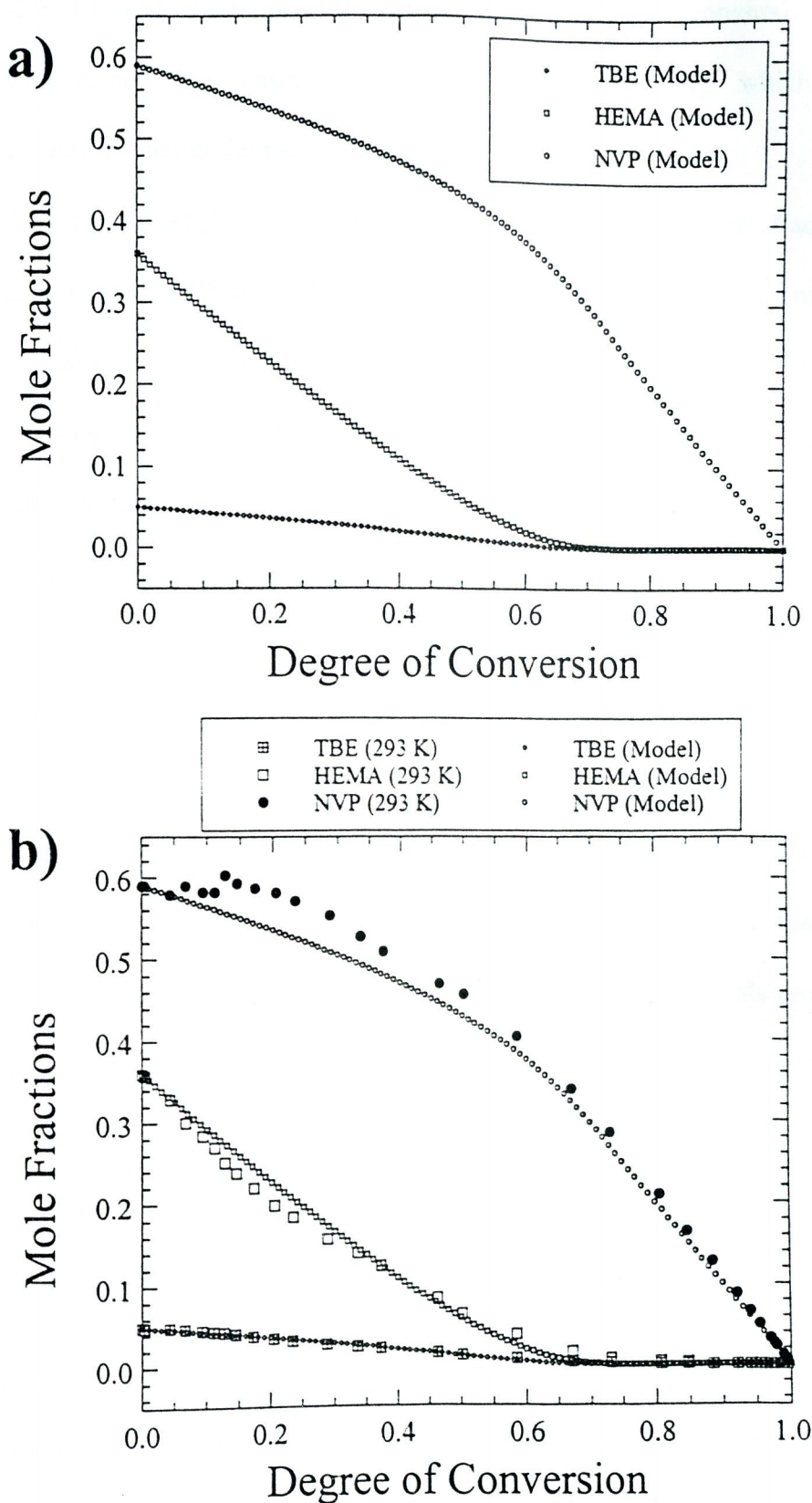


Figure 7.10. a) The results of the theoretical simulation based on Q - e values listed in Table 7.1, expressed in terms of mole fractions of the constituent monomers as a function of the instantaneous degree of conversion to copolymer for composite Mixture B. b) A comparison of the simulated data to the experimental data, recorded during the UV-cure of Mixture B as monitored with ^1H NMR spectroscopy.

- The observed retardation in the curing rate at the degree of conversion *ca.* 0.35 may herald the onset of diffusion controlled curing which is not accommodated in the model calculation.
- A probable explanation for the detection of higher mole fractions of unconverted NVP in the NMR experiments than is predicted by the model over the early stages of curing, may arise from the formation of shorter oligomers of polymer, which are still mobile enough to contribute to the liquid signal, and are therefore detected as residual uncured liquid monomer. This would also lead to calculated values for the instantaneous total degree of conversion that are underestimated, which would account for the apparent slight shift to the left in the first half of the plotted curing profiles for HEMA and TBE in Figure 7.10b.

These predominantly macroscopic features of the curing dynamics are now examined further in terms of the detailed information contained in the spectral lineshapes, which are influenced, among other things, by the free radicals produced by UV irradiation.²

7.3.3.2 ¹H NMR Chemical Shift and Linewidth Effects

Lineshape (and chemical shift) analysis provides a more microscopic picture of events at a molecular level. Figure 7.11 portrays the superimposed lineshapes of the three major monomer constituents in Mixture B recorded as a function of curing time (293 K). To facilitate interpretation of the rather convoluted dependence of the lineshapes on curing, the data are recast in the form of chemical shifts of resolved sub-peaks plotted as a function of curing time (Figures 7.12 through 7.14). Also reproduced in the plots are the curing profiles (dashed lines) along with the spectral

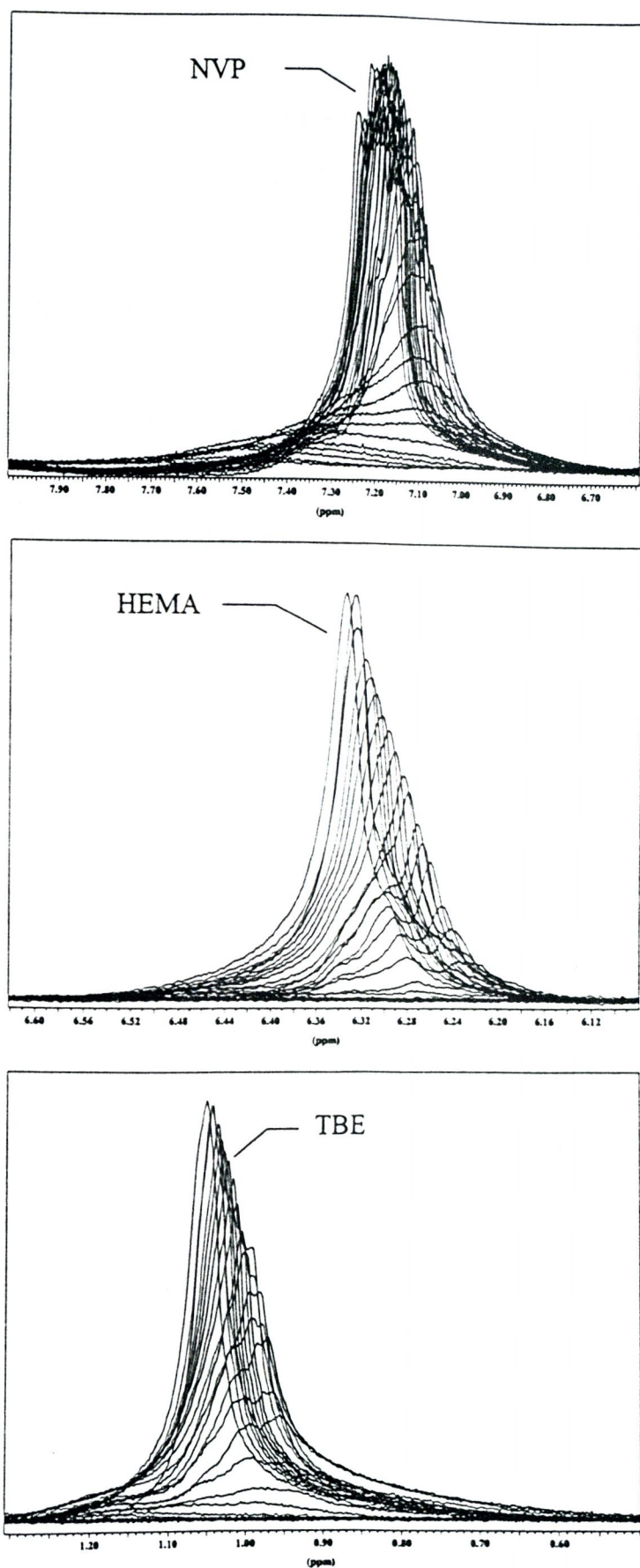


Figure 7.11. Overlaid NVP, HEMA and TBE ^1H NMR liquid spectral peaks recorded during the *in situ* UV-cure of composite Mixture B (293 K).

Mixture B

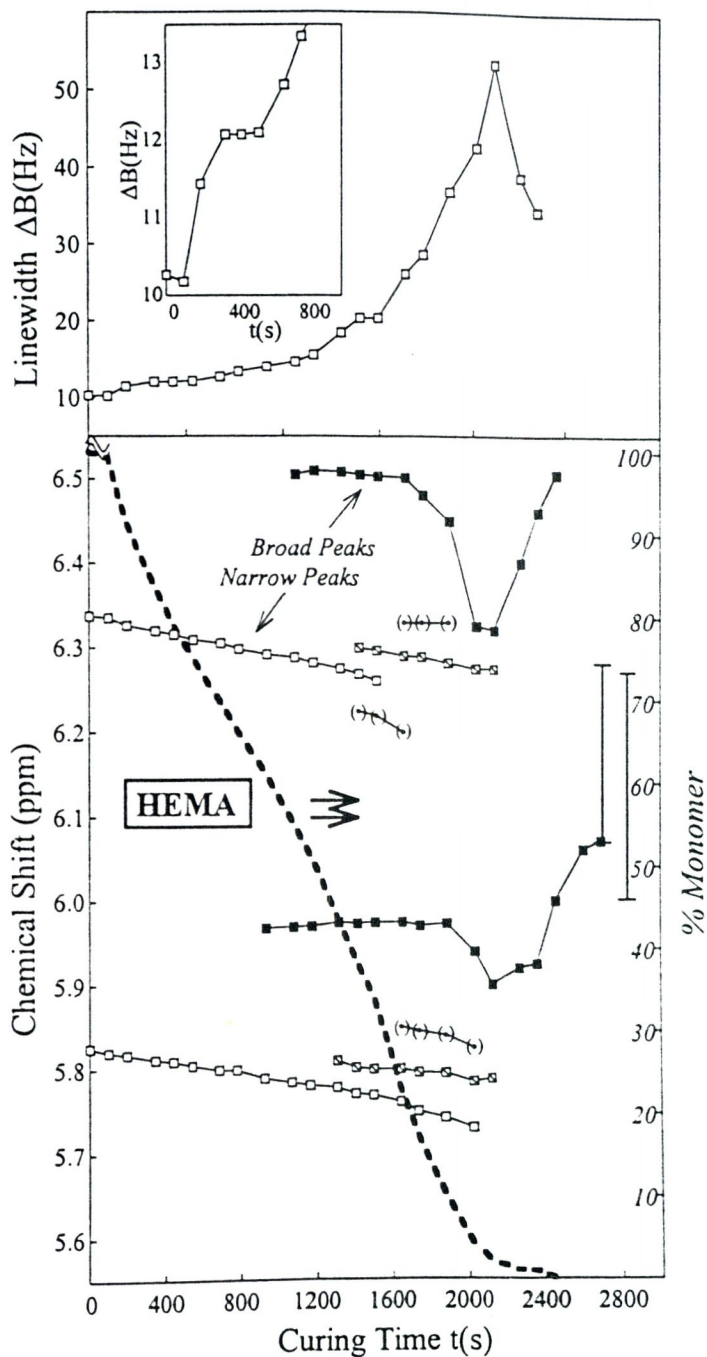


Figure 7.12. ^1H NMR chemical shift position (ppm) and peak linewidth (Hz) profiles of the HEMA component (peaks e and f) during the UV-photoinitiated cure of composite monomer Mixture B.

Mixture B

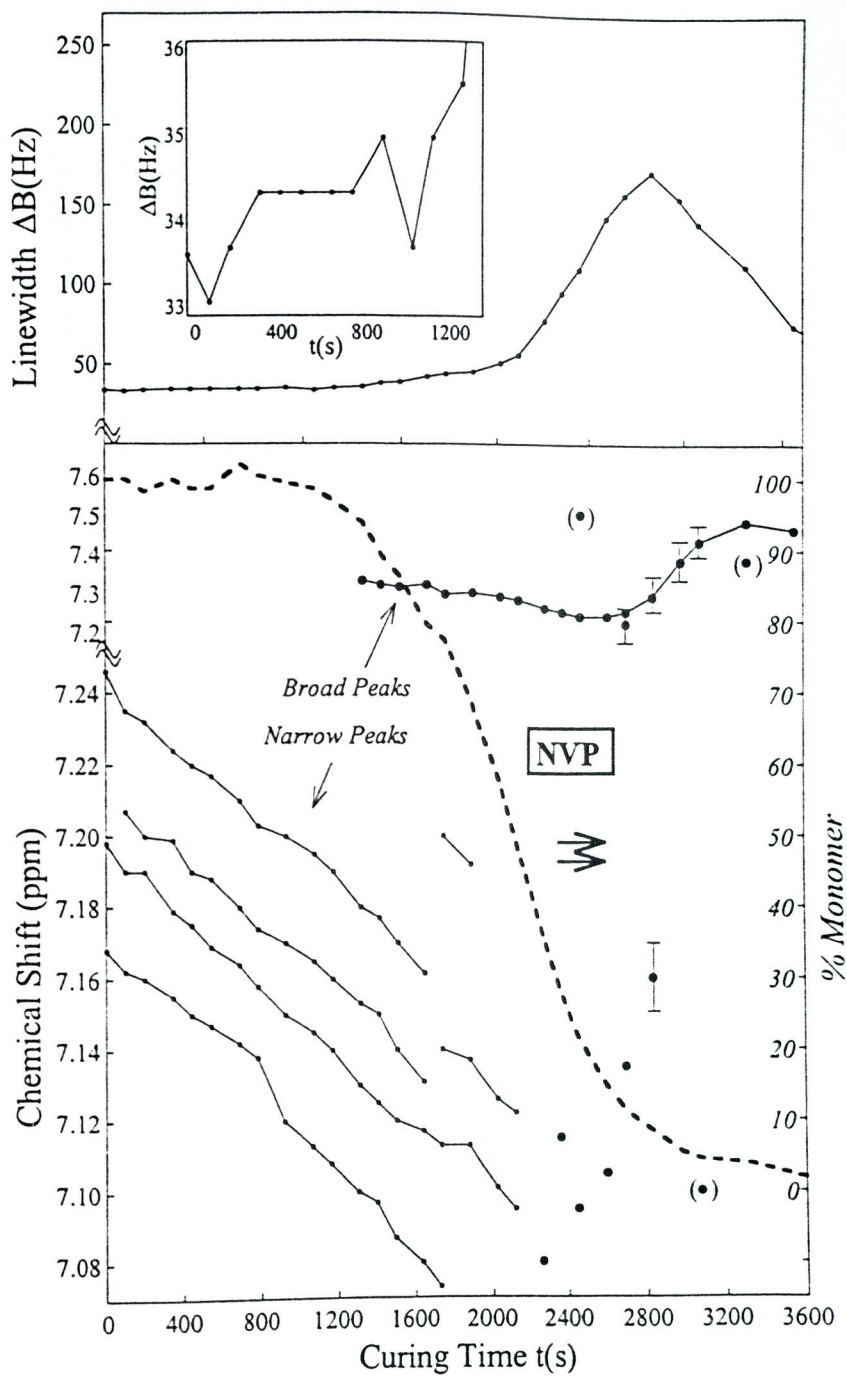


Figure 7.13. ^1H NMR chemical shift position (ppm) and peak linewidth (Hz) profiles of the NVP component (peak n) during the UV-photoinitiated cure of composite monomer Mixture B.

