UNIVERSITY OF SOUTHAMPTON

Investigations into the Morphological Control of Polymer Dispersed Liquid Crystal Materials

Richard Alan Paul Smith, BSc (Double Hons.), GRSC

Thesis submitted for the qualification of Master of Philosophy

Department of Chemistry

November 13, 1995

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Master of Philosophy

INVESTIGATIONS INTO THE MORPHOLOGICAL CONTROL OF POLYMER DISPERSED LIQUID CRYSTAL MATERIALS

by Richard Alan Paul Smith

Polymer dispersed liquid crystals (PDLCs) have been investigated. Initial work concentrated on studying common liquid crystal types in a poly(methyl methacrylate) matrix. Although useful for basic studies on PDLCs these were not suitable for potential application. Work on polyurethane dispersed liquid crystals was carried out as the polymer of choice has not previously been studied. This proved more fruitful; such materials displayed many properties desirable in applications. The morphology of these PDLCs was controlled by varying the cure regime. Finally thermal gradients have been postulated as a possible method of controlling off-state alignment of the liquid crystal in such composites; preliminary studies have been carried out and a range of further investigations is suggested to further study on these novel systems.

Contents

Acknowledgements

Suitable acknowledgements should go to George Attard and I must thank Geoffrey Luckhurst for his help.

For financial support I must thank the Department of Chemistry, GEC and Merck.

For help during the project I must thank Drs D Coates, S K Heeks and P Nolan.

I am most grateful to my dad, Gerald, for letting me loose on his Macintosh and for proof reading the introduction.

This dissertation is dedicated to Nayim of Real Zaragoza for scoring the greatest goal in the history of football in the 1994/1995 European Cup Winners' Cup Final.

Chapter 1. Liquid Crystals - An Introduction

Before understanding such a specific application of liquid crystalline materials as in polymer dispersed liquid crystal devices it is necessary to understand the basics of liquid crystalline behaviour and materials.

1.1. Overview

Liquid crystals (perhaps more correctly named anisotropic fluids) were first identified about a century ago with the discovery of an intermediate fluid phase between solid and clear liquid upon heating cholesteryl benzoate; the discovery is generally accredited to Reinitzer [1] although Lehmann investigated this intermediate phase, demonstrating its birefringence and eventually labelling the phase "liquid crystal" [2]. This work was largely unnoticed until much more recently when there has been a vast increase in interest and research in this field due to both its inherent scientific interest and potential in a wide range of applications, most notably in display devices [3].

There are two basic types of anisotropic fluid, each with distinct characteristics.

The first consists of solutions of amphiphiles (*eg*, oil and/or water mixed with a surfactant) and are primarily termed *lyotropic* liquid crystals. These systems are formed from solvent induced aggregation of amphiphiles into micelles and furthermore, as the amphiphile concentration increases, into a variety of complex, non-spherical aggregates, lamellar (layered) phases, for example. These are of considerable interest, partially due to the links that they have with biological systems (all cell membranes are liquid crystalline in nature); although fascinating they are not relevant to this work and so will not be discussed further.

The second type is not necessarily dependent on the presence of two or more different species of molecule. These are termed *thermotropic* liquid crystals and are of interest in this work. As their name suggests, these materials vary their ordering as a function of temperature.

1.2. Thermotropic Liquid Crystals

Consider a molecular crystal being heated. As energy is imparted to the system the interactions holding the crystal together are eventually overcome; thus at this point the crystal will melt, usually into an isotropic liquid. Sometimes some of the ordering present in the crystalline state remains in the system after melting and thus an anisotropic fluid phase is seen - a liquid crystalline phase.

The basis of this effect is determined by the degree of molecular anisometry; *ie*, deviation from spherical symmetry. If the molecules are, for instance, shaped like cigars, then it can intuitively be seen that the preferred molecular packing, in a crystal state and even in a fluid state, will be such that the long axes of the molecules will tend to lie parallel with each other.

If the molecules do not have enough energy to rotate, translate or vibrate into an organisation with more spherical symmetry, then this alignment will extend beyond the immediate molecules. If sufficient, this local orientational ordering will become long range ordering and will extend across thousands of molecules or more. It will be retained throughout a macroscopic sample (*ie*, any molecule will be aligned with all in its vicinity) and thus an anisotropic fluid phase is seen; this differs from a crystal where there is (theoretically) infinite positional and orientational ordering. This, then, is the basis of thermotropic liquid crystallinity. When sufficient heat energy is further imparted then the molecules will cease to be able to align as they reorient (vibrate, rotate, *etc*) to give an average shape further from this anisometry and thus a further phase transition to an isotropic liquid is seen.

The direction of the long range ordering is described by a unit vector known as the *director* - denoted by the symbol **n** [4]. Essentially the director defines the average local orientation of the molecules. This varies throughout a macroscopic sample (somewhat randomly). The degree of ordering - *ie*, how well the molecules align with respect to the director - is a much more involved concept and is measured by an order parameter; the most common measure is a second rank tensor [5], denoted **S** [6]:

$$S = \frac{1}{2}\overline{\left(3\cos^2\theta - 1\right)},$$

where θ is the angle of the molecular axis from the director **n**. Thus the ordering varies from 1 (perfect order parallel with the director) to 0 (perfect disorder) to -0.5 (perfect order orthogonal to the director).

It is obvious that departure of the phase from isotropy may well lead to some interesting effects; this is indeed the case. Perhaps the most striking and certainly the most beautiful is the birefringence that the phase anisotropy induces. Most crystals are birefringent and liquid crystals are no exception. This is best seen by using polarised light microscopy where incident light is first polarised, then passes through the sample (necessarily reasonably thin) and finally passes through an analysing Polaroid orthogonal to the first Polaroid. As **n** in the system varies in space, so the refractive index varies (the anisotropy induces two refractive indices - n_o along the director and n_e orthogonal to the director). This variation leads to rotation of light when passing through the sample and thus light will be transmitted by the sample through the analysing Polaroid. Each liquid crystal phase has characteristic *textures* that depend on the ordering of the director in the system and the presence of defects (regions where the director changes discontinuously).

The main kind of thermotropic liquid crystal currently used in commercial applications - mostly display applications - is termed *calamitic*. The constituent molecules tend to be very elongated with a relatively polar functional group on one end and are very well exemplified by the molecule 4-*n*-pentyl-4'-cyanobiphenyl (this is in fact a component of many commercial mixtures of liquid crystal). The two adjacent phenyl rings and the cyanide group form a rigid molecular backbone, this being the root of the anisotropic molecular packing. The alkyl chain is present to provide access to the liquid crystal phase by lowering the melting point (caused by disruption of the interactions of the rigid molecular core); the theoretical crystal-nematic transition would otherwise be above the point at which decomposition occurs. There is an enormous variety of these types of liquid crystal; the rigid core can be biphenyl, terphenyl, Schiff's base, ester; the end groups can be cyanide, nitro, halide; the terminal chains alkyl or alkyloxy, for example. These calamitic liquid crystals can form a variety of differently ordered phases.

To be of use in electro-optic systems, liquid crystals must be able to align with an applied (generally electric) field. This is the reason for the polar head group in the most common liquid crystalline materials. This polar group will obviously cause a non-uniformity in the dielectric behaviour of the material - a dielectric anisotropy caused by the anisotropic molecular polarisability, *ie*, one end of the "rod" will have a concentrated negative charge and the other by default a more positive one. Therefore a permanent dipole is set up along the length of the molecule which will evidently cause alignment in an electric field as the negative end of the molecule will tend to point towards the anode. There is a useful definition of this effect termed the *dielectric anisotropy* ($\Delta\varepsilon$); this in essence is the difference between the values of the dielectric constant parallel with the director ($\varepsilon_{\parallel}$) and perpendicular to the director ($\varepsilon_{\perp}$) and ($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$). A large dielectric anisotropy will thus result in a liquid crystal readily aligned by a field.

1.2.1. Nematic Phase

The least ordered of the liquid crystalline phases is termed *nematic* (often simply termed N) and is the most common in current display devices. The phase is fluid, with long range orientational ordering but no positional correlation; here the molecules align such that the principal molecular axis of each lies, on average, parallel with the director. Beyond this there is no ordering; in fact if the shape of the molecules is ignored then this phase, in terms of correlation of centres of mass, is identical to the isotropic liquid phase.

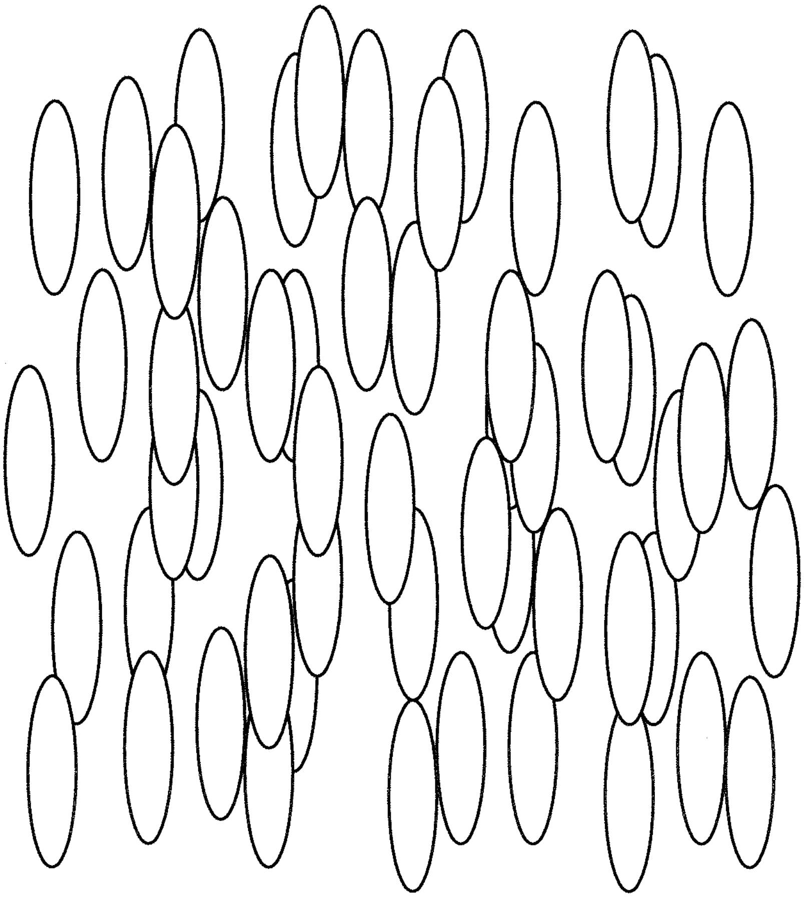


Figure 1.1. Idealised liquid crystal nematic phase

The optical texture of this phase (as seen using polarised light microscopy) is generally what is known as schlieren; this is a thread-like pattern with point singularities known as disclinations or point defects where the director orientation changes abruptly. It is also possible for the director to align perpendicular to the surfaces of the sample vessel (usually a glass slide) in which case light will evidently not be rotated and thus none transmitted. The phase is mobile and when subjected to mechanical stress will flash as ordering of the director in the sample is induced and altered; in fact flow will often be seen with no applied pressure.

1.2.2. Smectic Phases

More highly ordered phases are seen, however; there are many *smectic* phases (denoted S_A, S_B, *etc*, vaguely in chronological order of characterisation), in which the molecules tend to lie in layers, with the molecular cores lying alongside each other; motion of the molecules is preferred within rather than between layers. The simplest is the smectic A (S_A), which is similar to the nematic but the molecules tend to congregate in layers orthogonal to the main molecular axis. Other smectic phases exist where there are modifications to this basic layered form, including tilting of the director (S_C) and hexagonal packing (S_B). Still further types exist with these two effects combined (S_F and S_I).

1.2.3. Crystal Phases

There are a number of phases which are not exactly liquid crystalline in nature; these are more usually termed crystal phases due to the presence of significant long range three dimensional positional and orientational correlation. Originally these had been termed smectic phases (they are in some sense smectic phases with three dimensional ordering) but true smectic phases do not possess three dimensional positional correlations. The ordering is not theoretically infinite and so the phases are not truly crystalline in nature.

1.2.4. Chiral Phases

Of particular note are *chiral* phases. Introducing a chiral element into a liquid crystal molecule (even as subtle as hydrogen to deuterium) produces something of a helical packing in the ordering that occurs as a modification to the basic packing. Typically nematic and tilted smectic phases may be thus altered. Thus we see a chiral nematic phase (N* - formerly termed *cholesteric* as a result of the discovery of the cholesteryl benzoate mesophase) and chiral smectic phases (S* with subscripts as appropriate). These are of considerable importance for display technologies currently, due to certain interesting effects (the high polarisation) that they exhibit which are not of direct importance to this work [7].

1.3. Polymeric Liquid Crystals

Another important class of liquid crystalline material, and somewhat relevant to this work, consists of polymeric liquid crystals, of which there are two basic types.

A polymer chain is modified in one of two ways; either a mesogenic (liquid crystalline) unit is incorporated into the polymer chain to form a main chain liquid crystal polymer or is attached as a pendant to form a side (now known as side group) liquid crystal polymer.

These are of considerable interest and are increasingly being commercialised, *eg*, Kevlar, as used in armouring, which is formed from a liquid crystalline phase of a polyamide dissolved in oleum. A wide variety of other uses is possible, including optical data storage systems similar to compact discs.

1.4. Other Thermotropic Materials

It is appropriate to note that not only rod shaped molecules form thermotropic liquid crystalline phases; molecules shaped like a coin will have a tendency to align together and thus we see *discotic* liquid crystallinity; there are also liquid crystalline molecules shaped like bowls. In theory any molecule that deviates from spherical symmetry should form a liquid crystalline phase at some combination of temperature and pressure. There are also hybrid systems; for instance a disc-like central unit with pendant rod-like chains; such molecules can be used as models for polymeric systems [8]. There is also research into amphitropic materials (those which display thermotropic and lyotropic characteristics).

Chapter 2. Overview of Polymer Dispersed Liquid Crystals

Basically, a polymer dispersed liquid crystal (PDLC) material comprises a solid polymer matrix in which are dispersed microdroplets of a (typically nematic) liquid crystal.

This idea of dispersing anisotropic materials in an isotropic matrix to achieve selective refractive index matching is certainly not new [9] but the advent of liquid crystal technology has added new dimensions to the area. Liquid crystals may usually be aligned by electric fields and thus selective refractive index matching may be achieved in a hybrid system. A forerunner of this PDLC technology was the reverse idea, a device in which isotropic particles were dispersed in a liquid crystal "matrix" [10]. Still closer to the concept of microdroplets is to infuse a microfilter with liquid crystal [11].

Microdroplets proper have been formed by two methods. First a technology of emulsification of liquid crystal in a (necessarily water soluble) polymer to form encapsulated droplets - termed NCAP for nematic curvilinear aligned phase - has been developed with some success [12] and in fact is very close in terms of structure, operating principle and electro-optic response to the final idea of PDLCs proper. True PDLCs, the subject of this Thesis, are afforded by phase separation methods [13] and have the most potential of these polymer/liquid crystal composites in electro-optic applications [14],[15].

Two states exist for these devices; the "off" state which is highly scattering and the "on" state which is transparent. The off-state scatters due to refractive index mismatching between the randomly oriented liquid crystal droplets and the polymer matrix; the random orientation is brought about by uneven anchoring conditions at the liquid crystal/polymer interface leading to random director distributions (figure 2.1a); in the on-state these are aligned to effect refractive index matching ($n_o = n_p$) and thence a clear state is achieved (figure 2.1b). Switching between the two is achieved by applied electric field induced reorientation of the liquid crystal director.

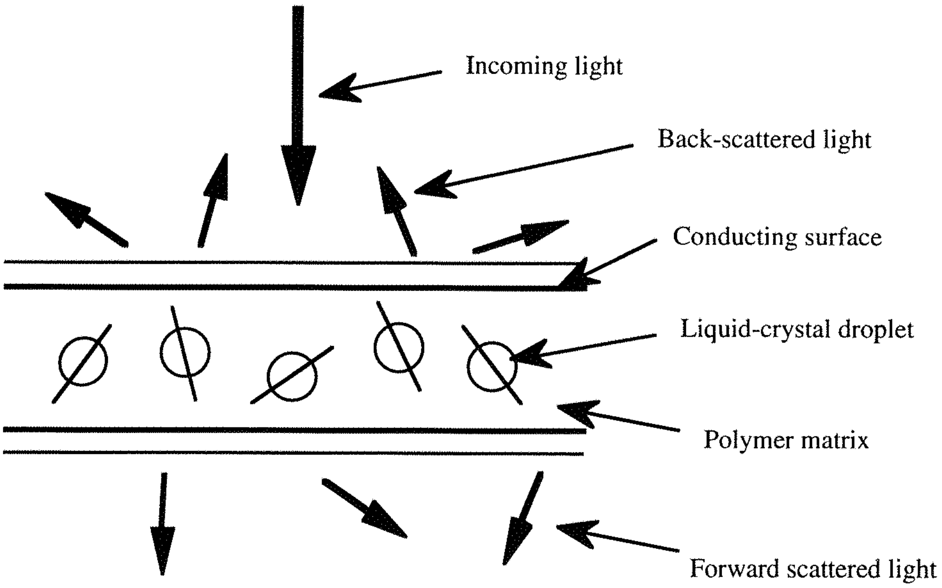


Figure 2.1a. PDLC off-state

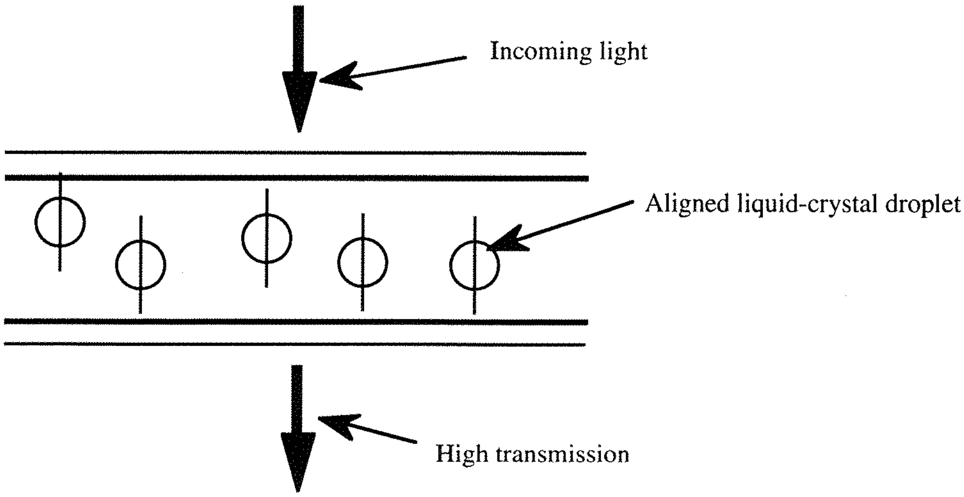


Figure 2.1b. PDLC on-state

A number of advantages that this type of material has over other technologies makes it an attractive proposition for development. The fabrication methods avoid many of the problems encountered in more conventional liquid crystal devices such as surface alignment, cell filling and sealing; the cells do not require Polaroids which therefore simplifies device design, reduces the cost, will often increase device lifetime in adverse conditions and reduces light loss in a cell in its clear state; the devices are capable of rapid switching times, offering greater speeds than, say, twisted nematic displays when the same liquid crystal is used; the ease of fabrications allows production of large area displays and devices; due to the nature of polymers it is easy thereby to manufacture flexible displays. The main problem with such materials is that the switching voltages can often be very high, thus potentially limiting use to large scale or permanent devices such as in houses or offices. Overall this technology is therefore one of great potential in the display device market [16].

Chapter 3. Formation of PDLCs

Polymer dispersed liquid crystal composites are formed by phase separation methods from an homogeneous and usually isotropic mixture of liquid crystal and prepolymer. There are three methods to afford the systems; polymerisation-, solvent- and thermally induced phase separation. Each of these may yield different results and in consequence a wide variety of morphologies is accessible; different structures can have different properties and therefore different application possibilities and so a wide variety of potential devices is conceivable, depending on the specifics of the cure.

3.1. Polymerisation Induced Phase Separation

Polymerisation induced phase separation (PIPS) generally uses either ultraviolet or chemical cure from an homogeneous liquid crystal/prepolymer mixture (although other methods have been reported [17]). In broad terms, the change in chemical potential of the polymer upon polymerisation results in the liquid crystal having reduced solubility in the forming polymer matrix [18], thus at some point the solubility gap is passed and the liquid crystal phase separates out by one of two mechanisms (see §**3.4**) [19]. Eventually the polymer gels and hence the droplet morphology is set.

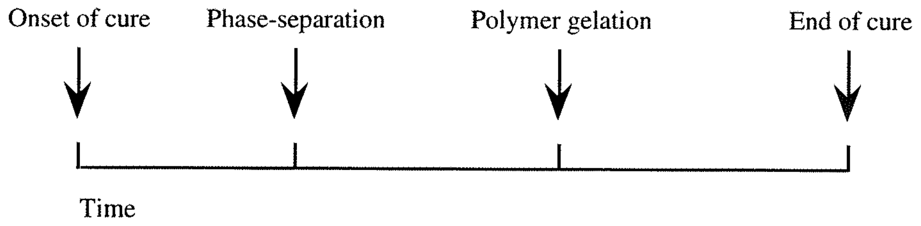


Figure 3.1. Schematic of PIPS

A variety of UV curable monomers have been used (acrylates and methacrylates for example) [20]; it is also common to use monomer/oligomer mixtures for this process [21]. These processes occur by step growth or chain reaction, with each usually resulting in one of two different morphologies [22]. Chain reaction mechanisms usually work quickly and result in large polymer strands forming quickly and phase separating from the lower mass mother solution; thus a so-called polymer ball morphology results with liquid crystal being in the continuous phase. Step growth gives a more even growth of the polymer; this results in the mother solution effectively increasing in molecular mass and thus the lower mass liquid crystals will become less soluble and so phase separate.

Of the thermosetting polymers, epoxy based systems (usually cured with amines) have been the most studied due to their availability and the ease with which copolymers may be formed to produce specific values for properties such as refractive index. Practically, any thermosetting system may of course be used and a polyurethane system is in fact described in this Thesis.

Two major factors affect the size of the droplets in PIPS systems; the materials used and the cure conditions.

The effect of the choice of materials is naturally system-specific and is not readily generalised. The aspects that affect the results include the reaction rate of the polymer precursor (effects discussed later) and the comparative densities of the two components [23,24].

The cure conditions can have a large effect on the end results; by far the most important factor being cure temperature which has a wide range of effects on the cure, many of which are interlinked and must be determined for each system although some points will naturally remain constant.

The main effect of a higher cure temperature naturally is to increase the rate of chemical reaction and so phase separation occurs more rapidly; the result is that smaller droplets are formed as the phase separation is forced upon the system with little time (in terms of molecular diffusion) for migration of the liquid crystal through the polymer in order to increase the droplet size; only localised phase separation is seen resulting in smaller droplets.

Also important is the degree of polymerisation which is normally greater with greater cure temperature; after completion of the reaction a higher degree of polymerisation will result in a more effectively phase separated system due to decreased solubility of the smaller liquid crystal in the polymer matrix. It is also the case however that higher cure temperatures will increase the solubility of the liquid crystal in the polymer initially although post-cure movement of the liquid crystal will reduce the content in the polymer matrix.

The effects of the cure temperature are rather interconnected so the characteristics of a product may vary in a complex manner with cure temperature, although the above-mentioned points are generally true.

In UV cure systems the intensity of the light that is used to cause the polymerisation is important; higher intensity naturally leads to a faster reaction with the subsequent effects already described. The concentration of any initiator is also important; the rate of reaction will be greater overall if there is more initiator.

3.2. Solvent Induced Phase Separation

Solvent induced phase separation (SIPS) is the most complex of the three methods as it involves a third component; a common solvent for a dissolved liquid crystal and thermoplastic. A given (homogeneous) solution is first formed and then the solvent is evaporated at a prescribed rate until a point is reached when eventually phase separation is seen (the point where the solvent can no longer support all of the two components in solution) and the liquid crystal forms droplets that eventually become locked in as the polymer gels (see figure 3.2)[25].

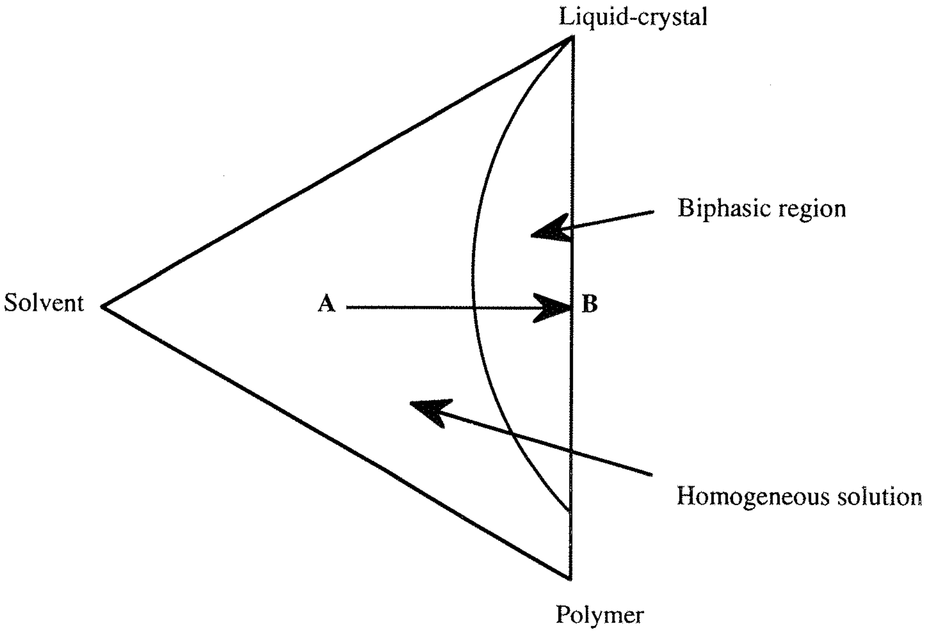


Figure 3.2. Schematic of SIPS. This ternary phase diagram shows that from the initial mixture at **A**, as solvent is removed, the line **AB** is traversed to point **B** in the biphasic region.

Factors affecting this method are the materials used and the rate of solvent removal. Removing the solvent rapidly will result in small droplets; as the polymer sets faster the liquid crystal is forced out of solution more quickly and the polymer gels more rapidly thus not allowing any further growth.

When devices are constructed using this method it is common to follow an uncontrolled SIPS process with a more controlled thermal process (see 3.3) as this method affords more control.

3.3. Thermally Induced Phase Separation

Thermally induced phase separation (TIPS) is achieved by cooling from a thermoplastic/liquid crystal melt. The liquid crystal and the polymer will have been chosen such that they are miscible above the melting temperature of the polymer. As cooling proceeds the miscibility gap is passed and phase separation affords the usual droplets.

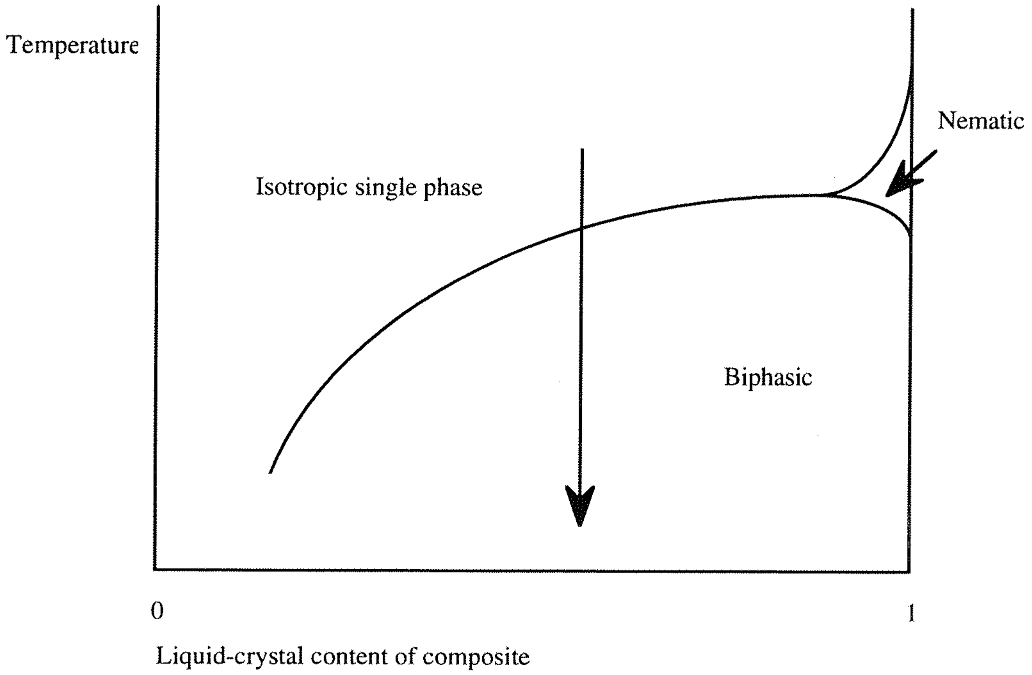


Figure 3.3. Schematic of TIPS

Factors affecting the cure are the materials and the cooling rate [26]. Faster cooling has the same effects as faster cure in PIPS or faster solvent removal in SIPS; smaller droplets result. Another effect of faster cooling is that more liquid crystal remains dissolved in the polymer upon cooling due to kinetic effects (less time elapses to allow the liquid crystal to phase separate from the melt).

3.4. Phase Separation Processes of PDLCs

The phase separation of PDLC systems is like that of any other mixture of materials in most respects except certain modifications sometimes have to be made to take into account the anisotropy of the liquid crystalline component. At first, the mother solution is (usually) an homogeneous mixture of liquid crystal and polymer. The phase separation process (often termed decomposition) occurs as the system cures (PIPS), cools (TIPS) or the solvent evaporates (SIPS), resulting either in phase separation of either the forming polymer, leading to a polymer ball morphology, or liquid crystal, leading to the generally more desirable microdroplet structure. Demixing occurs by either *binodal* or *spinodal decomposition* [27]; the specific process is determined by the second derivative of the free energy/composition curve.

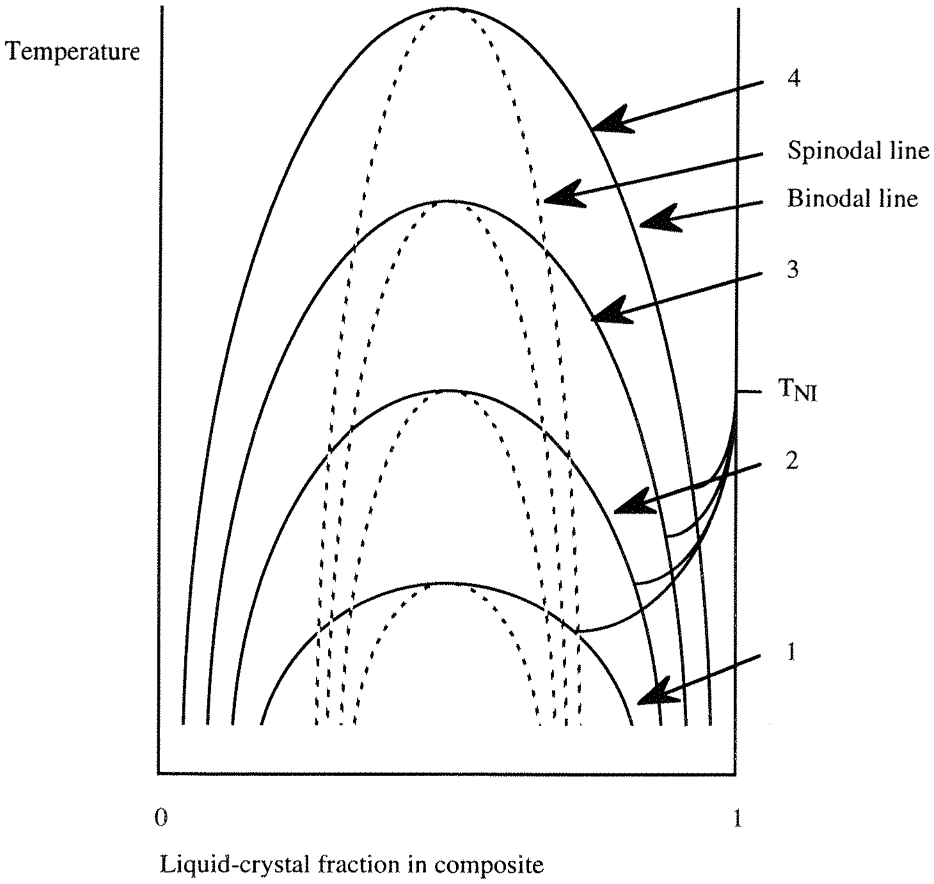


Figure 3.4. Phase diagram change upon polymerisation; the lines **1-2-3-4** refer to increased degree of cure with time

The change in the phase diagram associated with a PIPS process is illustrated in figure 3.4. The polymer is cured either thermally or photochemically and as it does the set of curves **1-2-3-4** is passed; thus for a given composition and cure temperature the phase separation curve (sometimes termed binodal line) is passed at some point. Above the curve is the stable (single phase) region - the free energy of the system is a minimum. Below the binodal line two regions are noted. First a metastable region in which the mixture remains homogeneous until a transition past the kinetic barrier to the more stable phase separated form by the binodal process. Below this region lies the unstable region where phase separation occurs by the spinodal process. A faster cure (more rapid progression from **1** to **4**) results in a more rapid progression into the unstable region of the phase diagram thus promoting spinodal decomposition. In a slower cure regime the system changes more slowly and thus more time is spent in the metastable region giving rise to binodal decomposition; morphologies seen in experiment have reinforced this idea repeatedly.

Note that this effect is much the same as the TIPS process as the curve of the phase diagram here is moving relative to a constant composition/temperature point, the reverse being true in TIPS; the SIPS process can also be thought of in these terms with increased solvent loss being equivalent to increased degree of polymerisation. Note also that the nematic to isotropic transition (T_{NI}) of the liquid crystal increases upon polymerisation.

The reverse of this phase separation has been investigated. There is a heat of mixing associated with the mixing/demixing point of a binary system; in PDLCs this heat depends on the degree of cure and the concentration of the liquid crystal; it has been shown that a minimum occurs with respect to liquid crystal content [28].

Also of note is the possibility of self-organisation of the liquid crystal droplets during formation [29], although this effect has not often been reported. In a SIPS process a spatial periodic distribution of droplet clusters can result; moreover it has been observed that orientational ordering of the symmetry axes of the droplet director configurations (see §**4.1**) can occur and so give potential control over film characteristics.

It can be of use in many polymerisation cure systems to cure above the phase separation point; cure below can lead to unwanted phase separation and large domains of either liquid crystal or polymer; naturally such cures will be followed by TIPS to afford more desirable products.

3.4.1. Binodal Decomposition

Quite simply, this process is phase separation by a nucleation and growth mechanism. In the metastable region of the phase diagram, random aggregations of liquid crystalline material in the mother solution result in the phase separation of randomly spaced and randomly sized droplets of the liquid crystal from the mother solution. Naturally the polymer may also form such agglomerates, resulting in randomly spaced balls of polymer phase separating from the mother solution. This is purely a chance mechanism which is often undesirable for applications as the characteristics of these randomly formed systems are usually not suitable (for example, the threshold voltages of systems may not be sharply defined because the liquid crystal is not uniform).