Mixture B

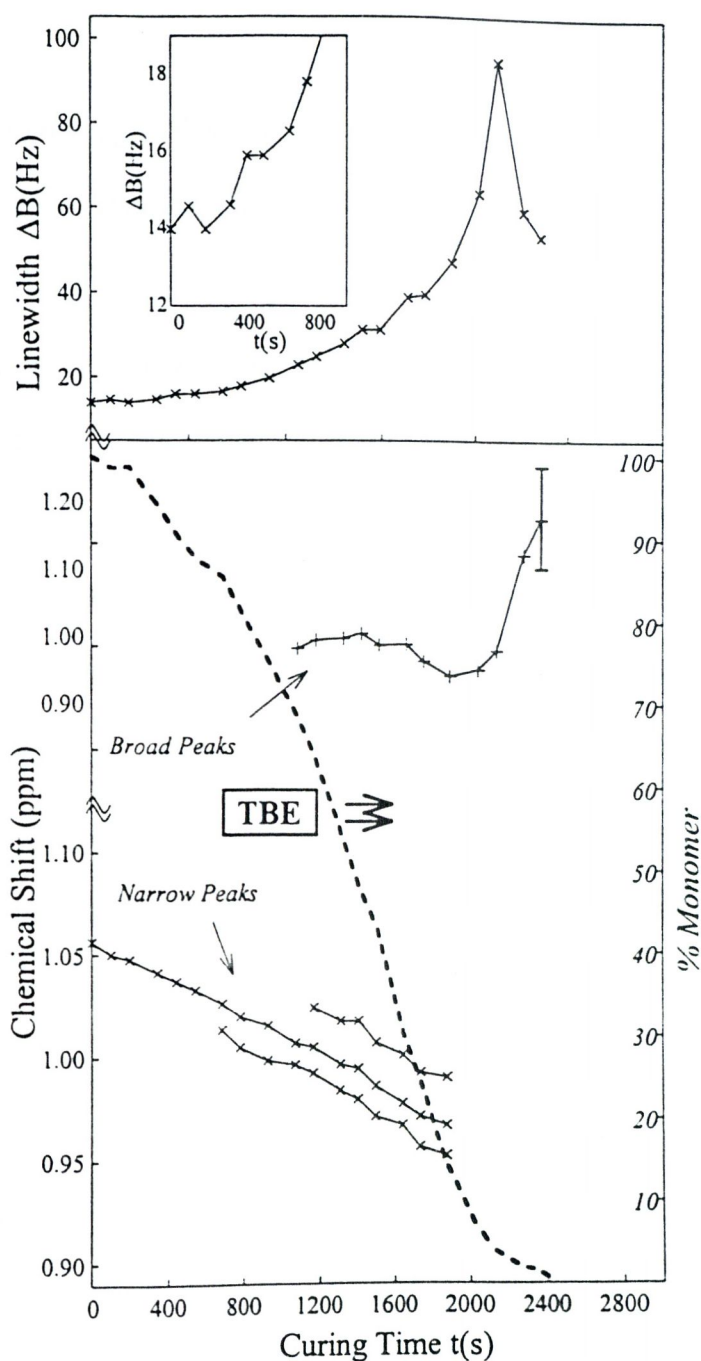


Figure 7.14. ^1H NMR chemical shift position (ppm) and peak linewidth (Hz) profiles of the TBE component (peak p) during the UV-photoinitiated cure of composite monomer Mixture B.

linewidths (ΔB) recorded as a function of curing time. The oscillatory dependence of ΔB on curing time in the initial phase of cure is included as an insert in each of the diagrams.

The following analysis of the response of the most complex, NVP, component creates an interpretational framework which also accounts for the responses of HEMA and TBE, components.

- There are a number of potential contributors to the observed oscillations in the initial part of the curing profile and the linewidth ΔB for $t \leq 700$ s: First, the dynamics of free radical generation and their subsequent influence on the NMR lineshape before being masked by the onset of larger scale effects due to the formation of oligomers of increasing length; second, the response to cure of superimposed constituent sub-peaks in the recorded NMR spectral lines, each exhibiting marginally different chemical shift behaviour with the progress of inhomogeneous polymerisation (see below); and third, the uniformity or otherwise of sample irradiation achieved and possible effects associated with the UV laser pulse rate of 20 Hz. A detailed analysis of these factors would require a further study involving a more focused series of experiments confined to the initial phase of the curing cycle. An immediate priority would be to quantify the free radical concentrations as curing proceeds using Electron Spin Resonance (ESR) and to carry out a more detailed analysis of lineshapes using model simulations.
- The coexistence of broad and narrow peaks for curing times in excess of 1300 s provides direct evidence of inhomogeneous cure in the composite monomer. Whether this is an inherent feature of the curing dynamics or is due to

experimental factors such as non-uniform UV irradiation of the sample will be the subject of further study, as discussed above.

- The decrease in linewidth ΔB and the concomitant increase in chemical shift at 85-90% conversion denotes the progressively dominant effect of remnant monomer and/or short oligomers that persist even to very long curing times. At this stage of nearly complete polymerisation, it is recalled that the contribution from the fully cured polymer far exceeds the bandwidth of the liquids probe and has been subsumed into the baseline.

An analysis of the overall pattern of chemical shift, linewidth and remnant monomer as a function of curing time is bound up with a comparison of the FTIR and NMR approach, as discussed in the section which follows.

7.3.3.3 Cure Profile of Monomer Mixture B by FTIR Spectroscopy: Comparison with NMR

Details of the experiments to measure the dynamics of the *in situ* UV-cure profiles of these composite monomer systems using Fourier transform infrared spectroscopy (FTIR) techniques have been described in *Chapter 6*. Figure 7.15 shows the UV-cure profiles of NVP and HEMA monomers in Mixture B measured in this way. The ability to monitor the conversion of TBE to copolymer was precluded due to its low concentration and the absence of a characteristic, well-resolved vinylidene bond absorption band in the IR spectra. The system was therefore treated as a two-component mixture of NVP and HEMA, and the reported values for their mole fractions were adjusted upwards to 0.62 and 0.38, respectively. Figure 7.16 shows the measured FTIR UV-curing profile of Mixture B re-plotted appropriately. The simulated curing profiles for NVP and HEMA, calculated using the computer programme based on the adjusted mole fraction values and the same $Q-e$ values as

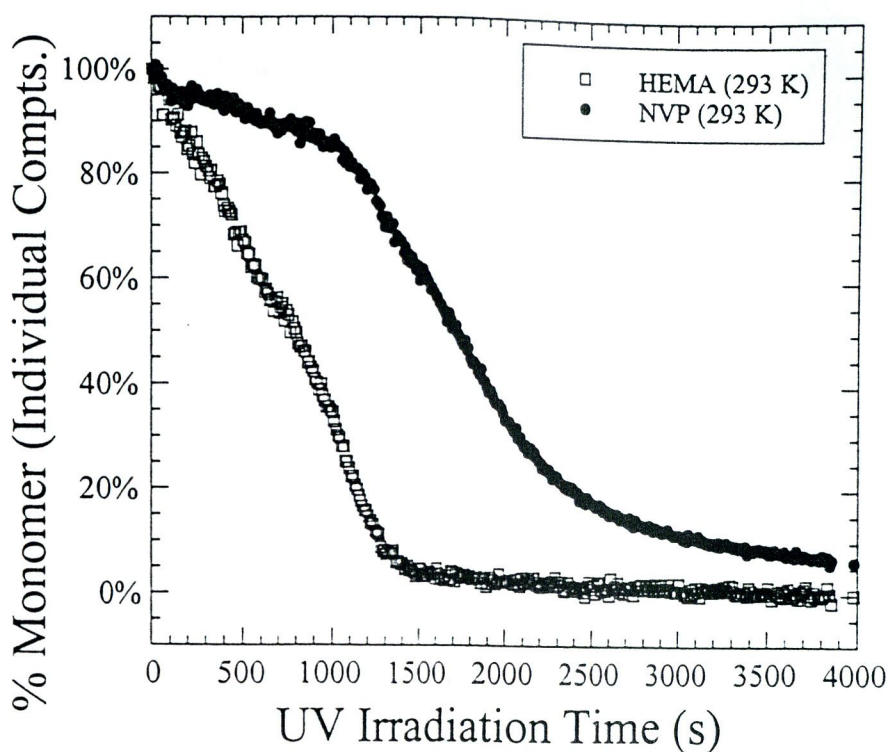


Figure 7.15. Curing profiles of NVP and HEMA in composite Mixture B (293 K) as measured using FTIR spectroscopy (*see Chapter 6*).

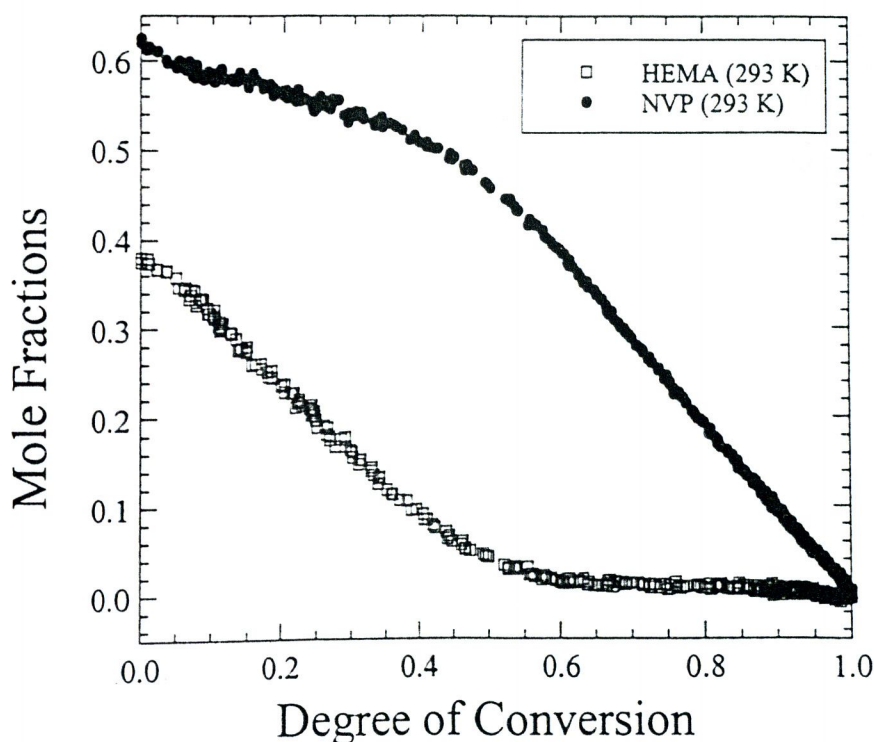


Figure 7.16. UV-curing profile of NVP and HEMA in composite Mixture B as measured using FTIR spectroscopy, expressed in terms of the mole fractions* of the constituent monomers as a function of the instantaneous degree of conversion to polymer (* *see text*).

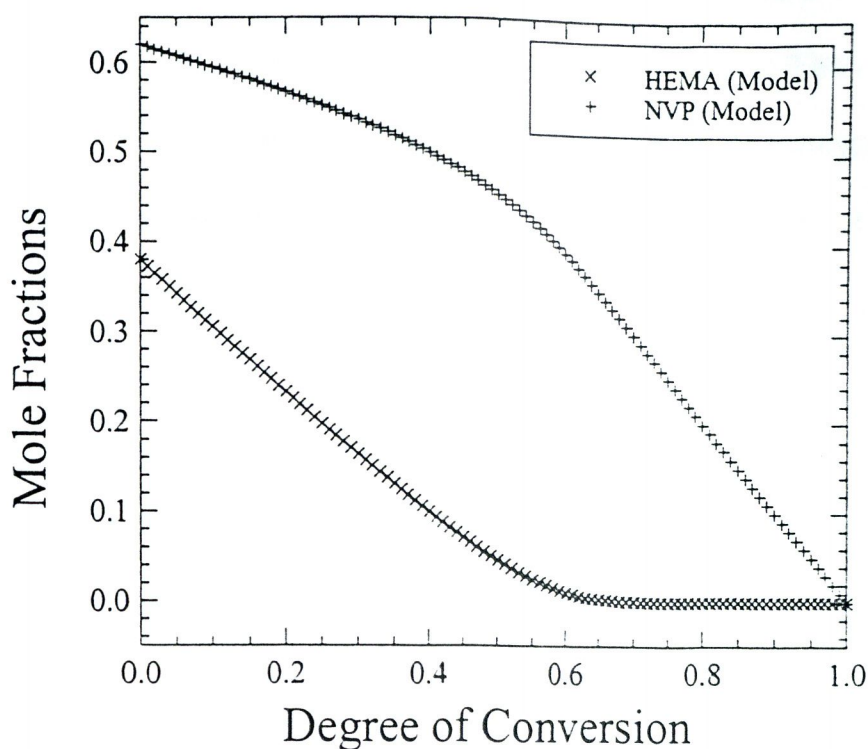


Figure 7.17. Simulated curing profiles of NVP and HEMA in composite Mixture B based on a 2-component model (*see text for details*). (Q - e values: NVP: $Q = 0.14$, $e = -1.14$; HEMA: $Q = 0.80$, $e = 0.20$).

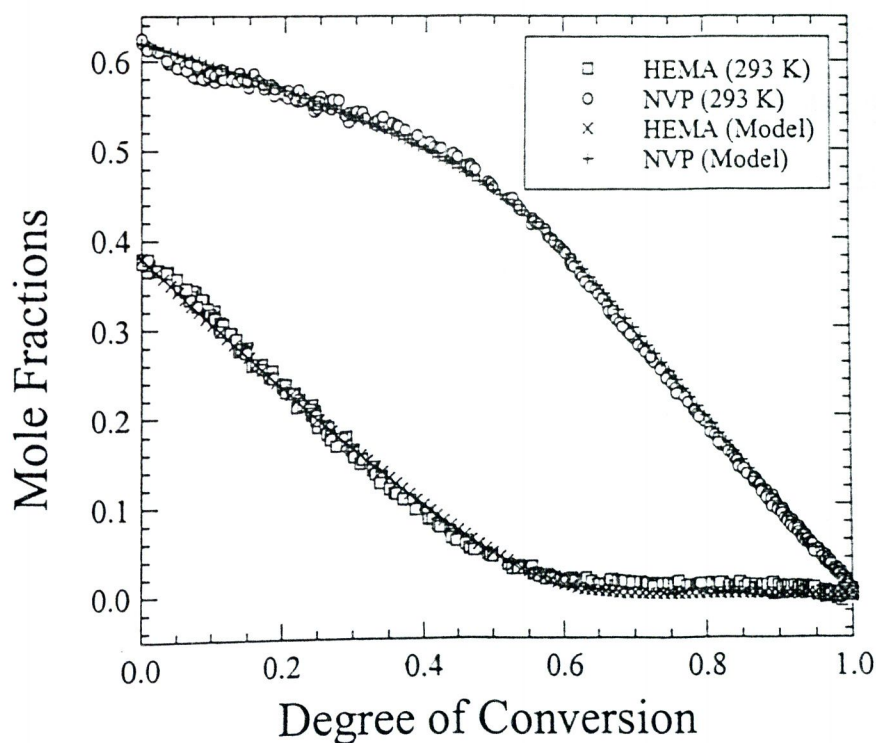


Figure 7.18. FTIR experimental UV-curing profiles of NVP and HEMA in composite Mixture B (293 K) *versus* the simulated curing profiles (based on a 2-component model- NVP: $Q = 0.14$, $e = -1.14$; HEMA: $Q = 0.80$, $e = 0.20$).

before, are furnished in Figure 7.17, to which the experimental data is compared in Figure 7.18. Since TBE cures at a rate that is intermediate between HEMA and NVP, its omission contributes to the slight overestimate of NVP curing rate and underestimate of HEMA curing rate in the model calculation. However, it is evident that the simulated data are otherwise in excellent agreement with the experimental FTIR UV-curing data for NVP and HEMA in Mixture B.

Casual inspection of Figures 7.15 and 7.8 reveals clear differences in the shape of the curing profiles of Mixture B as monitored by FTIR and NMR, respectively. Due to differences in the experimental configurations, the FTIR sample received a greater UV-light intensity than the NMR sample and cured more quickly as a result. However, it is the relative cure dynamics (i.e. the shapes of the cure profiles) rather than the kinetics (speed of cure) of these systems that primarily concern us here. Differences are most noticeable in the initial stages of cure; within the first *ca.* 1000 s, FTIR records a slow but progressive rate of cure in NVP whereas, in the case of NMR, the observed depletion of remnant liquid monomer is barely noticeable. Note also in this time regime that the NMR chemical shift of sub-peaks decreases almost linearly while linewidth ΔB changes very little (Figures 7.12 through 7.14).

To understand these differences, recall that FTIR monitors the depletion of C=C bonds *via* the progressive loss in intensity of the curing-sensitive bands listed in Table 6.2; this is the key first step in the polymerisation process. NMR linewidths, on the other hand, discriminate between liquid monomer and solid polymer on the basis of their characteristic motional correlation frequencies relative to the bandwidth of the probe (*ca.* 4 kHz), which establishes the cross-over frequency from liquid to solid in this experiment. Material with a correlation frequency greater than 4 kHz is deemed to be liquid-like (or a gel); material with correlation frequencies lower than 4 kHz is

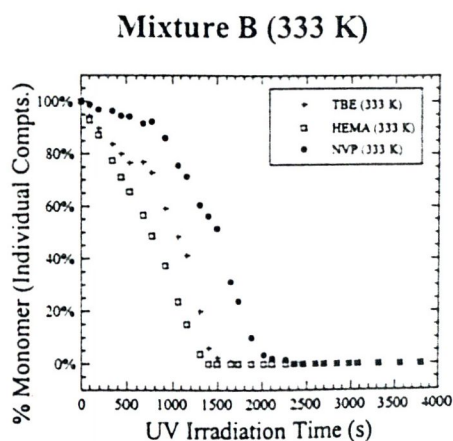
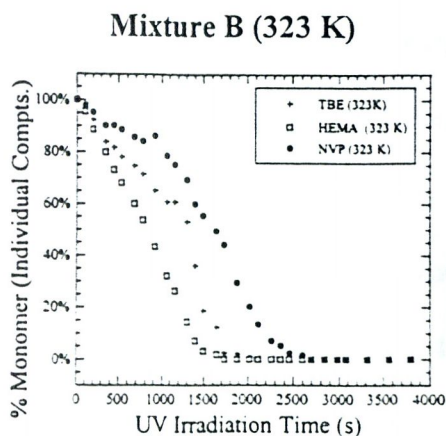
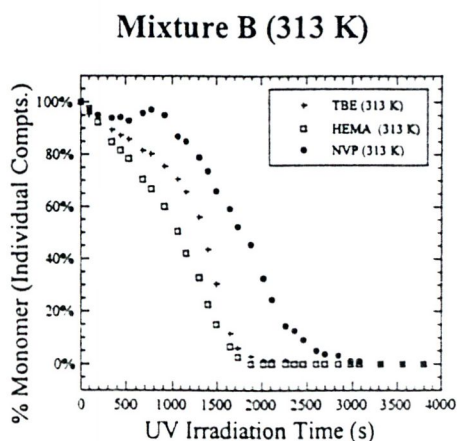
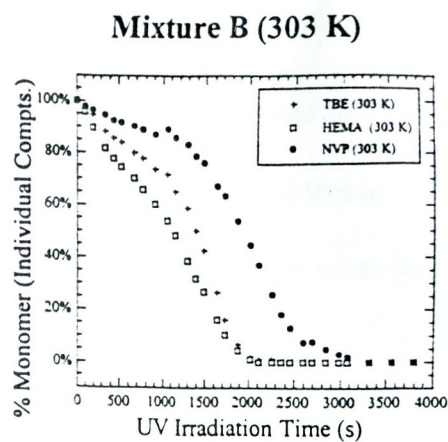
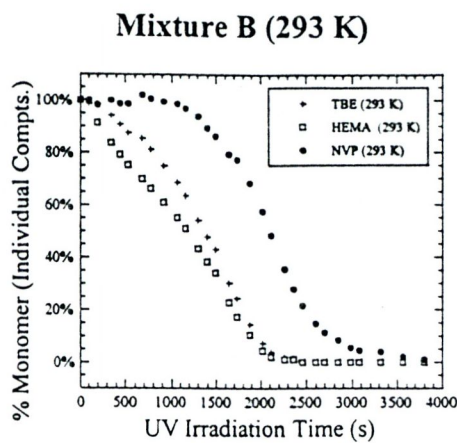
considered to be solid polymer and no longer contributes to the observed spectral peak.