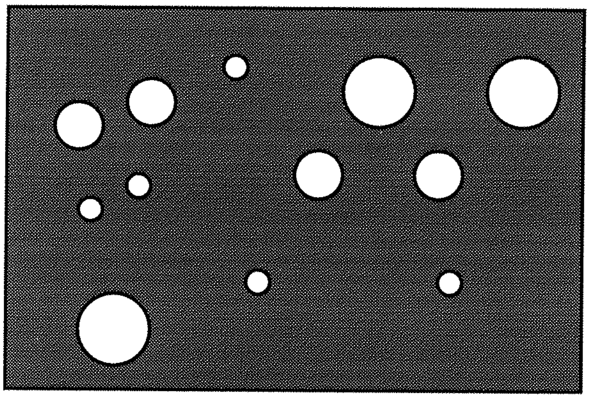


Figure 3.5. Binodal decomposition morphology

3.4.2. Spinodal Decomposition

This process is not as random as the binodal process and occurs in the unstable region of the phase diagram. It has been suggested that this form of decomposition is not different to binodal decomposition but is in fact a generalised form of the nucleation mechanism [30]. This mechanism causes minute perturbations of the local composition of the mixture to amplify with time [31]; the predicted structure is described in terms of a superposition of periodic modulations of a fixed wave length, random in amplitude, orientation and phase.

Thus the theory predicts uniform fluctuations of composition throughout a phase separating system. This leads to more uniform finished products and could also, in principle, lead to improved control over the characteristics of the composite (size and distribution of the droplets) as the parameters controlling the phase separation are more easily changed here than in the binodal decomposition process.

The spinodal decomposition process has been studied extensively [32,33]. The Flory-Huggins equation of the free energy of a binary polymer mixture is [34]:

$$\frac{\mathrm{F}}{\mathrm{kT}} = \phi \ln \phi + \frac{1-\phi}{N_{\mathrm{B}}} \ln(1-\phi) + \chi(1-\phi),$$

where ϕ is the volume fraction of the liquid crystal, N_{B} is the degree of polymerisation of component B (the polymer; the degree of polymerisation of the liquid crystal is taken to be 1), k is Boltzmann's constant and χ is an interaction parameter. As N_{B} increases from 0 (where the second derivative of F with respect to composition is positive and the system is thus stable), the free energy begins to assume a double well form which favours phase separation for certain concentrations.

The Cahn-Hilliard theory describes the initial progression of the spinodal process and uses the assumption that an inhomogeneous binary mixture can be described by a free energy thus:

$$F = \int \left[f(\phi) + \kappa (\nabla \phi)^2 \right] d^3 r ,$$

where $f(\phi)$ is the free energy density of an homogeneous system with concentration ϕ and κ is the interfacial energy constant [35].

Theories for isotropic polymer solutions [36] are useful starting points for modelling liquid crystalline systems as they have been studied more extensively and are closely related; the following relation is seen for the concentration diffusion in isotropic polymer solutions:

$$\frac{\partial \phi}{\partial t} = M . \left[\frac{\partial^2 f}{\partial \phi^2} \nabla^2 \phi - 2 \kappa \nabla^2 \nabla^2 \phi \right],$$

where t is the time and M is the diffusive mobility [37]. Whilst this is strictly valid for isotropic solutions it is also possible to apply this successfully to liquid crystalline systems [38] by considering the liquid crystal as a rigid rod solvent and the polymer as the solute. When in the early stages of decomposition the system behaves in a linear fashion with well defined periodicity and there is a maximum (resonant) growth wavelength which is calculated as follows ($\partial^2 f / \partial \phi^2$ is evaluated at the initial (*ie*, homogeneous) composition) - naturally this is where the droplets form:

$$\lambda = 2^{3/2}\pi - \left[\frac{\left({\partial^2 f}/{\partial \phi^2} \right)_0}{2\kappa} \right]^{-1/2},$$

where λ is the wavelength of the periodicity with maximum growth.

The time evolution of the structure factor is then given by:

$$S(q,t) = S(q,0)e^{2R(q)t},$$

where q is the scattering vector [39] and $R(q)$ is the growth rate. The structure factor is defined as the Fourier transform of the spatial correlation function of the dielectric constant at time t; it is proportional to the intensity of scattered light $I(q,t)$ and may therefore be determined from light scattering experiments to yield information on a curing system.

The growth rate, $R(q)$ is defined as:

$$R(q) = -Mq^2\left(\frac{\partial^2 f}{\partial \phi^2} + 2\kappa q^2 \right).$$

Now M and $\partial^2 f/\partial \phi^2$ will, in a polymerising system, vary with time and the degree of polymerisation and so will cause a variation in the light scattering when compared to a thermally quenched system; maximum scattering is seen at:

$$q_{\text{max}}^2 = \frac{-\partial^2 f}{4\kappa \partial \phi^2}.$$

Most commercially used liquid crystal systems, *eg*, E7, are mixtures; this can affect the end results and some success has been achieved in predicting such effects [40]; evidently such prediction is important to be able to achieve commercially viable products.

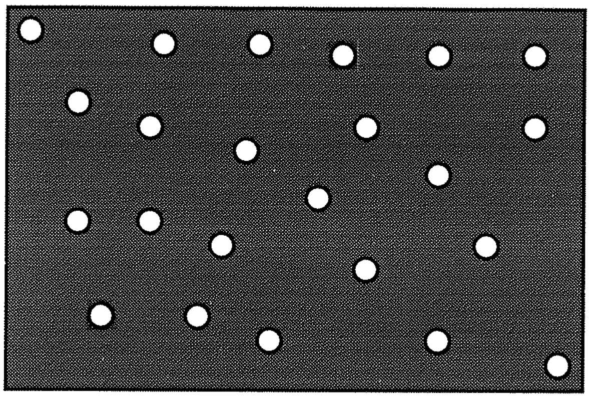


Figure 3.6. PDLC resulting from spinodal decomposition

Once the phase separation has begun and separate domains of polymer or liquid crystal have begun to form from the mother solution then further phase ripening (phase coarsening) mechanisms accentuate the effect although the uniform distribution of liquid crystal droplets is not necessarily lost if phase separation is good enough.

Much work has been done on the influence of the nematic-isotropic transition on the phase separation in a binary system where one species is liquid crystalline and the other species consists of spherical molecules [41,42]. Such effects are only important when the concentration of the isotropic component is below a certain limit (determined largely by the relative sizes of the isotropic and anisotropic interactions of the system).

3.5. Phase Ripening

After phase separation processes have occurred phase coarsening may occur; this can blur the difference between the two phase separation processes as the effects become less dependent on the initial decomposition mechanism. This effect is caused by thermodynamic pressure to minimise the interfacial free energy between the phases. Two processes are generally referred to: diffusion and hydrodynamic flow [43].

Hydrodynamic flow is strongly reduced at low temperatures due to the increase in viscosity, and also the diffusion process increases in rate with temperature. Thus at higher temperatures in the two-phase region more coarsening will be seen. If, then, a given material is cooled rapidly past the miscibility gap (thus reaching these lower temperatures) smaller phase domains (*eg*, droplet size) will necessarily result as the processes are much slower. This obviously makes the specifics of the phase separation and phase coarsening processes irrelevant.

If the polymer glass transition is passed on cooling then only the diffusion process can occur as evidently no flow occurs (at least on a reasonable time scale). Thus long term effects are governed largely by the diffusion of the liquid crystal in the polymer matrix; for long term applications diffusion must be negligible if the phase separation is not extremely good.

The Ostwald theory for interfacial tension driven phase ripening by diffusion leads to the result that:

$$d^3 \propto Dt/T,$$

where d is the minor phase droplet diameter, D is the diffusivity and T is the absolute temperature.

As the diffusivity usually increases with temperature above the first power (*ie*, greater than linear), higher temperatures will result in larger phase separated domain sizes.

Chapter 4. Operating Principle of PDLCs

To recap, PDLCs consist of micron sized droplets of liquid crystal dispersed in a polymer matrix. To understand the operating principle of these systems as electro-optic devices it is necessary to look at the film structures and from this explain how the films work. The morphology of the films is determined by the specific processing conditions employed but to describe the operating principle a basic morphology will suffice, wherein there is an isotropic polymer containing spherical droplets of a nematic liquid crystal.

In essence, the device will have a transparent state and an opaque (scattering) state; switching between the two is achieved by use of an applied electric field. The principle lies in the electro-optic response of the liquid crystalline material and selective refractive index matching of this material and the polymer matrix.

4.1. Nematic Director Configurations in Liquid Crystal Droplets

The very small size of the droplets induces large elastic distortions on the natural liquid crystal ordering due to curvature of the cavity. Unusual liquid crystal director configurations therefore result as this distortion competes with the anchoring of the liquid crystal director at the polymer interface and natural ordering of the fluid [44,45,46,47,48,49]. It is worth noting that a very powerful technique to explore the configuration of the liquid crystal droplet is nuclear magnetic resonance [50,51,52,53,54,55].

Two basic forms of anchoring at the polymer/liquid crystal interface are possible; the director could be anchored parallel with or perpendicular to the droplet interface. To illustrate the operating principle successfully it is not necessary to investigate all the possibilities of structure for each type of anchoring; it is only necessary to explain a few and all others follow intuitively from these - the basis of operation remains largely the same whichever configuration is considered.

4.1.1. Radial Configuration

With perpendicular anchoring there is the *radial* configuration, which is spherically symmetric, possessing splay deformation; it essentially consists of a central defect with the local director pointing towards the surface of the sphere. This is not birefringent, due to its spherical symmetry, and occurs when anchoring is strong or the droplet is large enough that the splay deformation energy is not too great. This is evidently not stable with an applied field as the director will attempt to align along the field direction thus altering the organisation to axial.

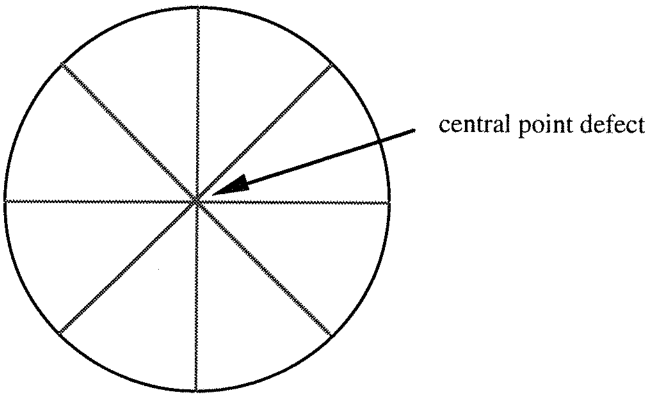


Figure 4.1. Radial director configuration

4.1.2. Equatorial Configuration

A further configuration seen with perpendicular anchoring is the *equatorial* configuration [56]. Factors contributing to this arrangement are weak anchoring, small droplet size and an applied field. Here there is an axis of symmetry through the centre of the droplet; if the anchoring is sufficiently strong then a line defect is seen around the equator corresponding to the symmetry axis. The axis defines conveniently a "droplet director"; this is a useful definition when describing electric field effects.

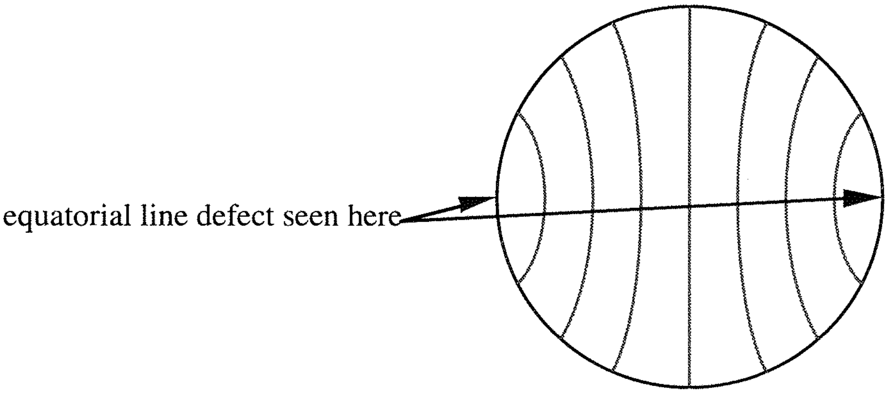


Figure 4.2. Equatorial director configuration

4.1.3. Bipolar Configuration

With tangential director anchoring there is the (most common) *bipolar* configuration. Here again the system exhibits cylindrical symmetry and therefore a droplet director, with point defects this time at the two ends of a diameter which corresponds to the symmetry axis.

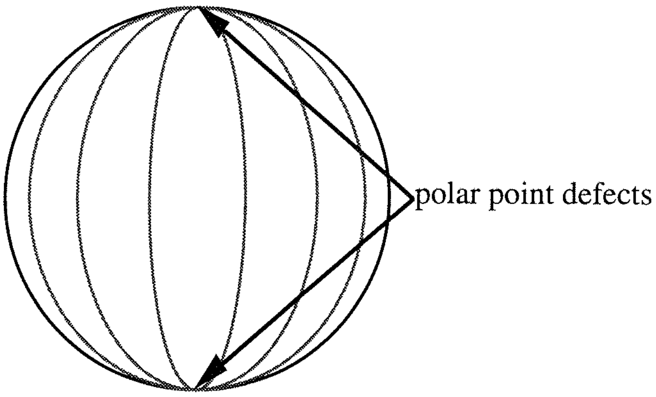


Figure 4.3. Bipolar director configuration

4.1.4. Axial Configuration

This droplet configuration is not common; the liquid crystal forces are usually such that a bipolar configuration is seen. Nevertheless this arrangement does occur and in it the liquid crystal ordering, again with tangential anchoring, is such that the directors lie in concentric rings about the droplet axis as shown in figure 4.4.

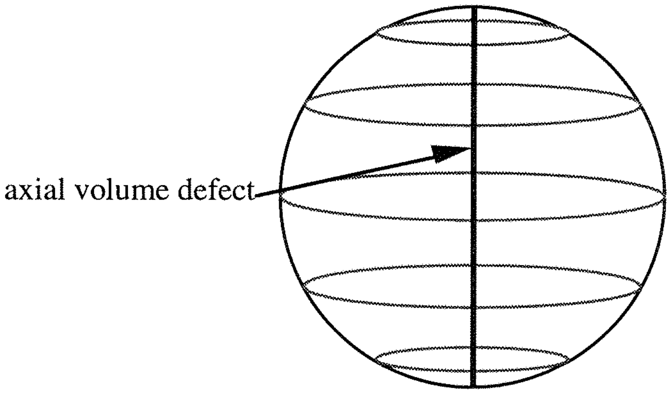


Figure 4.4. Schematic of axially configured droplet

4.1.5. Other Configurations

Many other configurations are possible [57] but, as noted, to describe them all is not necessary; far more detailed studies have been carried out and such a level of detail is not warranted here as it does not help to illustrate the principle of operation of PDLC devices.

It should, however, be noted that certain of the director configurations will be more desirable for some applications than others; for instance a bipolar configuration requires far less energy to realign than a radial droplet and so devices requiring low operating voltages would require more of the former and less of the latter configuration.

Introduction of a chiral element into the liquid crystal creates further interesting configurations; these are useful in colour PDLC applications but again it is beyond the scope of this work to elaborate [58,59,60,61].

4.1.6. Droplet Anisometry

Here it is wise to broach the subject of non-uniformity of droplets. Needless to say, none will ever be truly spherical although in many instances it is sufficient to assume spherical symmetry. When there is a degree of anisometry of the droplet the nature of the anchoring at the surface will be different depending on the position at the surface. Typically a droplet will be elongated along one axis; in the case, for instance, of tangential anchoring, this will promote the positioning of the two point defects to where the free energy is a minimum, *ie*, at the "ends" of the droplet. Similar effects will hold for any given configuration and naturally some configurations will be promoted over others; for instance, equatorial will be preferred over radial since the radial configuration will be destabilised by the imposition of an inherently anisotropic confinement.

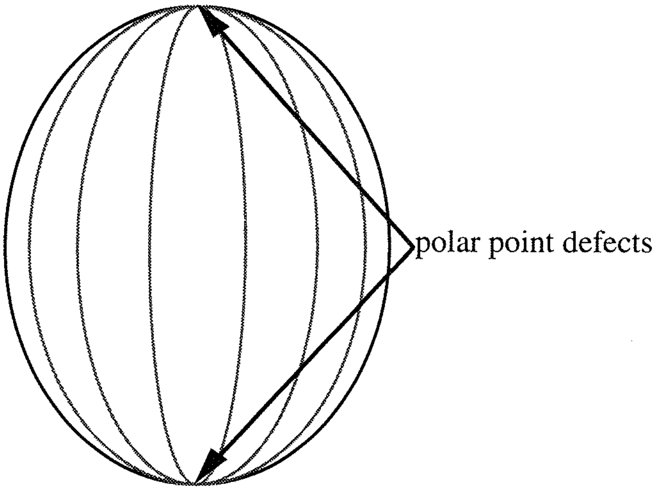


Figure 4.5. Elongated droplet with bipolar configuration

As a result of this promotion of a certain director configuration, the electro-optic characteristics will be strongly influenced by the shape of the liquid crystal droplet. Thus it is easy to envisage that control over the morphology of the system will allow a degree of control over the final electro-optic performance [62,63].

4.2. Operation

In electro-optic displays, polymer dispersed liquid crystal films are switched between a state which allows light to pass unimpeded and a state in which the light is scattered very efficiently [64,65,66,67].

4.2.1. Off-State

To be effective in the off-state, the droplets' size is chosen to be of the order of (but necessarily slightly larger than) the wavelength of light appropriate to the application and the film of the order of ten times that thickness. Naturally when all else is equal the liquid crystal droplets will adopt a minimum free energy director configuration, which is usually the bipolar configuration. In an uncontrolled film this will result in a random distribution of the droplet director, which in turn causes a refractive index mismatch between the liquid crystal droplets (the random distribution gives effectively a range of refractive indices between n_e and n_o) and the host matrix (clearly n_p cannot match all the range between n_e and n_o). Due to the size of the droplets [68] and the difference in the refractive indices these films are highly scattering and thus appear opaque [69,70]. Scattering intensity is influenced by the number of scattering events an incident photon experiences and the degree of mismatch at the droplet boundary. Thus a good degree of anisotropy of the refractive index is desirable to ensure off-state scattering is high; similarly a high droplet density ensures a large number of scattering events although it impairs on-state clarity. Interference caused by droplets of a size similar to the wavelength of light naturally causes intense scattering.

Thus if there is a sufficient density of droplets such a film will scatter extremely effectively [71]. For example, consider a film of thickness around 30μm with droplets of around 1μm (50% by volume); incident light will undergo many scattering events prior to leaving the film and so it is very efficiently scattered.

4.2.2. On-State

In the on-state the film, sandwiched between two conducting slides (usually indium tin oxide coated glass), appears transparent [72]. This is achieved by choosing the refractive index of the polymer to be the same as one of the refractive indices of the liquid crystal (usually n_o as most liquid crystals have positive dielectric anisotropy and thus align parallel with the field), such that when aligned by an electric field of sufficient strength, normally-incident light sees no changes of refractive index on traversing the film and thus is transmitted [73].

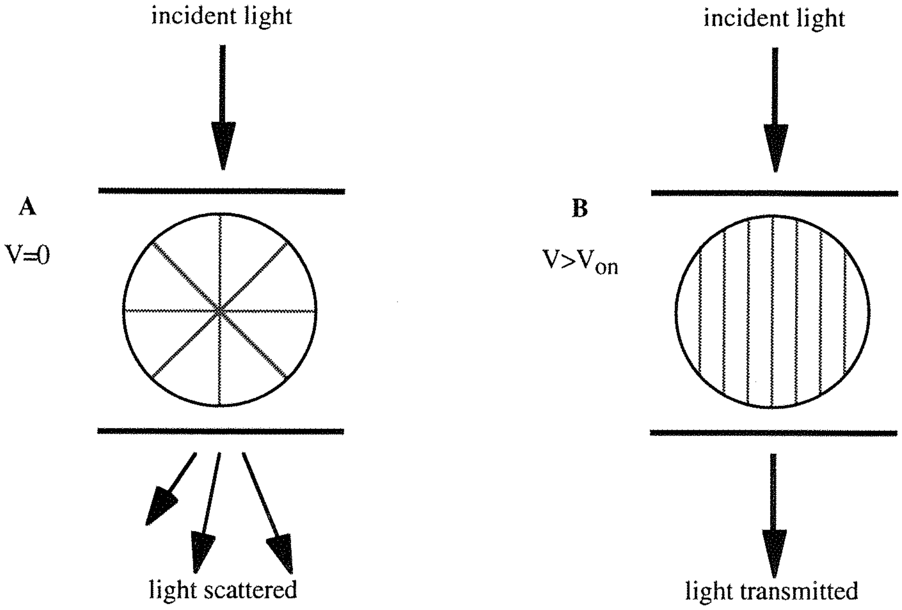


Figure 4.6. Basis of PDLC operation

Figure 4.6 shows the basis of operation. In **A** the normally-incident light sees a change in refractive index at the droplet boundary; on application of a potential in **B** the liquid crystal becomes aligned such that there is no change in refractive index on traversing the droplet boundary.

For the axial configuration, the liquid crystal director will try to align parallel with the field, in the case of those with positive dielectric anisotropy. When enough force is imparted to the droplet, to overcome the ever present elastic forces and those caused by confinement in a small volume, the droplet will essentially be seen to rotate such that the local (and thus droplet) director points along the direction of the field. If the refractive indices have been chosen appropriately then the film will become clear for viewing angles perpendicular to the film.

For the radial configuration the liquid crystal director will align with the field and be forced into an axial type configuration when the aligning energy overcomes the droplet forces; again the droplet director will be parallel with the field.

A bipolar droplet will effectively rotate such that the director lies parallel with the applied field.

When the applied field is removed, the droplets will again try to minimise their free energy. Although some cases of memory effects (*ie*, retention of the director states after removal of the field) in these systems have been observed [74], on the whole, the surface forces that caused the alignments in the first instance will prevail to return the droplets to their original configurations.

These effects may naturally be generalised to any configuration, with the main consideration being that the refractive indices of the polymer and the liquid crystal (n_o for a liquid crystal of positive dielectric anisotropy) be chosen such that they match on alignment by a field.

4.2.3. Anisometric Droplets

Droplet anisometry has a great effect on the on/off characteristics. In general the effects are to promote a certain configuration which remains fixed in the off-state during repeated on/off cycles. The anisometry of the droplet will increase the elastic deformation free energy and thus will in general increase the strength of the field required to align the droplet. The main benefit lies in the fact that these forces will rapidly force the original configuration to return once the applied field has been removed. Thus again control over this anisometry can be seen to be of use in final device attributes, for instance in reverse mode devices where the film is transparent in the off-state and an applied field will induce the usual opacity; in such a system the liquid crystal is aligned in the off-state such that there is no refractive index mismatch for incident light and in the on-state the liquid crystal is reoriented such that mismatch is achieved (see §**7.5**).

Chapter 5. Electro-optics of PDLC Materials

Generally, liquid crystal devices are switched on and off by application of electric fields and PDLCs are no exception. The main advantage over other systems involving liquid crystals is that these systems require no Polaroids; additionally no insulation or alignment layer is required.

To achieve electric switching, a conducting film needs to be placed at each surface of the film, typically this will be indium tin oxide; one layer will have an appropriate electrode pattern photolithographically defined such that information may be effectively displayed. Often these correspond to simple, directly driven display segments, but matrix addressing technology is usually a requirement for modern high information displays.

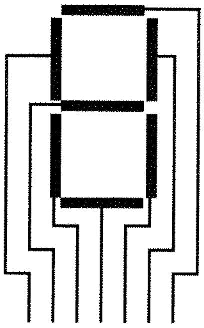


Figure 5.1. Schematic of basic direct drive display. The segments' earth electrode will be the entire reverse side of the display; each element must be directly driven.

5.1. Device Construction

These devices are easy to manufacture in principle. To illustrate, consider a system utilising a PIPS process to effect film formation. In this the liquid crystal/prepolymer mixture (either UV or thermally cured) is sandwiched between two substrates, with transparent spacers to ensure film uniformity. This set-up is then either exposed to ultraviolet light or heated to effect cure of the polymer and thus phase separation. The substrates themselves consist of glass or plastic coated with a layer such as indium tin oxide. This basic idea may be modified; it has been demonstrated that it is possible to cure using one substrate only and separate the cured film from the substrate.

5.2. Matrix Addressing

Matrix address systems are essential for modern high information content displays. Essentially matrix address systems consist of segmented electrodes that are connected in orthogonal rows and columns to produce display elements at the intersections (pixels) (figure 5.3 shows a related device - the active matrix address system). The rows of the matrix thus produced are activated sequentially in time and appropriate voltages applied in parallel to the columns such that each pixel at the intersections is either on or off. Each segment responds to the net root mean square voltage across it; if, then, the net voltage at the intersection is greater than some critical voltage, say V_{on}, then the segment will be activated. Naturally if this potential is not achieved the pixel will not be activated. The liquid crystal will of course relax back to the minimum energy configuration once the potential has disappeared; the driving must therefore be dynamic inasmuch as the pixel must be addressed again before the relaxation period is finished to keep the pixel activated; thus such drivers will cycle through the rows and columns with a periodicity less than the relaxation time of the liquid crystal.

This gives rise to a maximum number of rows that may be addressed for a given drive voltage and this is maximised when $V_{on}/V_{off}{\approx}1$ [75]. Obviously this number is desired to be as large as possible in order to impart the most information possible. This difference between V_{on} and V_{off} is in turn dependent on the slope of the electro-optic response curve (transmission *versus* applied voltage); if there is a sharp rise to clarity upon increasing the applied voltage then more rows may be addressed.

5.3. Electro-optic Response

A major factor in determining effective electro-optic response is uniformity of the display medium; in this case this corresponds to homogeneity of the sample and uniformity of the droplet size; any variations from the desired morphology (size, shape or orientation along the droplets' major axis) will result in a dispersion of the electro-optic response and thus a decrease in efficiency (sharpness of the response curve). For use in commercial devices, therefore, morphological control of these systems is desirable; thus control over the curing of the systems is of paramount importance.

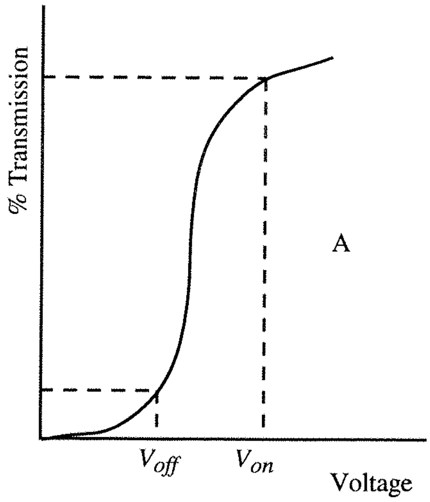


Figure 5.2a. Typical electro-optic response curve for PDLC film

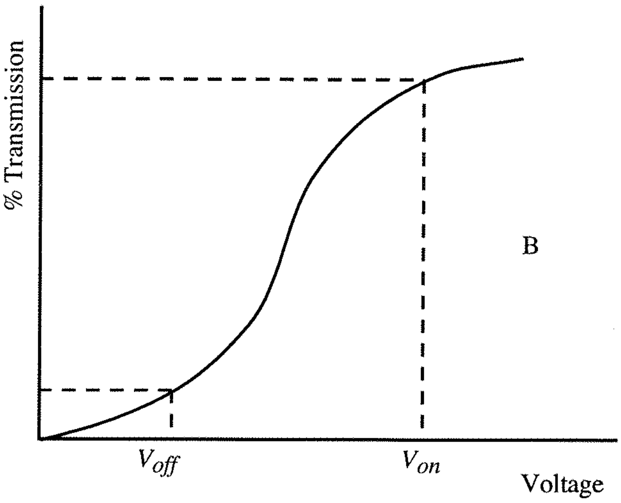


Figure 5.2b. Inefficient PDLC electro-optic response curve. The sets of scales are the same but V_{on}/V_{off} is clearly closer to unity in **A** than in **B.**

Even so, these factors are not the only ones that can cause poor response; the resistivities of the two components obviously play a major role in determination of the curve. As this is an electrical circuit, naturally some of the driving voltage will be dropped across the polymer and thus a reduction in the effective electric field as seen by the liquid crystal droplets [76]. Also as the droplet reorients the effective dielectric permittivity will change as the directors all align parallel with the field. In addition the liquid crystal may be considered to be in series with the polymer in the circuit and therefore a reduction in effective field (shielding) may be seen. Thus the response curve is bound to be non-ideal. It is desirable in these systems, as in other conventional liquid crystal displays, to have a liquid crystal with high dielectric anisotropy in order to achieve quick on-times and low threshold voltages. The elastic constant [77] of the liquid crystal used also affects the relaxation time which is proportional to K^{-1} (a higher elastic constant means a quicker response); the on-time is dominated by the square of V_{on}. The voltage requirement is proportional to the square root of the elastic constant so improvements in relaxation time will increase the voltage although within an acceptable regime.

In general, therefore, to achieve reasonable levels of addressing several problems must be overcome. A typical method of overcoming these is to use dual frequency addressing of the liquid crystal. These liquid crystals respond differently to electric fields when the frequency of the applied AC voltage changes - a cross-over point is seen where the dielectric anisotropy changes from positive to negative. This is relatively easily achieved with modern electronics but the biggest problem lies with the temperature range that the liquid crystal is addressable in; the crossover frequency rises exponentially with temperature [78,79]. This gives improved control over the on- and off-times of a device although the cost (in terms of required field) can be high (*eg*, 100V).

Although matrix addressing technology (noted above) is limited to single figure numbers of lines currently, active matrix addressing technology [80] may be used with even poor-response systems in small display devices [81]; such systems are excellent for projection displays and small screen applications [82] (figure 5.3)). These utilise non-linear response devices such as transistors in series with the display elements; the response is compatible with the fastest addressing time of the element and the effect then is to enable the stored charge to be dissipated across the display element in a time compatible with the response of the liquid crystal. The primary drawback is that the fabrication is additionally complicated by the presence of the transistor; thus the cost is increased and the display size limited [83].

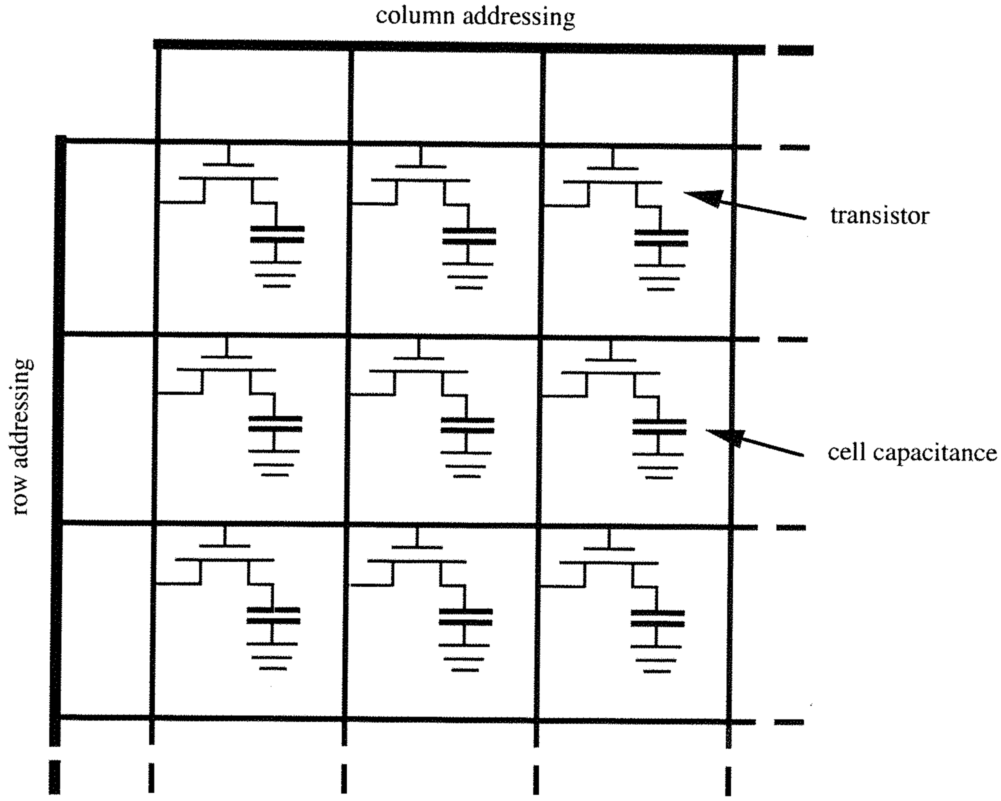


Figure 5.3. Schematic of basic active matrix address system

5.4. Factors Affecting Electro-optic Performance

As is evident, the performance of a PDLC material in a given application is dependent on a wide variety of factors; the materials used, the system morphology, the method of device construction [84]. Requirements generally include a high contrast ratio (essentially a comparison of transmission in the on- and off-states), low driving voltage, low power consumption, fast switching times, high film resistance, environmental stability (in fact resistance to any kind of degradation) and wide viewing angle. A tall order and a very complex one as most of these attributes are inextricably related.

5.4.1. Clarity and Transmission

These quantities need quite exact definitions; clarity is the measure of the sharpness of a viewed image (unscattered transmitted light/total transmitted light), whereas transmission is simply the amount of light that is able to pass through the film (transmitted intensity/incident intensity). It is possible to have high clarity with low transmission and *vice versa*. Measurements are generally carried out by UV-visible spectrophotometry using an integrating sphere for transmission and for clarity a haze meter or integrating sphere.

The main factor in determining the on-state clarity of a PDLC film is the match of (typically) n_o and n_p. When the match is close, more transmitted light will be unscattered and thus there will be a clear image. Normally incident light will naturally be of higher clarity than that incident off the normal; this is of course due to the mismatch of n_e and n_p. A good match is usually achieved by tailoring n_p (this is possible by subtle changes in the chemical structure of the polymer - very easy to achieve due to the enormous range of commercial polymers available currently). The effect of the liquid crystal in the composite is threefold; firstly, the inevitable dissolution in the matrix alters n_p; secondly, n_o is not that of bulk liquid crystal - this is due to the distortions imposed by the confinement in small cavities which prevent all the liquid crystal directors aligning exactly parallel; thirdly, the n_e of the liquid crystal increasingly affects the refractive index match as viewed off the normal.

In the off-state, the clarity and transmission is affected mainly by the birefringence of the liquid crystal and the size and density of the droplets. Obviously a liquid crystal with high birefringence will scatter more than one with a lower birefringence; a greater range of refractive index naturally causes greater mismatch with the polymer. When the droplets are of a size and spacing of the order of visible (or whichever wavelength is desired) light's wavelength then most scattering will be seen. Whilst this is desirable in the off-state, evidently this scattering will reduce the on-state clarity also - the system is not perfect; due to anchoring the liquid crystal director will not be aligned at the interface and thus residual scattering will be seen, meaning this effect is of importance. Film thickness increases the scattering in both off- *and* on-state but needless to say also the driving voltage required [85].

Temperature affects the refractive indices of the polymer and liquid crystal differently; Δn decreases with increasing temperature, reducing contrast, n_o generally increases with temperature and n_p decreases [86]. As a result, matching of the indices over a temperature range is usually difficult if at all possible and so a compromise at some mid point in the operating range is usually enforced.

Typically, a PDLC film for use in a device will be around 25µm thick, will have evenly spaced droplets around 1 micron in diameter, n_p=n_o and will have a highly birefringent liquid crystal such as E7 (Merck).

5.4.2. Contrast Ratio

Contrast ratio [87] is a useful standard of performance for any display device and is essentially a measure of the off- and on-state transmission, although there is more than one definition. The main contributor to contrast ratio is the light scattering but investigations have shown [88] that the method of perception and the definition of the ratio are important in its precise determination.

The first method of determining the contrast ratio is by measuring unscattered light (transmission or brightness in the on- and off-states) and the second method measures the light scattered (again comparing between on- and off-states)

The methods of improvement are largely covered elsewhere in this report; for instance the use of dual frequency addressing will inherently improve contrast ratio (besides the improvement in the speed of response) because of the enhanced degree of refractive index mismatch of the off-state.

It is fortunate that in these devices the natural forces causing realignment of droplet directors are such that the off-state scattering is easily sufficient to maintain a high contrast compared with the on-state.

5.4.3. Driving Voltage

As with other aspects of PDLCs, many factors affect the driving voltage of a PDLC film [89].

Most descriptions of PDLC films consider a spherical droplet. If this is the case, then no real distortion is required to realign the droplet as the two orientations are degenerate.

It is obvious that this is inaccurate - no droplet will ever be spherical; all will vary somehow, typically being elongated, and it is these often slight differences that account for the random alignment of the droplet directors and thus also the scattering and is obviously a requirement for a PDLC film.

These distortions also affect the driving voltage as more energy is required to align the liquid crystal [90,91]; the switching voltage for a bipolar droplet is:

$$V_B = \left(\frac{d}{3a}\right)\left(\frac{\rho_p + 2}{\rho_{lc}}\right)\left|\frac{\kappa(l^2 - 1)}{\Delta\varepsilon\varepsilon_o}\right|^{1/2},$$

where d is the film thickness, l (=a/b) is the ratio of the droplet semi-major axis (a) to the semi-minor axis (b), ρ_p is the resistivity of the polymer, $\rho_{l\text{-}c}$ is the resistivity of the liquid crystal, κ is the elastic constant of the liquid crystal [92] and $\Delta\varepsilon$ is the dielectric anisotropy of the liquid crystal. A low driving voltage is achieved with a thin film, near spherical droplet symmetry, a high dielectric anisotropy of the liquid crystal (allowing easy alignment by an applied field), large droplet sizes (less elastic force required to align the liquid crystal as the effects of confinement are reduced), low polymer resistivity (relative to the liquid crystal although this will naturally increase the power consumption) and high liquid crystal resistivity. It must also be stressed that the sheer size of the devices affects the overall driving voltage and power consumption so engineering devices must take into account such effects (losses in the indium tin oxide layer, *etc*) [93].

The electric field within a droplet is not necessarily simply related to that of the applied field [94]. The effects of shielding of the applied field by the dielectric and ionic conductive effects in the liquid crystal droplets [95] can be quite severe in altering the effective field - up to and even more than an order of magnitude. The dielectric problem is overcome by choice of low polymer resistivity as mentioned above; the liquid crystal used must be extremely pure (at least in terms of ionic impurity).

5.4.4. Response Time

Droplet shape is a primary factor in governing the speed of the response to applied fields [96].

In general the further a droplet is from spherical symmetry then the faster the response upon removal of an applied field but the slower the response when one is applied (a less spherical droplet will have a stronger force returning to equilibrium).

The relationship determining τ_{off} (time constant for relaxation to the off-state) is as follows:

$$\tau_{off} = \frac{\gamma_1 a^2}{\kappa(l^2 - 1)},$$

where γ_1 is the viscous torque/viscosity coefficient.

Response time (τ_{on}) is naturally also governed by the strength of the applied electric field and is proportional to E^2. Relaxation to the scattering state is exponential with some time constant τ_{off}. This relaxation rate is affected by the droplet anisotropy (as (l^2-1)), a useful fact because if small distortions are created in the droplets then the relaxation time is improved (a square relation) whereas the driving voltage is sacrificed much less (a linear relation).

Switching can be much improved by the use of dual frequency addressing of the liquid crystal. In such a dual frequency addressed system the liquid crystal is electrically switched between two forcibly aligned states (see §**6.1.1**).

Chapter 6. Optimisation of PDLC Materials

There are a number of factors that must be considered in order to improve the performance of a PDLC material.

6.1. Liquid Crystal

Even the simplest liquid crystalline material can behave in a quite complex manner and as such there are many factors that will affect overall device performance. Due to the complexity of these systems on a molecular level these factors are frequently interlinked and therefore it is often the case that the best compromise in PDLC characteristics will be as close as a material can get to the actual requirements.

Most commercial liquid crystalline materials are of the cyanobiphenyl type although there is considerable research into alternatives [97,98,99]. Such liquid crystals are often eutectic mixtures where the mixture's properties have been engineered to give the requirements of a materials for use in an electro-optic device - somewhat easier than attempting to engineer a pure material with the same requirements. E7 [100] is a good example and is quite common (see §**8.1**). The cyanobiphenyl type of liquid crystal is well characterised and widely used, particularly as eutectic mixtures which have very wide operating ranges and high dielectric anisotropy.

Natural requirements include fast response, high birefringence, high dielectric anisotropy and of course low cost; these are dealt with simply by choice and are described as necessary elsewhere. Two options for improvement are described below.

6.1.1. Dual Frequency Addressing

In many applications it will be of interest to use a dual frequency addressable liquid crystal in the device (or a mixture of conventional liquid crystal with, say, 10% of such a material). In essence these liquid crystals will respond differently to AC electric fields when the fields are applied at different frequencies; at some crossover frequency, f_C, the electro-optic response characteristic will change over from having negative to positive dielectric anisotropy [101].

When applied successfully in a device the liquid crystal can rapidly be switched between the aligned transparent state and a pseudo off-state (in which the directors are aligned at 90° to the on-state which is basically as effective as the random scattering state) simply by altering the applied field frequency [102,103]. In essence this gives rise to an increase in the slope of the transmission with respect to applied potential. This forced switching makes applications involving, for instance, fast switching times and high contrast far easier than relying on a more conventional relaxation mechanism which can be relatively slow [104,105].

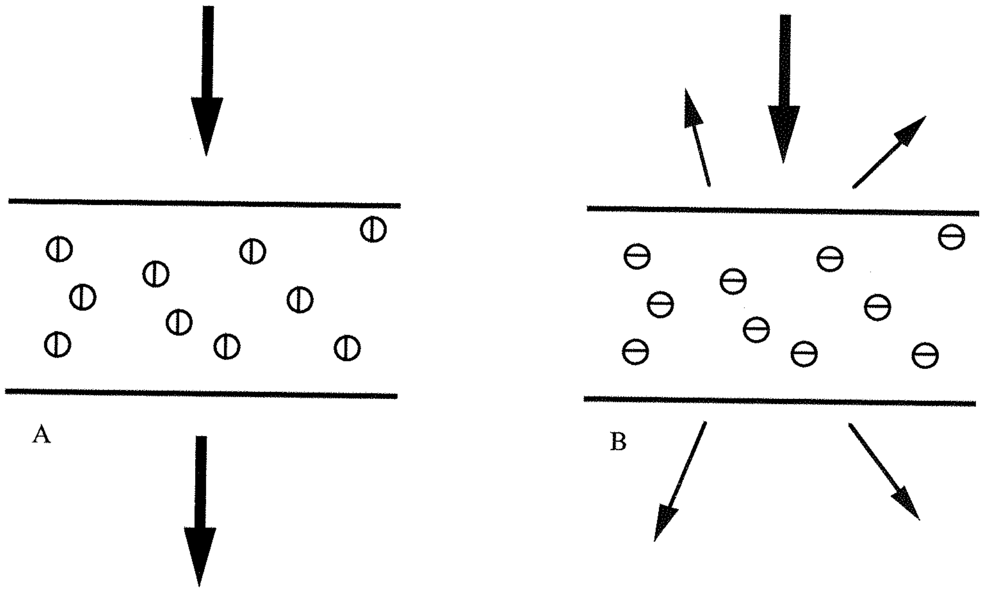


Figure 6.1. Schematic of dual frequency PDLC operation. In A, f_{applied} is greater than f_c; in B f_{applied} is less than f_c.

This technology is of particular importance in matrix address systems where rapid response is a particular requirement. Although the electronics involved in the construction are a little complex, current integrated circuit technology allows production of such devices with few problems.

6.1.2. Effective Temperature Range

As noted already, a wide operating range of the liquid crystal will be required to maintain a high birefringence in the operating range of the device; this is particularly true in the high temperature limit where a small change in temperature may alter the birefringence quite significantly. The low temperature limit is also important as the material must be fluid at low temperatures for outdoor applications. Over this range the refractive index or indices must also be consistent to avoid excessive mismatch with the n_p. There is now a reasonable range of commercial mixtures that are able to operate over ranges acceptable to most applications.

6.1.3. Alternatives

Various advances in liquid crystal technology have allowed parallel advances in PDLC technology; one of these is development of ferroelectric chiral smectic phases [106]. For example, most "normal" liquid crystals in display devices have characteristic switching times for basic applications of 1-10ms. Research has shown that ferroelectric [107] and antiferroelectric [108] liquid crystal materials can improve the speed of response by a factor of 10 to 100. Application of this improvement in PDLC technology has yet to be realised however; most requirements of PDLC devices would not benefit, although application in projection would benefit considerably.

6.2. Polymer

Many problems must also be tackled when optimising the polymer matrix; these interrelate with those of optimising the liquid crystal in a number of places, and also are connected in themselves.

The polymer cure regime is the most important factor in polymer matrix optimisation. It must be sufficiently fast such that production is as rapid as necessary and so a suitable choice of liquid crystal, polymer and phase separation method for the desired application must be chosen. This is often not easy; for instance with thermosetting materials a low temperature method, whilst desirable in that it reduces liquid crystal solubility in the polymer, will result in slow cure times, which is naturally undesirable for most kinds of production; naturally a hotter and thus faster cure will achieve the opposite.

Another facet of this problem is contamination of the liquid crystal by prepolymer. This only really applies in thermosetting cure systems where there is a relatively high degree of material (prepolymer) which is appreciably soluble in the liquid crystal. This is largely overcome by choice of formulation of cure system, and ensuring maximum possible cure. Photoinitiator in UV cured systems can be a problem, although it is possible to overcome this by use of a copolymerisable initiator [109].

Conversely there is the contamination of the polymer matrix by the liquid crystal (plasticisation of the polymer) [110,111]. Higher cure temperatures will naturally give rise to enhanced liquid crystal solubility in the polymer and so must be avoided if possible. It can be desirable also to make the polymer repeat unit and the liquid crystal less chemically compatible to reduce solubility in the polymer matrix [112]; certainly altering the structures of each has a noticeable effect [113].

Environmental stability is another factor to consider, although the nature of polymers makes this relatively easy to achieve. Specific applications will dictate the desirable characteristics required but most will be easy to achieve [114].

The use of polymeric liquid crystals is of great potential as it theoretically could reduce or remove off-normal haze but since these materials are often experimental in nature themselves specific application is not always easy. Nevertheless some have been developed [115].

6.3. Refractive Index matching

It is evident from the previous discussion that the appropriate refractive indices of the liquid crystal and the polymer must match closely to be of any use in a PDLC device; there must be sufficient scattering in the off-state and sufficient clarity in the on-state. Two main problems arise at this consideration - those of angle of view and temperature of the device. A further consideration of polymer matrix plasticisation by the liquid crystal is also worth noting but curing regimes are a primary factor in controlling this problem [116].

6.3.1. Angular Dependence

The previous discussions hold true only for normally incident light; all angles of view must be considered for any application that requires transmission other than perpendicular to the display (this, of course, means most applications).

Normally incident light will see little change in refractive index upon passing through the on-state polymer/liquid crystal interface. Evidently at other angles of incidence the light will be scattered proportional to the angle away from normal (the effective refractive index becomes further from n_0) [117]. Measurement of this is possible although multiple scattering and the anisotropy of the systems complicate anything other than an empirical approach to its correction.

Under ambient (*ie*, diffuse) lighting, photons entering the film will be from many directions and thus will be scattered into a range of angles. Some of these will encounter other droplets and be scattered again, others may reach the boundary of the device. Some of these will be trapped within the film and will back-scatter, others will be released from the film at some essentially random angle [118]. Thus the film will appear less clear. This angular dependence causes a "haze" [119] in the appearance of the film under diffuse (or ambient) lighting; this quantity is used to define film clarity [120].

Needless to say, haze is dependent on the materials used in the film; it is easiest to engineer n_p relative to n_o and this is what is usually done to improve film characteristics. The choice of the n_p/n_o ratio affects the angle of effective transmission and the angle of maximum transmission. The following assumes $n_e > n_o$, such is the case with E7, where $n_o = 1.520$ and $n_e = 1.745$ at 20°C.

When $n_p < n_o$ the angle of maximum transmission (which may be some way below 100%) is at the normal but the transmission tapers off quickly away from the normal.

If $n_p = n_o$ then the angle of maximum transmission is again at the normal. As the angle of view moves away from the normal the refractive index of the liquid crystal changes but since, for small angles, the main contributor to liquid crystal refractive index is n_o the match is still close. This also gives the broadest transmission peak.

It is sometimes desirable to have $n_p > n_o$, *eg*, in solar control applications (windows in sunny climes) where direct sunlight is to be avoided. Normally incident light is no longer that which has the greatest transmission. As the angle moves away from the normal, the match gets closer until reaching some desired angle where it is achieved (this depends on the choice of the refractive indices of the materials and in particular the birefringence of the liquid crystal).

A potentially excellent way of reducing or even removing this angular dependence of the light transmission would be to use a liquid crystalline polymer as the matrix for the system [121]. In such a system, theoretically at least, the polymer matrix would be formed from a nematic phase, thus affording an aligned matrix in which the refractive index changes with the angle of incidence of light, much like the liquid crystal in the droplets. As such it is conceivable that the indices of the polymer and the liquid crystal could be engineered such that they match over the entire hemisphere of viewing in the on-state, although this would be difficult to achieve because the actual values cannot be accurately predicted. In addition off-state alignment of the system during cure (*ie*, curing from the nematic phase) could be achieved trivially allowing greater control over the system characteristics. However current polymer liquid crystal technology is experimental in nature and as a result a material that not only has suitable n_e and n_o but also phase separates effectively is difficult to create.

6.3.2. Temperature Dependence

Mismatch in the n_p and n_e leads to scattering in the off-state, although inherently PDLCs scatter light so well that specific engineering is unnecessary. The specific birefringence of the liquid crystal, $\Delta n = n_e - n_o$, is largely the cause of the scattering.

This value, on the whole, decreases with increasing temperature [122] more quickly than n_p which results in increased scattering and thus improved off-state performance. It is obvious, however, that there will be similar effects in the on-state and so worse on-state performance will be expected.

At some temperature n_p will equal n_o by design. Due to the temperature dependence of both values it will not hold for all temperatures. Any deviation from this temperature will then naturally worsen device performance.

About the only way of alleviating this problem is to create a device that will operate at temperatures as far below T_{NI} as possible. The reason for this is that the rate of change of the refractive index of the liquid crystal with respect to temperature is higher near the nematic-isotropic transition, so the effect will be lessened when further from. It is also useful to choose a liquid crystal with a wide operating range for similar reasons. Additionally $\Delta\varepsilon$ is larger when T_{NI} is much greater than the operating temperature.

6.4. PDLC Morphology

As has been noted in several places, it is of great use to be able to control the specifics of the film morphology to allow a number of different potential applications. Various characteristics may be varied, including the size of the droplets in the polymer matrix. The droplets will never be perfectly spherical and some degree of control of their shape is possible, and thence orientation within the film. The droplet shape, in particular, can have quite dramatic effects on the operational characteristics of a PDLC device.

One simple quantity that is easy to control is the film thickness; this has a great effect on the film performance. Essentially a thicker film will drastically improve off-state scattering but will also reduce the on-state transmission and increase the threshold voltage.

A very direct alteration of the film morphology can be achieved simply by altering the relative concentrations of the two components of the system [123]. Very high concentrations of liquid crystal will result in a network of polymer formed throughout a continuous phase of liquid crystal [124]; slightly less will result in the reverse of the common morphology - that is a polymer ball morphology will be seen [125]; reduction still further will result in the characteristic microdroplet structure and finally a plasticised polymer matrix will be afforded at the solubility limit.

6.4.1. Droplet Size Effects

The elastic free energy of a liquid crystalline droplet is related to the degree of deformation of the liquid crystal director, thus a smaller droplet, with necessarily greater deformation, will have higher elastic energy than a larger droplet where the local director is on the whole less strained by the curvature-enforced strain. As a result greater fields are therefore required to reorient the liquid crystal directors in films where the droplets are small [126].

This is readily apparent in poorly prepared films (that is, those with uneven droplet size distribution); microscopic observation shows a range of sizes and application of an electric field gives a gradual transition from opaque to clear state, as previously mentioned. For most applications, therefore, control of droplet size is of great importance to give precisely defined characteristics.

The droplet size also affects the light scattering characteristics of a film. Naturally the specific application will determine the precise requirements (*eg*, back-scattering of light is a requirement in solar control applications, whereas in most other applications the light merely needs to be scattered, be it forwards or backwards).

One of the main factors in controlling the droplet size is the curing temperature, as already mentioned. It is seen in general that a higher cure temperature will give rise to smaller droplets due to a more rapid onset of phase separation. Control involves the alteration of the parameters of the cure regime to afford droplets of a size appropriate to the final application [127].

6.4.2. Droplet Shape Effects

The effects of droplet shape are related to those of droplet size and are of immense importance in determining how well a PDLC material functions. It is expedient to consider a droplet of elongated oblate spheroid shape; all other examples will follow intuitively as elastic free energy considerations will be similar.

Consider a bipolar configuration; the two point defects of the droplets will, in a spherical droplet, be randomly oriented. If the spherical symmetry is perturbed then there will inevitably be places where the strain on the director configuration is minimised. In the case of an oblate spheroid these points are obviously going to be the points where the curvature is maximised and thus we see the disclinations occurring at the "ends" of the droplet. The field therefore required to reorient the liquid crystal director is going to be higher as the volume elastic deformation free energy is higher - essentially the liquid crystal is held in the orientation defined by the droplet shape. Evidently this effect will be more pronounced for greater distortions from the spherical.

This effect has been shown to be true experimentally for threshold and saturation field; a lower field is required to achieve complete reorientation (or transparency in a device) in a film with less deformed droplets. Correspondingly these same elastic forces promote rapid relaxation of the film upon removal of an applied field.

An example where non-spherical droplet shape is of use is in reverse mode films. These films work essentially opposite to the normal PDLC film; they are transparent at zero field, application of the driving voltage causes them to become opaque. For example, if a film is created by, for example, applying a shear stress during polymerisation, the droplets will generally be slightly elongated, with all major axes parallel with the shear direction. Thus, assuming uniform droplet size (controlled by temperature of cure, for example), the director configurations will be predetermined and so off-state clarity will be achieved by choice of refractive indices such that the light transmitted will encounter no barriers and thus will be transmitted unscattered. Application of the field will bring about droplet director reorientation and the usual opacity due to refractive index mismatching.

Control of the droplet shape is of especial interest due to the strength of the effects. The conjecture of this work is that cure across a temperature gradient will enable control over the alignment of the anisometric droplets and thus greater control over the film characteristics.

Another method of achieving off-state alignment is by cure from a nematic liquid crystal/prepolymer phase. Droplets formed from such a mother solution will form such that the droplet director lies parallel with the mother solution director; alignment by an electric field during cure will thus give a uniform aligned phase. Such systems may also be utilised in reverse mode displays [128].

Chapter 7. PDLC Technology - Applications and Innovations

To recapitulate arguments presented previously, PDLC materials are a useful prospect for application, particularly of course in the area of display devices and glazing products. Also, due to advantages that these materials hold over other display types (lack of Polaroid requirement, ease of fabrication [129,130], *etc*), there is a wide range of potential markets in which PDLC technology will be competitive.

PDLCs are particularly suited to the production of low power consumption, large area displays and light valves; specific applications such as interior windows (screens and partitions), electronic displays (particularly projection displays), signs and automobile sunroofs are currently under development [131]. Display media are either PDLC or NCAP (these types are very similar in structure and behave in much the same way in applications) and several commercial products are available.

7.1. Dyed PDLC Materials

There are various options available in the pursuit of greater contrast ratio or coloured PDLC displays. First, those devices used in transmission mode may employ coloured backlighting; also it is quite possible to incorporate dyes into the materials either in the liquid crystal or the polymer matrix.

Liquid crystals may be 'doped' with dyes in such a way as to produce black and white or colour displays [132]. It is possible to use highly ordered pleochroic dyes in the liquid crystal to produce a film with both controllable absorption and scattering [133]. These devices are termed "guest-host" or "dyed phase change" displays. There are a number of factors that influence the performance of a given dye when in a solution with a liquid crystal [134] which must be considered in order to produce an effective device.

Such displays with pleochroic dyes operate as follows for a typical device. In the off-state when director orientations are essentially random, all polarisations of incoming light are absorbed by the dye and so the result is a black film. An applied field will orient the liquid crystal and the dye such that the dye's major molecular axis is perpendicular to the incident light path and therefore the absorption reduced resulting in a clear film. The net result in a device is to give greatly improved contrast ratio.

A coloured display based on this technology would consist of such a guest-host film mounted in front of a coloured fluorescent reflector. In the on-state, incident light passes through the PDLC with low scattering and absorption, thus leaving the coloured reflector open; this results in a high intensity, high purity on-state. In the off-state high levels of absorption and scattering are seen thus yielding a very dark state. Such a display could be thin and would not require backlighting as even low levels of ambient lighting would give high visibility. No Polaroids are required and thus both the cost and complexity of construction are reduced and also wide viewing angles are possible (up to 160°). Response times are good (whilst guest-host systems switch slightly more slowly than pure liquid crystal, response times are still of millisecond order). Flexible substrates may be used and, in general, fabrication is quite simple thus allowing large or non-standard shaped devices. Possibilities for application include integrated control panels and thick film touch switches.

Another method of producing coloured displays with dyes is to incorporate a non-pleochroic dye into the liquid crystal or polymer matrix [135,136]. The effect of incorporation in the polymer matrix is to increase reflections within the film which in turn increases the path length of the scattered light and thus producing coloured output light. These can be produced to give either coloured segments on a dark background or *vice versa*. Improved contrast may be gained by additionally incorporating pleochroic dyes into the liquid crystal; the contrast is also improved if parallax between the dyed area and the liquid crystal is removed by use of an appropriate dye in the polymer matrix. It is possible to produce patterns in films by these methods to give the triads required for a full colour display (note that despite the 2/3 light loss in this manner the resultant brightness is still better than that of more conventional liquid crystal displays). A big advantage with these is the thickness of the films; they are thin enough that three could be combined in series to produce complimentary or subtractive colour displays without the light loss associated with the triads.

Production problems are, at least theoretically, minimal as far as dyed materials go. Some methods of preparation may lead to chemical attack of the dye by, *eg*, reacting prepolymer but largely speaking these problems may be overcome.

The use of dyes in exterior applications naturally requires ultraviolet stable compounds; many dyes, however, tend to fade due to photoinduced degradation when exposed to continual solar radiation. Work is required in this field as few, if any, such UV stable dyes now available are suitable for such uses.

The only other problem particular to dyed films is the general loss of transmission; evidently the dye will absorb radiation in the on-state and not only the off-state. Most of the above techniques will nonetheless give reasonable characteristics.

7.2. Large Area Light Valves

The nature of the processes for PDLC construction allows the facile production of large area films for field-effect uses. Screens of the order of a square metre area have in fact been produced routinely. This is a huge advantage over other liquid crystal display materials as no easy means of producing large area uniformity and homogeneity (requirements for uniform response) is currently possible with other liquid crystal devices. The very nature of the production process ensures this uniformity is achieved in PDLC devices; a sandwich film of liquid crystal/prepolymer mixture and the conducting surfaces is produced easily and the mixture cured. Also the nature of the materials means that they are less dependent on this homogeneity but the polymer matrix acts as a permanent spacer. These are laminated generally to glass or plastic substrates to give rigidity to the device or in some cases the *in situ* cure gives a free-standing film. As a result these materials are highly competitive in the light valve market [137].

A potential problem is off-normal haze; most PDLCs will give a hazy transmission when viewed off-normal. It is possible to overcome this with the use of Polaroids [138], chiral liquid crystal (see later) or optimisation of the materials used (see previous discussion).

Such devices as are currently available [139] have all of the properties of conventional glass windows but naturally there is the advantage of light control. Only the requirements of mass, volume efficiency, thermal insulation, solar heat reflection and environment affect end use but the flexibility in application copes with most such restrictions.

As previously noted, transmission in the clear state can approach that of plain glass and a variable scattering state may be realised in a device to give shade without complete loss of visibility. Indeed, such devices are quite readily available commercially and can be used in offices, retail displays and the like where occasional privacy and light screening is an advantage.

Similar to this concept in practical terms is that of a light modulator or light valve, wherein transmission is dependent on incident light [140,141].

7.3. Automotive Applications

Light valves for use in cars have also been investigated. One of the largest problems in this respect is solar control [142,143]; as many cars are required to have large areas of glazing, for the reasons of visibility and aesthetics, there is the additional demand on the materials used to withstand the extra degradation due to ultraviolet light and also the heat absorption from the large areas involved. Solar control requires backscattering of the photons and thus prevention of absorption or transmission in order to keep down the solar energy behind the screen. There is the physical problem of production of a precise curved shape although this is not insurmountable. It is evident, therefore, that progress in this field is slower than in permanent, fixed applications such as in houses and office buildings.

The main use in cars is in information displays. Naturally this area is of great importance and as a result much research is involved with developing such technology. In-car displays will be required to be of three types; one for engine information, one for navigation (involving a moving map) and the third a multimode display for environmental and diagnostic information and control.

The option of PDLC devices in these systems is a good one due to the high brightness, ease of colour display fabrication, environmental stability and ease of creating shaped displays. The drawbacks of these displays are the high threshold voltages and the stringent requirements; a high contrast ratio, very wide temperature range (well outside human-acceptable conditions) and fast response speeds. Current PDLC technology is able to meet these specifications in most respects however; operating ranges of -15 to 80°C have been reported using certain liquid crystal mixtures although further research into wider-range nematic mixtures is needed to realise the potential in this market. The multimode and moving map display types require more attention from the driver and so a more likely scheme is to incorporate projection-mode heads-up displays (such as those used in military aircraft) into the vehicle so as to display information on the windscreen rather than the inherently less safe, conventional heads-down display. This requires high intensity projection to be effective in bright ambient lighting, a requirement which PDLC materials are well equipped for.

7.4. Projection Applications

Perhaps the type of application that PDLC materials are most suited to is that of projection. PDLCs have very high on-state transmission and low off-state absorption and so bright projected images with negligible heat dissipation are possible with PDLC devices. High power lamps may thus be used and so extremely good contrast ratios may be achieved with even current PDLC films [144].

PDLC light intensity modulators may be used in concert with dielectric mirrors to effect full colour projectors [145,146] where incoming white light is separated into the three constituent primary colours, the intensities of each beam of which are then modulated by a PDLC active matrix device (*eg*, polysilicon thin film transistor (TFT)), the light recombined by dichroic mirrors to result in a beam of the desired colour and intensity. The result is a high information content (*eg*, 500x500 pixels), low loss, efficient projection system. PDLC materials are competitive in active matrix systems [147] and continuing research has been prompted [148].

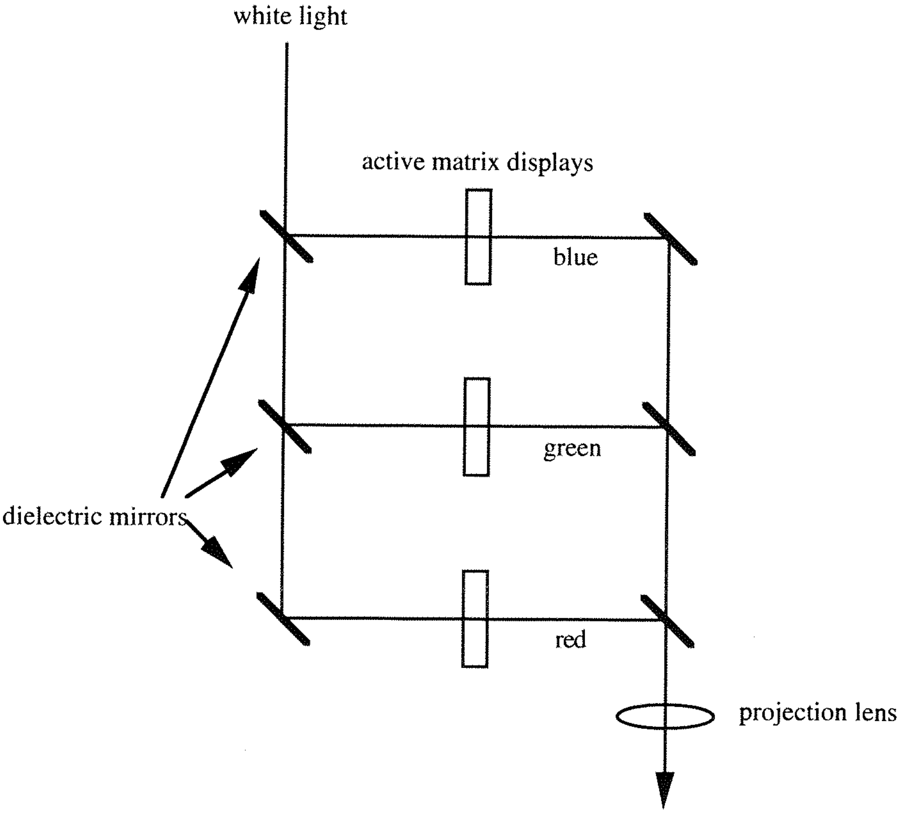


Figure 7.1. Schematic of a possible PDLC colour projection system

Such displays also have potential use in the (projection) television market. If they are able to be switched at video frame rates then naturally television displays will be achievable.

There are also further requirements for use in active matrix displays [149]. Low (10V) voltage operation is a requirement to improve the possibilities of use in TFT-type displays. In order to achieve this it is often of use to produce materials of the "polymer ball" morphology (that is, a continuous liquid crystal phase containing "balls" of polymer) with liquid crystal contents of around 75%. The PDLC film must display reasonable capacitance characteristics (holding ratio of both the liquid crystal and the polymer) to retain the charge when the addressing voltage has moved on. In addition there must be minimal hysteresis in the electro-optic response characteristics (that is, the on-curve must be the same as the off-curve) to facilitate reasonable grey scale capability.

7.5. Reverse Mode Devices

As has been noted, it is possible to produce PDLCs in which the on-state is opaque and the off-state is clear. These have applications in devices where there is some sort of failsafe requirement where the screen must be clear if there is a power failure. Early attempts [150] utilised liquid crystals with negative dielectric anisotropy which were aligned within a droplet using surfactants.

More recently, as noted, there has been research into dual frequency addressing and application of such liquid crystals in display devices. Various prototypes have been produced [151].

There are limitations on the use of dual frequency addressing, however. The crossover frequency, as with so many other liquid crystal parameters, is dependent on temperature (f_C increases with temperature). High voltages and low frequency fields cause dielectric heating of the liquid crystal (because of ionic impurities) and thus additional problems are imposed upon engineering of a workable device. The uppermost operating temperature is thus plainly limited, although the temperature dependence of f_C can be used to produce a temperature-dependent electro-optic switch [152]. Power consumption is also a problem; high frequencies increase the power consumption and so small areas only may be driven thus. As it stands today, high driving voltages (100V) are required although further developments will reduce this to a more viable level.

7.6. Polymer Network PDLCs

Most typical PDLC materials will contain around 50% liquid crystal. Naturally it is conceivable to use a still greater amount of liquid crystal to effect a film morphology other than the "Swiss cheese" type involving microdroplets. In these cases a reverse morphology is seen or in many cases a morphology of an aligned polymer network (PN) is present [153]. In both types there is a continuous liquid crystal phase throughout the device.

Typically the PN will be formed from a nematic phase of a liquid crystal/prepolymer mixture [154,155]; a liquid crystalline monomer/liquid crystal mixture (5:95) is homogeneously aligned over the substrate and photopolymerised from this nematic phase to give a polarised, scattering film. Another type involves a similar methodology to produce a reverse mode film [156]. A further development involving a liquid crystal/liquid crystalline polymer composite in a smectic phase has also been demonstrated [157].

Such devices will be more difficult to manufacture. Evidently the polymer is unable to contain the fluid and so a system will have to be sealed by something else. In addition more rigid casing will have to be used than is the case with normal PDLCs as the material is fluid or at least more flexible.

7.7. Polymer Dispersed Chiral Liquid Crystals (PDCLCs)

In principle, any type of liquid crystal may be used in a PDLC material. Certainly chiral liquid crystals are of interest for application in this way. These may be used to achieve a variety of effects but due to the nature of chiral liquid crystals colour displays are an obvious candidate for development [158,159].

A typical device [160,161] will scatter in the off-state and selectively reflect a colour in the on-state. The principle of operation is similar to that of a conventional PDLC but is modified by the fact that a chiral liquid crystal has a helical structure which can selectively reflect a given wavelength which is equal in length to the helical pitch. The liquid crystal is required to have a negative dielectric anisotropy and so will align perpendicular to an applied field, resulting in a helical structure that is parallel with the field and incident light; the pitch is inversely proportional to the concentration of chiral dopant in the liquid crystal mixture. Three such devices could be used in reflective devices and transmissive devices with grey scales and full colour.

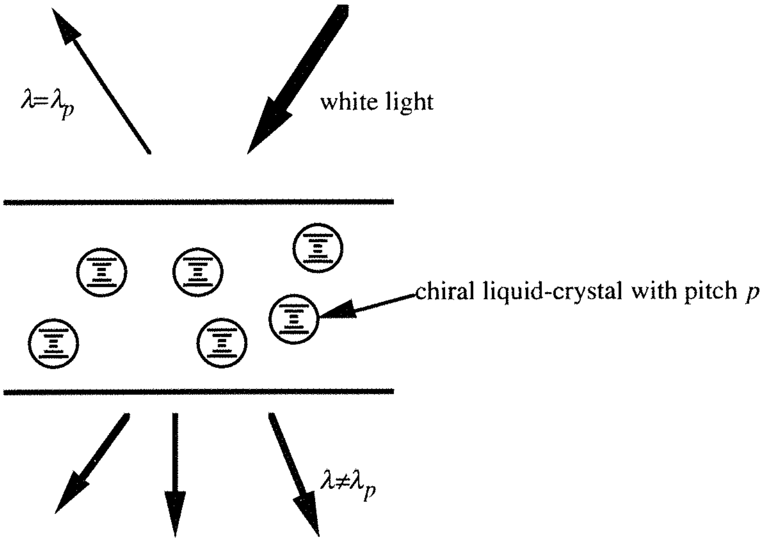


Figure 7.3. Schematic of reflective PDCLC

Another application is in haze free light shutters. Many conventional PDLC approaches to light shutters are unable to overcome the problem of off-normal haze. It is possible to use chiral liquid crystals to overcome this problem in a polymer network device [162]. Similar to this, a polymer stabilised chiral liquid crystal dispersion has been developed [163] which is able to operate in three modes; normal- and reverse modes [164] and colour reflecting (this is a bistable mode that selectively reflects light [165]).