Chemical shifts of resonant nuclei are sensitive to their immediate environment and, in this respect, are a closer analogue, in the context of curing, to the FTIR response. Thus, both NMR chemical shifts and FTIR manifestly respond to the depletion of C=C bonds and the consequent formation of short oligomers which still retain a liquid-like mobility within the parameters of the NMR experiment, thereby leaving the NMR linewidths and perceived remnant monomer levels reasonably invariant. This is in keeping with the observed behaviour in Figures 7.15 and 7.8.

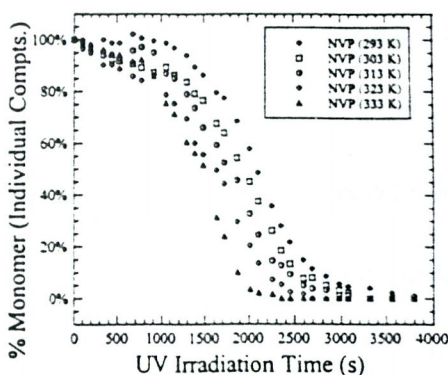
In summation, the FTIR spectroscopic curing experiments directly monitor the actual conversion of monomer double bonds, whereas the NMR curing experiments, where spectral responses to changes in molecular motions are recorded, can only reflect the extent of monomer converted to polymer with motional correlation frequencies of 10^3 Hz or less. Representation of curing dynamics is, in one way or another, technique-dependent. However, the unique worth of the NMR experiments lies in their ability to monitor the cure profiles of multiple components in the composite systems, even when present at fairly low concentrations, due to the superior spectral resolution achievable using this technique.

7.3.3.4 Cure Profile of Monomer Mixture B *versus* Temperature

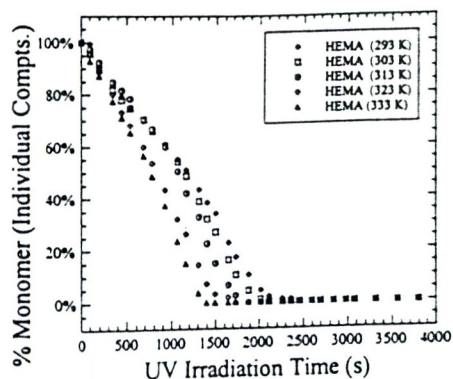
Liquid NMR UV-curing profiles of the three main monomer components of Mixture B were recorded over the temperature range of 293 K to 333 K, as an aid in further elucidating the cure behaviour of the mixture, in order to develop and refine practical manufacturing protocols for high quality lenses produced from this composite material. Figure 7.19 shows five UV-curing profile plots, recorded at 10 K



NVP in Mixture B (293 K to 303 K)



HEMA in Mixture B (293 K to 303 K)



TBE in Mixture B (293 K to 303 K)

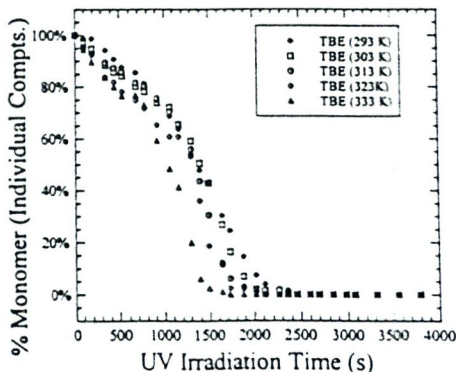


Figure 7.19. UV-cure profiles of composite Mixture B and the individual monomer components over the temperature range of 293 K to 333 K.

intervals over this temperature range, and also three composite plots of the measured temperature behaviour of the individual NVP, HEMA and TBE monomers in Mixture B. As expected, the curing rate of each component monomer is observed to increase progressively with increase in temperature.

7.3.3.5 Cure Profile of Monomer Mixture B by ^{13}C NMR

^{13}C NMR liquid spectroscopy experiments were also conducted to examine the UV-curing profile of Mixture B. The inverse gated pulse sequence (*Chapter 3.2.1.2*) was used to suppress selective peak enhancements due to the NOE effect and thereby ensure the quantitative nature of the spectral information. Assignments for all of the peaks in the ^{13}C NMR spectrum of Mixture B are provided in Figure 4.18. Figure 7.20 shows a stacked plot of the ^{13}C NMR spectra collected during an *in situ* UV-curing experiment (293 K), with characteristic peaks for NVP and HEMA indicated, and the measured peak intensity data are plotted against time in Figure 7.21. The data are broadly comparable to the findings of ^1H NMR experiments. The longer T_1 relaxation times for ^{13}C nuclei impose significantly longer pulse recycle delay times, which means that fewer spectra, even when obtained with a minimum number of scans, can be collected over the course of a cure process. The low natural abundance of ^{13}C , combined with a lack of opportunity for co-addition of multiple scans within the curing time-frame of the sample, results in the spectra recorded having poor signal to noise ratios and the errors associated with peak intensity measurements in the cure profile plots are correspondingly large. These limitations place severe constraints on the reproducibility and ultimately on the usefulness of such ^{13}C NMR measurements, particularly for monitoring curing processes that occur over a time-frame of less than a few hours.

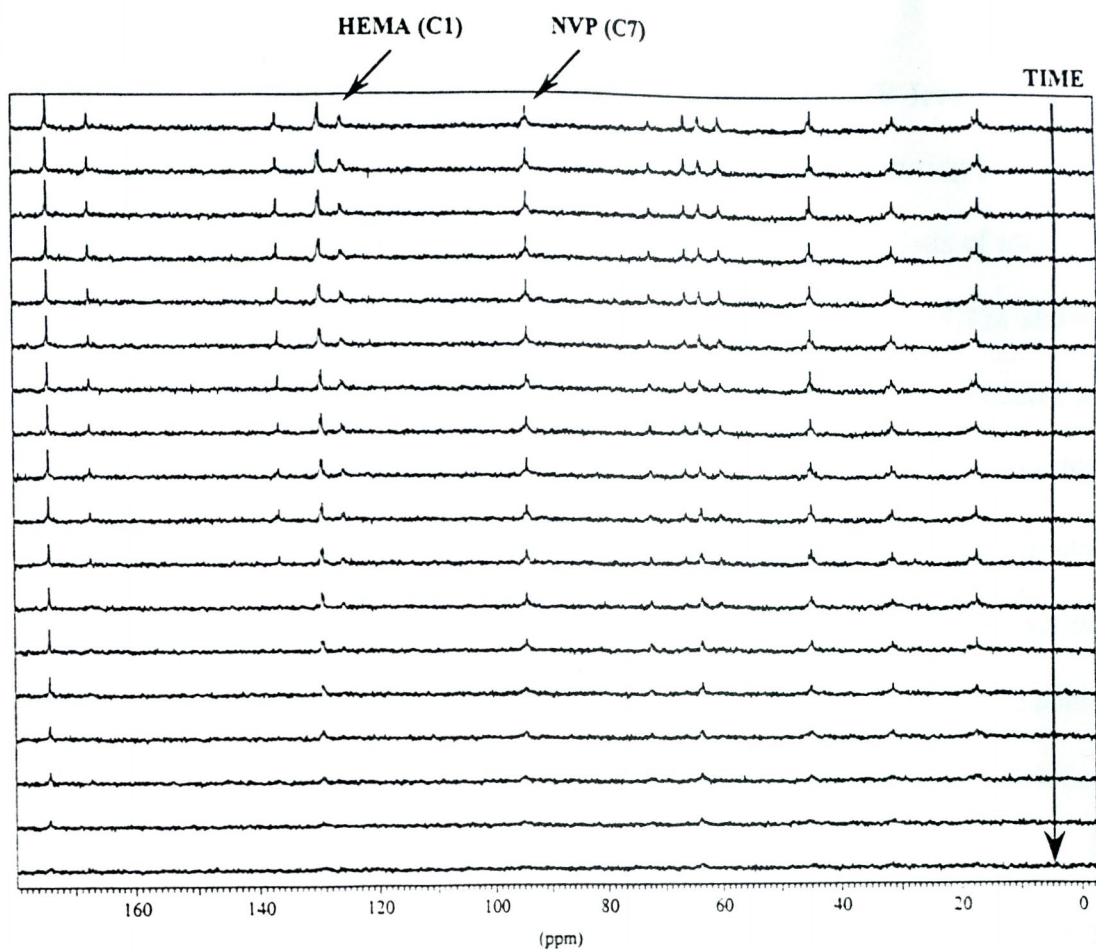


Figure 7.20. Overlaid ^{13}C NMR liquid spectra (293 K) from the UV-photoinitiated cure of composite monomer Mixture B.

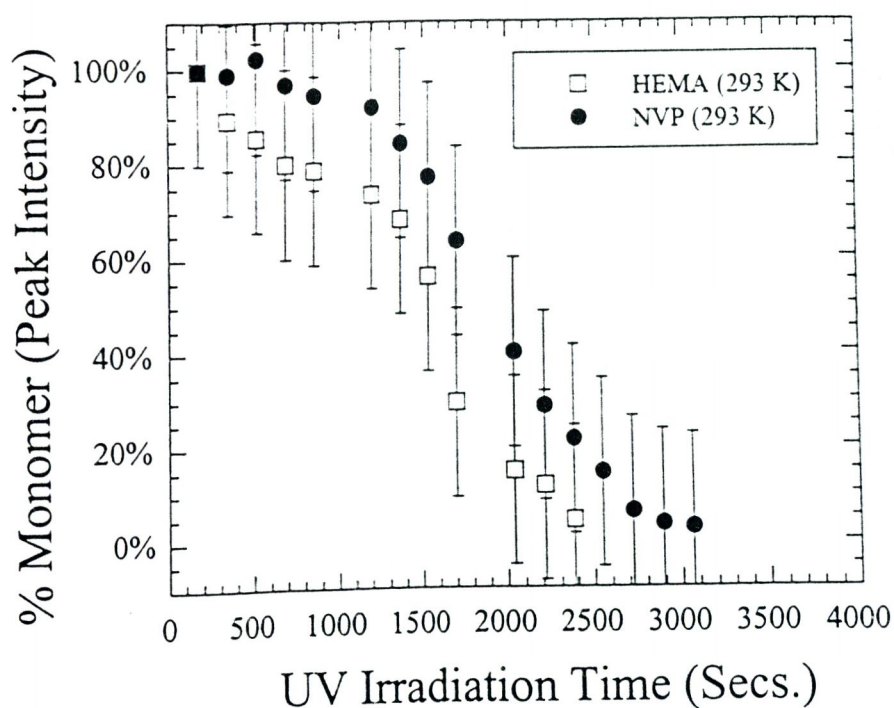
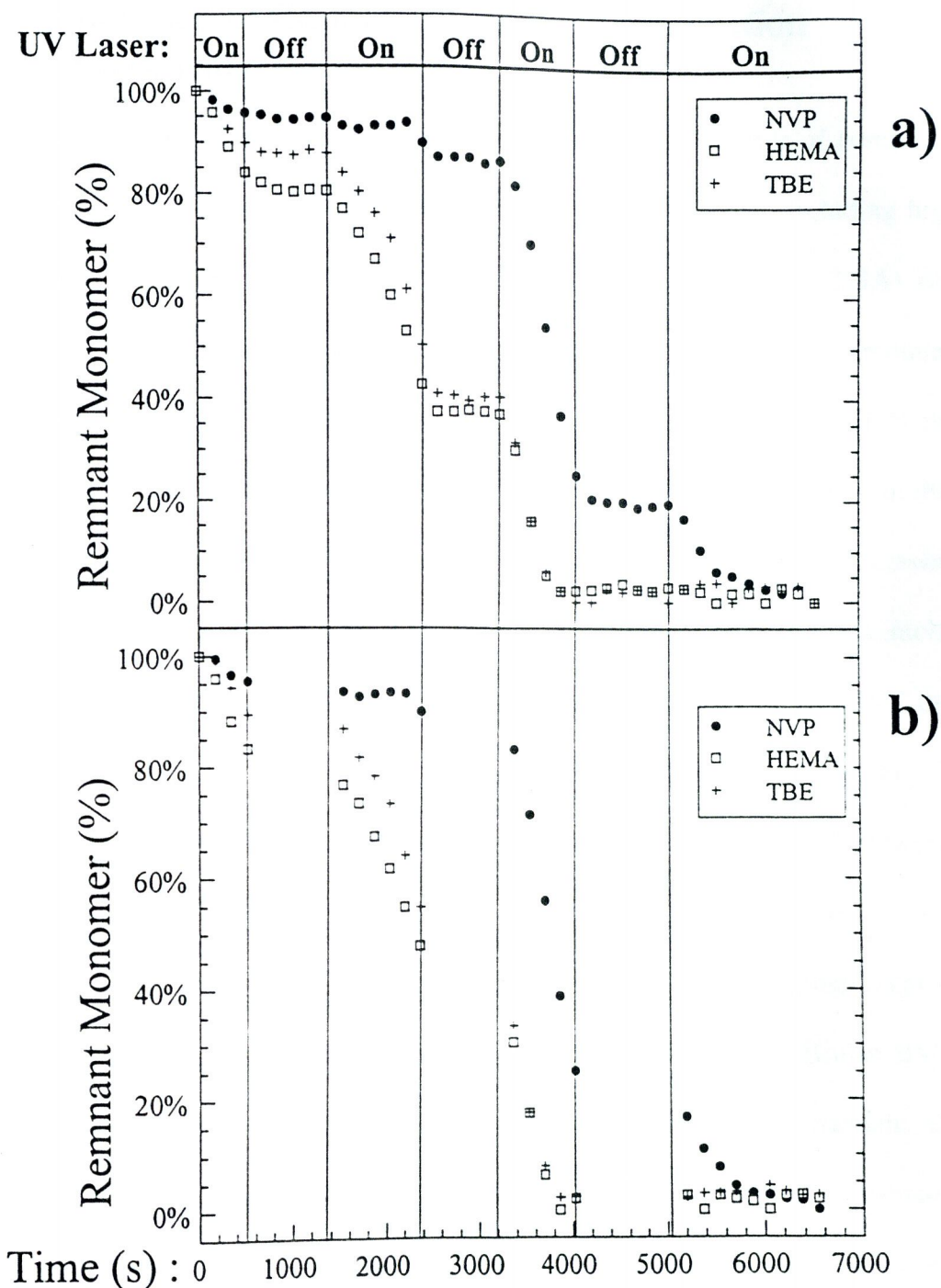


Figure 7.21. Curing profiles of HEMA and NVP in Mixture B as a function of UV-curing time (293 K) determined from ^{13}C NMR measurements. The large errors arise from poor signal to noise ratios in the spectra.

7.3.3.6 Cure Profile of Monomer Mixture B with Intermittent UV-Irradiation

Liquid ^1H NMR spectroscopy was used to record the *in situ* curing profile of composite Mixture B, while the sample was exposed to alternating periods of incident UV light and total darkness within the modified CIDNP probe. Figure 7.22a shows the resulting intermittent cure profile with the light exposure conditions indicated at the top of the plot. A continuation of cure during the 'dark' periods, most noticeably in the time periods immediately after cessation of illumination, is observed, albeit at a greatly reduced rate. It may be that the exothermic UV-photoinitiated polymerisation process generates enough local heat energy in the sample to continue to produce some free radicals by thermolysis (rather than by photolysis) of the initiator in the absence of UV-light; or it may be an inherent feature of the curing dynamics.¹²

The experiment was repeated with the inclusion of short inversion recovery experiments (*see Chapter 5*) recorded during the periods of darkness, to approximately measure the changes in the ^1H spin-lattice (T_1) relaxation times of each of the components over the course of the UV-curing process (Figure 7.22b). The results of these measurements for each component are tabulated in Figure 7.22c. The data clearly indicate a decrease in T_1 relaxation times with progression of cure, resulting from an increased hindrance to molecular mobility as system first gels and then solidifies. These results may provide a means of optimising experimental acquisition parameters: the progressive reduction in relaxation times means that the pulse recycle delay time may be appropriately shortened over the curing process, permitting the collection of a greater number of spectral scans or of more individual spectra within the same time period.



c)

	$T_1(s)$		$T_1(s)$		$T_1(s)$		$T_1(s)$
NVP	1.25		1.07		0.61		0.42
HEMA	0.51		0.44		0.35		---
TBE	0.22		0.21		0.20		---

n.b. T_1 values have an associated error of approximately $\pm 30\%$.

Figure 7.22. The curing profile of composite Mixture B was recorded (a) while the sample was illuminated intermittently with UV light. The experiment was then repeated (b) with ^1H spin-lattice (T_1) relaxation times recorded for each of the monomer components of the curing mixture (c) during the periods when no UV light was incident on the sample.

7.4 Experimental Results: Thermal Polymerisation Experiments

Experiments to examine the thermally initiated cure behaviour of composite monomer Mixtures H, I and J exploited thermal analysis techniques, including high temperature ^1H NMR liquid spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). While monomer Mixture H was formulated for this study out of academic interest, Mixture I and J are currently used in the manufacture of commercial contact lenses. The systems differ in composition in that Mixture J contains glycerol (10% by weight), which acts as a diluent and a processing aid, whereas Mixture I does not (Table 4.1), but they otherwise consist of equimolar ratios of the active monomer components (Table 7.1). Trace amounts of IMVT dye added to Mixture I do not effect the thermal cure behaviour of the system. A comparison of cure behaviour of these two systems therefore reveals the influence that the addition glycerol has on the thermal polymerisation profile of the mixture.

The higher temperatures used to thermally initiate the *in situ* polymerisation of the samples in the NMR probe were achieved and maintained with the Bruker BVT-1000 temperature controller unit. While this arrangement could maintain the temperature in the sample area of probe to within ± 1 K, minor temperature fluctuations at the higher temperatures produced larger variations in the measured spectral response, which resulted in relatively 'noisier' thermal cure profile plots than those obtained from similar experiments to measure the UV-photoinitiated cure profiles of the composite monomer mixtures at room temperature.

7.4.1 Copolymerisation Reaction Profile of Monomer Mixture H and Comparison with Theoretical Simulation Results

Liquid ^1H NMR spectroscopy was used to examine the *in situ* thermally initiated curing profiles of NVP, HEMA and TBE monomers in the composite Mixture H at 343 K. Figures 7.23a and 7.23b show offset and overlaid images of the successively acquired spectra from the thermal cure experiment. The cure profiles, measured from the integrated peak areas and plotted as % (residual) monomer against curing time are shown in Figure 7.24. A noticeable change in the curing behaviour of NVP is again evident beyond 600 seconds once the HEMA and TBE components approach completion. Figures 7.25 and 7.26 indicate the corresponding comparison between theory and experiment. Comparably good agreement is achieved, indicating that the simulated thermal cure profiles still match the experimental data reasonably well at this elevated temperature in Mixture H.

7.4.2 Thermal Cure Profiles of Monomer Mixtures I and J

Figures 7.27a and 7.27b show offset views of the multiple spectra collected during the ^1H NMR thermal curing profile measurements of *in situ* polymerisations (333 K) of Mixtures I and J, respectively. Experiments were conducted at a number of selected temperatures between 333 K and 383K as part of a study to develop and refine a practical manufacturing protocol for high quality lenses. The effect of applying a 'thermal ramp' heating procedure was also investigated, whereby the curing temperature was raised from 338 K to 373 K at a rate of 1 K per minute, and then held isothermally at 373 K for a 2 hour 'post cure' period. Figures 7.28a and 7.28b show the thermal curing profiles of NVP and HEMA, cured at 333 K, 343 K and under 'thermal ramp' conditions, in Mixtures I and J, respectively. A number of conclusions can be drawn from these cure profiles:

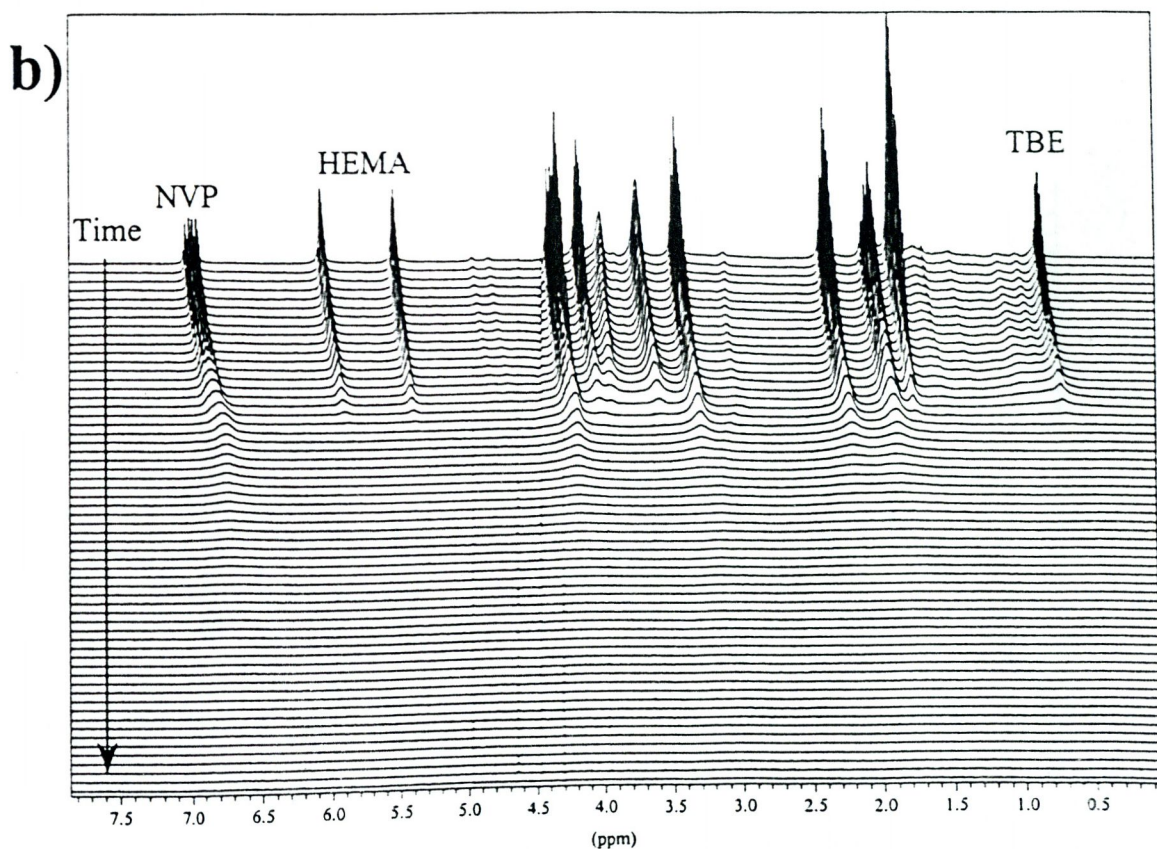
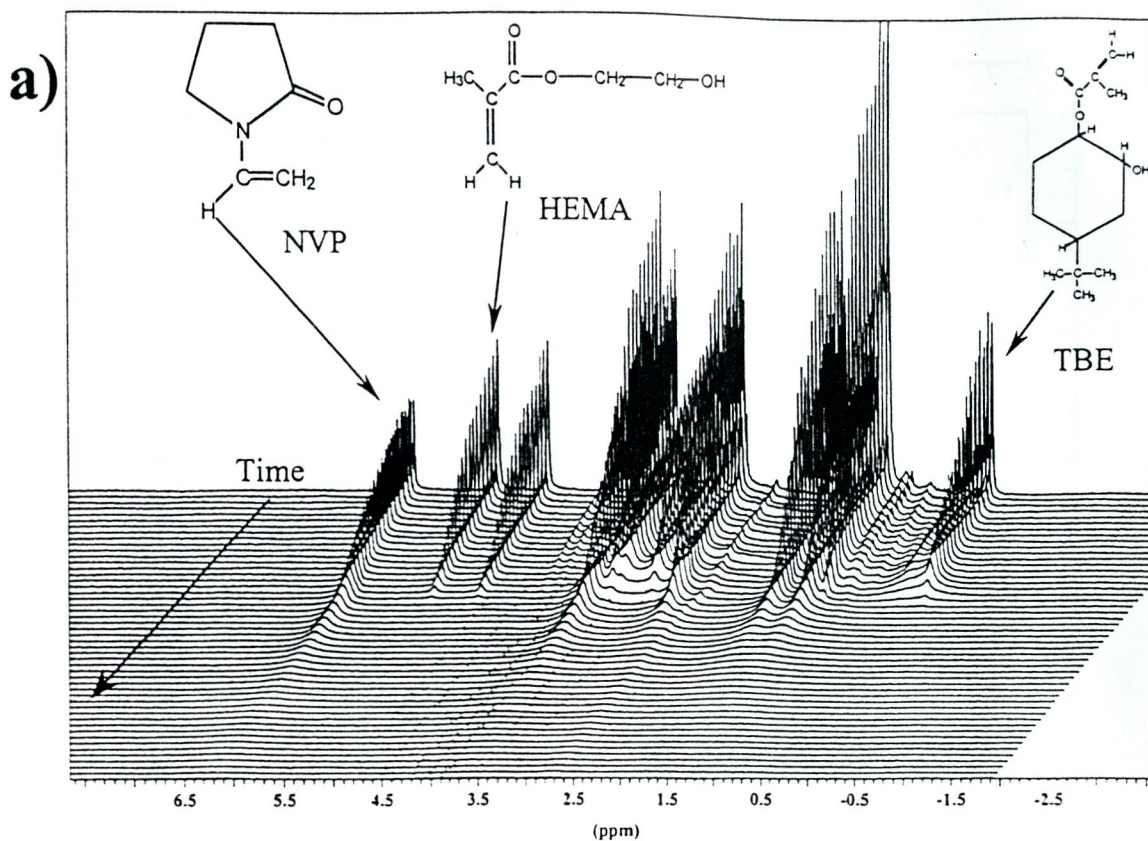


Figure 7.23. The *in situ* ^1H NMR curing profile of the thermally initiated cure (343 K) of the composite monomer Mixture H, shown with successively acquired spectra (a) offset and (b) overlaid, illustrating the spectral changes recorded over the course of the thermal polymerisation process.

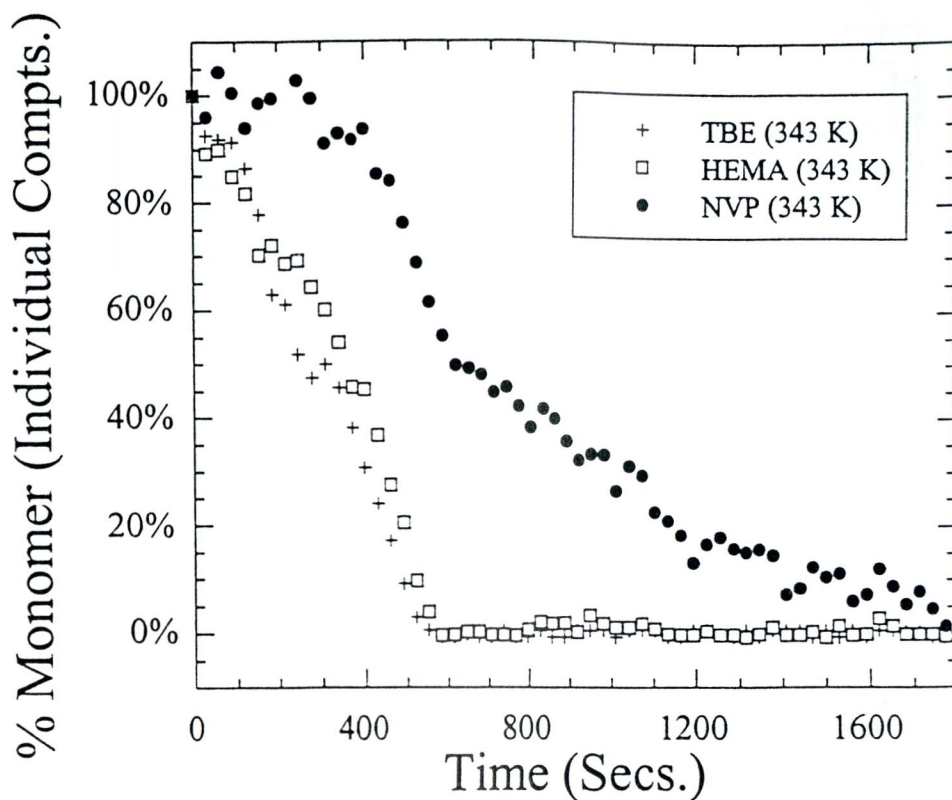


Figure 7.24. Curing profiles of the three constituent monomers in Mixture H as a function of thermal curing time (343 K).

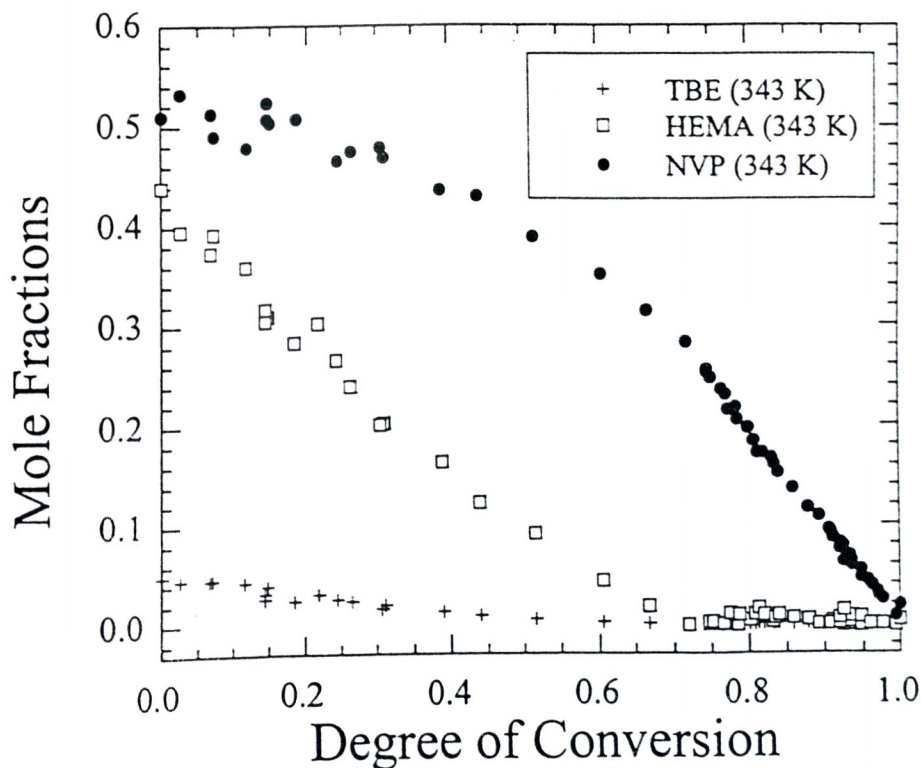


Figure 7.25. Mole fractions of the constituent monomers in the composite Mixture H as a function of the instantaneous degree of conversion to copolymer (343 K).