7.8. Other Applications

Although of high potential in the displays market, PDLC technology may also be utilised in ways other than display devices.

One application possibility that has been developed is to use a controlled TIPS process with a polymer/liquid crystal mixture to produce a read/write optical data storage system [166]. In this a laser will write with a small area, high intensity pulse and erase with a larger area, lower intensity pulse. The high intensity and the small area would give rise to higher temperatures and would cause faster cooling rates resulting in a small droplet, spinodal type morphology. The other laser pulse would result in lower temperatures and the writing beam would reside on the medium for a greater time, thus leading to slower cooling and a larger domain size. The resulting morphological difference could be detected by a reading system and so information could be stored. The obvious application here is erasable compact disc technology.

A novel application for PDLCs is their use as partially exposed systems [167]. In such a film the surface of the material is not, as with conventional PDLCs, the polymer but liquid crystal droplets are exposed to the surrounding environment. This facilitates surface studies due to the optomechanical response of the liquid crystal which can be induced by gas flow [168]; as a result, gas flow sensing and boundary layer investigations [169] are thus enabled using this technology.

Photoinduction of a liquid crystal phase transition has also been demonstrated in PDLCs [170] and could have potential use in photorecording systems, although as yet no feasible systems have been developed.

Another interesting application is in the production of holographic gratings using controlled diffraction [171] but again further research is required before a workable system is developed.

There is a variety of related technologies to polymer dispersions. Glass dispersed liquid crystals have been demonstrated [172] and these have similar characteristics to PDLCs. A forerunner of PDLC technology involved the dispersion of particles in a continuous liquid crystal phase; this achieves electro-optic characteristics similar to PDLCs; recently there has been work on similar materials involving the dispersion of small inorganic particles in a nematic liquid crystal [173].

PDLCs also have applications in areas other then those involving light. Liquid crystals can be applied in acoustics due to their anisotropic conduction of sound; PDLCs have been demonstrated in acousto-optical transducers [174].

Chapter 8. Aims of the Project

It has been stressed in the previous chapters that the effects of processing conditions on PDLC materials can be exploited to optimise the performance of a PDLC material for particular use in a device.

The initial aim of the project was to investigate the effects of varying the thermal treatment of PDLC materials. In particular in this work the idea of curing across a temperature gradient was to be considered. It is well established that varying the temperature of cure affects PDLC morphology but the idea of deliberate inhomogeneity of temperature during a cure has not been considered.

Various potential morphologies have been postulated for such a regime. One is that there will be a gradual change through such a sample; from a spinodal morphology at one end, wherein there are small and evenly spaced droplets, to a binodal morphology at the other, where there are large, irregular domains. Another is that the droplets may be anisometric; for example, egg or tear shaped where the "small end" lies facing the hotter region and the larger end facing the cooler; the potential with this morphology is that the liquid crystal will inherently be aligned in the off-state of such a film and so greater control over the device may be achieved.

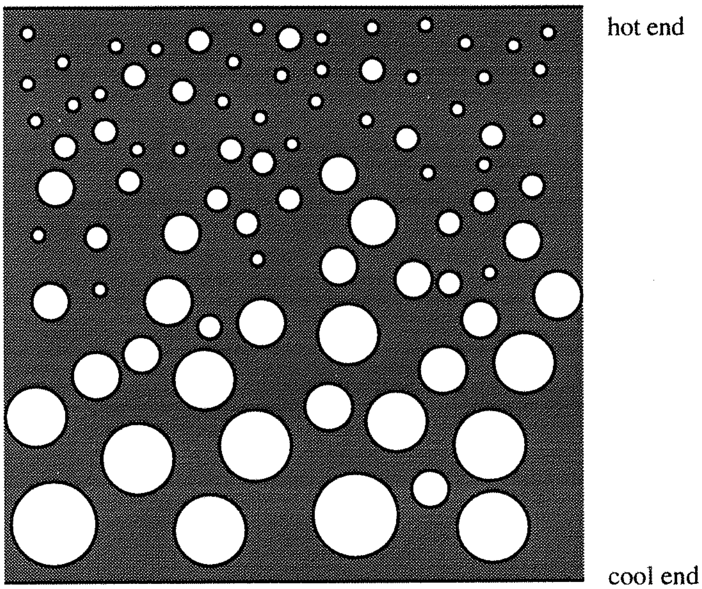


Figure 8.1. Possible morphology from thermal gradient cure. Smaller droplets are predominant in the hot, spinodal regime whereas larger droplets prevail in the cooler binodal regime.

More fundamentally the establishment of the relation of the morphology of a PDLC to the underlying phase separation processes was to be determined. Below is presented a schematic of the initial plan.

A: Planning Phase.
Aims: Selection of the polymer matrix and liquid crystal materials and familiarisation with prior art.

B: Preliminary Experimental Phase.
Aim: Development of experimental methodology for the determination of phase diagrams and scanning electron microscopy (SEM).

C: Main Experimental Phase.
Aims: Relation of PDLC morphology to thermal conditions, determination of post-cure PDLC composition, assessment of the relationship of PDLC morphology and device performance.

8.1. Phase A - Planning

A1: On-line search for publications concerning PDLCs.
A2: Assessment of relevance of papers; 0 (no relevance) to 3 (essential).
A3: Acquisition of all papers of rating 3, any of rating 2 or 1 with easy availability.
A4: Acquisition of papers on fundamental aspects of spinodal decomposition.
A5: Detailed study of relevant papers.
A6: Input of information into database.
A7: Discussion of preliminary experiments.
A8: Review and planning.

The literature review is contained in the preceding chapters.

At this stage the following points were decided upon: the liquid crystal for use in preliminary work was to be 5CB (4-*n*-pentyl-4'cyanobiphenyl) [175] and that for use in more detailed study the commercial mixture E7 [176]. The structures are given below.

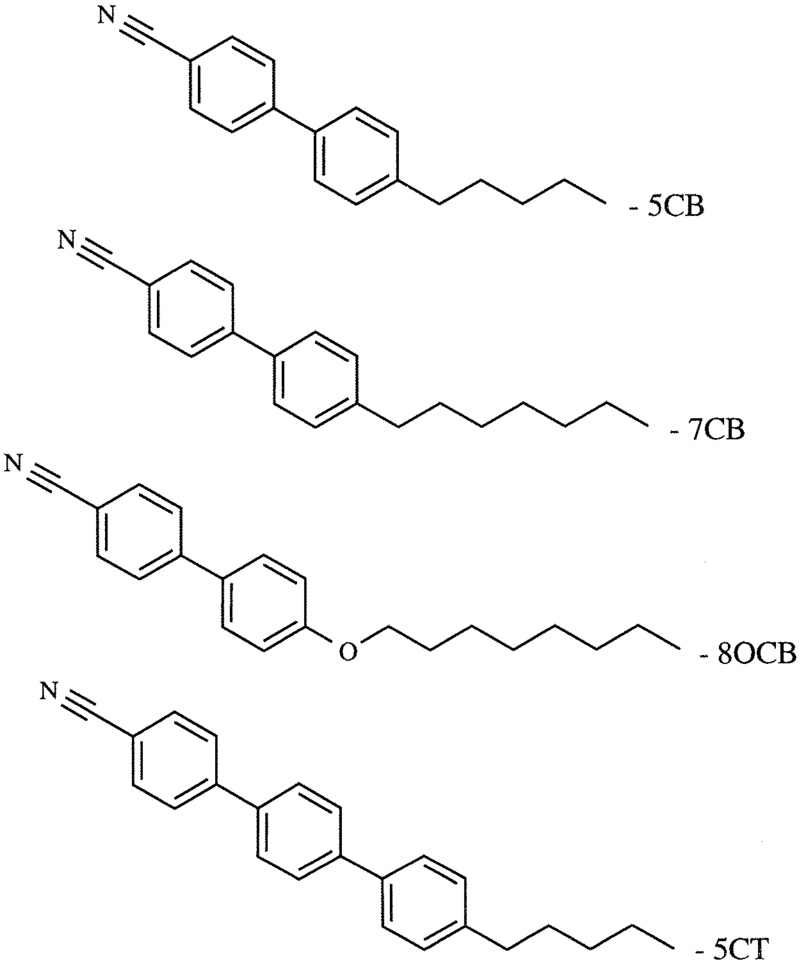


Figure 8.2. 5CB and other components of E7. 5CB (51% of E7), 7CB (4-*n*-heptyl-4'-cyanobiphenyl) (25%), 8OCB (4-*n*-octyloxy-4'-cyanobiphenyl) (16%) and 5CT (4-*n*-pentyl-4'-cyanoterphenyl) (8%).

The polymer for use in preliminary experiments was to be a poly(methyl methacrylate) (PMMA) system. PMMA is very common and well studied in many different systems; in addition it is readily available and chemically convenient for study (ready dissolution in a wide variety of common solvents, *et cetera*). As the phase separation processes in the differing methods are in many respects similar it was decided that the use of a SIPS process followed by controlled TIPS process was adequate to model the effects of variation of thermal cure variations in a thermosetting system.

The polymer for the main body of experiment was to be a thermosetting polyurethane as little work to date had been carried out on such systems; in the main thermosetting epoxy based polymers have been studied. Initially α,ω-hydroxylated polybutadiene, to be cured with an aliphatic diisocyanate such as 1,6-diisocyanatohexane, was the system of choice.

Further details of experimentation emerged; 1; the amount of 5CB in the polymer matrix was to be determined by optical, electro-optical, thermo-optical [177] and calorimetric analysis [178] and 2; the possibility of deuterium NMR studies was raised and as a result the synthesis of specifically deuterated 5CB was to be carried out [179].

8.2. Phase B - Preliminary Experimental

B1: Preparation of varying PMMA/5CB and PMMA/E7 mixtures.
B2: Determination of experimental set-up to afford viewing of phase separation.
B3: Investigation of cooling and heating on selected composites.
B3.1: Construction of the phase diagram.
B3.2: Preparation of selected compositions for SEM and electro-optic analysis.
B4: Investigation of the effects of processing history on the morphology.
B4.1: Combination of the morphological data with the phase diagram of PMMA/E7.
B5: Collation of findings.
B6: Review and planning.

This stage largely proceeded as above. The SEM analysis was deferred until a later date at this point.

8.3. Phase C - Main Experimental

C1: Selection of the polymer matrix.
C1.1: Investigation of systems in the ratios required for full polymerisation.
C1.2: Investigation of the cure kinetics over the applicable temperature range.
C1.3: Determination of the glass transition (T_g) of the resultant polymer matrix.
C1.4: Selection of the best formulation.
C2: Main Experimental.
C2.1: Preparation of ternary mixtures (diol, diisocyanate and liquid crystal).
C2.1.1: Construction of phase diagram over the slow cure range of temperatures.
C2.2: Cure of ternary mixtures at various temperatures.
C2.2.1: Characterisation of electro-optic response.
C2.2.2: Investigation of the morphology.
C2.2.3: Determination of completeness of phase separation.
C2.3: Selection of materials for use in work on thermal gradient cure.
C3: Thermal gradient cure regimes [180].

Naturally this phase of the project was experimental in nature and thus the most subject to unforeseen problems, detailed later in the chapter.

Additional work was to be the formation of cross linked matrices and photographs of the PDLC materials.

Chapter 9. Poly(methyl methacrylate) Composites Work

After the initial literature review the second phase of the project, investigation into liquid crystal/poly(methyl methacrylate) composites, was undertaken.

9.1. Experimental

Based on phase A of the work, the next (initial experimentation) phase of the project was to be work on poly(methyl methacrylate) (PMMA) composites. These were chosen as such composites are relatively well studied and the material is well characterised; as a result it was deemed prudent to choose such a system to gain a feel for the area.

It was decided to produce composites of four kinds in this phase of the project. Two molecular masses of PMMA were to be studied; low mass [181] and very high mass [182]. Both liquid crystal types were to be used 5CB and E7. An uncontrolled solvent induced phase separation process was to be used, using dichloromethane - chosen as it is a good solvent, very volatile and so unlikely to remain dissolved in the polymer matrix to any great extent. Following this, the samples were to be heated and a controlled thermally induced phase separation monitored.

The structures of the two liquid crystal materials have already been given. PMMA is formed from photopolymerisation of methyl methacrylate.

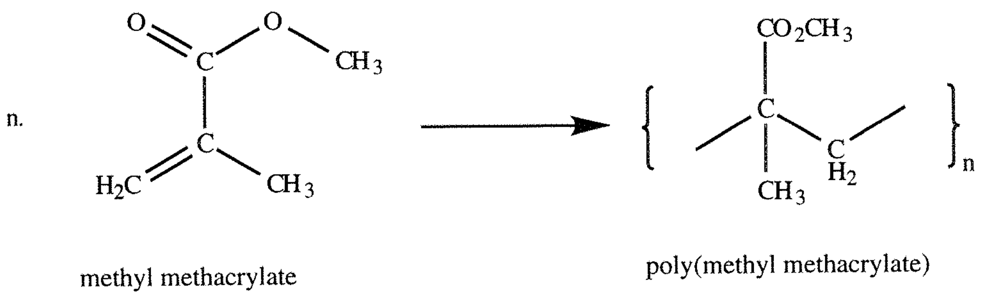


Figure 9.1. PMMA

Eight samples of each pairing of liquid crystal and polymer were prepared as follows. The compositions were 10-70wt% (mass percentage increasing incrementally by 10wt%) liquid crystal in the composite, the rest being composed of the PMMA.

Above this concentration was deemed to be unfeasible as in such systems the polymer is incapable of forming a continuous polymer matrix for the liquid crystal.

The appropriate amount of liquid crystal was placed in a glass tube (0.1g for the 10wt%, 0.2g for the 20wt%, *etc*) and to this added enough PMMA to make the sample up to 1g (0.9g, *etc*). To each of these mixtures was then added dichloromethane (5ml) [183] and the systems allowed to mix thoroughly (stoppered vial, left for at least 48h with regular shaking and no loss of volume).

Microscope samples were prepared as follows. A drop of the mixture was placed on a microscope slide and spread out thinly (approximately 50-100μm thickness). The slide was then heated to about 50-60°C for 12h to remove the solvent, thus effecting uncontrolled SIPS and ensuring that the mixture was a homogeneous mixture; this temperature was deemed insufficient to volatilise a significant quantity of liquid crystal from the sample over this time. The sample was then ready for microscopic inspection.

DSC samples were prepared as follows. Half ml samples of the mother solution were taken and placed in similar tubes. These were again heated to about 50-60°C but for a longer period (48h) due to the thickness of the sample. Once the samples had lost as much solvent as possible they were very carefully broken up to avoid glass contamination from the tube and a 20-30mg sample collected for analysis. The sample was then placed in a standard aluminium DSC sample pan and scans taken; the purge gas used was nitrogen [184]. Two heating/cooling cycles then followed; the data from the first cycle was not recorded (it was to ensure thorough removal of solvent and mixing of the samples - preliminary microscopy investigations indicated full mixing at the elevated temperatures used in these cycles), both halves of the second cycle were recorded and analyses of any detectable transitions carried out.

It was soon noted from initial studies that the very high molecular mass PMMA was not suited to the work of interest. The compositions took an undesirable length of time to dissolve even with regular mixing (much longer than the two days needed for the lower mass material), were too viscous (difficult to work with and in addition high viscosity is conducive to incomplete homogenisation of the sample) and overall took much longer to form workable samples than the low mass PMMA; thus the work reported here is solely on the low mass PMMA system.

Further to this, the preparation of SEM and electro-optic analysis samples was deferred until a later time. Additionally, as noted later, the phase diagram was difficult to determine and as such efforts were concentrated on more fruitful investigations using DSC.

9.2. Microscopy Studies

Microscopy studies were carried out as follows. After the initial uncontrolled solvent induced phase separation on the microscope slides (60°C for 2h), the mixtures were heated to a homogeneous mixture at approximately 150°C. These samples were then observed at various cooling rates.

It was soon noticed that the 5CB composites were not at all phase separated up to 30wt%; after cooling to below T_{NI} no birefringent droplets were observed; as it is unlikely that any droplets present would have been solely radial in director configuration (a state that would give no birefringence) it is inferred that no phase separation occurred at all, particularly as the macroscopic sample remained perfectly transparent. At 40wt% several small droplets were observed and on increasing the liquid crystal content greater numbers of droplets were seen in the composites. These findings agree well with DSC data (see later).

One consistent observation was leeching out of liquid crystal above the solubility limit. The surfaces of the composites were found to be coated with a film of liquid crystal (noted first by being slick to the touch and then by the fact that this coating was birefringent), indicating that the polymer matrix contracted and liquid crystal leeched out by a diffusion process during the experiments. The amounts involved were deemed insufficient to affect the results although it should be noted that such an effect renders potential devices less effective. It was also noticed that a continual layer of liquid crystal was seen (indicated by a schlieren texture under the microscope) at the glass surface in the higher liquid crystal concentrations; presumably this was the same effect as leeching at the air interface although the difference between the interfaces could potentially cause preferential leeching at one surface.

Heating and cooling tests confirmed well known observations. The composite, after the uncontrolled SIPS, was heated to the isotropic mixture. It was noted that a small amount of liquid crystal vaporised when the temperature exceeded about 150°C; this was identified by birefringence of condensate on the microscope lens. The trend in the results discussed below confirmed expectations so the amount of loss from this vaporisation was deemed to be inconsequential for relative comparisons (as with the leeching effect) although the absolute values may have been affected. The actual temperature at which an isotropic mixture was achieved was very difficult to ascertain due to the very gradual nature of the change; this mixing occurred invariably above the nematic-isotropic transition of the liquid crystal and as such the lack of contrast between the brilliant nematic phase and dark background severely impaired the detection; rotation of the Polaroids did not improve the view. Once in the isotropic phase the systems were cooled at varying rates, to afford differing phase separation conditions. As a result of these observation difficulties (no easy means of overcoming this problem could be invented within the time available) the phase diagram investigations were essentially curtailed.

The size and number of the droplets are controlled by a number of factors as previously noted. The amount of liquid crystal in the mixture will obviously determine this; the more liquid crystal that is present then the more droplets there will be beyond the solubility limit and ultimately the droplet size will be larger. The temperature affects this also; a higher temperature will necessarily increase the solubility of the liquid crystal in the polymer and so reduce the droplet size. A high cooling rate will force the liquid crystal out of the polymer solution by spinodal decomposition and allowing less time for phase coarsening to occur and so smaller droplets will result as the liquid crystal content exceeds its solubility; conversely a lower cooling rate leads to binodal decomposition and phase coarsening occurs so larger droplets will form.

Extremely fast cooling rates (plunging into liquid nitrogen) resulted in no instant phase separation at all; indeed phase separation was only seen if such samples were then warmed to room temperature, where eventually small droplets formed; this would have been due to extremely slow movement at such low temperatures followed by a speeding up of the diffusion at ambient temperature. Ultimately a very slow phase separation was seen resulting in large droplets as described later.

A quick cooling rate (say 20°Cmin^{-1}) with the 50wt% 5CB composite resulted in droplets of less than 1μm forming (fairly uniform spacing and narrow distribution of sizes). Over the course of days these droplets increased in size slightly to about 1μm, presumably due to slow diffusion of the liquid crystal molecules through the polymer matrix (*ie*, slow phase coarsening). The mechanism of phase separation here is deemed to be spinodal decomposition due to the even nature of the droplets' distribution.

Slow cooling rates (1°Cmin^{-1}) resulted in much larger droplets forming (around 5-10μm in this case of 1°Cmin^{-1}); this is attributed to a nucleation and growth mechanism as the resultant morphology is one of very large droplets randomly and unevenly distributed through the polymer matrix. Again, phase coarsening was subsequently seen.

Lower liquid crystal concentrations did not phase separate as noted. There was a correlation, as would be expected, between the concentration of the liquid crystal and the droplet density; higher concentrations of liquid crystal giving a more dense distribution of droplets. Also droplet size was ultimately affected; higher liquid crystal concentrations giving slightly larger droplets; this is explained by a greater degree of phase coarsening caused by the thermodynamic pressure from the high liquid crystal concentration in the matrix.

The droplets themselves showed the "Maltese cross" appearance characteristic of the bipolar droplet director configuration, although a detailed study of the distribution of director configurations was not undertaken.

Nematic to isotropic transition temperatures (termed the nematic-isotropic transition) for the droplets corresponded roughly to those of pure 5CB (35°C) but in all cases a slight (2-3°C) depression of the transition was seen. This depression is caused by two main factors; droplet size and impurities. Small droplets are essentially less pure due to the effects of the interface on the bulk material and thus have lower transitions; monomer impurities will necessarily depress the transition.

Work on E7 composites produced some interesting results. In the main these results were similar to the 5CB composites with a few notable differences.

First, the E7 phase separated from the composite at a lower concentration than 5CB. This can be attributed to the fact that E7 is a mixture of four components; each component will have differing solubility in PMMA and some of the components (possibly the cyanoterphenyl liquid crystal due to the molecular dissimilarity with the polymer repeat unit) evidently phase separate at lower concentration. In addition, the droplet density in these composites was larger than with the 5CB and the droplets themselves were larger; this is attributed to the mixture overall being less soluble in the polymer matrix than the 5CB. Similar correlations with liquid crystal content were observed (more droplets with increasing concentration, *etc*).

Clearing temperatures of the droplets were not easy to obtain in this case. It is entirely likely that different droplets would have had slightly different compositions due to slight differences in phase separation circumstances; thus some droplets were seen to have higher transition temperatures than pure E7 (indicative of a higher concentration of 5CT in these droplets), others had lower transitions than pure E7 (T_{NI} =61°C). In all cases, a broad range of transition temperatures was seen (approximately 55°C to 65°C but tending to be on the high side indicating perhaps preferential phase separation of higher mass/transition components of the liquid crystal mixture). Droplet size and impurity factors are a little more difficult to ascertain in this case due to the inherent complexity of the system. The droplet density was higher than with 5CB mixtures, the droplet sizes were less uniform and generally larger (1-3μm at 50wt% after cooling at 20°Cmin^{-1}).

The nematic-isotropic transition measurements for the 5CB composites showed repeatability within 1°C and errors within 2°C of "true" temperatures; twice this for E7 due to the complexity of the mixture. Droplet size measurements also showed good repeatability; similarly prepared samples were indistinguishable.

9.3. DSC Results

Various transitions were observed and analysed using the DSC technique, each is described individually.

As noted above, the method for analysis involved drying a small amount of the polymer/liquid crystal/DCM solution, extracting a sample for analysis, passing the material through one heating/cooling cycle and following this with the recorded second cycle for analysis. The reason for this lies in the uncontrolled method of phase separation used for the preparation; the samples were required to be phase separated under more controlled conditions for a proper analysis and thus the first cycle was ignored to ensure thorough mixing and solvent loss.

The pure polymer was also tested against polymer dissolved in dichloromethane (subsequently evaporated) to check that there was no significant difference between the two. Indeed there was not; in fact almost no difference could be detected and thus for these purposes the amount of dichloromethane remaining in the polymer matrix was considered to be negligible, if present at all.

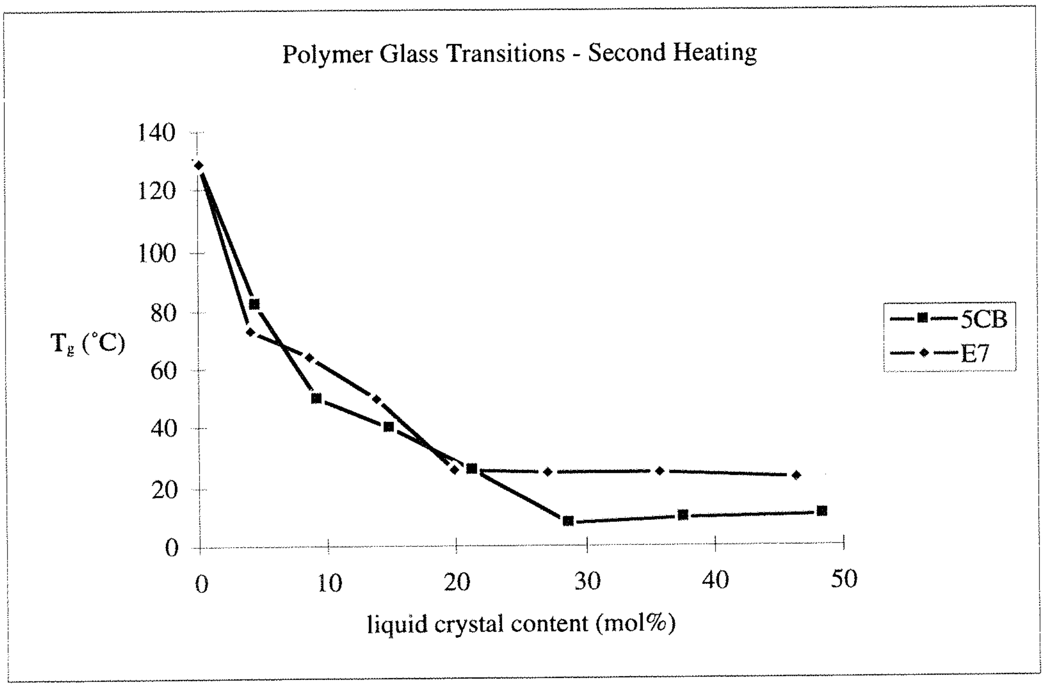
Repeatability of T_{NI} measurements was good (within 2°C for 5CB, 5°C for E7); that for the PMMA T_g within 5°C. Errors as follows; ±10°C for T_g, ±10JK^{-1}mol^{-1} for ΔC_p; ±2°C for T_{NI}, ±0.05 for $\Delta S_{NI}/R$ of 5CB; ±5°C for T_{NI}, ±0.1 for $\Delta S_{NI}/R$ of E7.

9.3.1. Glass Transitions

First, from the data given in figure 9.2a, it is obvious that addition of liquid crystal to the polymer depresses the glass transition temperature, considerably in this case of PMMA. This effect is due to plasticisation of the polymer matrix by dissolution of the liquid crystal. The glass transition, essentially a co-operative cessation of segmental motion of the polymer strands, is depressed upon increasing the concentration of solute in the polymer matrix. If there is matter (liquid crystal in this case) disrupting the interactions of the polymer then the degree of co-operation between the polymer strands is reduced; *ie*, there will be greater freedom of movement at a lower temperature than if no impurities were present. Thus the transition is depressed as less energy is required to allow this greater movement.

These results also show that at some point the effect attenuates with respect to increased liquid crystal content. This attenuation is due to the solubility limit of the liquid crystal in the polymer matrix being attained; after a certain point no further reduction is seen as no further liquid crystal is dissolved - phase separation is seen.

It had been predicted that the E7 composites would show higher glass transitions across the board than the 5CB composites due to an anticipated lower solubility but this is not shown with any clarity by the results. The first heating runs do seem to indicate a higher final glass transition with the E7 (after attenuation of the reduction). However this is not disproved either. Mechanically the E7 composites were tougher than the 5CB, all else even (although this does not necessarily indicate a higher *thermal* glass transition) and for a given concentration of liquid crystal there was a greater degree of phase separation with the E7 composites which implies lower solubility and therefore the likelihood of a higher transition.



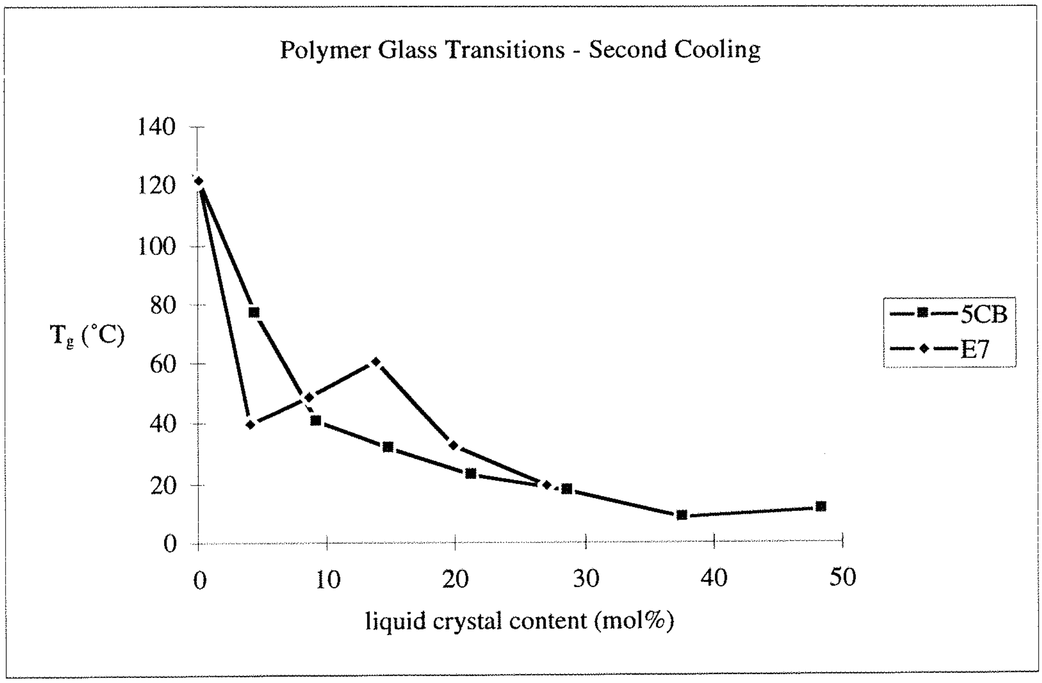


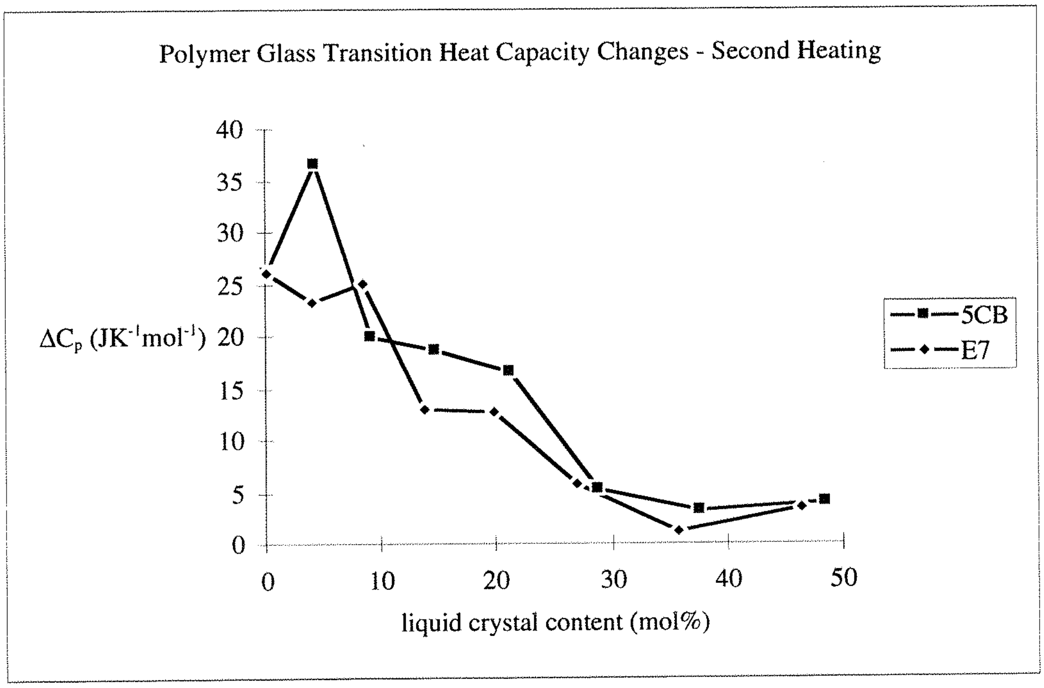
Figure 9.2a. PMMA glass transition temperatures

The associated heat capacity changes, shown in figure 9.2b, were calculated based on the amount of polymer present alone. The repeat unit of the polymer was used as the basis for the mole (-C-C(CH_3)(CO_2CH_3)-; M_r=100.11375gmol^{-1}).

These data show that increasing the liquid crystal content of the composites decreases the heat capacity change associated with the glass transition, *ie*, it becomes a weaker second order transition. This is again explained by the plasticisation effect the liquid crystal has on the polymer matrix. As the polymer has increasing liquid crystal content, its intermolecular interactions become diluted as the liquid crystal is vastly more fluid and interacts only weakly with the matrix, thus progressively increasing the degrees of freedom of movement of the polymer below the transition (the polymer is more fluid) whilst having less effect on the more fluid phase above the transition. So the heat capacity change is reduced as the difference between the two states (below and above the transition) is reduced.

There is apparently an initial leap in the size of the glass transition of the 5CB composites. This can be rationalised in two ways; either there is greater freedom for the polymer to absorb energy above the transition (possible caused by freedom of the liquid crystal) and/or less freedom below at this point (possible caused by restriction of motion of the polymer due to the liquid crystal filling the available free space). A more detailed study of this is required for greater information to give a better explanation.

It is also noticeable that the E7 composites appear to have slightly less of a heat capacity change than those of the 5CB. This is not certain as the difference is quite small and within experimental error. E7 may be less compatible with the polymer than 5CB; that is to say, a greater amount of disruption of the polymer matrix' binding forces (and therefore its means of absorbing thermal energy) occurs at a given concentration. Again it should be noted that E7 is a mixture which can give rise to unpredictable effects. It is not unlikely that, because of this complication, certain components remain within the polymer matrix preferentially whilst others remain within droplets and this could have a great effect on the systems; this would, again, need more detailed study, possibly by NMR to determine the location of liquid crystal molecules.