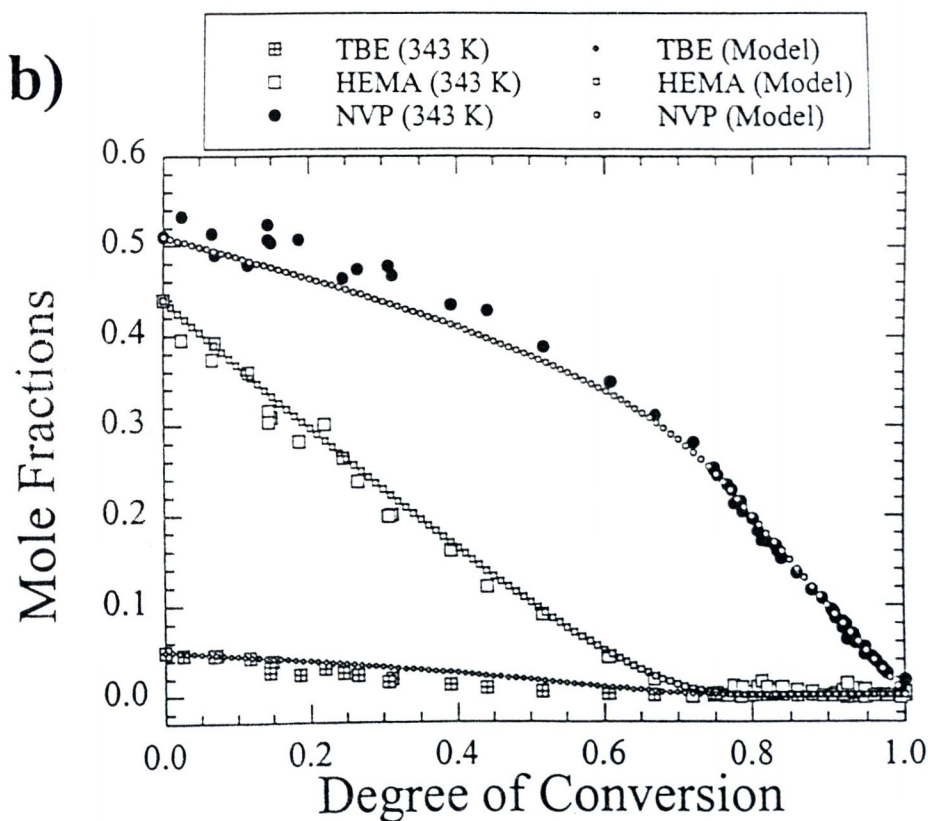
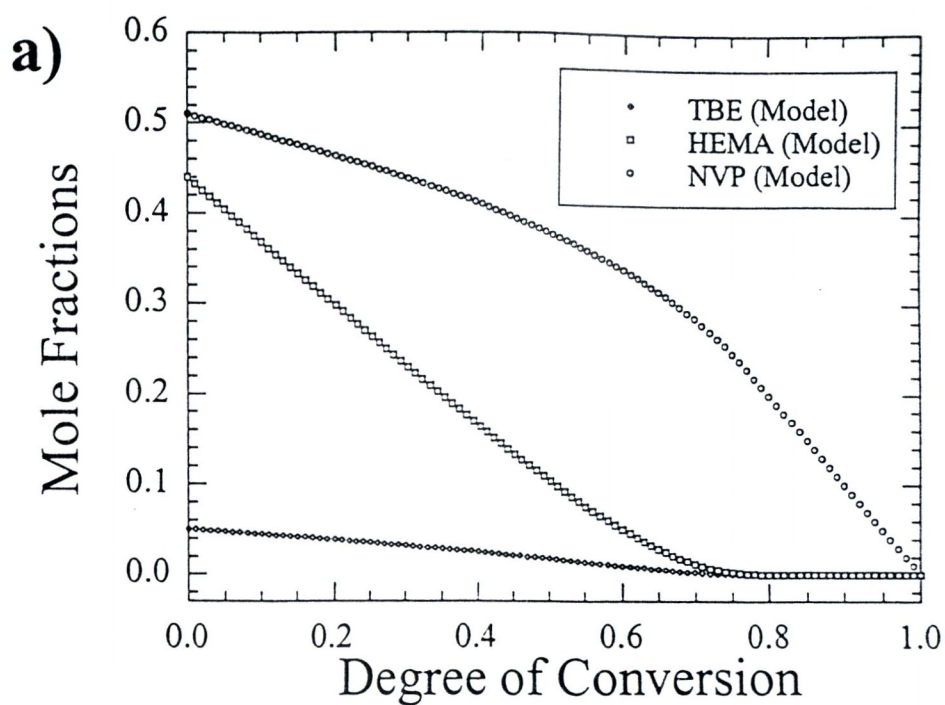
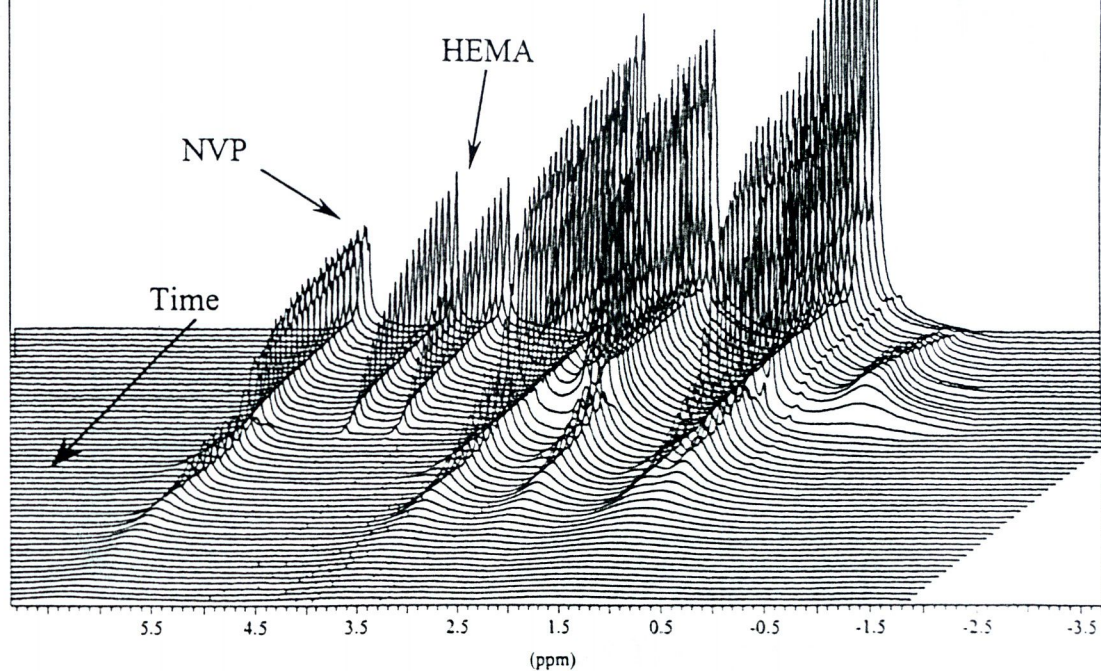


Figure 7.26. **a)** The results of the theoretical simulation based on $Q-e$ values listed in Table 7.1, expressed in terms of mole fractions of the constituent monomers as a function of the instantaneous degree of conversion to copolymer for composite Mixture H. **b)** A comparison of the simulated data to the experimental data recorded during the thermal cure of Mixture H as monitored with ^1H NMR spectroscopy.

a)

Mixture I



b)

Mixture J

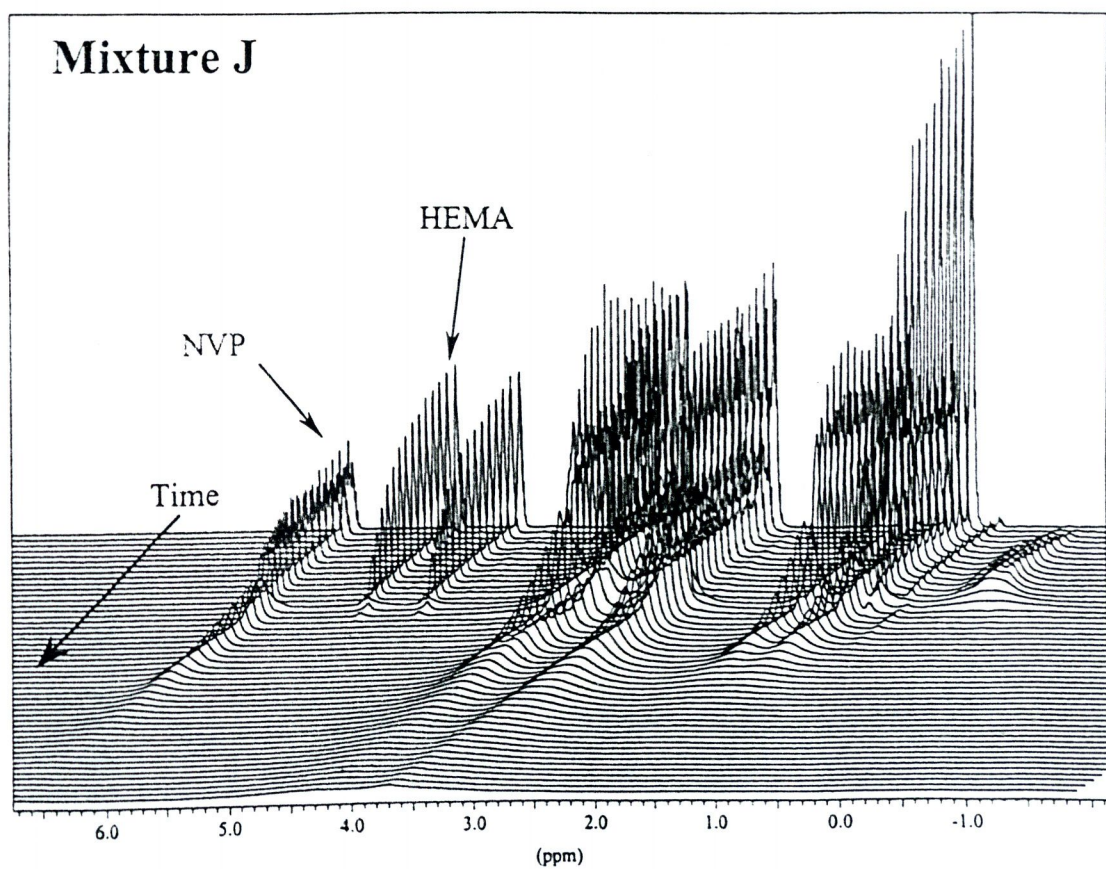


Figure 7.27. ^1H NMR thermal curing profiles of the *in situ* polymerisation of Monomer Mixtures a) I and b) J (333 K).

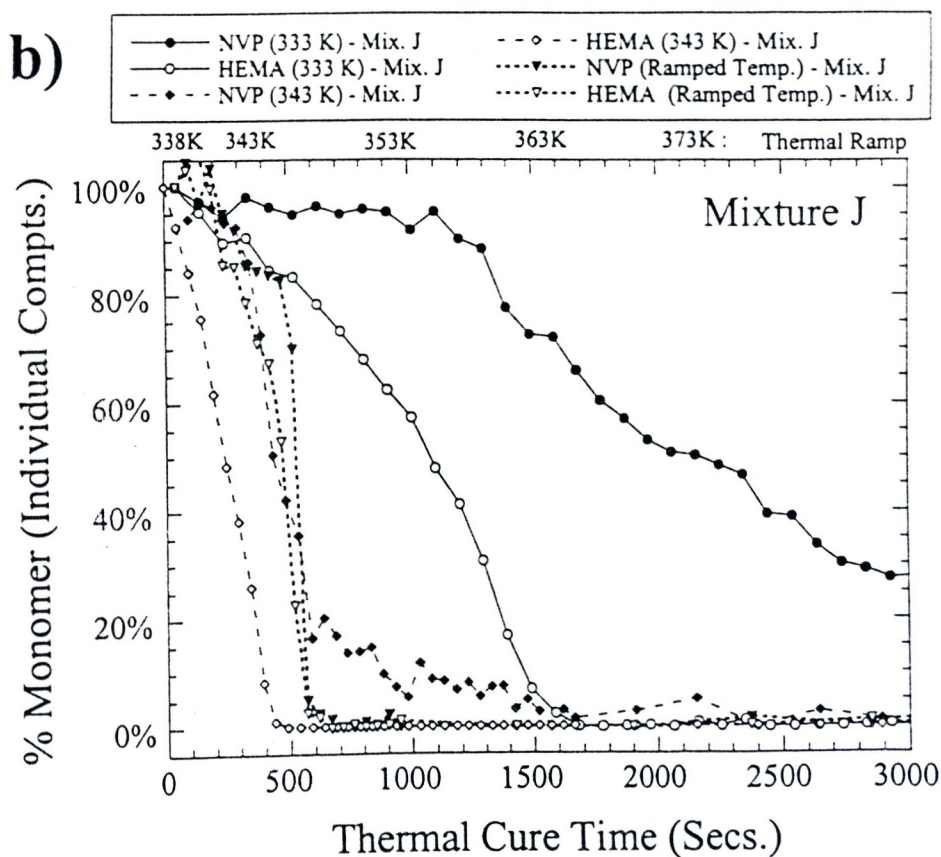
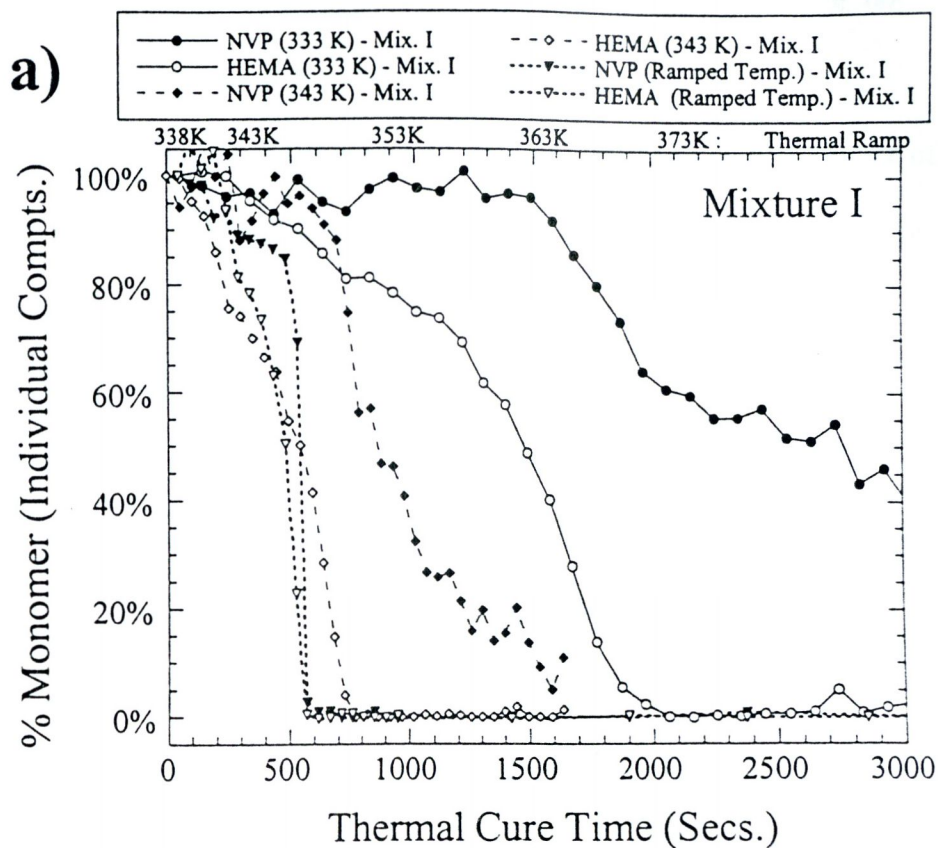


Figure 7.28 Thermal Curing Profiles of NVP and HEMA in **a)** Mixture I and **b)** Mixture J (333 K, 343 K and under Thermal Ramp Conditions).

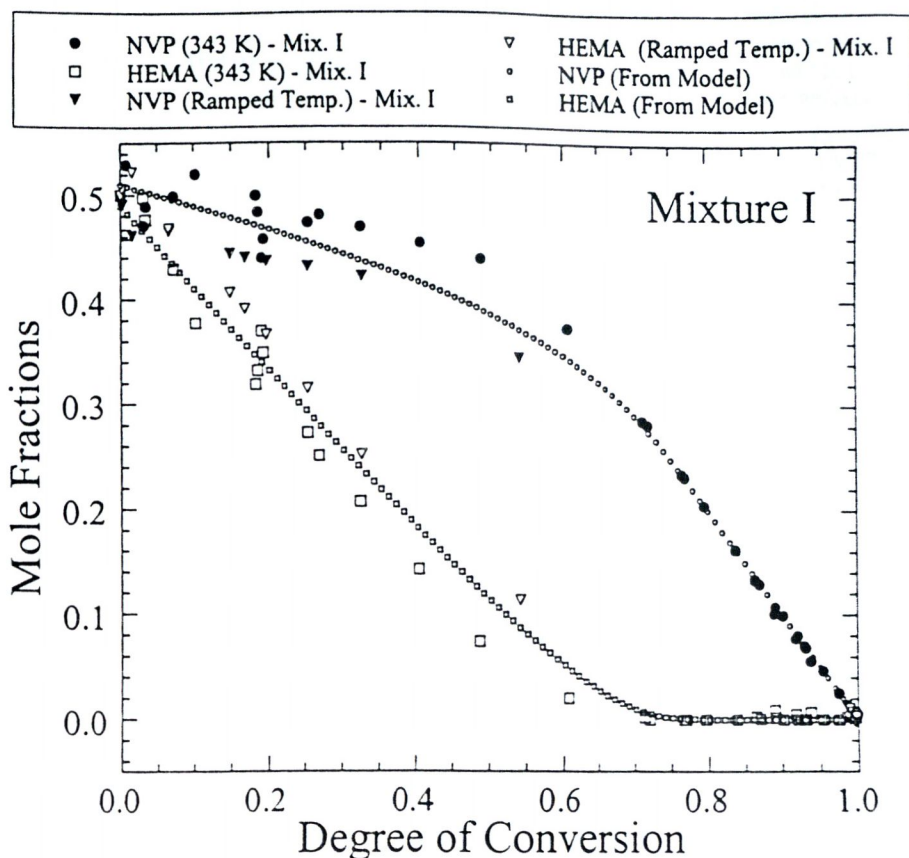
- As expected, the polymerisation rate is greatly increased for both mixtures when conducted at the high temperature of 343 K.
- In agreement with findings reported in the literature,²⁵ the presence of glycerol in Mixture J facilitates faster and more extensive thermal cure profiles for NVP and HEMA than those achieved in its absence (Mixture I) at three different curing temperature conditions.
- The ‘thermal ramp’ heating protocol is significantly more effective at thermally curing both the HEMA and NVP components of the two mixtures to completion, within a shorter time-frame, than either of the two isothermal experiments.

The thermal curing profiles for Mixtures I and J, at 343 K and under thermal ramp conditions, are compared to simulated data in Figures 7.29a and 7.29b. While the simulated data agree well with the experimental data obtained at 343 K, it compares less favourably with the experimental data from the ‘thermal ramp’ cured samples of the two mixtures. This arises from the fact that the model assumes steady state conditions for the generation of free radicals,¹⁹ which is not the case when the temperature is changed continually over the course of the cure process.

7.4.3 TGA Measurements of the Volatility of the Liquid Mixtures

Mixtures I and J were examined using thermogravimetric analysis in order to evaluate their volatile nature over the temperature regimes used in the thermal curing experiments. Figures 7.30a and 7.30b show the resulting thermographs recorded for Mixtures I and J, respectively, heated from 293 K to 873 K at 5 K per minute in a constant flow of dry nitrogen gas. It is evident under these conditions, which are similar to those used in some manufacturing protocols, that the mixtures experience

a)



b)

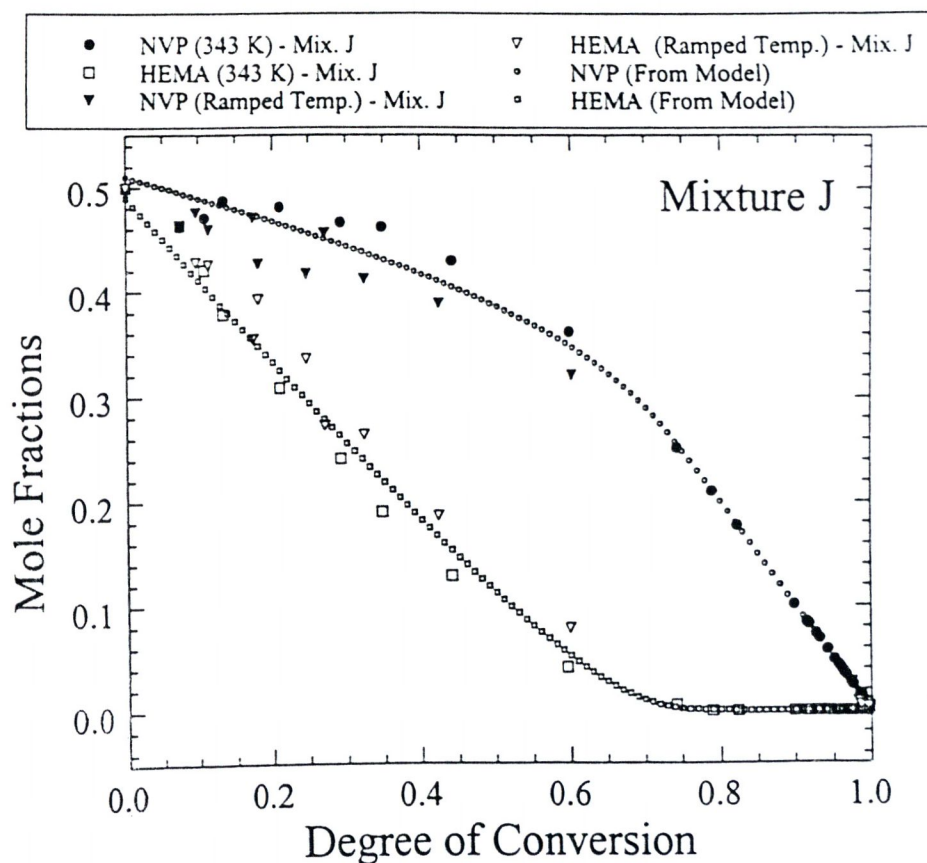
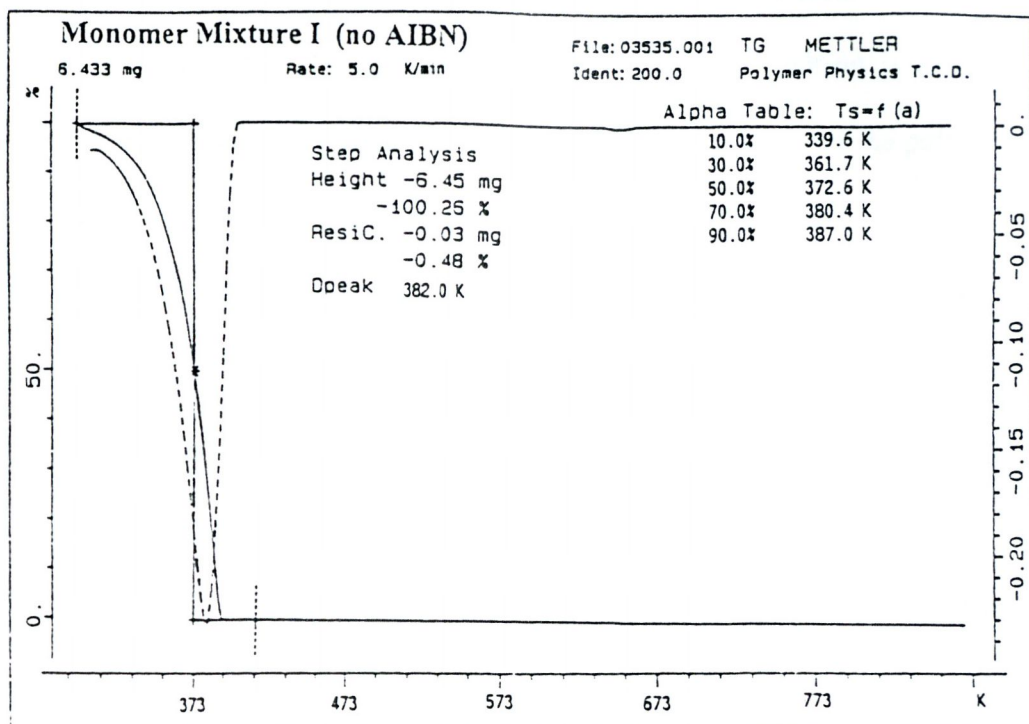


Figure 7.29. Comparisons of simulated data to experimental thermal curing data (343 K and Thermally Ramped Conditions) for a) Mixture I and b) Mixture J.

a)



b)

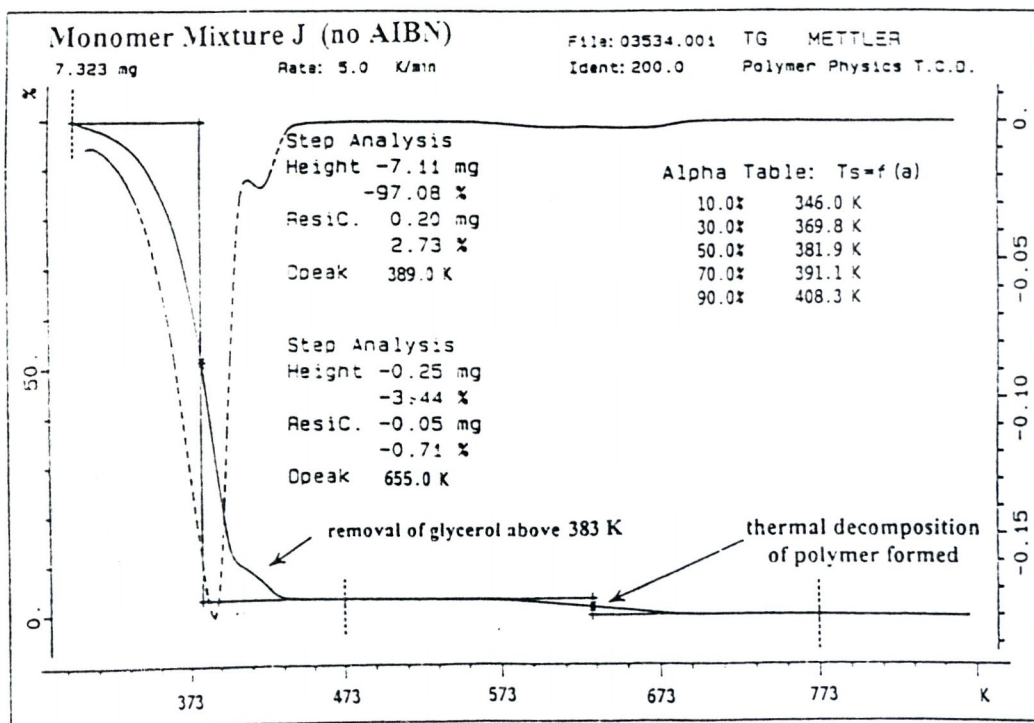


Figure 7.30. Thermogravimetric Analysis of the thermal volatility of the liquid monomer Mixtures a) I and b) J with increasing temperature while exposed to a constant flow of dry nitrogen gas.

weight losses, even at relatively low temperatures. If one of the components is more volatile than the others then it is possible that the mixture composition is altered, which in turn, would have implications for the final physical properties of the polymer produced. The weight loss profiles of Mixtures I and J differ as follows:

- The loss of the glycerol component from Mixture J occurs above about 383 K. The addition of glycerol to the mixture reduces the overall rate of loss of the other monomer components, probably *via* a hydrogen bonding effect, as is reflected in delayed weight loss (*i.e.* peak value shifted from 382 K to 389 K).
- The presence of glycerol facilitates the thermal polymerisation of a small percentage of Mixture J (3.44% by weight) under these conditions, even in the absence of AIBN thermal initiator. The thermal decomposition of the polymer thus formed occurred at *ca.* 655 K.

Sample tubes and cells were sealed in NMR and FTIR curing experiments. However, some sample weight losses were recorded during DSC thermal curing experiments.

7.4.4 DSC Analysis of the Thermal Cure of Mixtures I and J

A series of differential scanning calorimetry (DSC) experiments were conducted on samples of monomer Mixtures I and J, to examine the effects of glycerol on the curing behaviour and final physical properties of these systems. Details of these experiments and their findings are presented in Table 7.2.

Degassed samples of each mixture were ‘thermally cured to completion’ in the DSC instrument, by heating from 303 K to 473 K at 10 K per minute (Figure 7.31a). The exothermic ‘heat of polymerisation energy’ liberated, in terms of calories per gram of sample, was recorded in order to establish the ‘total cure energy’ for each

mixture, so that the degree of cure might be estimated in other samples by comparison with these values.²⁷ The samples were then subjected to a second thermal heating cycle to check for residual uncured monomer (none was detected) and to measure the quasi-static glass transition temperatures (T_g) of the polymers thus formed (Figure 7.31b). While the measured heats of polymerisation recorded were approximately the same for the two mixtures (109 cal/g) the T_g of the polymer formed from Mixture J was approximately 22.5 K lower than for Mixture I, due to the plasticisation effect of the added glycerol component.

Samples of Mixtures I and J, which had been thermally cured at 333 K for 80 minutes *in situ* in NMR experiments (*see Section 7.4.2*), were heated from 303 K to 473 K at 10 K per minute in the DSC to measure residual exothermic heats of polymerisation arising from uncured monomer. Mixture I was found to contain approximately 20% uncured material while Mixture J had only 15% uncured monomer, in agreement with the NMR results, which indicate that the addition of glycerol increases the rate and extent of polymerisation found in these systems.

Degassed Mixture I and J samples were isothermally cured by DSC at 333 K for 120 minutes and the resulting exotherms were recorded (Figure 7.32a). From the recorded times to achieve maximum rate of cure for the two mixtures, it was clear that the addition of glycerol to Mixture J resulted in an increased cure rate at this temperature (*see Table 7.2*). The heats of polymerisation recorded were less than expected, probably due to the weight loss in the mixtures during isothermal cure (approximately 10%). The amount of remnant monomer in these samples was measured with a ramped heating cycle (Figure 7.32b) and the T_g 's of the polymers formed determined in the second heating cycle. As before, Mixture J had cured to a

Table 7.2. DSC experiments to measure the thermal cure behaviour of monomer Mixtures I and J.

DSC Experiments:	Mixture I	Mixture J
<u>'Complete' Thermal Cure</u> Exothermic Heat Energy (303 K to 473K @ 10 K/min.): T_g of polymer formed (2nd cycle - mid point):	109.14 cal/g 380.98 K	109.00 cal/g 358.24 K
<u>Residual Un-cure in NMR (333 K / 80 min.) Samples</u> Residual Exothermic Heat Energy (303 K to 473K @ 10 K/min.): (Extent of Un-cure):	22.06 cal/g (ca. 20%)	16.13 cal/g (ca. 15%)
<u>Residual Un-cure in DSC (333 K) Samples</u> Exothermic Heat Energy* (Isothermal - 333 K for 120 min.): Time to Peak (maximum) Rate of Cure Residual Exothermic Heat Energy (Dynamic - 333 K to 473K @ 10 K/min.): (Extent of Un-cure): T_g of polymer formed (2nd cycle - mid point): (* n.b. ca. 10% sample weight loss recorded).	63.80 cal/g 61.84 min. 24.29 cal/g (ca. 23%) 379.60 K	57.44 cal/g 58.59 min. 18.78 cal/g (ca. 18%) 354.91 K
<u>Residual Un-cure in 'Thermal Ramp' Samples</u> Exothermic Heat Energy (Thermal Ramp: 338 K to 373 K @ 1 K/min.): Residual Exothermic Heat Energy (Dynamic - 303 K to 473K @ 10 K/min.): (Extent of Un-cure): T_g of polymer formed (2nd cycle - mid point):	98.86 cal/g 6.73 cal/g (ca. 6%) 378.00 K	95.93 cal/g 3.36 Cal/g (ca. 3%) 358.47 K
<u>Residual Un-cure in 'Thermal Ramp' + 'Post-Cure Period' Samples</u> Exothermic Heat Energy (Thermal Ramp: 338 K to 373 K @ 1 K/min.): <u>+ Post-Cure Process (373 K for 120 min.)</u> Residual Exothermic Heat Energy (Dynamic - 303 K to 473K @ 10 K/min.): (Extent of Un-cure): T_g of polymer formed (2nd cycle - mid point):	97.90 cal/g 0.37 cal/g (ca. 0.3%) 380.65 K	98.16 cal/g 0.05 cal/g (ca. 0.05%) 358.14 K

Note: Temperature Values $\pm$ 0.3 K; Energy Values $\pm$ 2%, (though larger errors may result from sample weight loss).

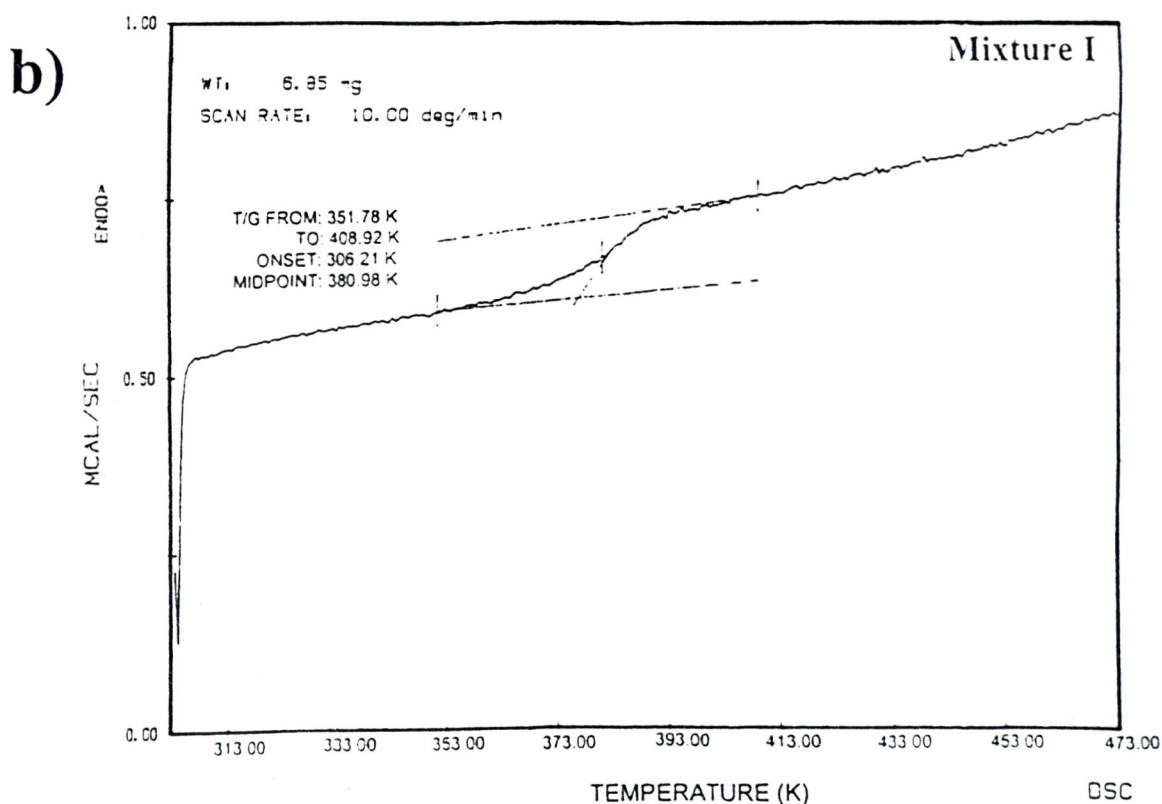
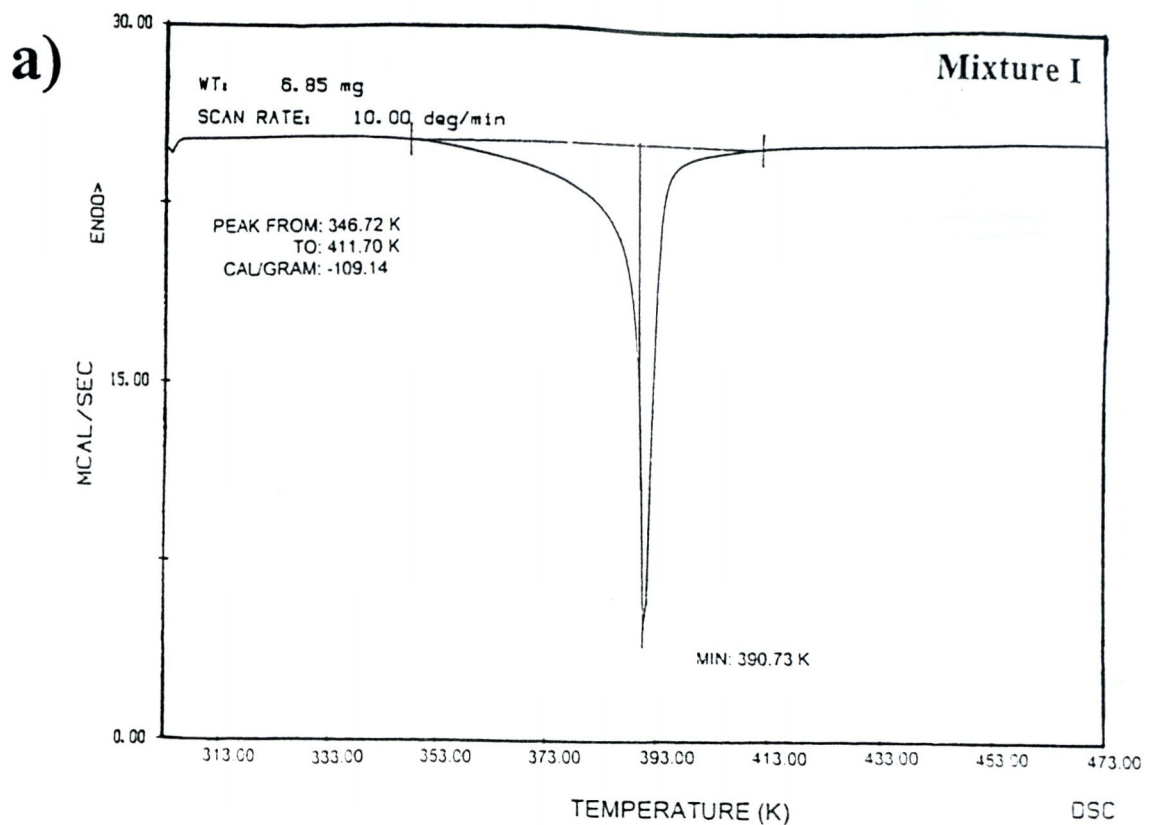


Figure 7.31. DSC profile of **a)** the 'Complete Thermal Cure' of a sample of monomer Mixture I (293 K to 473 K @ 10 K/min.). The sample was then subjected to a second thermal cycle **b)** to check for residual uncured monomer and to determine the glass transition temperature (T_g) of the polymer formed.