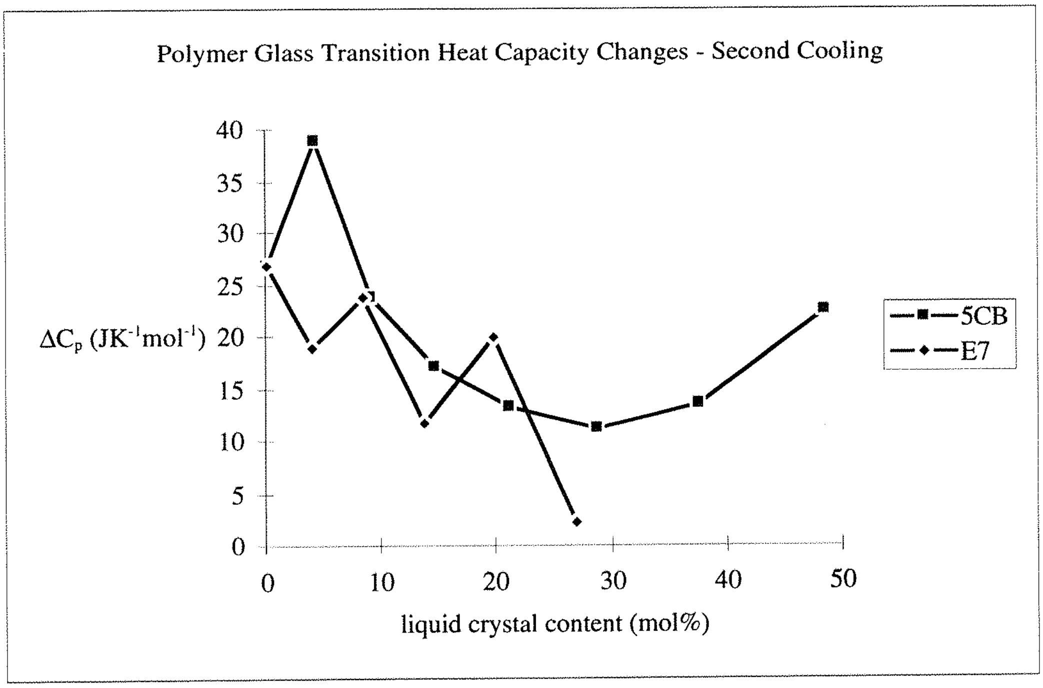
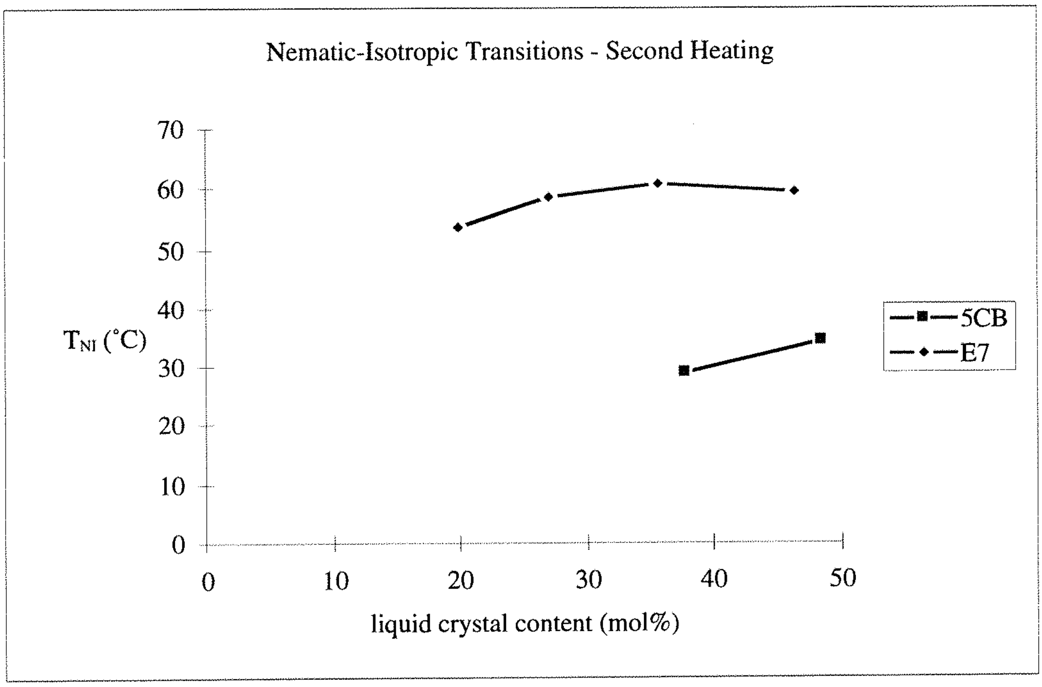


Figure 9.2b. PMMA glass transition heat capacity changes

9.3.2. Liquid Crystal Nematic-Isotropic Transitions

The nematic-isotropic transition temperatures are presented in figure 9.3a. Only the higher concentrations of liquid crystal in the composites showed characteristic clearing points. This is due to solubility in the polymer matrix; at lower concentrations no liquid crystal phase is seen in the composites. Evidently the liquid crystals are both quite soluble in the polymer, 5CB more so than E7. This agrees with the results obtained by microscopy.

It is also apparent that the clearing temperature of E7 is lower in the composites than in the bulk (61°C), and similarly for 5CB (35.1°C). Contributory factors are that the polymer itself contains remaining lower mass monomer that is appreciably soluble in the liquid crystal, which would thus depress the transition temperature, and also that the droplets are small, leading to a reduction in the transition temperature. The fact that E7, used in these experiments as it is a common commercially used liquid crystal, is a mixture of components again complicates the picture; each of the components will interact differently with both the polymer and each other and thus an unforeseen effect could occur, such as 5CB (51% of the E7 mix) could be disproportionately dissolved in the liquid crystal phase more than the polymer matrix which would of course lead to a lower transition temperature than might otherwise be expected. This is not likely; microscopy observations showed some E7 nematic-isotropic transitions to be higher than the bulk E7 transition; this would of course indicate preferential solution in the polymer matrix of 5CB. However the two are not necessarily inconsistent as the two sets of equipment may have been calibrated differently.



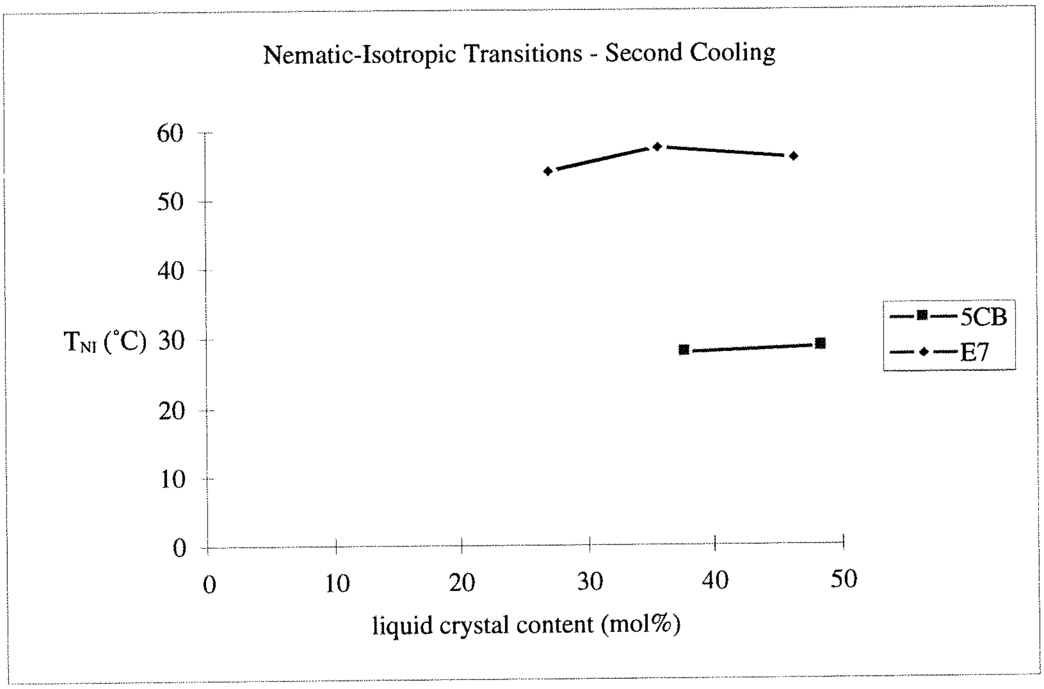
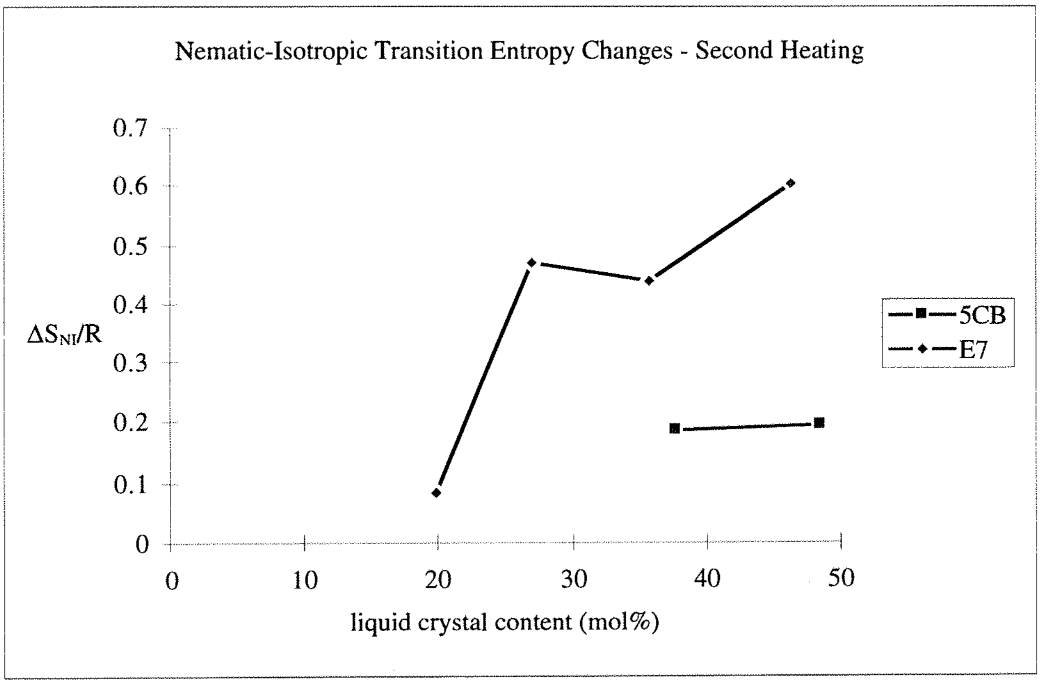


Figure 9.3a. Liquid crystal nematic-isotropic transition temperatures

The data for the entropy changes at the nematic-isotropic transition, given in figure 9.3b, were calculated based on the total liquid crystal content; that is, hypothetical complete phase separation without adjustment for any liquid crystal dissolved in the polymer matrix.

It is seen from the data that the liquid crystal is contained substantially within the polymer matrix as a plasticiser. The inference is gained due to the difference between the transition entropy as measured and calculated and the transition entropy of the bulk liquid crystal. From the second heating data it is particularly clear that there is very little liquid crystal present as phase separated droplets at about 20mol% E7; thus a rough estimate may be made of the fraction of liquid crystal that is contained in droplets and thus also contained in the polymer matrix given the size of the entropy change of pure E7 [185]. Again, this needs additional work to gain the necessary information for a fuller analysis.

As would have been expected, E7 has a higher transition entropy change than 5CB, consistent with that of the bulk liquid crystal (some of the components of E7 have a higher order parameter than 5CB and the mixture is therefore more highly ordered). The bulk values are 0.36 for 5CB and 0.45 for E7. For the E7 composites the $\Delta S_{NI}/R$ becomes higher than that for the bulk material; this lends further credence to the theory that preferential phase separation of higher order parameter components of the mixture occurs and the 5CB component remains dissolved in the matrix. It is worth stating that no easy comparison between the numbers is possible, however, due to the fact the results were calculated on the total amount of liquid crystal contained in the composites and not the amount contained in the droplets.



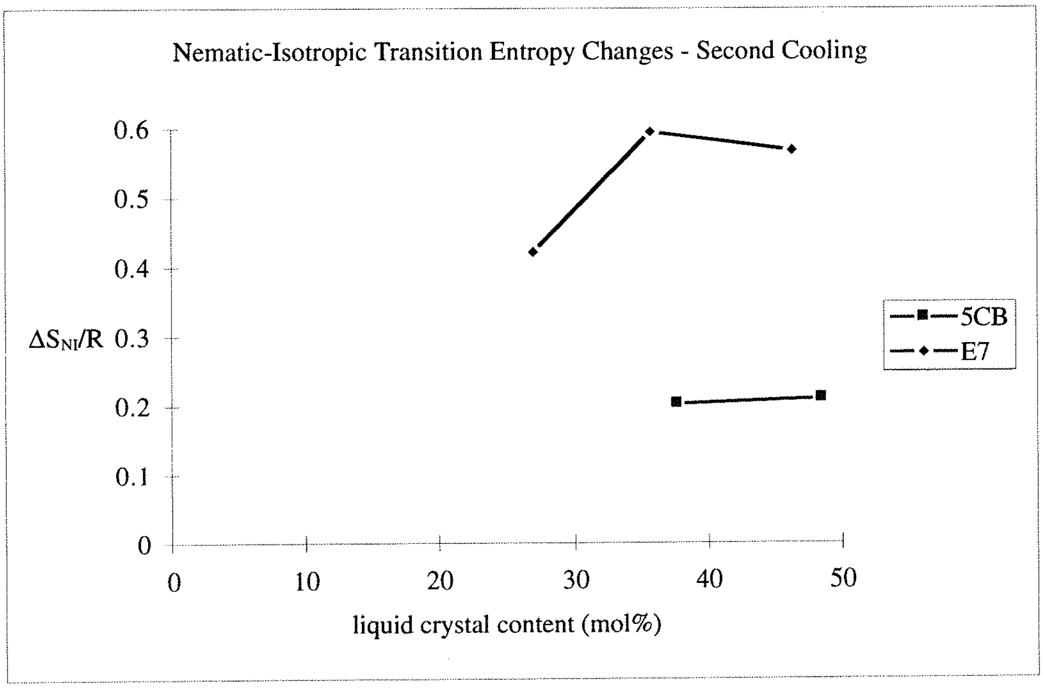


Figure 9.3b. Liquid crystal nematic-isotropic transition entropy changes

9.4. Summary

This phase clearly showed that PDLCs are easy to form, albeit in an uncontrolled manner. Control was not easy to achieve and so these systems are not readily exploitable for use in the marketplace.

Microscopy showed that droplets in these systems were quite large on the whole; although fast cooling rates from the homogeneous phase resulted in small droplets (about 1μm) initially, further phase ripening resulted in droplets of a larger diameter. Higher liquid crystal concentrations of course resulted in a higher droplet density. Transition temperatures of the liquid crystals were confirmed; 5CB in the composites showed a lower transition temperature than the bulk liquid crystal; E7 showed a higher transition, explained by the disproportionate dissolution of the higher transition components in the liquid crystal phase over the polymer matrix.

DSC largely confirmed prior art, theoretical expectations and microscopy studies, insofar as the expected glass transition depression was observed and the nematic-isotropic transition temperatures of 5CB were lowered. The nematic-isotropic transition of E7 was consistent, within experimental error, with the explanations given.

Chapter 10. Polyurethane Composites Work

The next phase of the project was to produce novel polyurethane/liquid crystal composites; this was the main experimental Phase C. Urethane groups are generally formed from the reaction of an alcohol with an isocyanate.

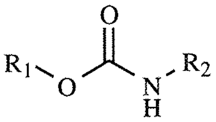


Figure 10.1. Polyurethane functional group. R_1 and R_2 in the following correspond to alkyl chains linking with other units.

10.1. Initial Experiments - Polymer Selection

As with the PMMA composites both 5CB and E7 were to be investigated in mixtures with some polyurethane matrix. The polymer matrix was to be a simple system based on 1,6-diisocyanatohexane [186] cured with α,ω-hydroxylated polybutadiene [187].

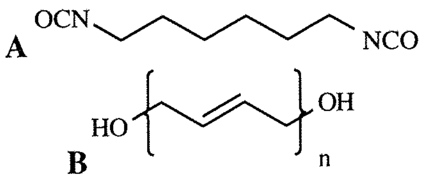


Figure 10.2. Initial polyurethane materials. 1,6-Diisocyanatohexane (**A**) and α,ω-hydroxylated polybutadiene (**B**).

The methodology used was quite simple; a glass tube containing the appropriate mass of diol was placed in a ready-warmed poly(ethylene glycol) [188] bath and the diisocyanate added in the correct volume by syringe (accurate to 0.01ml). The system was then allowed to cure; the end point was determined initially by simple mechanical testing (*ie*, the point at which the material was consistently stiff to mechanical pressure over a time scale of hours) and visual observation. Composite systems were formed simply by adding the appropriate mass of liquid crystal into the diol before the addition of the diisocyanate.

The polybutadiene diol was found to be far too viscous, even at elevated temperatures, to produce a system easy to create and manage. As a result the diol to be studied was then chosen to be hexanediol [189]; this was subsequently found to be much more amenable to experimentation.

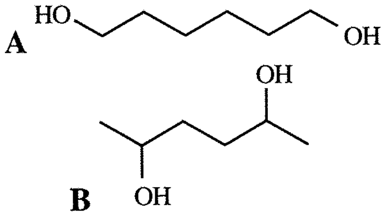


Figure 10.3. Hexanediols. 1,6-Hexanediol (**A**) and 2,5-hexanediol (**B**).

10.1.1. 2,5-Hexanediol with 1,6-Diisocyanatohexane

The first tests were varying the ratios of 2,5-hexanediol and 1,6-diisocyanatohexane (10mol% diol:90mol% diisocyanate, 20:80, . . ., 90:10); the possibility of forming an incomplete prepolymer/liquid crystal system for later, final cure in an actual device had been considered and so for these thermosetting PIPS systems a range of mixtures was tested to check the viability of the such a proposition.

The alcohol was weighed into a glass vial and the vial placed in a test tube rack in a poly(ethylene glycol) bath at 60°C. The diisocyanate was added by syringe, the volume to be added having been calculated exactly, and once added the mixture was agitated to ensure homogeneity and then the mixtures left for 24h.

The result was as predicted; 10mol% diol:90mol% diisocyanate and 90:10 were fluids; 20:80 and 80:20 were more viscous fluids; 30:70 and 70:30 were very viscous fluids; 60:40 and 40:60 were soft, opaque white solids; 50:50 was a hard, opaque white solid. The two 30:70 mixtures looked to be a good choice for a prepolymer system. Polarised light microscopy of a small fragment of the 50:50 mixture showed that it contained a birefringent spherulitic structure as is common with semicrystalline polymers. This 1:1 hydroxyl:isocyanate mixture was seen as a clear candidate for use as a standard for further investigation as it was plainly well phase separated and well cured, leading to easy preparation and easy analysis.

Naturally any device would require a system without this light scattering spherulitic structure to function well. Cross linked polymers are usually unable to crystallise and are often clear and as a result it was decided to perform experiments on a linear system (for simplicity) and a cross linked system (for realism). Another possibility was to introduce defects in any semicrystalline structure with a non-linear unit such as 1,3-phenylene diisocyanate. The main thrust, however, was the introduction of glycerol to effect a network structure.

10.1.2. 1,6-Hexanediol with 1,6-Diisocyanatohexane

1,6-Hexanediol is a white solid at room temperature; in the experimental conditions used this material melted fairly quickly (within 20s). Initial experimentation soon showed that the 1,6-hexanediol reacted too quickly with the 1,6-diisocyanatohexane (2 to 3min at 140°C, 15min at 100°C) to allow much scope within the experiment. In addition the resultant polymer was highly scattering and very hard, in comparison with that formed from 2,5-hexanediol; as a result of this and the rapid cure this avenue was abandoned. The samples were white in colour and as noted were highly scattering; it is likely that the polymer formed is semicrystalline in nature although, as this avenue was abandoned, no further tests were carried out.

10.1.3. 2,5-Hexanediol and Glycerol with 1,6-Diisocyanatohexane

To afford a network structure (thus avoiding crystallisation of the polymer) it was decided to use glycerol [190] to cross link the otherwise linear system.

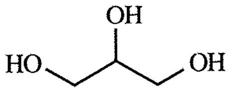


Figure 10.4. Glycerol.

Because glycerol is notable for its being extremely hygroscopic (water would be expected to react with the isocyanate much faster than the alcohols used) it was dried by partial distillation of about 10%, to remove residual water, immediately before use.

The methodology needed to be modified to produce known ratios of glycerol and 2,5-hexanediol. Stock mixtures of glycerol and 2,5-hexanediol were made up such that the percentage of hydroxyl functions (ratio as 2,5-hexanediol:glycerol) in the mixture was 98.1:1.9, 96.0:4.0 and 93.9:6.1 [191]. Apart from this the 1:1 isocyanate:hydroxyl ratio was maintained and the cure otherwise proceeded normally. Four samples were prepared at each stage, one each of the glycerol-containing alcohol mixtures and a fourth simply 2,5-hexanediol to form the linear polymer for comparison.

The first samples were held at 80°C; the glycerol-containing systems became elastic during the reaction and full cure was effected after 8h (determined by simple mechanical tests; the samples were unyielding to mechanical pressure); after this cure the systems were clear, slightly rubbery solids and when cooled they hardened considerably although not completely. The clarity was a good indication that no crystallinity was present and the elasticity a good indication of cross linking. The linear system by comparison was, after cure, a hard opaque solid.

The second samples were held at 100°C and similar results were obtained excepting that full cure was apparently reached after about 5h. The cross linked solids were again clear and were more "rubbery" (that is, lower Young modulus) than those cured at 80°C; this can easily be explained by the higher temperature of the bath. By comparison the linear system was opaque and remained very solid even at elevated temperatures of 100°C showing no signs of softening whatsoever.

The samples cured at 80°C, when heated to 100°C, softened considerably at first and then solidified slightly (to the same degree as those already cured at 100°C) indicating further cure. This observation is entirely consistent with established theory; a greater degree of cure is seen at a higher temperature.

Further tests with a 140°C bath resulted in complete cure after about 90min and overall a much faster reaction rate; the mixtures became viscous within 1min and within 30min the cross linked systems were rubbery as before.

For basic investigation of the systems a cure at 80°C was chosen before further work involving different temperature cures. The 2,5-hexanediol base was chosen as the standard as it could evidently allow a good range of temperatures and curing times for investigation.

Polarised light microscopy was carried out on these polymers. The linear polymer, whilst birefringent, showed no easily visible spherulites at room temperature. The birefringence disappeared completely on heating to 140°C. The three cross linked systems all behaved similarly under the microscope. Faint birefringence was seen in all of them which disappeared on heating. It is notable that all the polymers retained their macroscopic structure despite the heating; no liquefying was seen although the cross linked materials softened to a great extent.

10.2. Polyurethane Composites

Naturally some initial trials on these materials were carried out before a larger body of experimentation to "fine tune" the results.

Repeatability of the measurements: T_{NI} ±2°C for 5CB and twice that for E7; droplet size was repeatable to the same degree as the PMMA composites. There was no observed difference between consecutive heating cycles.

10.2.1. Initial Tests

Stock mixtures of 2,5-hexanediol and glycerol were prepared again; the mixtures were chosen to be 0.18% (allowing a very small amount of cross linking) and 1.74% glycerol (again an arbitrary amount of glycerol but enough to give a reasonable degree of cross linking); again the percentage indicates the amount of hydroxyl functions in the glycerol, the remainder being hydroxyl in the hexanediol [192].

The work carried out was again based on a 1:1 ratio of hydroxyl:isocyanate and was carried out in the same way as before, the only modification being that the liquid crystal was added into the alcohol before being placed in the bath of poly(ethylene glycol). Polypropylene vials were used for the cure in these cases to afford easy removal of the sample (glass vials had to be broken to access the composites thus causing problems of contamination). It must be noted here that any impurity in the polypropylene vials (unreacted monomer, *etc*) could potentially have affected the results; however any DSC or microscopy samples were cut from the centre of a sample so as to be representative of the pure sample.

Preliminary tests showed that the mesogenic materials were miscible with neither the alcohol mixtures nor the isocyanate. In addition the ternary mixture was also immiscible so far as could be ascertained (*ie*, the liquid crystal clearly was not miscible in the homogeneous diol-diisocyanate phase) but after a very short time (60s at 80°C) complete miscibility was attained; evidently on this evidence the liquid crystals are both miscible in some small oligomeric version of the polymer.

The first experiment carried out was a comparison of four alcohol mixtures (1,6- and 2,5-hexanediol, the 0.18% glycerol in 2,5-hexanediol and the 1.74% mix) cured with 1,6-diisocyanatohexane, at 80°C for 24h; each of the four was made with and without 5CB liquid crystal (25wt%).

The 1,6-diol systems both cured very quickly in comparison with the 2,5-diol based mixtures; both systems were completely opaque within 5min; this is attributed to a more rapid phase separation in these systems than in the 2,5-hexanediol systems, caused by longer polymer chains quickly passing the miscibility point with the mother solution.

The remaining six systems cured more slowly. In particular the three composite materials cured slightly slower than the pure polymer systems, as would be expected; that is the systems were slower to reach similar viscosity to the pure polymer. Again the cross linked systems showed elasticity during the early stages of cure. All the systems were left in the bath for 24h to effect full cure. The three 2,5-diol based systems without liquid crystal were all clear solids after this time; the three 2,5-diol composites were opaque, essentially similar in appearance to the PMMA dispersions prepared in the earlier work.

Microscopic analysis was carried out on samples cut from the six 2,5-hexanediol based systems; these were all roughly 2mm by 2mm by 1mm. Heating and cooling were carried out at a rate of 10°Cmin^{-1}.

The three pure polymers all showed some faint birefringence; this was retained even at elevated temperatures (140°C). Spherulites, more prevalent in the non-cross linked systems, melted at about 140-150°C in all cases leaving a very faint birefringence.

The composites were all well phase separated; liquid crystal, present in the characteristic droplet morphology, cleared at 27°C in all three cases; the droplets in the linear polymer matrix were about 3-4μm, those in the 0.18% cross linked 4-5μm and those in the 1.74% were 3μm. The morphology was unaffected by the heating/cooling regime; droplets remained exactly as before once they had been heated and cooled. Some of the liquid crystal leeched out and vaporised at these elevated temperatures; this was seen visually and the resultant condensate was birefringent as is characteristic of liquid crystals so it could be nothing else; this is similar to what was seen with the PMMA composites although in these polyurethane composites no leeching out occurred under ambient conditions unlike the effects seen with the PMMA work. Again, this loss by vaporisation was deemed to be insufficient to affect the trends in the results; in fact the absolute values were apparently unaffected as the liquid crystal transition temperatures observed under the microscope remained unchanged after repeated heating to this point.

An initial test in curing a 1:1 (molar) mixture of 2,5-hexanediol and 1,6-diisocyanatohexane with 20wt% 5CB was carried out, the idea being some form of *in situ* preparation of a film composite. In this the sample was prepared on a microscope slide, placed on the hot-stage used in the microscopy analysis; the three components were carefully added and mixed thoroughly. It was soon noted that the immiscibility of the system was problematic; there were large volumes of pure liquid crystal phase and homogenisation proved difficult. As a result this test proved inconclusive and it showed that future microscope slide preparations were probably best taken form a partially cured system.

10.2.2. Composites - Finding the Miscibility Gap

A set of polyurethane composites containing E7 was prepared to find at which composition of liquid crystal in the polymer was most viable for study. To do this, the 1:1 diol:diisocyanate was chosen and made up as composites with 0, 10, 20, . . ., 60wt% E7. These were cured, as before, at 80°C for 24h.

Again, during the cure all the systems were homogeneous and isotropic. In the early stages of cure (after 1h) the pure polymer system became viscous as with the 5CB composites.

All of these systems scattered light after 72h. The pure polymer system showed some light scattering - approximately 5mm thickness would obscure transmission; those above showed a great deal of scattering (a small chip obscured all transmission). The 0-30wt% liquid crystal composites were all solids but the 40-60wt% were distinctly biphasic, wherein a solid mass was surrounded by a continuous liquid crystal phase. The latter systems evidently were not of interest to this project as any potential system for use in a device would have to be solid.

Precisely the same experiment was carried out using 5CB as the liquid crystal and in this similar results were obtained. However the 10wt% composite was similar in appearance to the pure polymer; this clearly indicates that 5CB (being a single component liquid crystal) has some solubility in the polyurethane synthesised here. Any higher content showed a great deal of scattering. The 40wt% system was borderline in terms of formation of a solid sample; two were prepared and one was more or less a solid, the other was closer to the solid mass surrounded by liquid crystal.

10.2.3. Thermal Gradient Work

The thrust of the project was to be the production of samples cured in a thermal gradient. A mixture of isocyanate and alcohol was prepared as before; in this the approach taken to reducing polymer crystallinity was by introducing defects into the polymer using of 1,3-phenylene diisocyanate [193].

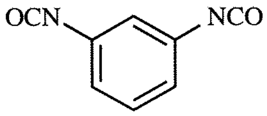


Figure 10.5. 1,3-Phenylene diisocyanate

Preliminary tests on the systems showed that the non-linearity of the phenylene diisocyanate reduced crystallinity and removed it in high enough concentration (20wt%). For the tests the concentration used was 4.5mol%.

A mixture of 4.5% 1,3-phenylene diisocyanate in 1,6-diisocyanatohexane was prepared; this was cured with 2,5-hexanediol with 30wt% 5CB as the liquid crystal component. Again the 4.5% is molar rather than by mass and the ratio of isocyanate to alcohol was 1:1. The sample was prepared in the usual manner and cured for approximately 2h before removing a sample and placing on a warmed microscope slide. At this point a second microscope slide was placed on top of the first to form a sealed system; regular thickness was maintained by placing new aluminium foil at the ends of the slides [194]. The sample was then cured (one end on a hot-plate at 150°C and the other on a cylindrical brass heat sink (15cm diameter, 10cm depth)) for 24h; the separation between the temperature extremes was 3cm, leading to a gradient nominally of 40°Ccm^{-1} although the temperature drop was unlikely to have been uniform. After this time the sample was studied using polarised light microscopy. The sample itself was approximately 50μm thick but slightly thicker at the cold-cure end.

The hot-cured end of the sample was significantly different to the cold end. The polymer was not birefringent; this indicates that the high temperature prevents any crystallinity in conjunction with the irregularities imposed by the phenylene diisocyanate; the system forms in such a disordered state that spherulites cannot form. Liquid crystal droplets were spherical, high in density, regularly sized (about 2μm) and evenly spaced (a qualitative assessment of spacing slightly larger than the size of the droplets themselves); this being consistent with spinodal decomposition morphology (see §**3.4.2**).

The cold cured end was characteristic of binodal decomposition and significant phase coarsening; the droplets were unevenly spaced, unevenly sized but generally large (about 15μm). The polymer itself displayed some crystallinity which was unexpected; it is postulated that a difference in the reactivity of the two diisocyanates was the cause; if the diisocyanatohexane cured more quickly than the phenylene diisocyanate (or *vice versa*) then it is conceivable that the polymer would be formed with no (or few) "kinks" in the chains, until perhaps later during the cure when the concentration of unreacted phenylene diisocyanate had increased greatly.

Lastly, across the middle of the sample there was a gradual transition from the spinodal morphology to the binodal morphology; throughout the sample all the droplets were spherical. However as the sample was so much longer than its thickness (relative to the direction of the thermal gradient), it was difficult to predict from this what the morphology resulting from a transverse temperature gradient would be.

A further sample was then prepared to attempt to view the effects of such a transverse temperature gradient. The mixture was prepared as before with the 1,3-phenylene diisocyanate mixture, 2,5-hexanediol and 30wt% 5CB. After about 2h a drop was placed on a microscope slide on the hot-plate at 150°C. Again, this was covered with another slide with foil spacers, and on top of this a water bath was placed in intimate contact with the top slide (and refilled regularly) to try to ensure some form of thermal gradient would exist across the sample [195]; the bottom of the system would be 150°C and the top 100°C and the sample in the middle physically and thermally. The possible effects of convection currents in the system were ignored for the initial test.

Polarised light microscopy was inconclusive; as any effects were likely to have been parallel with the line of sight in such an analysis it is difficult to see how the bottom would be different from the top of the sample. Focusing on different depths in the sample was not fruitful; the sizes of the droplets could not be ascertained owing to the density of the droplets obscuring the view. As it was, the system looked homogeneous so far as could be ascertained; the liquid crystal droplets were very small (1μm at most), as would be expected with a cure regime between 100°C and 150°C. A transverse section through the sample, carried out to avoid distortion of the structure, and then scanning electron microscopy on such a sample would be necessary to determine the exact morphology.

10.3. DSC Results - Linear Systems

Many of the samples prepared were studied by differential scanning calorimetry, as with the PMMA composites. The first set of results, given here, refers to those composites that were formed from a simple, linear polymer with no cross linking. To better present the results, the calculated data are appear according to type of transition rather than individual sample.

Errors and repeatability were fair in these samples after the first heating cycle; for the polymer T_g ±10°C, with ΔC_p ±20JK^{-1}mol^{-1}; for the liquid crystal T_{NI} ±2°C for 5CB and twice that for E7 with $\Delta S_{NI}/R$ ±0.05 in both cases.

The data from the first heating cycles have a higher error margin than the following two cycles due to the inherent uncertainty in a newly cured system. For the polymer, T_m ±10°C, $\Delta S_m/R$ ±0.02, T_g ±15°C and ΔC_p ±30 JK^{-1}mol^{-1}; for the liquid crystal ±5°C for both T_{NI} and ±0.1 for $\Delta S_{NI}/R$. The trends are well defined throughout the plots and in the first heating plots particularly the relative positions of the data are not so clear and must be treated with caution.

10.3.1. Polyurethane Crystal Transition

One of the more noticeable transitions on the DSC traces was a large first order peak at high temperature indicative of a polymer crystal transition (the point at which the polymer spherulites melt into an isotropic glassy form); see figure 10.6a. Microscopy data confirmed this transition as the crystal transition of the polymer. The polymer crystal transition is much as it is with any other first order transition except that it will disappear in most instances after one heating cycle; the polymer thereafter is too viscous or slow moving to reform a crystalline state upon even a slow cooling cycle and the polymer sets into a glassy phase as it is unable to form the semicrystalline state within the spherulites. Again this observation was reinforced by polarised light microscopy - any spherulitic character of the polymer was seen to disappear on heating and never return. The following data for the crystal transition were calculated based on the theoretical amount of polymer present.

It is apparent from the plot that the semicrystalline nature of this polyurethane is basically unaffected by the presence of liquid crystal; no change is seen on addition of liquid crystal to the polymer.

This crystal transition is lost after the first heating. As noted this is due to the high viscosity of the system; once the crystallites have melted then, unless cooled slowly, the polymer strands move too slowly for the spherulites to reform and a glass results.

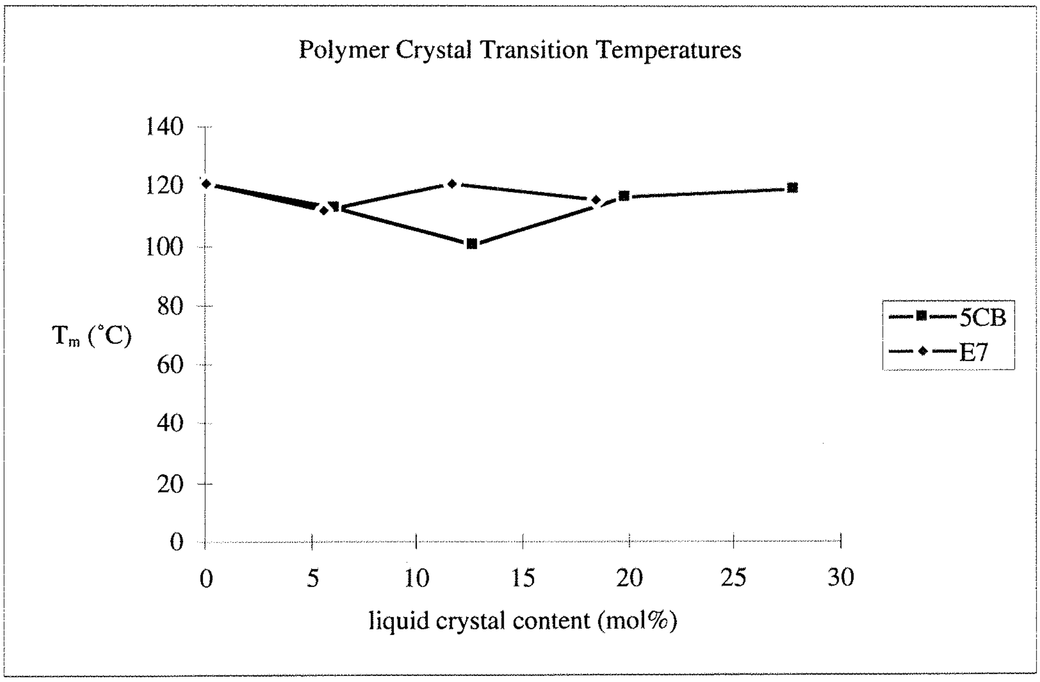


Figure 10.6a. Polyurethane crystal transition temperatures

The entropy change on melting the polymer is higher than that of the liquid crystal nematic-isotropic transition (figure 10.6b), this is of course indicative of a higher order in the spherulites than the more fluid nematic phase. Additionally, since not all of the polymer is present in the form of crystallites the true transitional entropy is higher; it is difficult, however, to estimate the actual volume present in crystalline form *vs* that in glass form. It is interesting to note that the transitional entropy increases on addition of liquid crystal. In addition the transitions are stronger in the E7 composites than in the 5CB composites. The first explanation for this is that more polymer is present in a semicrystalline form than is the case with the pure polymer; this is plausible from the viewpoint that in the pure polymer the interspherulitic space is filled with polymer glass whereas it is conceivable that in a composite some of this random structure is replaced with the liquid crystal. Another explanation could be that crystallinity is actually promoted somehow in the composites; either the polymer co-crystallises with liquid crystal or the polymer preferentially forms spherulites when liquid crystal is present. It is possible that, for example, nuclear magnetic resonance spectroscopy would give a clue as to the truth of this but certainly the results given are not sufficient for anything other than postulation; more specific work is required.

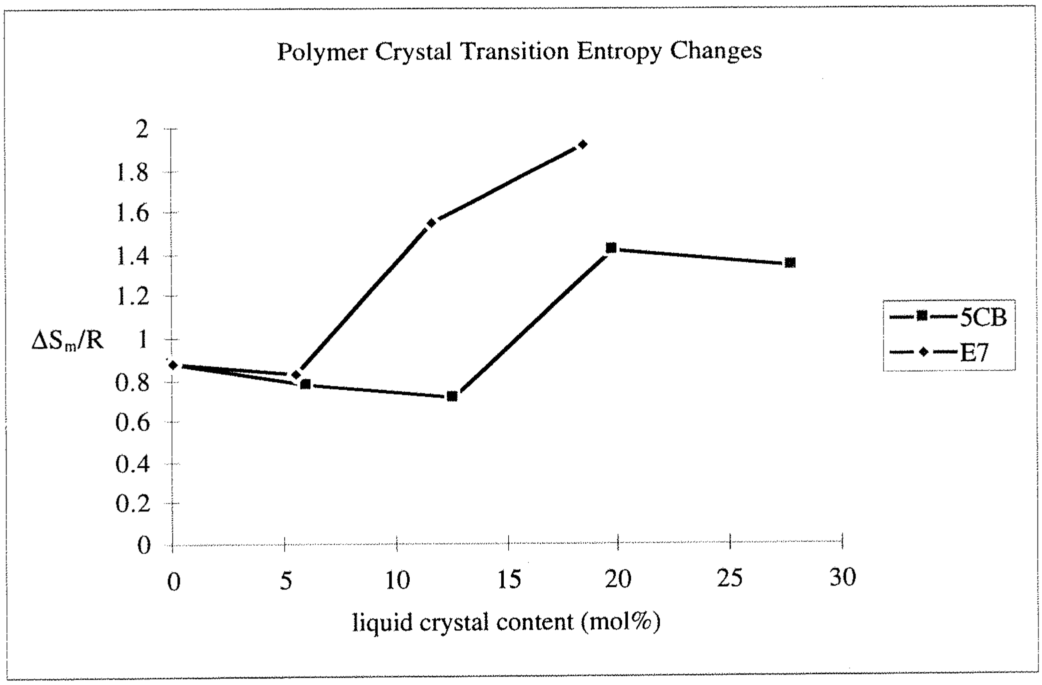


Figure 10.6b. Polyurethane crystal transition entropy changes

10.3.2. Polyurethane Glass Transition

Another transition characteristic of polymers is the glass transition. On a macroscopic scale, this often corresponds to the softening point of a polymer when heated. It is a function of the glassy state of a polymer; as far as these polyurethanes are concerned it corresponds to the polymer not contained within spherulites. On a molecular level the glass transition corresponds to a co-operative cessation of segmental motion of the polymer strands - in some sense where the polymer begins (on heating, or ceases on cooling) to move like a randomly oriented liquid. Unlike a crystal transition, this does not disappear after one heating/cooling cycle but is always present. Glass transition temperature is affected by molecular mass of the polymer; a longer chain of the same repeat unit will have a higher glass transition temperature (the strands are less prone to moving relative to each other as there are more attractive interactions). Plasticisers lower the glass transition by interfering with molecular interactions, thus with these composites, as was noted with the PMMA composites, it was likely that such effects would be seen and perhaps be quite marked.

In these thermally cured systems, the heating/cooling cycle exceeds the polymer's cure temperature by 120°C; it is entirely likely, then, that additional cure would occur and be manifested as an exothermic peak on the first cycle and an increase in the glass transition temperature on the second. Three plots are shown for the temperature and heat capacity changes; those on the first heating cycle, those on the subsequent cooling cycle and those on a second heating cycle for comparison with the first (figure 10.7a).

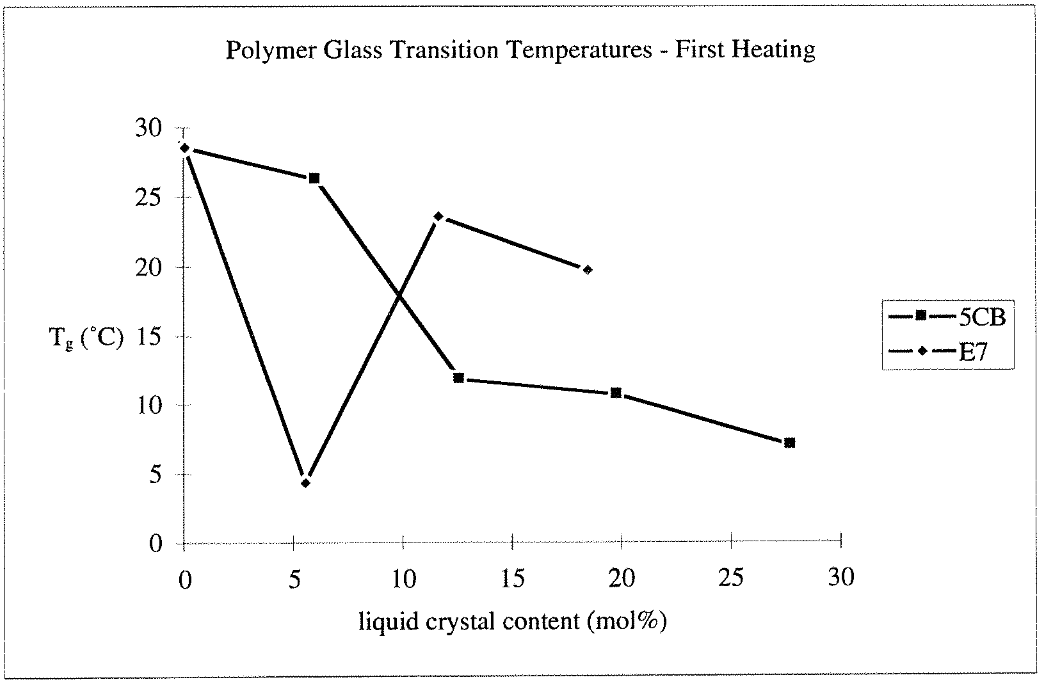
The first observation from the plots is the depression of the glass transition on addition of liquid crystal to the system. Whilst the same effect was seen with the PMMA composites, here the depression is perhaps not as marked although the glass transition of the PMMA is generally much higher than in these and so direct comparison is not possible.

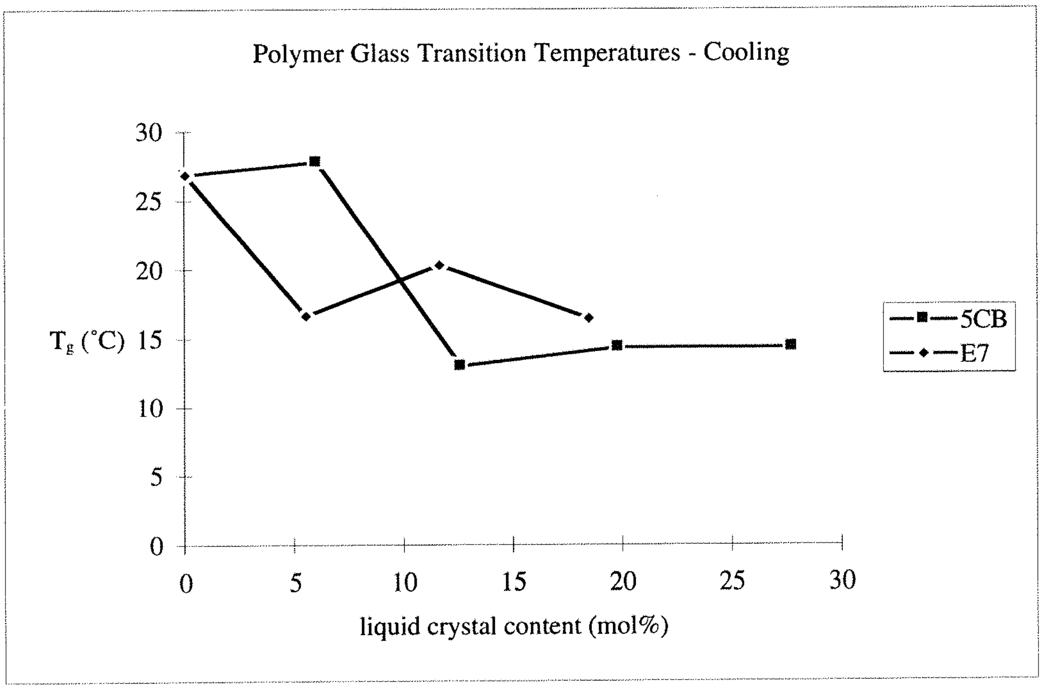
The explanation for the drop is the same as in the PMMA composites; the liquid crystal is soluble to a certain extent in the polymer and as a result disrupts the interactions thus depressing the transition temperature.

It is possible that the liquid crystal is much less soluble in the polyurethane than in the PMMA. Certainly the high density of urethane groups would contribute to a large polarity difference between the two chemical types; thus a reduction in solubility of the liquid crystal in the polymer could be expected. As a result the depression of the transition would be expected to be smaller as it is. Simple observation agrees with this theory; the composites phase separated at lower concentrations of liquid crystal in the polyurethanes than in the PMMA composites.

There is no notable difference in glass transition between the two composite types. Either they have similar overall solubility in the polymer matrix or the liquid crystal dissolved in the matrix in each case has a similar effect. It might have been expected that the 5CB would be more soluble than the E7 and thus give a more marked reduction (as with the PMMA); this does not seem to be the case, however.

The glass transition increased after the first heating cycle. An exothermic peak indicative of further cure was seen at high temperature(see below), thus an increase in the glass transition would be expected.


Polymer Glass Transition Temperatures - First Heating
30
25
20
T_g (°C) 15
10
5
0
0
5
10
15
20
25
30
liquid crystal content (mol%)
5CB
E7


Polymer Glass Transition Temperatures - Cooling
30
25
20
T_g (°C) 15
10
5
0
0
5
10
15
20
25
30
liquid crystal content (mol%)
5CB
E7

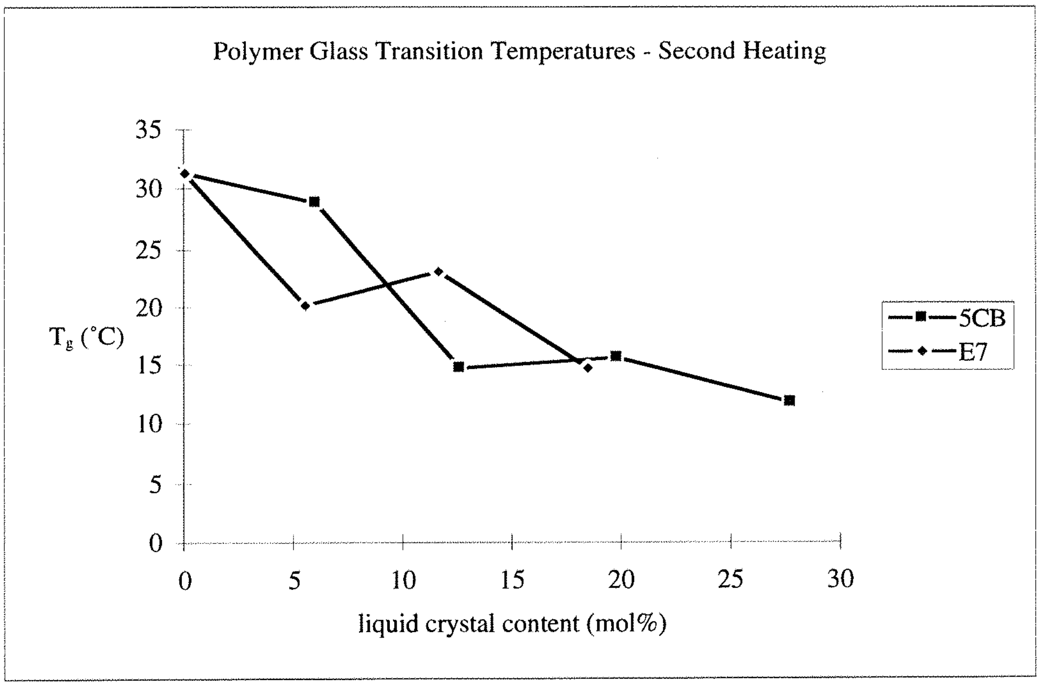
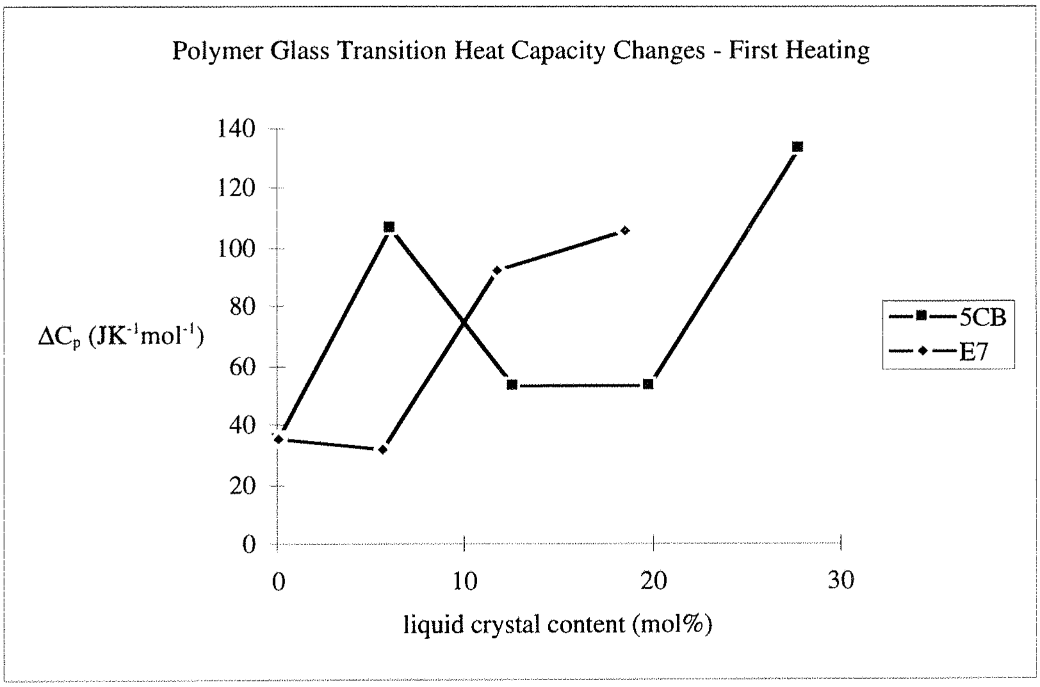
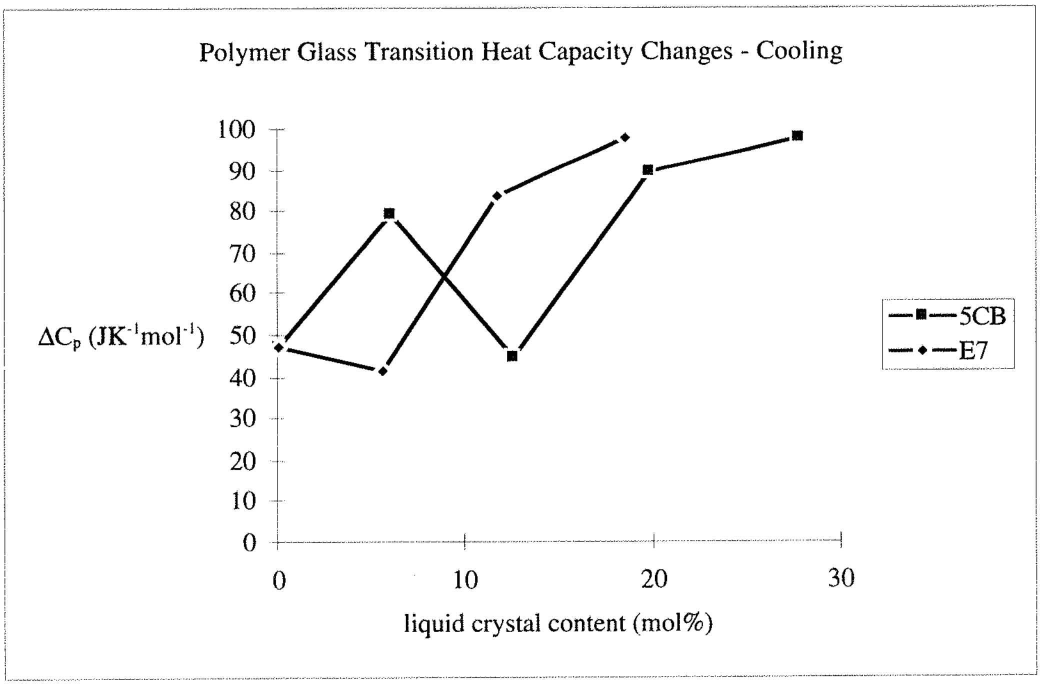


Figure 10.7a. Linear polyurethane glass transition temperatures

Figure 10.7b shows is an upward trend in the strength of the transition on increasing the liquid crystal content, in contrast to the PMMA composites in which there was a marked downward trend.

This indicates that either more polymer is present in the glass phase than the semicrystalline phase (although this would disagree with one of the possibilities for the increased size of the crystal melting point) or that the composite is better able to absorb thermal energy above the transition due to an increased amount of freedom of movement. The latter is intuitively more likely as the crystal transition also seems to be enhanced.


Polymer Glass Transition Heat Capacity Changes - First Heating
ΔCp (JK⁻¹mol⁻¹)
140
120
100
80
60
40
20
0
0
10
20
30
liquid crystal content (mol%)
5CB
E7


Polymer Glass Transition Heat Capacity Changes - Cooling
ΔCp (JK⁻¹mol⁻¹)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
liquid crystal content (mol%)
5CB
E7

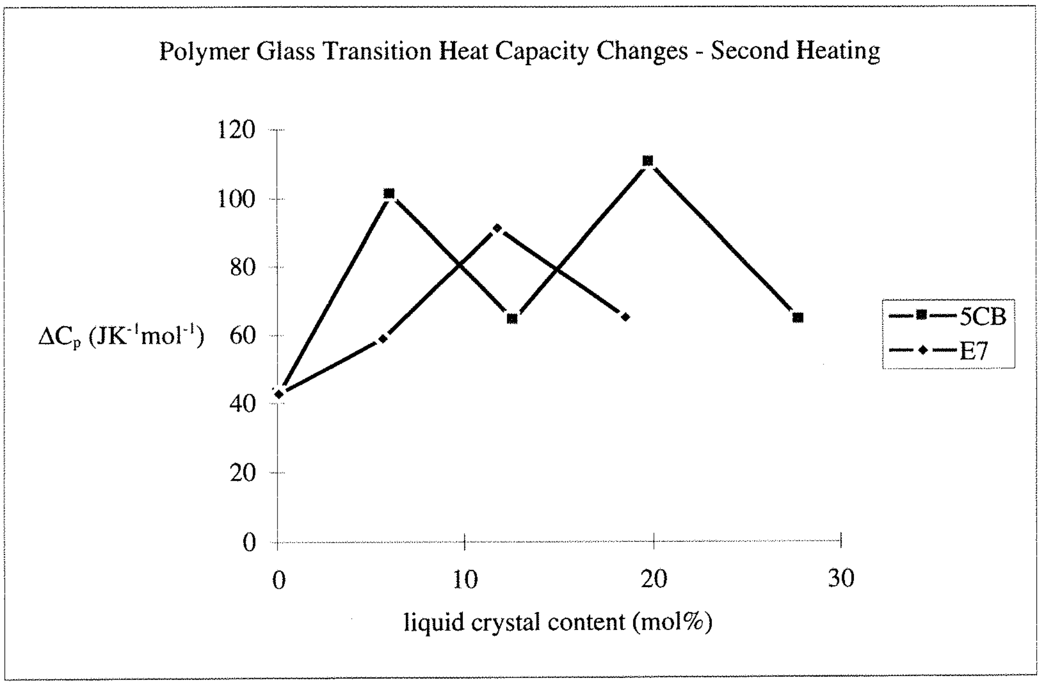


Figure 10.7b. Linear polyurethane glass transition heat capacity changes

10.3.3. Liquid Crystal Nematic-Isotropic Transition

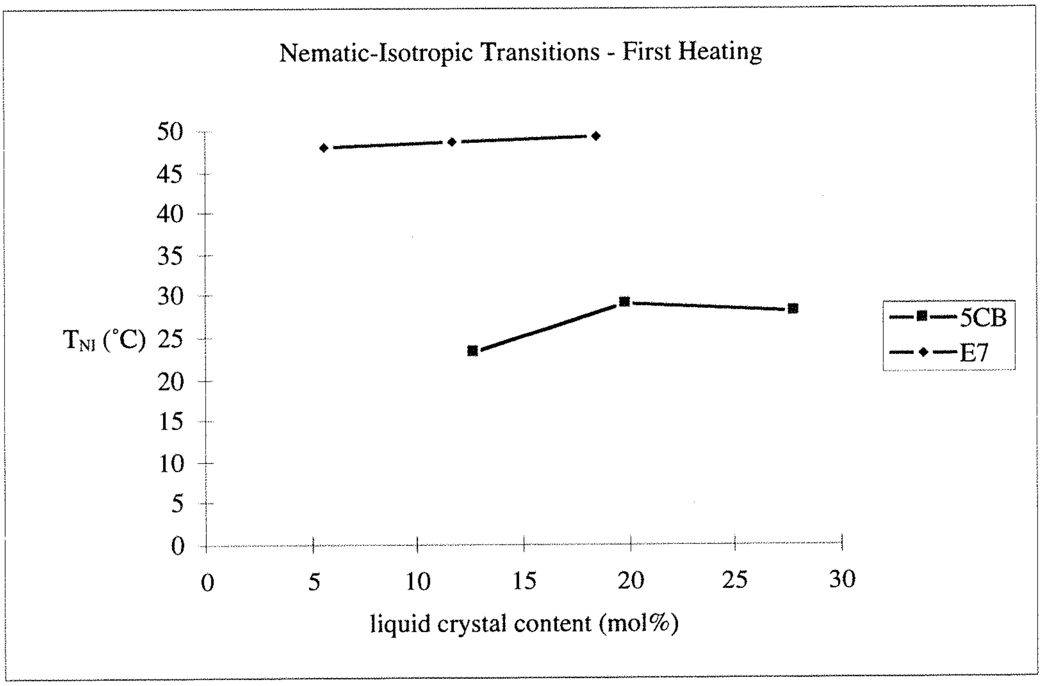
The nematic-isotropic transition is first order but tends to be much smaller (*ie*, with less enthalpy and entropy change) than a crystal to nematic transition where considerable energy is required to break the bonds and the difference in entropy between a crystalline solid and relatively disordered liquid is marked; nematic phases have a degree of order much closer to isotropic than crystalline.

Both of the liquid crystals involved in this work are extensively used and well characterised. They both form a nematic phase at room temperature; 5CB has a nematic-isotropic transition at 35.1°C and E7 becomes isotropic at 61°C. For bulk E7, $\Delta S_{NI}/R$ at 61°C is 0.45 and for 5CB it is 0.36 at 35°C.

The data in figure 10.8a show that in most cases the nematic-isotropic transition of the liquid crystal is reduced compared with that of the pure material. As with the PMMA composites, this implies that the small droplets observed under the microscope reduce the transition due to the confines of such a small cavity and in this case more so that impurity affects the transition temperature also.

It is worth noting that when the second heating cycle was run, the transition disappeared for lower concentrations of liquid crystal. This can be interpreted by an increased solubility of the liquid crystal in the polymer matrix; once heated the first time, the polymer is mobile enough to allow liquid crystal to dissolve and when cooled this effect is retained such that fewer droplets abound - this would manifest as a reduction in the transition enthalpy and even its removal (as was seen).

The single composition which retained a liquid crystal nematic-isotropic transition on the second heating has a higher temperature than that of pure E7. It is likely that the higher-transition components will preferentially phase separate out into the droplets with the lower-transition components remaining in the polymer matrix; thus the effective transition temperature would be higher.



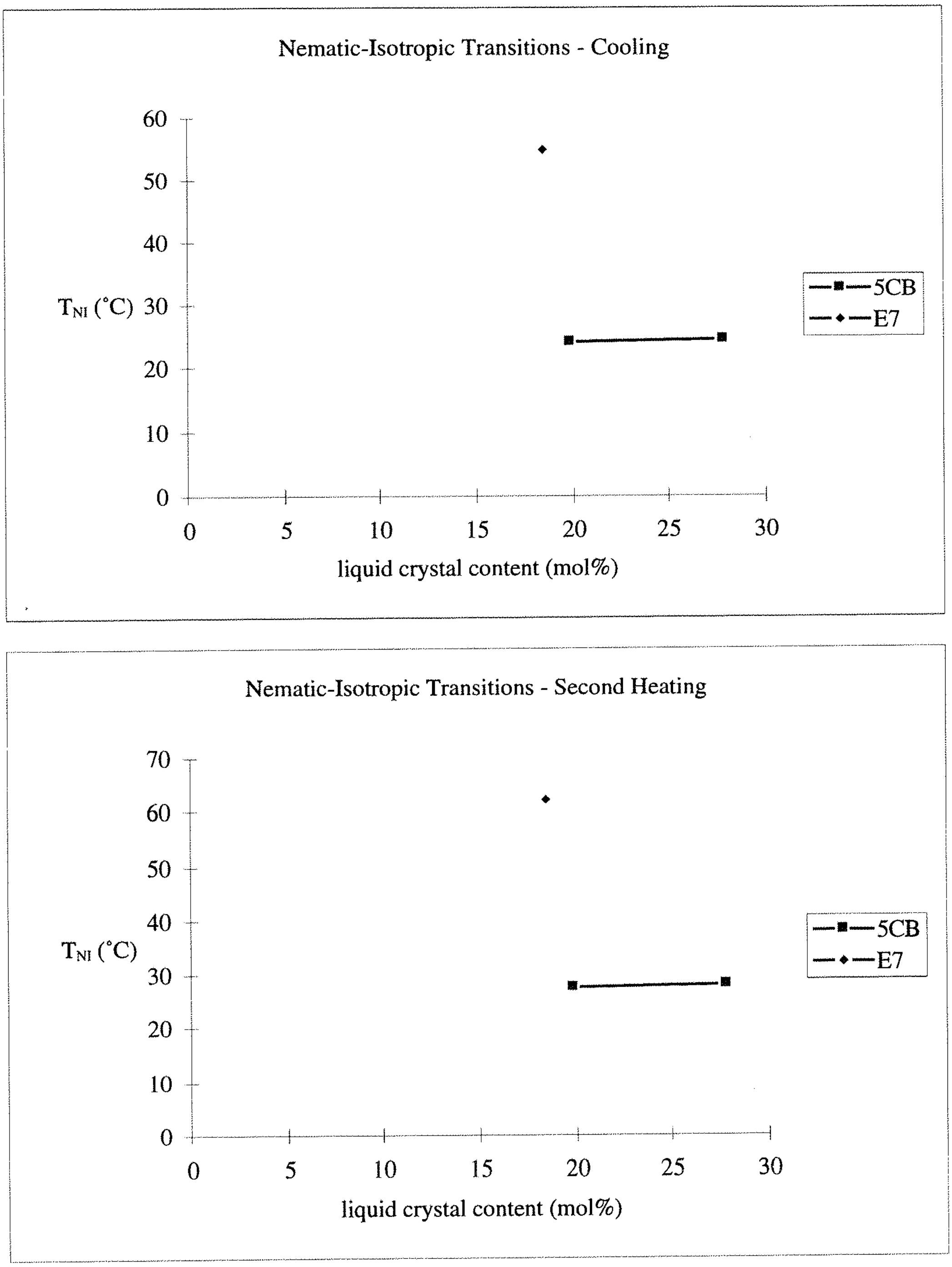


Figure 10.8a. Liquid crystal nematic-isotropic transition temperatures (linear systems)

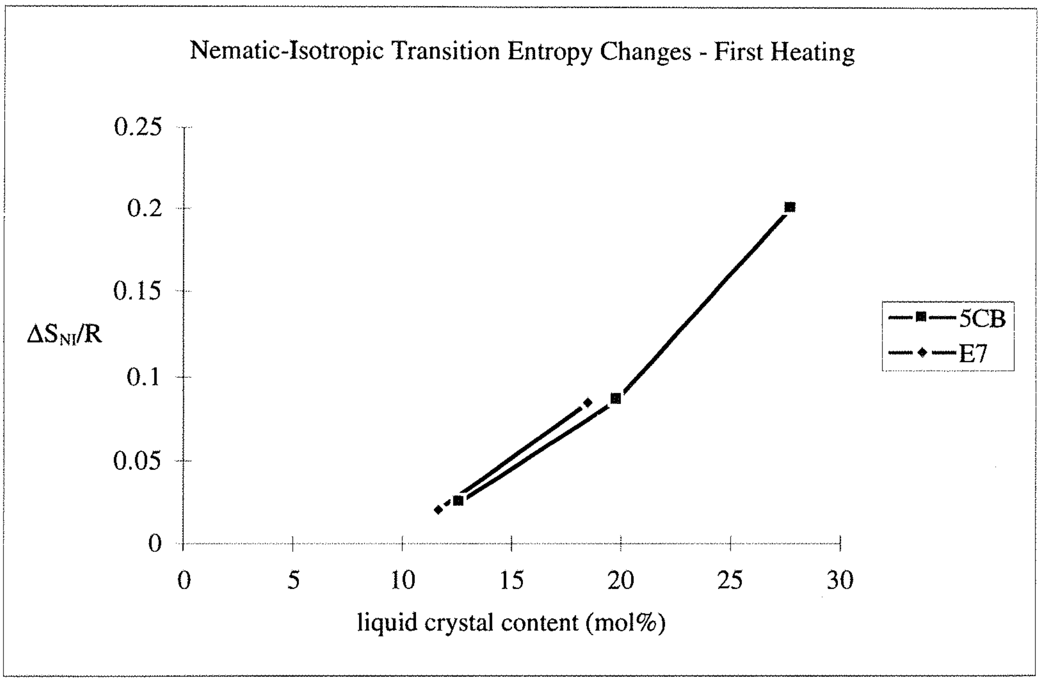
The data for the entropy changes presented in figure 10.8b were calculated based solely on the mass of the liquid crystal component in the mixture.

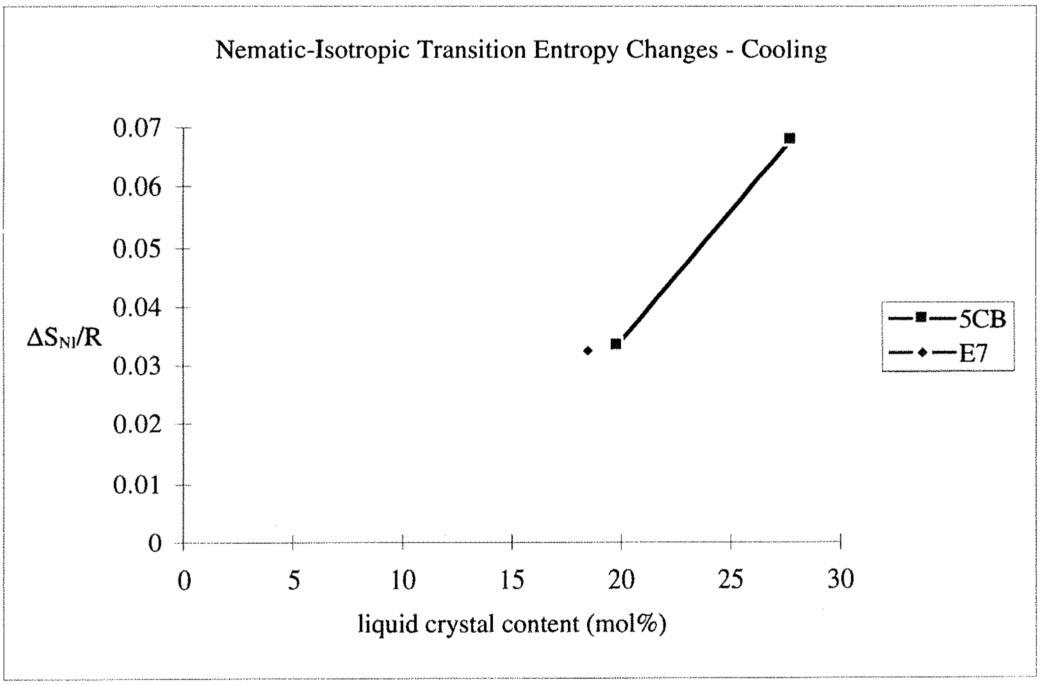
As can be seen, the strength of the transition increases on increasing the concentration of liquid crystal. This is entirely expected as there is a solubility limit of liquid crystal in the polymer, above which phase separation will occur. It is conceivable that an accurate study of this effect could give the precise concentration at which phase separation would occur for a given polymer although certainly in this work insufficient data is available.

Another interesting point is a reduction of the strength of the transition in passing from the first heating cycle to the second. The likelihood is that the liquid crystal dissolves further in the polymer once heated and so less liquid crystal is present in pure form to undergo a transition.