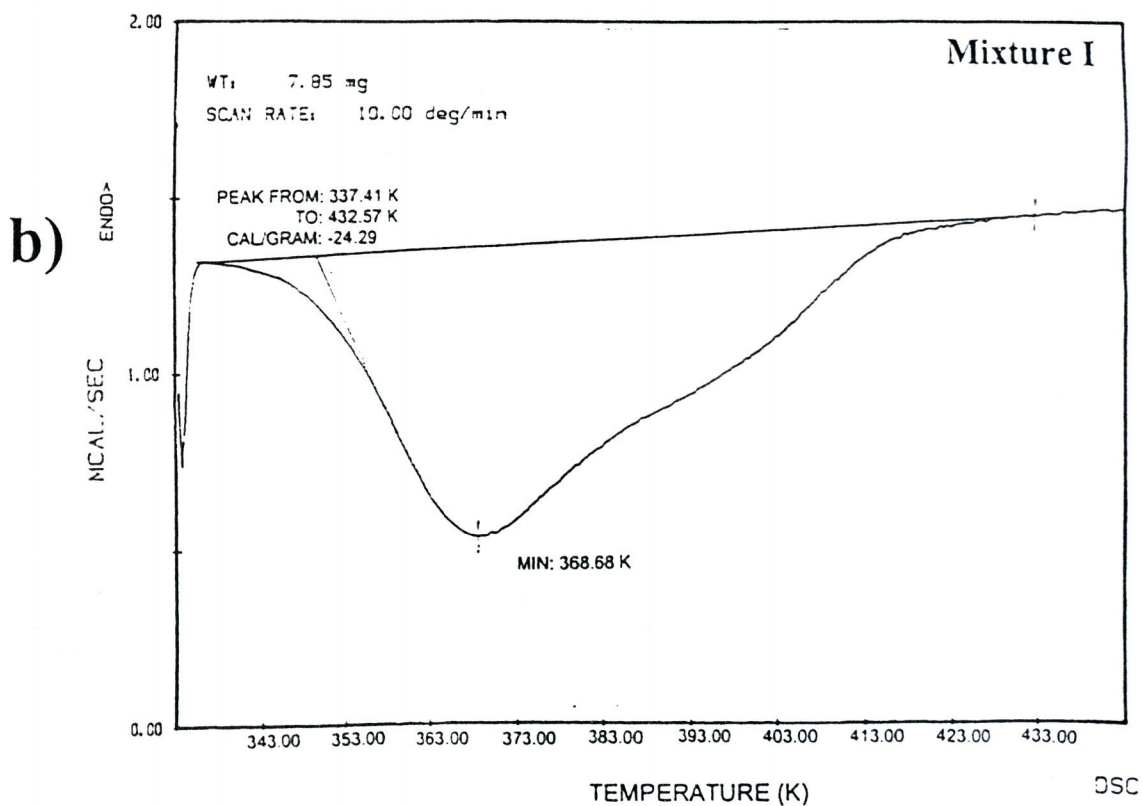
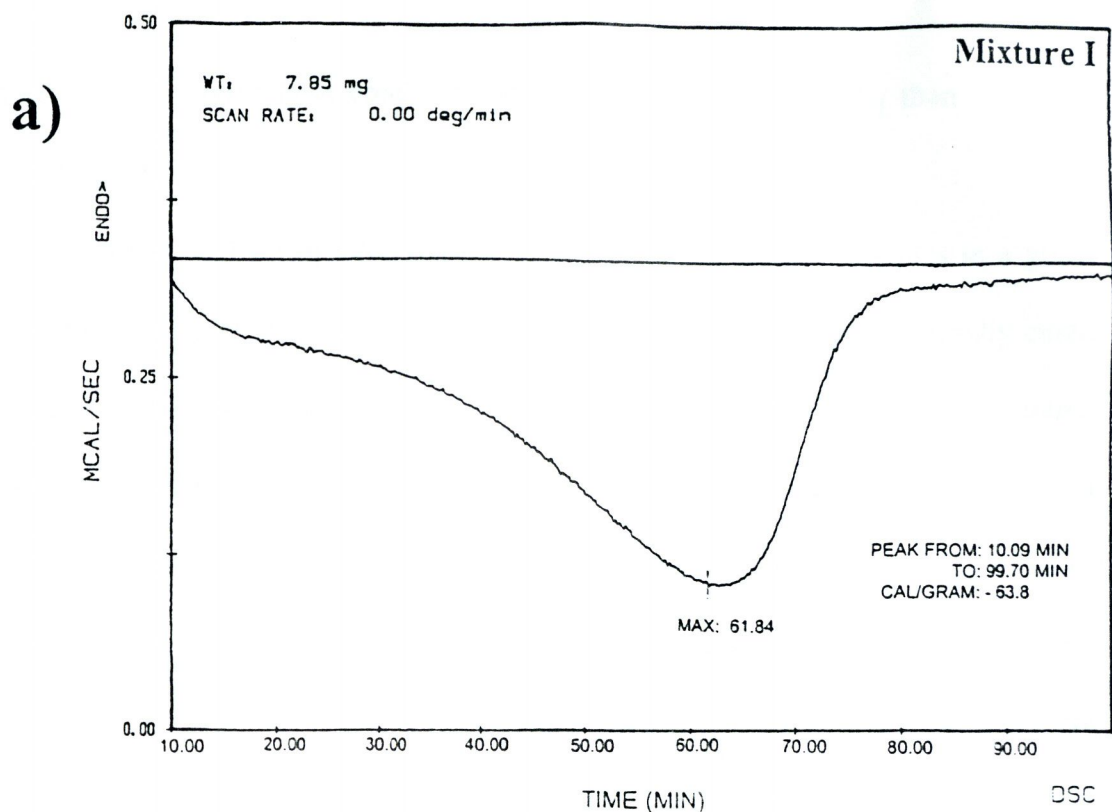


Figure 7.32. DSC profiles of **a)** the 'Isothermal Cure (333K)' of a sample of monomer Mixture I. The sample was then subjected to a second, dynamic thermal cycle **b)** (293 K to 473 K @ 10 K/min.) and exothermic thermal polymerisation of residual un-cured monomer was recorded.

greater extent under these conditions and also exhibited a lower T_g than Mixture I (see Table 7.2).

In the final set of DSC experiments used to explore the variables in a given manufacturing protocol, degassed samples of the two mixtures were thermally cured using the 'Thermal Ramp' heating conditions, *i.e.* 338 K to 373 K at 1 K per minute. The amount of remnant monomer and the T_g 's of the polymers formed were recorded as before. These experiments were then repeated with the inclusion of a 'post cure' period of 120 minutes at 373 K, to determine if the addition of such a heating cycle could further reduce the extent of uncured monomer in the samples. The results were dramatic, with a measured reduction in uncured material from *ca.* 6% and 3% to *ca.* 0.3% and 0.05%, for samples of Mixtures I and J, respectively (see Table 7.2).

While DSC is an indispensable tool for studies of the curing behaviour of polymeric systems in general, it often cannot provide the more subtle information concerning the differential cure profiles of the components of composite mixtures available from NMR or FTIR experiments. It is in this respect that the information obtained from the NMR and FTIR spectroscopic techniques as previously described is both unique and complementary, again reinforcing the merits of a multi-technique approach.

7.5 Conclusions

The novel use of high resolution liquid NMR spectroscopic techniques to probe in real time the thermal and UV-photoinitiated curing dynamics of a number of composite monomer systems of both academic and commercial interest has been described. Additional corroborative data from FTIR spectroscopy and from thermal analysis techniques were also presented. The observed curing profile responses were

fitted to model simulations generated by a new program,²⁰ based on $Q-e$ parameters, which is applicable to an N-component monomer mixture. The agreement based on published reactivity ratios for NVP and HEMA and those of a reasonable analogue for TBE was found to be good. Differences in the curing profiles as observed by NMR and FTIR spectroscopic techniques were rationalized in terms of their relative sensitivities to short and longer-range effects in the curing monomer systems.

Specific information regarding the curing behaviour of the composite systems proved useful in the development of suitable manufacturing protocols for commercially important contact lens products. The generic information obtained in this study has clarified the relationship between macroscopic properties and microscopic behaviour of the cured systems and, conversely, will facilitate the tailoring of new composite polymers to meet specific applications.

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Chapter Eight

Concluding Remarks and Future Work

8.1 Developments and Key Findings

The development of a novel methodology, which uses the high resolution liquid nuclear magnetic resonance (NMR) spectroscopic technique to continuously monitor in real time the thermal, chemical or UV-photoinitiated curing dynamics of multi-component monomer systems, has been described and its principles of operation fully explained. This and the more conventional FTIR spectroscopic technique were used to profile the curing dynamics of the major individual monomers in composite mixtures, principally NVP, HEMA and TBE. These systems are of both academic and commercial interest, specifically in the manufacture of high quality and high value hydrogel contact lenses.

The monomer conversion responses obtained from these two techniques were fitted to model simulations generated by a new numerical implementation, written by D.C. Douglass, which is applicable to N-component monomer mixtures. Agreement, based on published reactivity ratios of the monomer components, was good, thereby validating the methodology and instilling confidence in the overall validity of the NMR approach. Analysis of the changes in lineshape and chemical shift of the characteristic peaks in NMR spectra as curing proceeds provided unique additional information on the dynamic events at a molecular level in the curing systems.

A detailed spectroscopic study of each of the individual components of the systems, using liquid NMR, FTIR and UV-Visible techniques, was primarily conducted to facilitate characteristic peak assignments in the spectra of the complex

mixtures. This information in itself proved to be of significant value, in that it established an extensive 'spectroscopic database' of these commercially important materials for future reference purposes. Key information, such as the spectroscopic identification and ability to approximately quantify the ratios of the two isomers of the TBE species, for example, was also forthcoming in this study.

A study of the relaxation behaviour of the liquid systems was carried out, again primarily as a precursor to the NMR curing experiments, in order to establish appropriate acquisition parameters that ensured the quantitative nature of the NMR spectral data recorded. Additional information regarding the molecular dynamics in these systems was of further scientific interest.

Radiometry techniques, including a liquid phase chemical actinometer system, were successfully used to measure the UV light intensities employed in the photocuring experiments. Measurements were also made using thermal analysis techniques, including DSC and TGA, to examine the effectiveness of an actual industrial protocol - a ramped thermal heating method - achieve optimal curing conditions. This is an important practical issue in the production of good quality lenses.

The information provided in this thesis underpins an understanding of the overall curing dynamics of these composite monomer mixtures and has already provided important guidance in establishing suitable protocols in the manufacturing processes used in the production of high quality hydrogel contact lenses.

8.2 Future Work

Overall agreement between the theoretical model simulations of the curing profiles of multi-component monomer systems generated using Douglass's numerical

implementation software and those obtained by experimental measurement is satisfying. Interpretation in some instances must be viewed as tentative pending further, more detailed, investigation. Two areas of study immediately come to mind. First, it would be interesting to quantify free radical concentrations, particularly in the initial stage of curing: Electron Spin Resonance (ESR) or susceptibility measurements may accomplish this if the free radicals are sufficiently long-lived. Second, examination of possible differences between pulsed, synchronised irradiation and data acquisition, as opposed to continuous irradiation, may offer another avenue for probing the free radical activity. A more detailed analysis of NMR lineshapes and chemical shift changes over the course of the cure process, perhaps using model simulations, is also a consideration for the future.

The novel methodology developed here, *i.e.* the use of continuously recorded ^1H NMR spectra to monitor in real time, the thermal, chemical or photo-initiated differential cure behaviour of individual monomers present in multi-component monomer mixtures, is already finding applications in studies of other systems. The technique is currently being used successfully by other researchers here in the Physics Department, Trinity College, to examine the curing behaviour of different monomers and crosslinkers present in various 'molecular imprinted' polymer systems, both with and without the addition of 'template' species. These experiments benefit from increased spectral resolution achieved by using a newer, higher field, 400 MHz spectrometer. This study is being conducted as part of the ongoing European 'MICA' project.

This methodology has the potential to be used for studying any one of a plethora of potentially important applications and the unique information, accessed by monitoring changes in spectral lineshapes and chemical shifts may provide significant

fundamental additional insight into the curing behaviour of multi-component systems at the molecular level.

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Overall agreement between the theoretical model simulations of the curing profiles of multi-component monomer systems generated using Douglass's numerical

implementation software and those obtained by experimental measurement is satisfying. Interpretation in some instances must be viewed as tentative pending further, more detailed, investigation. Two areas of study immediately come to mind. First, it would be interesting to quantify free radical concentrations, particularly in the initial stage of curing: Electron Spin Resonance (ESR) or susceptibility measurements may accomplish this if the free radicals are sufficiently long-lived. Second, examination of possible differences between pulsed, synchronised irradiation and data acquisition, as opposed to continuous irradiation, may offer another avenue for probing the free radical activity. A more detailed analysis of NMR lineshapes and chemical shift changes over the course of the cure process, perhaps using model simulations, is also a consideration for the future.

The novel methodology developed here, *i.e.* the use of continuously recorded ^1H NMR spectra to monitor in real time, the thermal, chemical or photo-initiated differential cure behaviour of individual monomers present in multi-component monomer mixtures, is already finding applications in studies of other systems. The technique is currently being used successfully by other researchers here in the Physics Department, Trinity College, to examine the curing behaviour of different monomers and crosslinkers present in various 'molecular imprinted' polymer systems, both with and without the addition of 'template' species. These experiments benefit from increased spectral resolution achieved by using a newer, higher field, 400 MHz spectrometer. This study is being conducted as part of the ongoing European 'MICA' project.

This methodology has the potential to be used for studying any one of a plethora of potentially important applications and the unique information, accessed by monitoring changes in spectral lineshapes and chemical shifts may provide significant

fundamental additional insight into the curing behaviour of multi-component systems at the molecular level.

Appendix I

Computer program for the simulation of oligomer concentrations throughout the course of polymerisation of an N-component monomer composite system ($N = 2, 3, 4 \dots$).

Written By D.C. Douglass (1998).

3-Component Version:

'POLY3.BAS, DCD, 03-18-98: Use with "PRT SC" keys for hardcopy.

'THREE Component monomer mix.

'Free radical Polymerization of a three component monomer mix.

'Kinetic parameters must allow all monomers to be completely polymerized.

'PowerBasic Copyright 1989-1995 by Robert Zale.