There was an anomalous high calculated result for the entropy change of the 10wt% E7 composite; $\Delta S_{\text{"NI"}}/R \approx 7$ and therefore plainly too high to be the entropy change of the nematic-isotropic transition. It was noted that at a similar temperature in the composites a distinct endothermic peak was seen, albeit at a slightly higher temperature than the 61°C of the E7 nematic-isotropic transition (see below). It is quite likely that the two peaks were superimposed at this point thus resulting in a large apparent nematic-isotropic transition for this composite. Even this superimposition would be unlikely to account for the strength seen and so a further endothermic transition must therefore be responsible; if the E7 was in a crystal phase (which is unlikely) then superheating of the liquid crystal past its melting point could lead to melting occurring at the nematic-isotropic transition. The latter is perhaps the most likely given the strength of the transition; there is no other obvious mechanism. This result should be treated with scepticism and is not plotted.

Comparison with the bulk values (0.36 for 5CB and 0.45 for E7) shows that the transitions are apparently reduced somewhat. As with the PMMA composites the results were calculated on the total liquid crystal content and not just that contained within the droplets, so the values are lower than the "real" values. Disruption of the order due to the restrictions of the small space involved would reduce the order in the nematic phase and thus the entropy of the transition, which could in part account for the reduction in the transition strength.


Nematic-Isotropic Transition Entropy Changes - First Heating
0.25
0.2
0.15
0.1
0.05
0
$\Delta S_{NI}/R$
0
5
10
15
20
25
30
liquid crystal content (mol%)
5CB
E7


Nematic-Isotropic Transition Entropy Changes - Cooling
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
$\Delta S_{NI}/R$
0
5
10
15
20
25
30
liquid crystal content (mol%)
5CB
E7

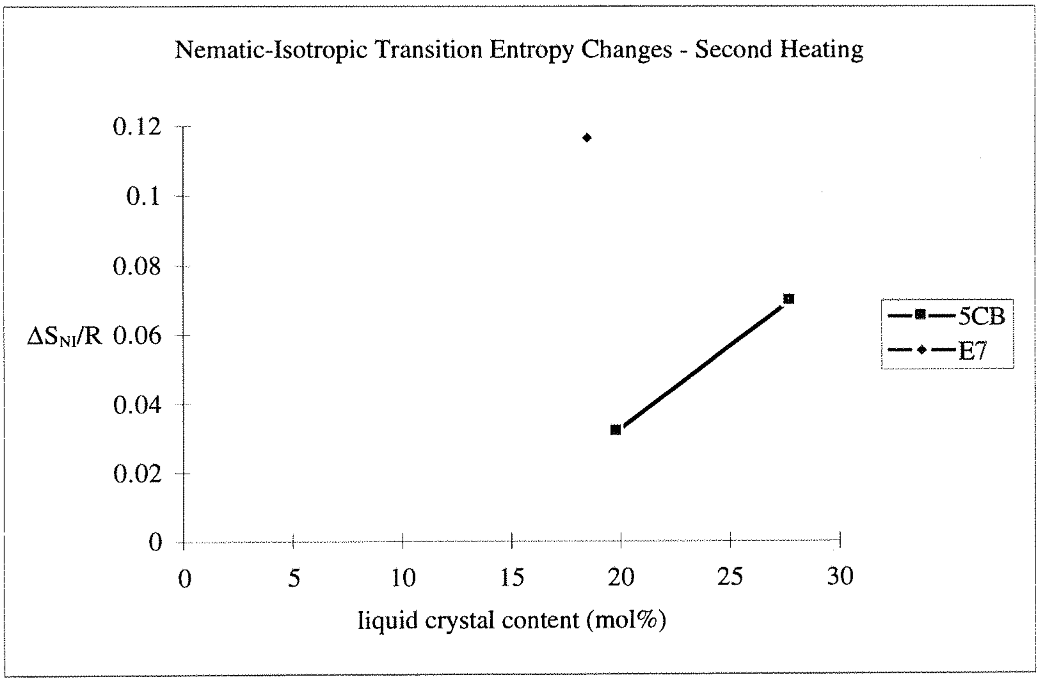


Figure 10.8b. Liquid crystal nematic-isotropic transition entropy changes (linear systems)

10.3.4. Other Transitions Observed

Three additional transitions were also observed in some of the DSC experiments; first the 5CB crystal-nematic transition and second an unknown transition of the composites. The third transition is not quantified here; at the top end of the first heating cycles in some of the composites an exothermic peak was observed. It is hypothesised that this corresponds to further reaction of alcohol and isocyanate, *ie*, further cure of the polymer. This hypothesis is reinforced by the increase in the glass transition temperature of the polymer. The former two transitions are discussed later.

The liquid crystal 5CB exhibits a crystal-nematic transition at 23°C. On the first heating run of higher concentration composites an endothermic peak was observed at about 13°C (figure 10.9). The entropy change at the transition ($\Delta S/R \approx 1$ to 2) is considerably larger than the observed nematic-isotropic transition as should be expected for a crystal melting into a mostly disordered state. As with the nematic-isotropic transition this peak is less visible at lower concentrations due to the solubility limit of the liquid crystal in the polymer. Unlike the nematic-isotropic transition this peak was not observed on the following cycles; this is due to the viscosity of the system combined with the small cavity size making the liquid crystal unable to crystallise; instead the fluid becomes more viscous and eventually forms a glass. E7 does not exhibit such a transition as it is a mixture which is therefore more or less incapable of forming a cohesive crystalline structure. The bulk value for the transition is $\Delta S_{CN}/R=6.46$; the reduction is caused by the basis of the calculation being the total amount of liquid crystal and a possible reduction in the transition due to the spatial confinement.

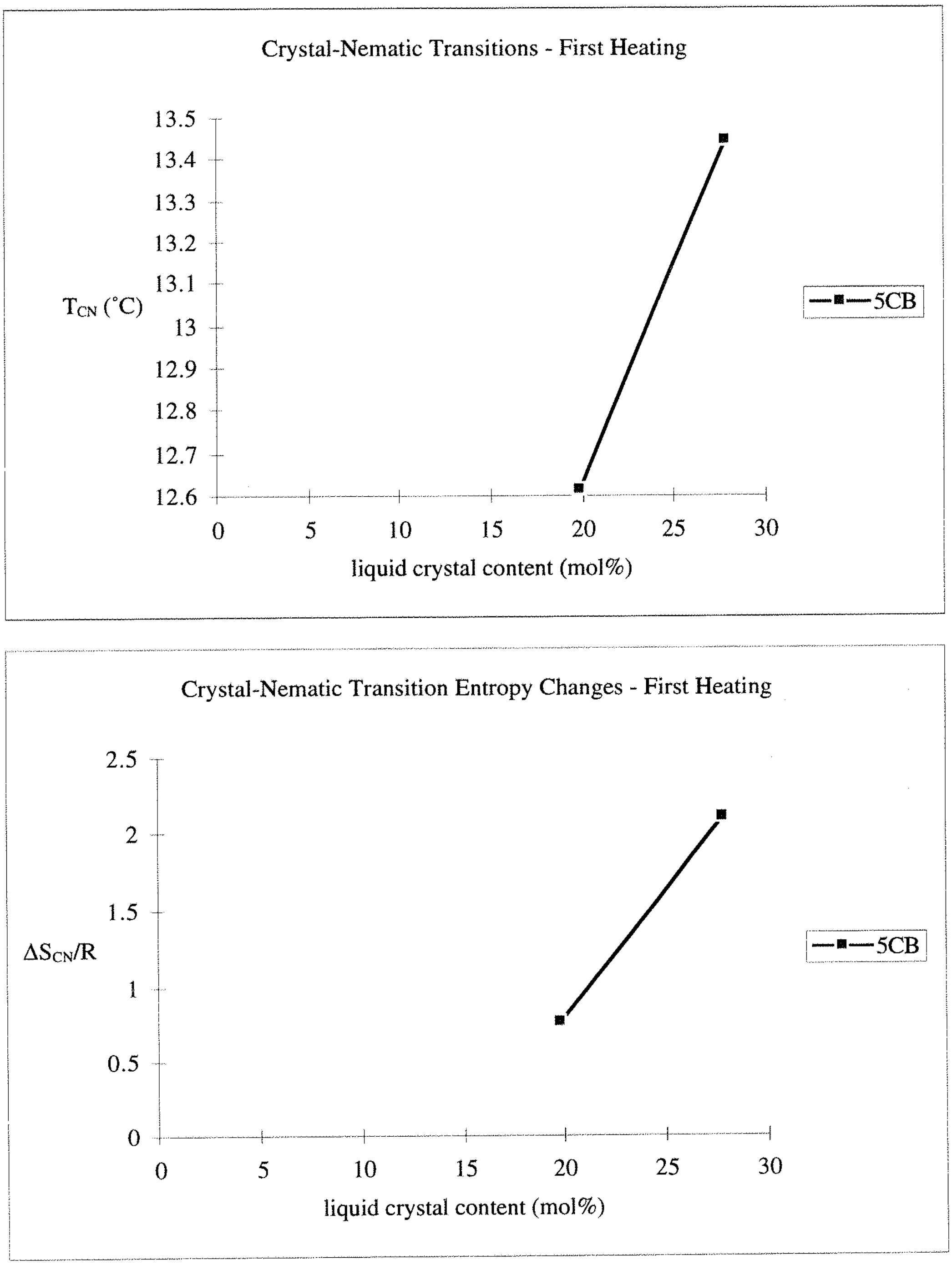
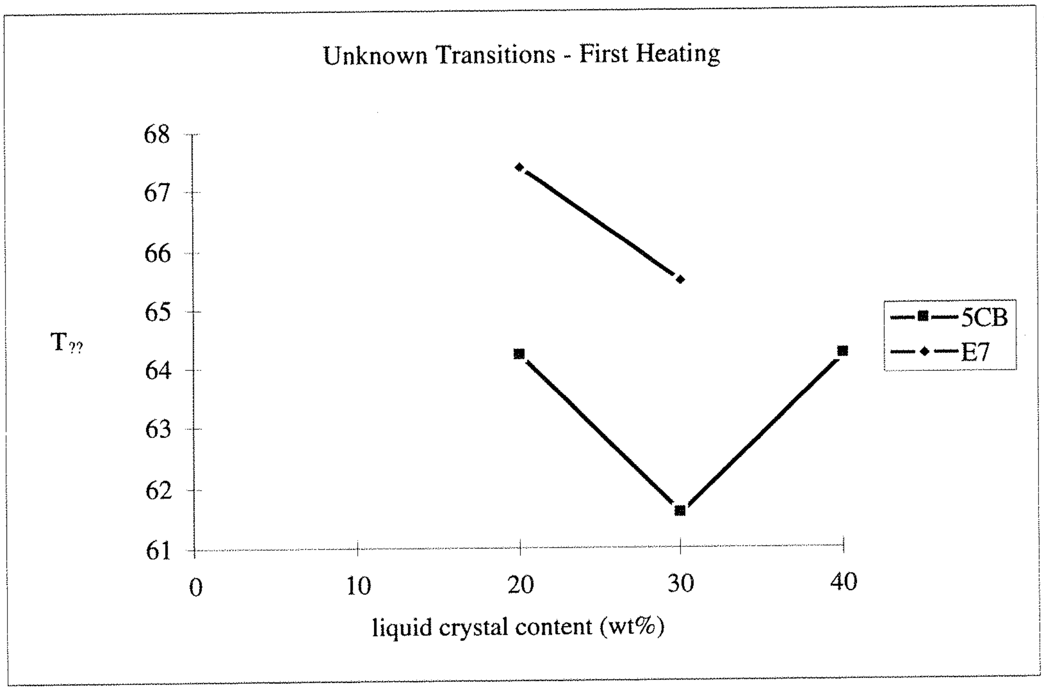


Figure 10.9. 5CB crystal-nematic transition (linear systems)

As noted, a transition was also observed at a temperature of about 65°C in many of the composites (figure 10.10). At first it was a little difficult to distinguish between this and the E7 nematic-isotropic transition but this peak was also observed in the 5CB composites. There is little pattern to the observation except that it increases in strength with increasing liquid crystal concentration and it is larger in the E7 composites than in the 5CB. It is logical to assume that it is, therefore, connected with the liquid crystal in some way although the reason why is obscure. It may be that the polymer crystallites or the glassy phase changes in some way; this is perhaps unlikely as the transition is not seen in the pure polymer although this lends credence to the idea that the liquid crystal interacts positively with the polymer (such as being co-crystallised). As noted in the 10wt% E7 composite the transition seems to be concurrent with the nematic-isotropic transition; as a result the point is not plotted below. Again, NMR techniques could be exploited to give further information on this transition.



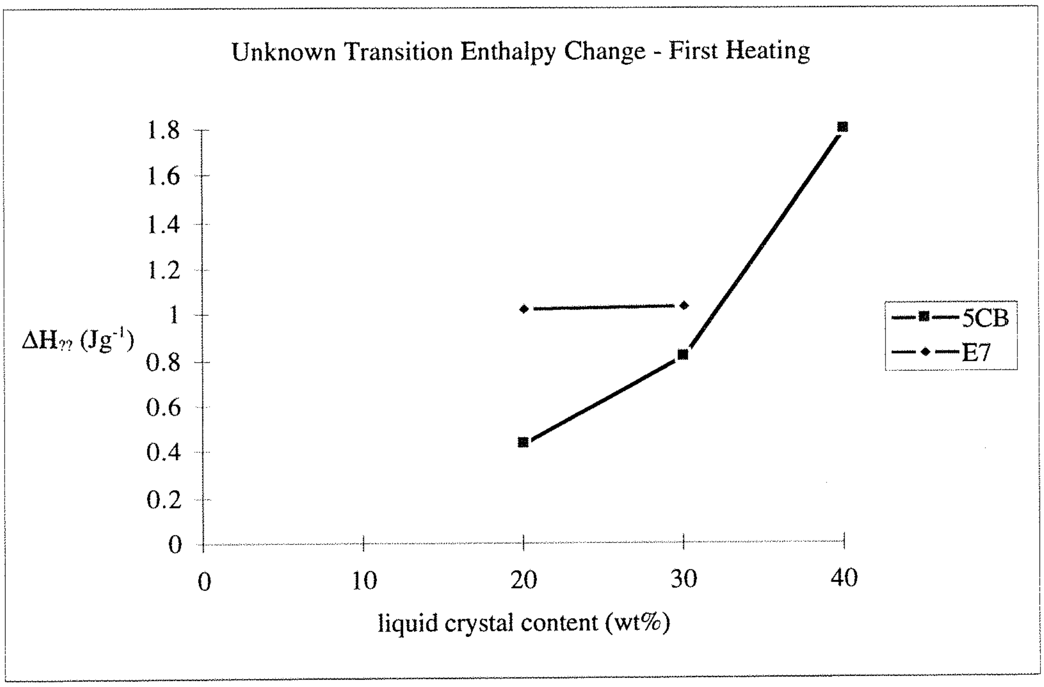


Figure 10.10. Composites' unknown transition (linear systems)

10.4. DSC Results - Cross Linked Systems

The presence of spherulites (polymer crystallites) caused a slight modification to the work. As polymer spherulites scatter light any potential device would have to be constructed from a polymer with no such effect.

In general in the DSC results the main transitions of interest remained - the glass transition of the polymer and the nematic-isotropic transition of the liquid crystal. Errors were as with the linear polymers.

10.4.1. Polyurethane Glass Transitions

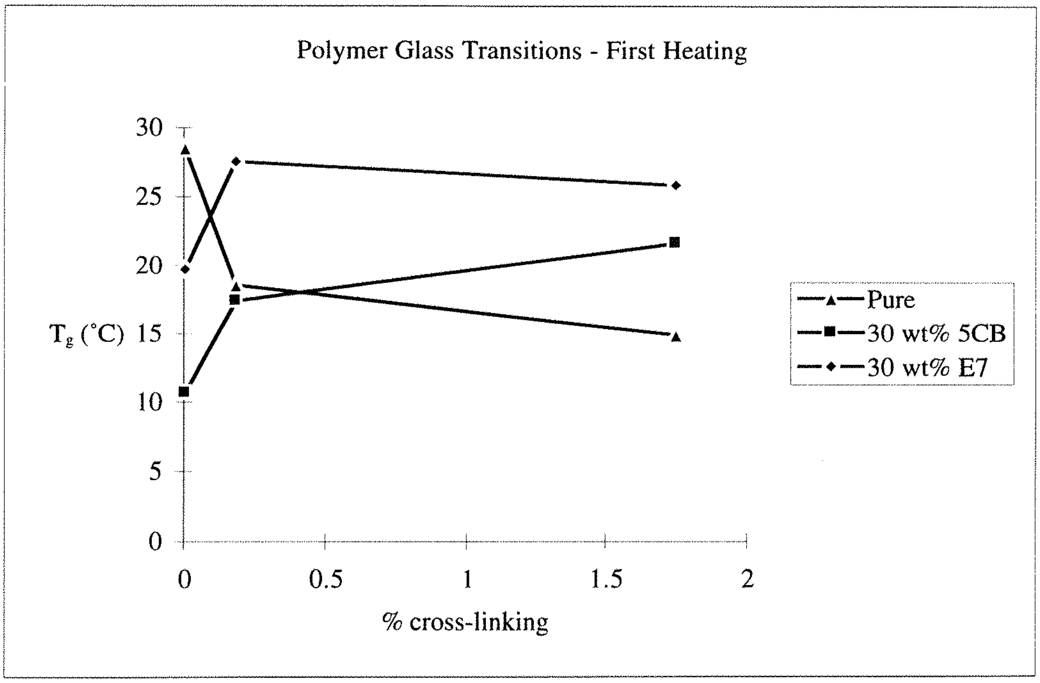
The glass transition occurred much as with the linear systems. For the DSC analysis, three systems are compared in figure 10.11a; the pure polymer, 30wt% 5CB and 30wt% E7 over a range of degrees of cross linking (0, 0.18 and 1.74% - see §**10.2.1**).

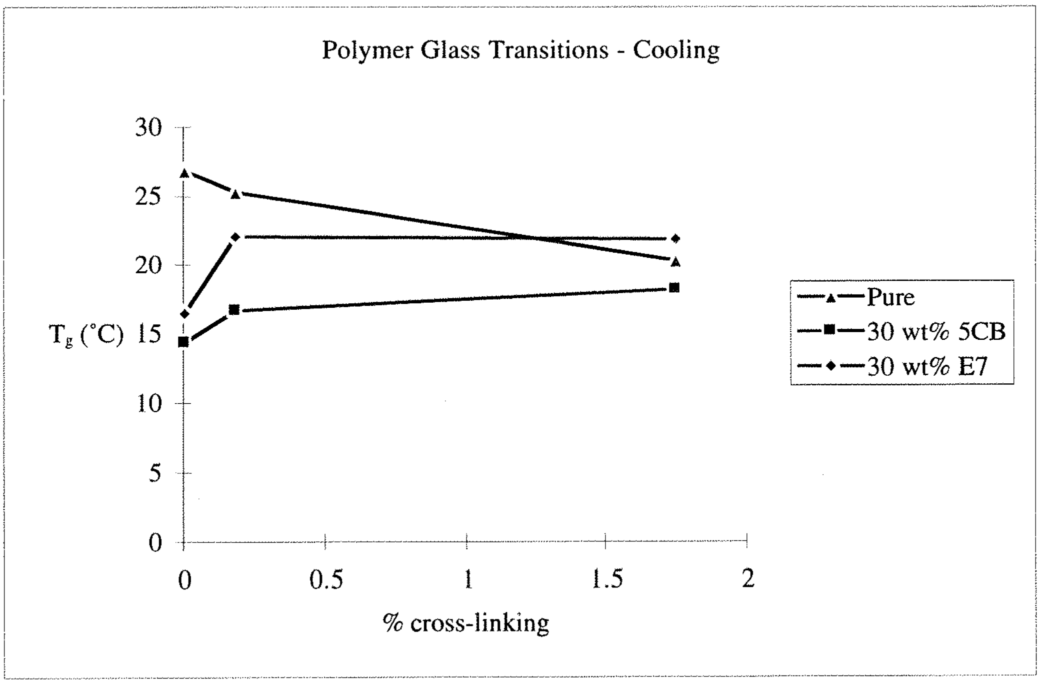
Increasing the cross linking density in the pure polymer depresses the glass transition. The network structure decreases steric hindrance and negatively affects the intermolecular interactions as the degree of cross linking increases; the strands of the polymer are held in less-than-ideal conditions for interaction (*ie*, order is disrupted considerably) and the strands are more free to move, so the glass transition is depressed as there are less attractive interactions present.

Addition of liquid crystal naturally decreases the glass transition due to plasticisation; moreso for the 5CB composites due to its greater solubility in the polymer than E7.

Addition of cross linking into a *composite* actually *increases* the glass transition temperature. In such a system it is perhaps better to compare the glass transitions of these cross linked composites with that of the pure elastomer and then say that the difference between the two is reduced. If the polymer is linear then the liquid crystal will inhibit the interactions (plasticise the polymer matrix) whereas in a cross linked system there would be greater free volume in which the liquid crystal could reside without adversely affecting the transition - even increasing it by restricting the degrees of freedom of the polymer in the more solid state below the transition. It may also be considered that a liquid crystal will plasticise a linear polymer matrix more readily than a cross linked polymer matrix on the grounds of molecular similarity; a liquid crystal would be likely to be less similar to an elastomer than a linear polymer of the same basic type and so would plasticise a cross linked matrix less readily than a linear one.

The results of the first heating cycle for the pure polymer show that as the degree of cross linking increases the transition drops considerably. This is likely to be due to the high viscosity during polymerisation; in the pure polymer compared with the composites the viscosity would be higher than those containing liquid crystal, thus restricting the degree of polymerisation. The second heating cycle confirms the supposition that the heating increases the glass transition by increasing polymerisation.


Polymer Glass Transitions - First Heating
30
25
20
T_g (°C) 15
10
5
0
0
0.5
1
1.5
2
% cross-linking
Pure
30 wt% 5CB
30 wt% E7


Polymer Glass Transitions - Cooling
30
25
20
T_g (°C) 15
10
5
0
0
0.5
1
1.5
2
% cross-linking
Pure
30 wt% 5CB
30 wt% E7

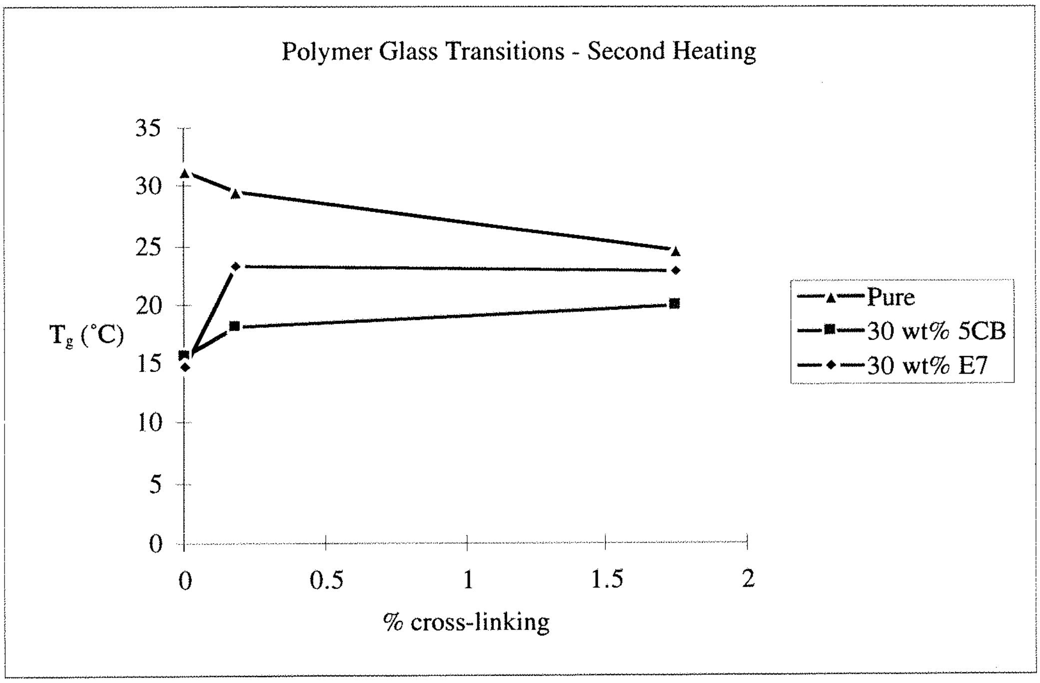
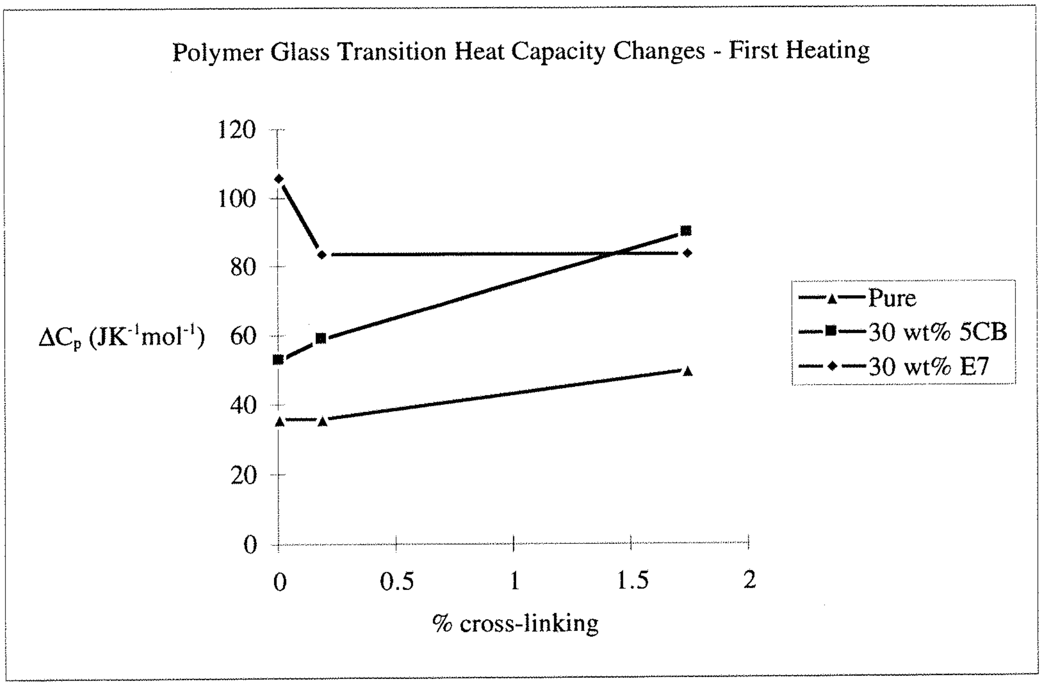


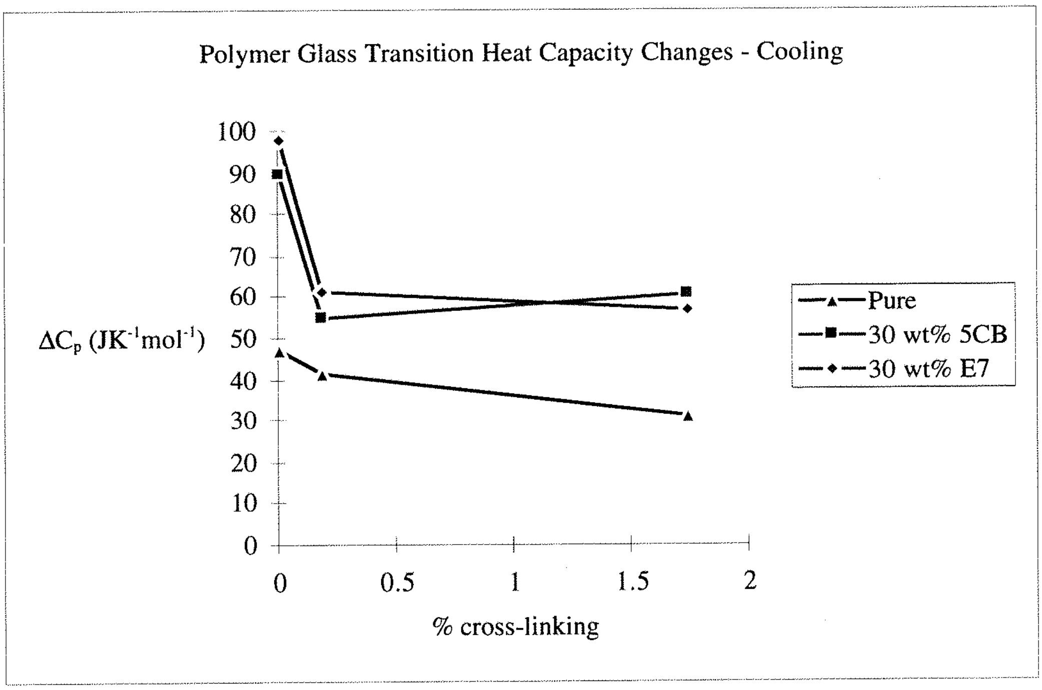
Figure 10.11a. Cross linked polyurethane glass transition temperatures

The first observation from the glass transition heat capacity change plots (figure 10.11b) is that the heat capacity change is greatly reduced on addition of cross linking agent into the system. This is explained by the fact that the cross linking means that the system is held in similar conformations above and below the transition, so the similarity reduces the degrees of freedom for movement; thus we see a weaker transition.

Addition of liquid crystal to the system increases the heat capacity change greatly with no difference between 5CB and E7. If liquid crystal is contained in the polymer matrix, then this is easily explained. Below the transition the liquid crystal is held fairly rigidly by the polymer and so cannot move; above the transition movement is facilitated and therefore more degrees of freedom are available to absorb heat, so therefore the transitional change in C_p is larger.

The drop in the strength of the transition on addition of crosslinker is more pronounced in the case of the composites than in the pure polymer. This is attributed to less liquid crystal being present in the polymer matrix which by the same arguments as previously reduces the size of the transition.


Polymer Glass Transition Heat Capacity Changes - First Heating
120
100
80
60
40
20
0
ΔCp (JK-1mol-1)
0
0.5
1
1.5
2
% cross-linking
Pure
30 wt% 5CB
30 wt% E7


Polymer Glass Transition Heat Capacity Changes - Cooling
100
90
80
70
60
50
40
30
20
10
0
ΔCp (JK-1mol-1)
0
0.5
1
1.5
2
% cross-linking
Pure
30 wt% 5CB
30 wt% E7

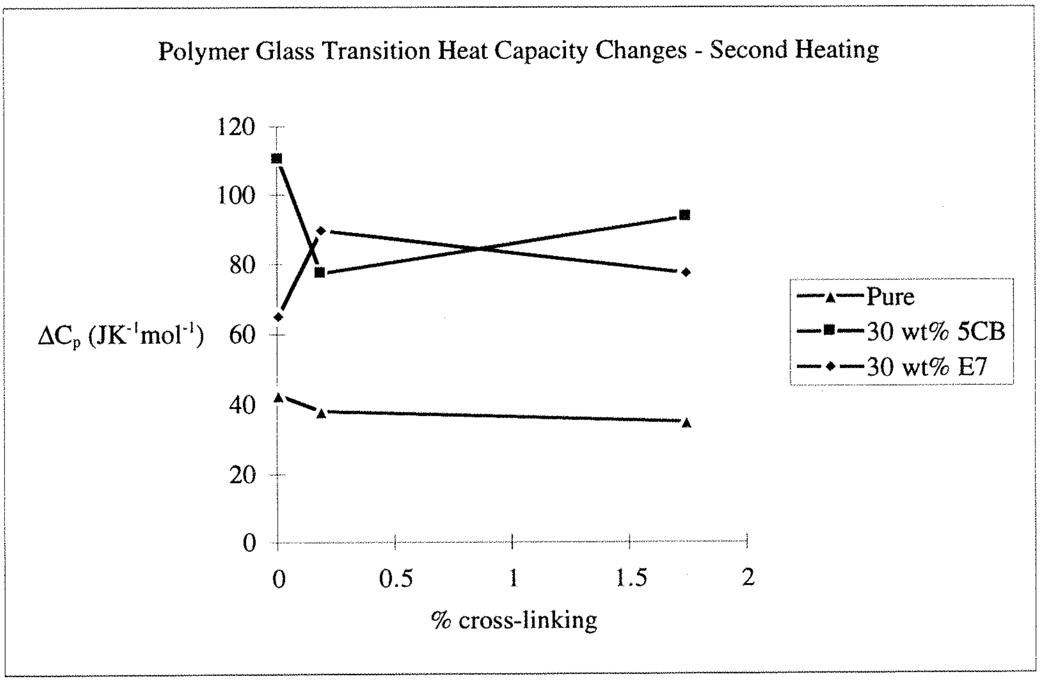


Figure 10.11b. Cross linked polyurethane glass transition heat capacity changes

10.4.2. Liquid Crystal Nematic-Isotropic Transition

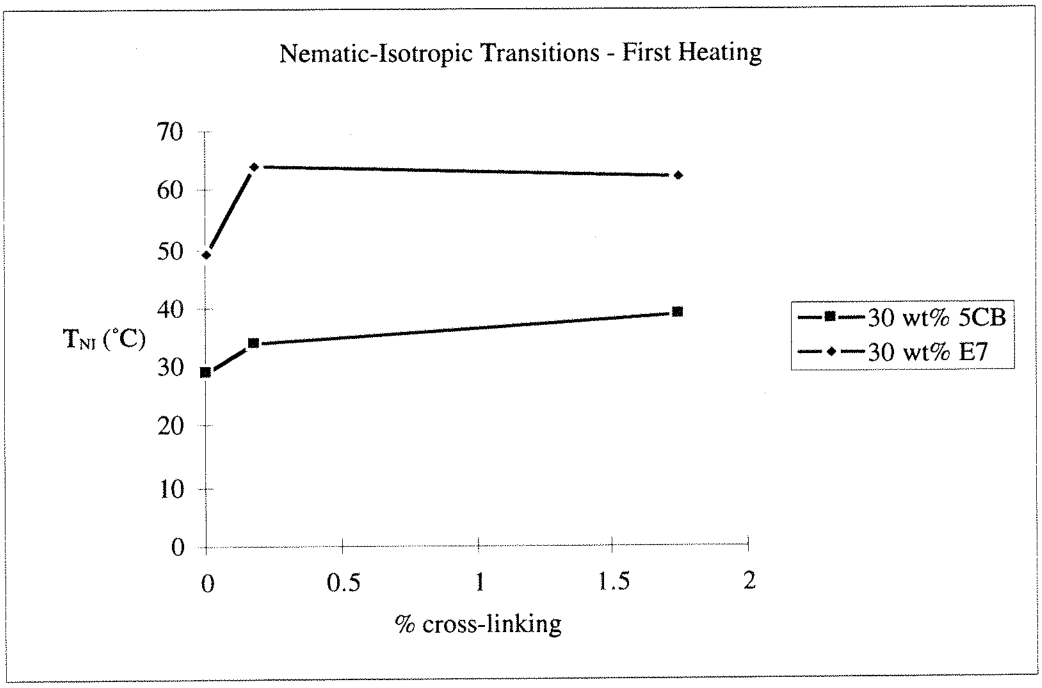
The other key transition is the nematic-isotropic transition of the liquid crystal. Two types of composite were studied; 30wt% liquid crystal (E7 and 5CB) with increasing cross linking. 30wt% was chosen as being a good phase separated system to investigate.