'Main Program

\$COMPILE EXE

\$OPTIMIZE SPEED

\$CPU 80386

\$INCLUDE "promath.inc"

Defdbl A-h, O-z: Defint I-n 'Fortran Convention

CLS

' Get Input Parameters from a file

INPUT "Input Parameter File Name? ", A\$

OPEN A\$ FOR INPUT AS #3

INPUT #3, p0\$, q0\$

PRINT p0\$, q0\$

INPUT #3, Q1, e1, p1\$

INPUT #3, Q2, e2, p2\$

INPUT #3, Q3, e3, p3\$, p4\$

INPUT #3, M1#, M2#, M3#, p5\$

PRINT "Q1= "; Q1; " e1= "; e1, p1\$

```

PRINT "Q2= ";Q2;" e2= ";e2, p2$
PRINT "Q3= ";Q3;" e3= ";e3, p3$
PRINT p4$
PRINT M1#;" ";M2#;" ";M3#;" ";p5$
PRINT "OK TO PROCEED?: (ANYKEY/N)"
p6$ = INPUT$ (1)
IF p6$ = "N" OR p6$ = "n" THEN
    PRINT " Calc. STOPPED: PRESS ANY KEY": STOP
END IF

```

```

NVAR = 2% ' Number of Dependent variables
np = 100 ' Number of steps in theta
DIM Y(1 TO NVAR), S1!(np), S2!(np)
DIM DS1!(np), DS2!(np)
SHARED Rc11, Rc12, Rc13, Rc22, Rc23, Rc33, Index
SHARED DS1!(), DS2!()

```

'Normalize initial concentrations'

```

Rt = M1# + M2# + M3#
M1# = M1# / Rt: M2# = M2# / Rt: M3# = M3# / Rt

```

'Initial values

```

Y(1) = M2#: Y(2) = M3# ' Note shift in indices!
' X=1-theta, X0 = 1#
S1!(0) = CSNG(Y(1)): S2!(0) = CSNG(Y(2))

```

' Form kinetic matrix

```

r11 = Q1 * Q1 * EXP(- e1 * e1): r12 = Q1 * Q2 * EXP(- e1 * e2) / 2#
r13 = Q1 * Q3 * EXP(- e1 * e3) / 2#
r22 = Q2 * Q2 * EXP(- e2 * e2): r23 = Q2 * Q3 * EXP(- e2 * e3) / 2#
r33 = Q3 * Q3 * EXP(- e3 * e3)
' r sub i,j = r sub j,i

```

'Change variables from (a1,a2,a3,a4) -> (X=1-th,a2,a3,a4)

Rc11 = r11: Rc12 = r12 - r11: Rc13 = r13 - r11

Rc22 = r11 - 2# * r12 + r22: Rc23 = r11 - r12 - r13 + r23

Rc33 = r11 - 2# * r13 + r33

H# = 1.1# / CDBL(np) ' Magnitude of H, & Sign of H is dealt with within SUB Derk

'This assignment assures that initial step is a full step,ie thetastep

HMIN# = 0#: MAXSTEPS = 100%: EPS = 0.0000001#

thetastep = 1# / CDBL(np)

FOR K = 0 TO np - 1: Index = K

X0 = 1# - CDBL(K) * thetastep: X1 = 1# - (CDBL(K) + 1#) * thetastep

CALL DERK(Y(), NVAR, X0, X1, EPS, H#, HMIN#, HNEXT#, MAXSTEPS)

S1!(K+1) = CSNG(Y(1)): S2!(K+1) = CSNG(Y(2))

NEXT K

' Make boxes and tics

SCREEN 12 ' VGA 640X480

VIEW ,0 ' Make whole screen black

VIEW (0,17) - (310,327), 0 ' Open Viewport for plotting Y(i) vs Theta

WINDOW (0,0) - (1,1) ' Set Scale of Viewport

LINE (0,0) - (1,1), 7, B ' Draw box

' Print axis labels

LOCATE 22, 20,1,7,7: PRINT CHR\$(233)

LOCATE 2, 1: PRINT "Y(i)"

FOR I = 1 TO 9: xtic! = CSNG(I)/10 ' Make X-axis tics

IF I = 5 THEN

LINE (xtic!,0) - (xtic!,.03)

ELSE

LINE (xtic!,0) - (xtic!, .02)

END IF

NEXT I

FOR I = 1 TO 9: ytic! = CSNG(I)/10 ' Make y-axis tics

IF I = 5 THEN

LINE (0,ytic!) - (.03,ytic!)

ELSE

```

    LINE (0,ytic!) - (.02,ytic!)
END IF
NEXT I
'Print Header
LOCATE 1, 25: PRINT "Parameter File: " + A$

' Plot Y(i) results
p! = CSNG(np)
st! = 1! / p!
PSET (0,S1!(0)) ' Set initial point for curve #2
FOR I = 1 TO np - 1
    LINE - (I * st!,S1!(I)), 7, ' Line in grey
NEXT I
PSET (0,S2!(0)) ' Set initial point for curve #3
FOR I = 1 TO np - 1
    LINE - (I * st!,S2!(I)), 7 ' Line in grey
NEXT I
T! = 1! - S1!(0) - S2!(0)
PSET(0,T!) ' Set initial point for curve #1
FOR I = 1 TO np - 1: Jdex! = CSNG(I) * st!
    LINE - (I * st!,1! - Jdex! - S1!(I) - S2!(I)), 7 ' Line in grey
NEXT I
CIRCLE (0.18!,S2!(18)),.011! ' Make label on curve #3
PSET (0.16!,S1!(16))
DRAW "BD1BL4R8H4G4" ' Label curve #2 with a triangle
PSET (0.12!,1! - 0.12! - S1!(12) - S2!(12))
DRAW "NG3NE3NF3H3" ' Label Curve #1 with a cross

VIEW (328,17) - (638,327), 0 ' Open New Viewport for Plot of F(i) vs Theta
WINDOW (0,0) - (1,1)
LINE (0,0) - (1,1),7,B
LOCATE 22, 61 : PRINT CHR$(233)
LOCATE 2, 42 : PRINT "F(i)"
FOR I = 1 TO 9: xtic! = CSNG(I)/10 ' Make X-axis tics

```

```

IF I = 5 THEN
    LINE (xtic!,0) - (xtic!,.03)
ELSE
    LINE (xtic!,0) - (xtic!,.02)
END IF
NEXT I
FOR I = 1 TO 9: ytic! = CSNG(I)/10 ' Make y-axis tics
    IF I = 5 THEN
        LINE (0,ytic!) - (.03,ytic!)
    ELSE
        LINE (0,ytic!) - (.02,ytic!)
    END IF
NEXT I

' Plot F(i) results
st! = 1! / p!
PSET (0,DS1!(0)) ' Set initial point for curve #2
FOR I = 1 TO np - 1
    LINE - (I * st!,DS1!(I)), 7 ' Line in grey
NEXT I
PSET (0,DS2!(0)) ' Set initial point for curve #3
FOR I = 1 TO np - 1
    LINE - (I * st!,DS2!(I)), 7 ' Line in grey
NEXT I
DT! = 1! - DS1!(0) - DS2!(0)
PSET (0,DT!) 'Set zero for curve #1
FOR I = 1 TO np - 1
    LINE - (I * st!,1! - DS1!(I) - DS2!(I)), 7 ' Line in grey
NEXT I
CIRCLE (0.18!,DS2!(18)),.011! ' Make label on curve #3
PSET (0.16!,DS1!(16))
DRAW "BD1BL4R8H4G4" ' Label curve #2 with a triangle
PSET (0.12!,1! - DS1!(12) - DS2!(12))
DRAW "NG3NE3NF3H3" ' Label curve #1 with a cross

```



```

VIEW (0,350) - (638,478) 'Open Viewport for printing parameters.
WINDOW (0,0)-(1,1)
LINE (0,0)-(1,1),7,B
LOCATE 23,4
PRINT "Put Results in File? (Y/N)";
b$ = INPUT$ (1)
CLS: LOCATE 23,4
LINE (0,0)-(1,1),7,B
IF b$ = "Y" OR b$ = "y" THEN
  CLS: LOCATE 23,4
  INPUT "File Name? ", D$
  FB = INSTR(D$, CHR$(46)) ' Detect presence of ".", i.e. an extension.
  FA = LEN(D$)
  IF FB = 0 THEN ' If no extension
    NAM$ = LEFT$(D$,7): EXT$ = ""
  ELSE ' If extension present
    ROOT$ = EXTRACT$(D$,CHR$(46)) ' Parse into before and after "."
    EXT$ = RIGHT$(D$,FA+1-FB)
    NAM$ = LEFT$(ROOT$,7)
  END IF
  ES = NAM$ + "Y" + EXT$: FS = NAM$ + "F" + EXT$
  OPEN FS FOR OUTPUT AS #1
  OPEN ES FOR OUTPUT AS #2
  PRINT #1, "Parameter Source File: " + A$
  PRINT #2, "Parameter Source File: " + A$
  PRINT #1, "Theta"; "      F-EDMA"; "      F-HEMA"; "      F-VP"
  PRINT #2, "Theta"; "      Y-EDMA"; "      Y-HEMA"; "      Y-VP"
  PRINT #2, 0!, S1!(0), S2!(0), 1! - S1!(0) - S2!(0)
  FOR K = 0 TO np - 1: Kdex! = CSNG(K + 1) * st!
    PRINT #1, K, DS1!(K), DS2!(K), 1! - DS1!(K) - DS2!(K)
    PRINT #2, K+1, S1!(K+1), S2!(K+1), 1! - Kdex! - S1!(K+1) - S2!(K+1)
  NEXT K
  CLS: LOCATE 23,4

```

```

PRINT "F() Data Saved in "; CHR$(34) + F$ + CHR$(34);
PRINT ": Y() Data Saved in "; CHR$(34) + E$ + CHR$(34)
ELSE
PRINT "NO DATA SAVED"
END IF
LOCATE 24,2
PRINT "Q1=";Q1;" e1=";e1,"M1(0)=";CSNG(M1#)
LOCATE 25,2
PRINT "Q2=";Q2;" e2=";e2,"M2(0)=";CSNG(M2#)
LOCATE 26,2
PRINT "Q3=";Q3;" e3=";e3,"M3(0)=";CSNG(M3#)

DO: LOOP WHILE INKEY$ = "" ' Wait for signal to remove plots.
CLOSE 1, 2, 3
END 'Main Program

' FUNCTION used by SUB Derk() //////////////////////////////////////
Function Sign (X1, X2) PUBLIC
If X2 <> 0# Then Sign = Abs(X1) * X2 / Abs(X2) Else Sign = Abs(X1)
End Function

' FUNCTION used by Derk() //////////////////////////////////////
Function Dmax1 (X1, X2) PUBLIC
If X1 > X2 Then Dmax1 = X1 Else Dmax1 = X2
End Function

'Subroutine to define RHS of (dy/dx=RHS) for each diff. eqn.
SUB Derivs (X, Y(), Dy(), N) PUBLIC
LOCAL d
d = 1# / (Rc11 * X * X + X * 2# * (Rc12 * Y(1) + Rc13 * Y(2)) + _
Rc22 * Y(1) * Y(1) + Y(2) * (Rc33 * Y(2) + 2# * Rc23 * Y(1)) )
Dy(1) = (Rc12 * X + Rc22 * Y(1) + Rc23 * Y(2)) * Y(1) * d
Dy(2) = (Rc13 * X + Rc23 * Y(1) + Rc33 * Y(2)) * Y(2) * d

```

END SUB 'Derivs

%%%

' Module : Diffeqns.bas was Promat10.bas
' Type : Integrate A Set Of Differential Equations
' Library: Promath Version 2.0
' Copyright 1992 - 1993 TeraTech, Inc. All rights reserved
' Copyright 1989 Hammerly Computer Services, Inc.

%%%

%%%

' Derk Integrates A Set Of Diff. Eqs. Over An Interval Using
' Fifth-order Runge-kutta Method With Adaptive Step Size.
' This Routine Calls Rk5 To Do The Integration

%%%

Sub Derk (Ystart(), Nvariables, X1, X2, Eps, H1, Hmin, Hnext, Kmax) PUBLIC

Maxsteps = 10000

Tiny = 1d-30

Redim Yscal(Nvariables), Dydx(Nvariables), Y(Nvariables)

X = X1

H = Sign(H1, X2 - X1)

Kount = 0

For I = 1 To Nvariables: Y(I) = Ystart(I): Next I

For Nstp = 1 To Maxsteps

Call Derivs(X, Y(), Dydx(), Nvariables)

IF Nstp = 1 THEN ' Modification of DERK() by DCD 03/08/98

DS1!(Index) = CSNG(Dydx(1))

DS2!(Index) = CSNG(Dydx(2))

END IF

For I = 1 To Nvariables

Yscal(I) = Abs(Y(I)) + Abs(H * Dydx(I)) + Tiny

Next I

If (X + H - X2) * (X + H - X1) > 0# Then H = X2 - X

Call Rk5(Y(), Dydx(), Nvariables, X, H, Eps, Yscal(), Hdid, Hnext)


```

If (X - X2) * (X2 - X1) >= 0# Then
  For I = 1 To Nvariables
    Ystart(I) = Y(I)
  Next I
  If Kmax Then Kount = Kount + 1
  Exit Sub
End If
If Abs(Hnext) < Hmin Then
  Print "Stepsize Smaller Than Minimum."
  Exit Sub
End If
H = Hnext
Next Nstp
  Print "Too Many Steps."
End Sub

```

```

'/////////////////////////////////////////////////////////////////

```

```

' Rk4 Advances A Solution Vector Y(N) Of A Set Of Ordinary Diff.
' Eqs. Over A Single Small Interval H Using Fourth-order Runge-kutta
' Method.

```

```

'/////////////////////////////////////////////////////////////////

```

```

Sub Rk4 (Y(), Dydx(), N, X, H, Yout()) PUBLIC

```

```

  Redim Yt(N), Dyt(N), Dym(N)

```

```

  Hh = H * .5#

```

```

  H6 = H / 6#

```

```

  Xh = X + Hh

```

```

  For I = 1 To N

```

```

    Yt(I) = Y(I) + Hh * Dydx(I)

```

```

  Next I

```

```

  Call Derivs(Xh, Yt(), Dyt(), N)

```

```

  For I = 1 To N

```

```

    Yt(I) = Y(I) + Hh * Dyt(I)

```

```

  Next I

```

```

  Call Derivs(Xh, Yt(), Dym(), N)

```

For I = 1 To N

Yt(I) = Y(I) + H * Dym(I)

Dym(I) = Dyt(I) + Dym(I)

Next I

Call Derivs(X + H, Yt(), Dyt(), N)

For I = 1 To N

Yout(I) = Y(I) + H6 * (Dydx(I) + Dyt(I) + 2# * Dym(I))

Next I

End Sub

'////////////////////////////////////

' Rk5 Performs A Single Step Of Fifth-order Runge-kutta Integration

' With Local Truncation Error Estimate And Corresponding Step

' Size Adjustment. Routine Adapted From Numerical Recipes By

' William H. Price Et Al.

'////////////////////////////////////

Sub Rk5 (Y(), Dydx(), N, X, Htry, Eps, Yscal(), Hdid, Hnext) PUBLIC

Fcor = .0666666667#

Safety = .9#

Errcon = .0006#

Redim Ytemp(N), Ysav(N), Dysav(N)

Pgrow = -.2#

Pshrnk = -.25#

Xsaved = X

For I = 1 To N ' Save Initial Values

Ysav(I) = Y(I)

Dysav(I) = Dydx(I)

Next I

H = Htry ' Set Step Size To Initial Trial Size

1 Hh = .5# * H ' Take Two Half Step Sizes

Call Rk4(Ysav(), Dysav(), N, Xsaved, Hh, Ytemp())

X = Xsaved + Hh

Call Derivs(X, Ytemp(), Dydx(), N)

Call Rk4(Ytemp(), Dydx(), N, X, Hh, Y())

```

X = Xsaved + H
If X = Xsaved Then
    Print "Stepsize Not Significant In Rkqc."
Exit Sub
End If
Call Rk4(Ysav(), Dysav(), N, Xsaved, H, Ytemp())
Errmax = 0#
For I = 1 To N
    Ytemp(I) = Y(I) - Ytemp(I)
    Errmax = Dmax1(Errmax, Abs(Ytemp(I) / Yscal(I)))
Next I
Errmax = Errmax / Eps
If Errmax > 1# Then
    H = Safety * H * Errmax ^ Pshrnk
    Goto 1
Else
    Hdid = H
    If Errmax > Errcon Then
        Hnext = Safety * H * Errmax ^ Pgrow
    Else
        Hnext = 4# * H
    End If
End If
End If
For I = 1 To N
    Y(I) = Y(I) + Ytemp(I) * Fcor
Next I
End Sub

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

```

Sub Rkde (Ystart(), Nvariables, X1, X2, Nstep) PUBLIC
    Nmax = 30
    Redim V(Nvariables), Dv(Nvariables)

    For I = 1 To Nvariables

```



```

    V(I) = Ystart(I)
Next I

X = X1
H = (X2 - X1) / Nstep
For K = 1 To Nstep
    Call Derivs(X, V(), Dv(), N)
    Call Rk4(V(), Dv(), Nvariables, X, H, V())
    X = X + H
Next K
For I = 1 To Nvariables
    Ystart(I) = V(I)
Next I

End Sub

```

3-component parameters file called by the program above:

"Input Parameters for THREE component polmerization Calc."

"Kinetic parameters"

0.14#, -1.14#, "Q1, e1: VP"

0.88#, 0.24#, "Q2, e2: TBE"

0.80#, 0.20#, "Q3, e3: HEMA"

"Initial Concentrations"

59#, 5#, 36#, "M1(0), M2(0), M3(0)"

Appendix II

Publications:

'Dynamics of Water Molecules in Polymers'

F.M Colye, S.J. Martin, V.J. McBrierty; *Journal of Molecular Liquids*, **69**, 95 (1996).

'Understanding Hydrated Polymers: the Perspective of NMR'

V.J. McBrierty, S.J. Martin, F.E. Karasz; *Journal Molecular Liquids*, **80**, 179 (1999).

'Curing of Polymer Composites - 1. NMR Characterization of Component Monomers'

S.J. Martin, J.E. O'Brien, J. Dowling and V.J. McBrierty; *European Polymer Journal*, **34**, 1817 (1998).

'Curing of Monomer Composites - 2. The use of NMR to monitor real time curing dynamics'

S.J. Martin, V.J. McBrierty, J Dowling, D.C. Douglass; *Macromolecules Rapid Communications*, **20**, 95 (1999).

'Curing of Monomer Composites'

S.J. Martin, V.J. McBrierty, J Dowling, D.C. Douglass; *Proceedings of the Sixth Annual International Conference on Composites Engineering, Orlando, Florida, (ICCE/6) pp.549 (1999).*

'The Curing Dynamics of Complex Monomer Mixtures in Real Time'

S.J. Martin, V.J. McBrierty, D.C. Douglass; *to be submitted to Macromolecules*