It is clear from the nematic-isotropic transition temperature plots (figure 10.12a) that increasing the degree of cross linking raises the clearing temperature of the liquid crystal.

In the case of the 5CB the clearing temperature is almost the same in these composites as it is in the pure liquid crystal; thus the 5CB may be considered to be very well phase separated from the polymer with the cross linking improving the purity, most likely by means of increasing the dissimilarity of the two components.

In E7 the transition appears to be higher than in the pure state. This clearly indicates preferential phase separation of the higher-transition temperature components from the polymer matrix. This can be explained as follows. In a cross linked system, the higher-transition liquid crystal components are effectively less similar to the polymer matrix that contains them and therefore it would be expected that they would phase separate preferentially into the liquid crystal droplets than in a linear polymer matrix, whilst the lower-transition components remain in the matrix to a greater extent due to a greater molecular similarity. Effectively this would give a higher nematic-isotropic transition and this idea is partly confirmed by the glass transitions of the polymer matrices; these are higher in the cross linked materials, perhaps indicating greater phase separation.

It is also seen that the clearing temperature increases from first to second heating. Due to further cure that is seen at higher temperatures, impurities in the droplets will decrease as the prepolymer reacts further. Increased molecular diffusion at elevated temperatures will cause liquid crystal to reside preferentially in the droplets and so they will increase again in strength (note this agrees with the observation of increased polymer glass transition temperature due to decreased plasticisation). This also agrees with the observation of the higher transition temperatures for the E7 composites; further cure results in larger droplets and increased phase separation and polarisation of the whereabouts of the various components (lower-transition components in the polymer matrix and higher-transition components in the droplets).



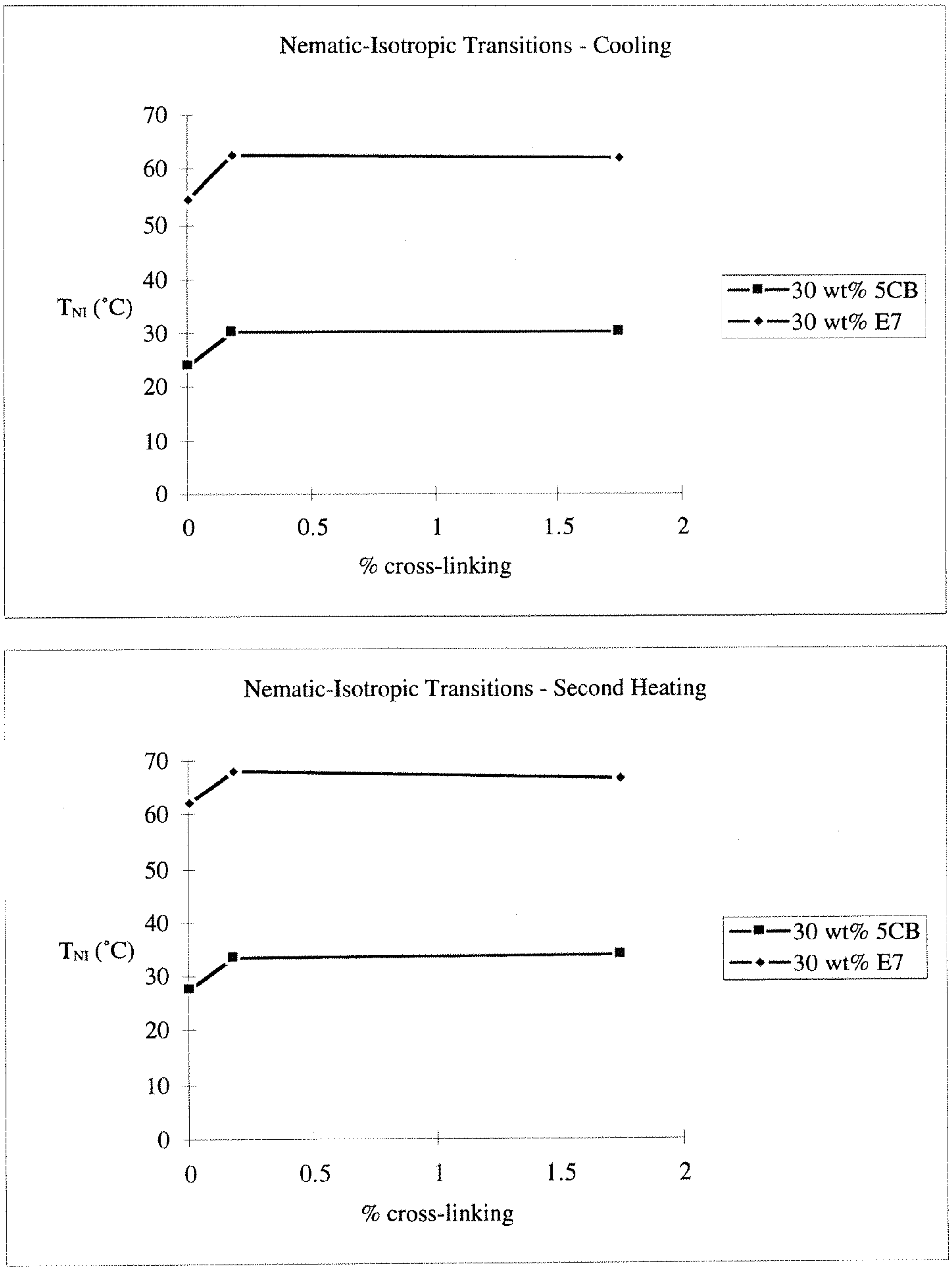


Figure 10.12a. Liquid crystal nematic-isotropic transition temperatures (cross linked)

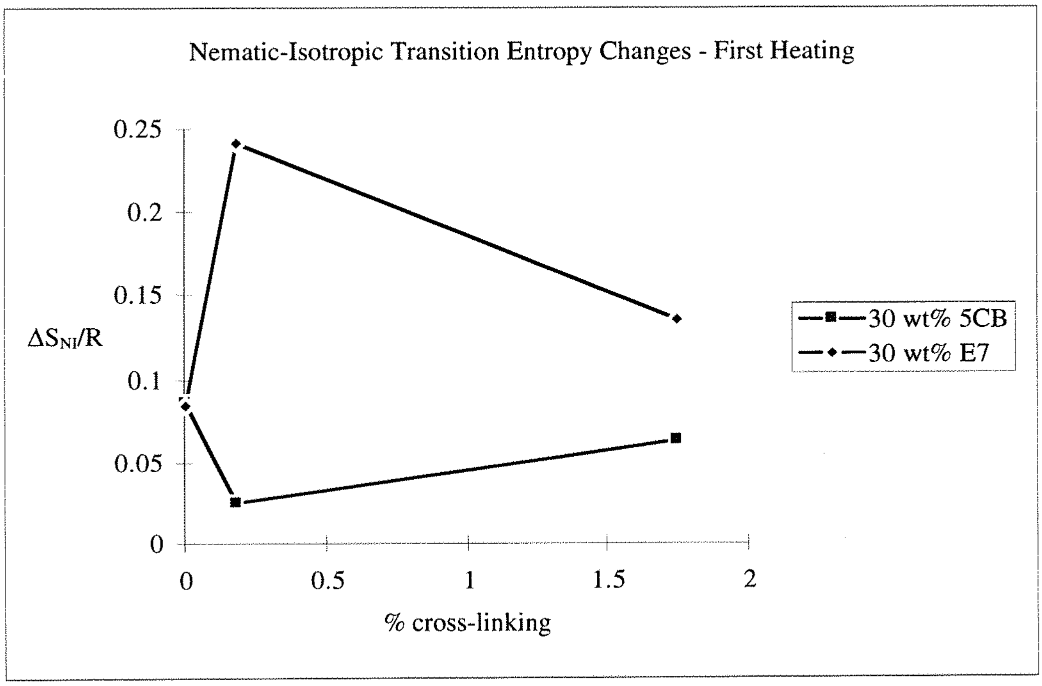
As with previous results, these entropy data presented in figure 10.12b were calculated based on the total amount of liquid crystal initially incorporated in the sample; in both cases 30wt%.

First from these data it is seen that E7 composites exhibit larger entropy changes on clearing than 5CB; this is precisely what would be expected based on bulk liquid crystal properties - the E7 is more ordered in its liquid crystalline state with a greater order parameter than is the 5CB.

It is also observed that the entropies associated with the transitions are lower on heating a second time. This is possibly because more liquid crystal is contained within the polymer as it becomes more soluble at higher temperatures. This does not contradict the theory that the droplets are purer, however; the droplets are mostly composed of liquid crystal and therefore fluid, so the polymer would not stay in solution there. Within the polymer matrix, the situation is naturally far more viscous and so demixing is not at all rapid.

No clear trend is seen on increasing the degree of cross linking, contrary to what might have been expected.

A reduction in transition strength similar to that seen in the linear systems is also seen.



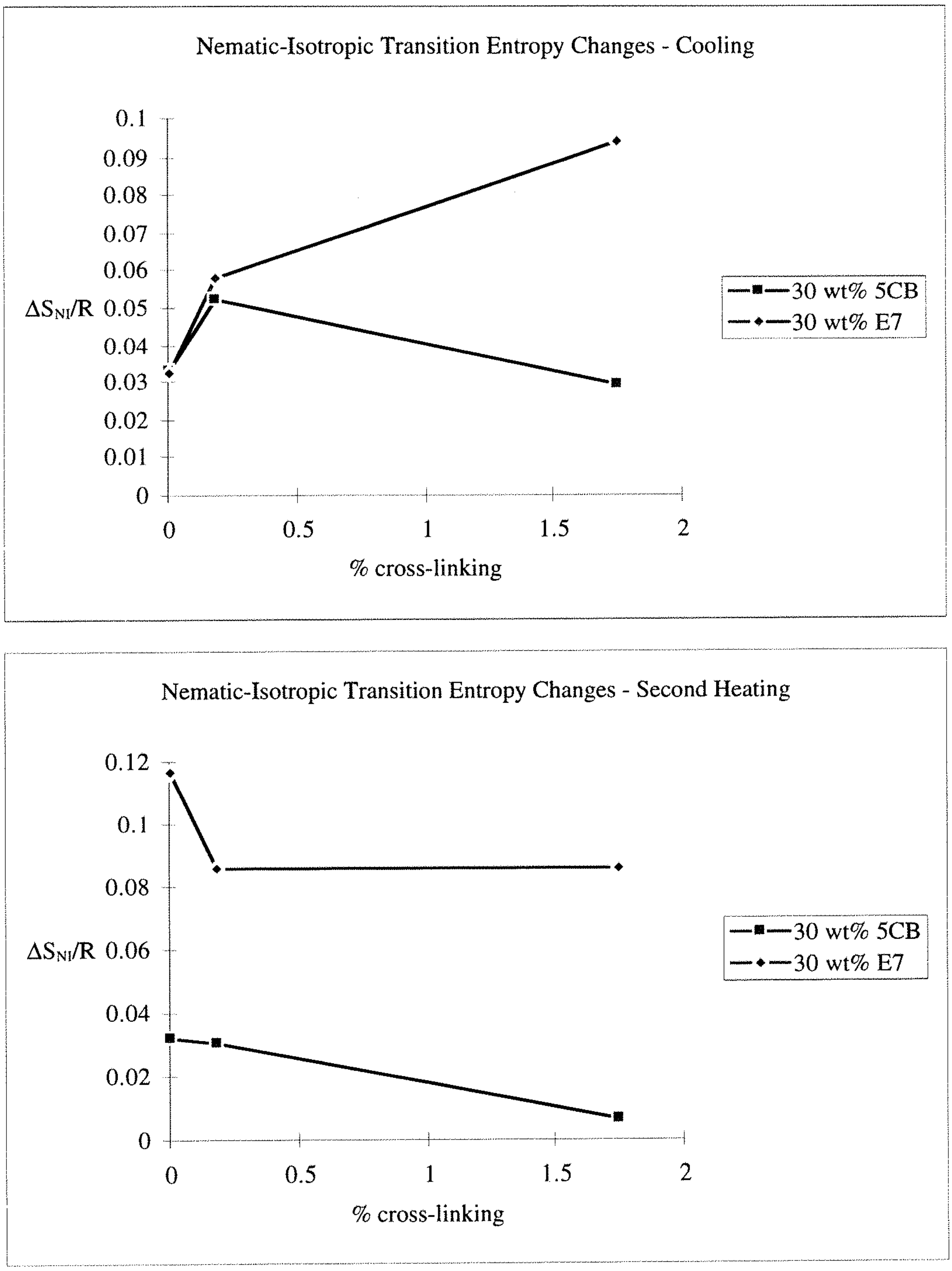


Figure 10.12b. Liquid crystal nematic-isotropic transition entropy changes (cross linked)

Chapter 11. Discussion and Further Work

The main thrust of this work had initially been to investigate a variety of polymer dispersed liquid crystal composites for subsequent use in systems where a thermal gradient was to be used to try to control the morphology.

In the first instance it must be stated that many samples were prepared for study by scanning electron microscopy - a crucial section of the work due to the detailed structural information it readily provides. Due to uncontrollable circumstances, these results are not available for discussion.

Secondly a large number of optical micrographs was taken of the samples detailed in the previous chapters. Again the results cannot be shown here due to uncontrollable circumstances.

Thirdly a detailed isothermal DSC study of the polyurethane composites was to be undertaken to yield information on cure at different temperatures. This work could not be undertaken, again due to uncontrollable circumstances.

Phase A

The first part of the project involved a detailed literature study concerning polymer dispersed liquid crystals. The results of this search are presented in Chapters 1 to 7.

The materials are easy to formulate and three types of system are identified. First, a polymerisation induced phase separation where a chemical cure of the polymer forces phase separation of the polymer from the mother solution of liquid crystal/prepolymer. Secondly, a solvent induced (properly solvent evaporation induced) phase separation, where the solvent in a ternary liquid crystal/solvent/polymer system is evaporated, thus forcing phase separation as the miscibility gap is passed. The third method is temperature induced, wherein a liquid crystal/polymer melt is cooled, thus again forcing phase separation as the miscibility gap is passed.

Each method leads to basically the same morphology; ideally a continuous polymer matrix containing microdroplets of liquid crystal of a diameter approximately equal to the wavelength of incident light to cause scattering.

The method of operation of a device is to use an electric field to alter the orientation of the liquid crystal director in a controlled manner so as to match the refractive indices of the polymer and the liquid crystal microdroplets, thereby producing a transparent film. Thus a typical PDLC film is effective as a light shutter.

Varying the cure regime of a PDLC affects its morphology and thus its characteristics; for instance a smaller size of microdroplet causes a smaller wavelength of light to be scattered. The idea of the project was to alter the cure regime in such a way as to cause phase separation across a thermal gradient as a possible method of controlling the electro-optic characteristics.

Phase B

The work carried out in this phase of the project was aimed at gaining insight into the general formation of polymer dispersed liquid crystal films. There are several publications covering dispersions of cyanobiphenyl materials in PMMA; the results detailed in Chapter 9 agree largely with the published results.

The work clearly showed that polymer dispersed liquid crystal materials are easy to construct. The suitability of PMMA as a matrix for cyanobiphenyl liquid crystals is perhaps doubtful; a high degree of phase separation is desirable but these composites showed 5CB to be too soluble in the polymer, evinced by the lack of phase separation until a loading of 30 or more wt%. Additionally both 5CB and E7 leeched out of the polymer matrix with a time scale of hours; certainly no operational device could be created with such a characteristic. Despite these drawbacks, the systems were eminently suitable for the preliminary studies on PDLC behaviour.

Apparent from an early stage was the difference in film morphology caused by varying the rate of cooling (and thus phase separation) of the composite (§**9.2**). Whilst the phase diagram itself was difficult to determine for these systems (although investigation of this would be useful for further work), the final morphology after cooling gave the expected rate-morphology relationship. Slow cooling resulted in binodal morphology (random size and spacing); faster cooling resulted in spinodal morphology (regular size and spacing); still faster cooling resulted in no immediate phase separation at all (the polymer gels, leaving the liquid crystal unable to phase separate).

Upon droplet formation, the polymer showed the expected plasticisation, manifested by the depression of the glass transition. The liquid crystal also agreed with expectations that there would be a slight depression of the nematic-isotropic transition, thought to be due to the small cavity restrictions. E7 showed interesting nematic-isotropic transition characteristics; a broad range of transition temperatures (55°C to 65°C) across the range of composition, including some transitions above the normal E7 nematic-isotropic transition (61°C). This is attributed to preferential phase separation of certain of the components of the mixture - 5CB is thought to be more soluble in the polymer matrix than the higher-transition components (K21, M24, T15) and so the droplets may well have a higher nematic-isotropic transition.

For these systems, however, the specific materials chosen would not be appropriate for commercialisation. There are many grades of acrylic resin available and a suitable system involving for instance E7 could theoretically be constructed. As has been noted, however, this SIPS process is not easy to control to a satisfactory degree - thus the requirement for work on PIPS.

Phase C

Recent work on thermosetting matrices has concentrated mainly on epoxy resins, although this has not been exclusive; the major reason for this is the wide availability of epoxy resins. As a result, polyurethanes were chosen here as a novel medium for the liquid crystals.

Clearly the choice of raw materials gave a very basic polyurethane type; whilst perfectly suitable for this work, a more detailed study on this and other potential systems would need to be undertaken to optimise the polymer matrix, although the results indicated that the composites produced had many favourable properties.

First, the linear polyurethane formed from the reaction of 2,5-hexanediol with 1,6-diisocyanatohexane was studied as a potential medium (§**10.1**). This polymer showed a high degree of crystallinity so further work was carried out using glycerol as a cross linking agent effective at low levels in the prevention of crystallinity (§**10.1.3**).

Preliminary investigations (§**10.2.1**) showed a high degree of phase separation of the composite and a reasonable size of liquid crystal microdroplet (of the order of microns). As such further work was subsequently concentrated on these materials.

A range of composites was then produced (§**10.2.2**), showing that the desirable morphology of liquid crystal microdroplets was maximised at about 30wt% of liquid crystal (either 5CB or E7).

Further work towards a potential product would have to result in sufficient mismatch and match of n_e and n_o with n_p respectively for a potential device to work effectively; no control was imposed over the refractive indices of the polymers chosen. Further to this aspect a 24 or 18h cure regime is too long for viable production; this is, however, linked with droplet size and thus film characteristics and so a more suitably tailored system would have to be devised although the systems in many respects look promising.

Some interesting results were found for the crystal transition of the linear polymer (§ **10.3.1**); increasing the liquid crystal content of the system apparently caused an increase in the strength of the transition, although the temperature was unaltered. As noted, this could be due to an increase in the proportion of the spherulitic form of the polymer as the liquid crystal displaces the randomly oriented glassy phase from the interspherulitic space. Alternatively there is the possibility of a co-crystallinity; a very interesting idea which would need more thorough investigation, for instance using the NMR techniques noted below.

Paradoxically, there was also an increase in the strength of the glass transition of the polymer on increasing the concentration of liquid crystal in the composites (§**10.3.2**). Whilst the transitions are different in nature (the crystal transition is first order and the glass transition is second order) the observations are perhaps counterintuitive, unless the liquid crystal has as positive influence on both the crystalline form and the glass form. It is possible to envisage an increase in the amount of polymer present in the semicrystalline phase due to volume displacement by the liquid crystal and also that liquid crystal trapped in the polymer glass (as might be expected from such a polymer as was used) would cause an increase in the heat capacity change.

The location of the liquid crystal within the composites would perhaps be best investigated by NMR techniques; these are fairly well established in the field of PDLCs and part of the project was to synthesise partially deuterated 4-*n*-pentyl-4'-cyanobiphenyl (see Appendix 1). An obvious extension to this work is then to carry out a sequence of experiments on this basis to observe the location of the liquid crystal in the composites based on the variation of the position of the peak due to the differing surroundings (deuterons contained in a liquid crystal molecule dissolved in the matrix will have a somewhat different environment to those surrounded by liquid crystal). A very interesting method of analysis is the use of magnetic resonance imaging, which currently can measure down to less than 10μm; further developments of this technology would allow *in situ* measurements of the location of the liquid crystal perhaps even without the necessity of deuteration (field gradient methods work best for proton NMR, however).

The liquid crystal itself behaved predictably; a small depression of the nematic-isotropic transition compared to that of the pure material was observed, consistent with previous observations (**10.3.3**).

Within the work on linear polyurethane composites, an unknown transition was observed at roughly 65°C (§**10.3.4**). Easily confused with the E7 nematic-isotropic transition at first, its presence in the composites containing 5CB showed that it was a genuine effect, dependent on the presence of liquid crystal. NMR techniques would perhaps give information on this transition as it seems to be connected with the liquid crystal so there would quite likely be a characteristic signal from the liquid crystal in an unusual environment.

The DSC results for cross linked PDLCs showed no unusual behaviour but minor effects on the transitions were observed (§**10.4**). The main objective in the use of a cross linked polymer matrix was to remove the polymers' crystal-induced birefringence, which was successful.

A high degree of phase separation is apparent in the polyurethane composites; this is ideal for commercialisation. This high degree of phase-separation, caused by chemical dissimilarity between the mainly hydrocarbon liquid crystal molecules and the high density of highly polar urethane moieties in the polymer, should be maintained in potential products. A reasonable range of polyurethane resins is available which should ensure that a sufficiently polar polymer matrix could result. This avenue of work lies mainly on development of a suitable polyurethane matrix to ensure adequate phase separation.

The size of the liquid crystal microdroplets is also reasonable for application; whilst in many cases the droplets formed were larger than the wavelength of visible light (the aim of most PDLC applications), within the framework used it would have been quite possible to produce droplets of a suitable size; in this instance it was not necessary. Again a straightforward development is apparent to control the droplet size to a sufficient degree.

The thermal gradient work was inconclusive (§**10.2.3**). Several problems were apparent at an early stage and these took time to overcome; a limited amount of information was thus obtained in the time frame of the experimentation. The evidence seems to be that rather than the formation of anisometric microdroplets within a film there is a gradual change from larger droplets in a binodal morphology (slow cure) to small droplets in a spinodal morphology (fast cure). A thin film prepared with a transverse thermal gradient will have inherent problems; the thickness of the glass slides in comparison with the thickness of the sample would (at a first approximation) account for most of the heat loss across the sample; evidently this restriction would cause a severe attenuation of the effects of a gradient cure regime unless a very large gradient was to be imposed, which is undesirable. A thinner glass cover could of course be used but would lead to difficulties in production imposed by the fragility of such a system.

As a result it seems that this approach to morphological control of PDLCs is not the best option available. Further work on gradient cure regimes must be undertaken to gain a greater insight into such systems; repeating the work performed with full SEM analysis would be the first step in such a project. The relationship of the film structure to the electro-optic characteristics would be the main aim. In theory, anisometric liquid crystal microdroplets would be a non-energy intensive method of off-state alignment (*ie*, no potential would have to be applied to achieve the state).

Appendix 1. Synthesis of Liquid Crystal 4-*n*-Pentyl-4'-cyanobiphenyl-αd_2

The synthesis of this specifically deuterated liquid crystal was performed to facilitate NMR studies on any samples subsequently prepared in order to determine the molecular orientational ordering in the dispersed microdroplets. Deuterium NMR has been used for some time to study the ordering in (most notably cyanobiphenyl-based) liquid crystals [196,197,198,199,200,201]. As PDLCs are relatively new, therefore, such NMR techniques already developed have been easy to apply to these composite systems [202]. Largely the techniques are aimed at determining the director configurations within a liquid crystal microdroplet but naturally this is not the only application of the technique; for example, liquid crystal dissolved in the polymer matrix could easily be identified because of its different environment.

As the different director configurations of the liquid crystal in a droplet give characteristic deuterium NMR signals, the use of NMR is therefore of great importance in any study devoted to attempting to control the shape and orientation of the droplets within a PDLC. As such, the liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl-d_2 was synthesised, specifically deuterated in the α-position on the alkyl chain to facilitate NMR studies by yielding a simple spectrum. The method followed was the standard procedure developed by Gray *et al* for the synthesis of alkylcyanobiphenyls; Friedel-Crafts acylation of bromobiphenyl with valeryl chloride followed by reduction to the alkyl and finally cyanation to afford the finished liquid crystal [203].

4-*n*-Pentanoyl-4'-bromobiphenyl

A mixture of valeryl chloride (14.5g, 120mmol) and 4-bromobiphenyl (28g, 120mmol) in dichloromethane (100ml) was added drop-wise, with stirring, to aluminium trichloride (16g, 120mmol) in dichloromethane (100ml) at 0°C over a 30min period. The mixture was then allowed to warm to ambient temperature and stirred for 24h.

The reaction mixture was then added to water (250ml) and separated. The aqueous phase was washed with dichloromethane (3x100ml). The combined organic phase was then dried over anhydrous magnesium sulphate, filtered and the solvent removed by rotary evaporation.

The resultant solid was recrystallised from aqueous ethanol to yield 4-*n*-pentanoyl-4'-bromobiphenyl (25.7g, 81mmol; 68% yield) as characterised by infrared spectroscopy (strong carbonyl stretch characteristic of adjacency to an aromatic ring).

4-*n*-Pentyl-4'-bromobiphenyl-d_2

Ether (100ml) was added drop-wise, under reflux, with stirring, to dry aluminium chloride (19.8g) and lithium aluminium deuteride (2.6g). To this was added 4-bromo-4'-*n*-pentanoylbiphenyl (7.43g, 23mmol) in deuterated chloroform (50ml) drop-wise over 30min. The mixture was then heated and stirred under reflux for 22h.

After cooling, deuterium oxide (100g) was added drop-wise with extreme caution over 60min. Further to this, 37% deuterium chloride in deuterium oxide (30ml) was added drop-wise over 30min, followed by stirring until all solids had dissolved and the mixture was cool.

The mixture was separated. The organic phase was washed with water (3x100 ml), saturated brine (3x100 ml) and finally water (100ml). The combined aqueous phases were then extracted with ether (500ml).

The combined organic phases were then dried over magnesium sulphate and the solvent removed after filtration. The solid was recrystallised from ethanol and dried to yield 4-*n*-pentyl-4'-bromobiphenyl-d_2 (5.8g, 19mmol; 82% yield) characterised by infrared spectroscopy (loss of carbonyl stretch).

4-*n*-Pentyl-4'-cyanobiphenyl-d_2

Cuprous cyanide (3.5g, 40mmol) was added to a solution of 4-*n*-pentyl-4'-bromobiphenyl-d_2 (5.78g, 19mmol) in *N*-methylpyrrolidinone (30ml). The mixture was then heated under reflux for 1h.

Taking care to remove the threat posed by evolved $HCN_{(g)}$, the mixture was poured into a mixture of ferric chloride ($FeCl_3.7H_2O$, 50g) in dilute hydrochloric acid (7.5ml cHCl in 53ml water). This mixture was shaken and then extracted with ether (3x50ml). The combined organic phase was then treated with activated carbon and further to this dried over anhydrous magnesium sulphate.

The solvent was then removed, the residue was purified by column chromatography (silica, eluted with petroleum ether/toluene with increasing toluene concentration), the fractions collected and reduced to afford the crude product which was distilled under vacuum (0.1mm mercury) to afford pure 4-*n*-pentyl-4'-cyanobiphenyl-d_2 (2.72g, 11mmol; 57% yield). The material had a clearing point at 32-33°C; the same value as literature for 5CB-αd_2 [204].

Appendix 2. Heat Transfer through a Composite Wall [205]

Part of the initial aim of the project was to attempt to make a PDLC composite under a thermal gradient; ultimately to see if this would be a possible means of controlling film morphology and therefore device characteristics.

Naturally an understanding of the science behind such a system would be necessary in order for its full potential to be exploited.

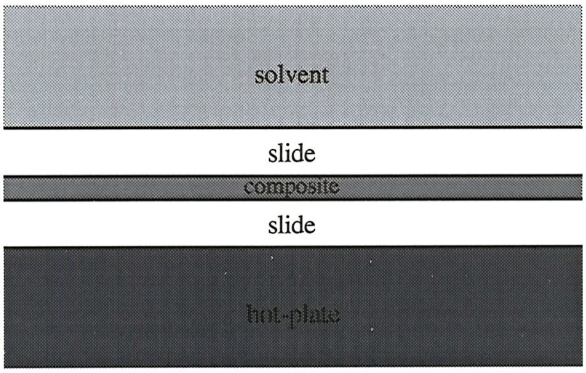


Figure A2.1. Idealised schematic of thermal gradient cure set-up

In the system shown in figure A2.1, the lower side of the composite sample is on a constant-temperature hot-plate and the upper face under a constant temperature heat sink (the solvent bath).

As the hot-plate generates heat at some temperature and the solvent bath accepts the heat and boils at a lower temperature, it is evident that a thermal gradient and flow of thermal energy is present.

The main form of heat flow through the system is by conduction; radiation naturally cannot occur and convection is of a minor concern, and then only applies to the liquid prepolymer/liquid crystal mixture.

The system itself consists of a hot-plate, above this the lower glass slide, above this the composite, above this another slide and on top boiling solvent or constant temperature solvent. Each piece of the set-up of course has a certain thickness and certain thermal conductivity. In the case of the materials actually used in the experiments, the thermal conductivities of all of them are not known and thus a further, more thorough investigation would require a set of materials with known properties. It is nevertheless possible to give an overview of heat flow through a composite wall in a general sense.

The temperature at one end of the system (pictured at the bottom in figure A2.1) is some T_1 and at the top where the liquid resides there is some T_4 which will be defined, say, by the boiling temperature of the liquid, the temperature of the hot-plate being controlled. The interfaces of the slides and composite are defined as T_2 at the lower face and T_3 at the upper face of the sample.

Heat flow through a solid is determined by conduction only. The basic equation for description of heat conduction in one direction through a block of area A and thickness x is the Fourier equation:

$$Q = -\mathrm{k}\frac{A}{x}\left(T_2 - T_1\right),$$

where Q is the heat flow rate, k is the thermal conductivity constant of the block and T_2-T_1 is the temperature difference. Another way to write this is in differential form:

$$q = -\mathrm{k}\frac{\mathrm{d}T}{\mathrm{d}x},$$

where q is the heat flux. In the above example the heat flows through three distinct layers; the lower slide in contact with the hot-plate (thermal conductivity k_{s1}, thickness x_{s1}), the PDLC composite (thermal conductivity k_c, thickness x_c) and the second glass slide (thermal conductivity k_{s2}, thickness x_{s2}). The lower surface of the slide, in contact with the hot-plate, is of course at some known temperature T_1, the lower face of the composite is T_2, the top face T_3, the top face of the top slide at the (known) solvent temperature T_4. The interesting part of the system is of course the temperature drop across the composite - T_3-T_2.

Naturally the heat flow is equal in all parts of the system, thus application of the Fourier equation yields:

$$Q = -\frac{\mathrm{k}_{s1} A\left(T_2 - T_1\right)}{x_{s1}} = -\frac{\mathrm{k}_c A\left(T_3 - T_2\right)}{x_c} = -\frac{\mathrm{k}_{s2} A\left(T_4 - T_3\right)}{x_{s2}}.$$

At this stage all the variables would be known except T_2, T_3 and k_c.

It must here be stated that k_c changes with time as the system cures; naturally the thermal conductivity changes with the changing nature of the curing material. A first approximation would be to assume that it is constant and then to introduce the change.

So for this first approximation it is possible to calculate the temperature drop across the sample in the following manner.

Rearranging the Fourier equation for the system gives:

$$T_2 - T_1 = -\frac{Q}{A}\left(\frac{x}{\mathrm{k}}\right)_{\mathrm{s1}} ; T_3 - T_2 = -\frac{Q}{A}\left(\frac{x}{\mathrm{k}}\right)_{\mathrm{c}} ; T_4 - T_3 = -\frac{Q}{A}\left(\frac{x}{\mathrm{k}}\right)_{\mathrm{s2}} .$$

Summation and rearrangement gives:

$$Q = \frac{-A(T_4 - T_1)}{\left(\left(\frac{x}{\mathrm{k}}\right)_{\mathrm{s1}} + \left(\frac{x}{\mathrm{k}}\right)_{\mathrm{c}} + \left(\frac{x}{\mathrm{k}}\right)_{\mathrm{s2}}\right)} .$$

Thus, given some approximation to the thermal conductivity of the composite it is possible to calculate the overall heat transfer. From this it is possible to calculate the temperature drop across the composite and thus a reasonable model of the actual conditions of the cure of the composite could be obtained.

A more thorough description would of course require $\mathrm{k_C}$ to change with time.

Appendix 3. Differential Scanning Calorimetry

Much of the analysis of the PDLC composites was performed by differential scanning calorimetry. Since it was such a major part of the experiments, an explanation of the technique and its relation to the results presented in this Thesis is given.

The basis of this technique is to measure the differential heat flow required to maintain a sample of material (here a composite material) at the same temperature as a reference. Scanning linearly over a temperature range at a predetermined rate results in differential scanning calorimetry.

Investigations of liquid crystals involve the analysis of phase changes, for instance most of the cyanobiphenyl series melt from a crystalline state into a nematic phase and then this changes into an isotropic liquid upon passing the nematic-isotropic transition. Each of these transitions has an associated enthalpy change which can be measured using a variety of thermal analysis techniques, in this case differential scanning calorimetry.

The experiments used a Perkin-Elmer DSC-7 unit equipped with an Intracooler I to reach temperatures as low as -30°C. A sample, typically 20-25mg (larger than the 5mg generally used for DSC due to the small transitions involved), was cut from the desired material and trapped in a standard aluminium sample pan. This was placed in the analysis pan of the DSC unit, with an empty aluminium pan in the reference cell to compensate for the energy absorbed by the sample container. Typically a heating/cooling cycle was programmed into the controlling PC at a rate of 10°Cmin^{-1}. As the cycle was passed, data was collected for later interpretation.

Once a DSC cycle is complete, a plot of heat flow (*ie*, C_p) *versus* time (a linear relationship with temperature due to the constant heating/cooling rate). First order phase transitions show as peaks or troughs depending on the nature of the transition (exothermic or endothermic). The analytical technique involves measuring the area of such a peak, which gives the enthalpy change in per unit mass. The onset of the transition is recorded along with the actual transition temperature. From this, if the relative molecular mass of the material is known, then the molar enthalpy change can be calculated. Since the temperature of the transition is also known then the entropy change associated with the transition can also be determined; this value is useful in liquid crystal research and is usually represented as $\Delta S/R$ to give a dimensionless parameter for ease of comparison. Second order transitions such as polymer glass transitions are also measurable; they appear as steps in the trace, corresponding to an increase in the heat capacity at a given temperature.

The work carried out involved composites; each material had characteristic transitions; the results were factored in each for the amount present in the sample (*eg*, the liquid crystal transitions were calculated based on the theoretical mass of liquid crystal in the composite alone).

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[175] M_r 249.348gmol^{-1}; courtesy Merck Ltd.
[176] This is an eutectic mixture common in display devices; commercially known as "Licrilite". An effective molecular mass of 271.74106g(mole liquid-crystal molecules)$^{-1}$ was calculated based on the composition; courtesy Merck Ltd.
[177] Thermo-optical analysis using an Olympus BH-P polarising optical microscope equipped with a Linkam THM 600 hot-stage, TMS 90 temperature controller and eyepiece graticule and stage micrometer for measurements.
[178] Differential scanning calorimetry using a Perkin-Elmer DSC-7 equipped with an Intracooler I.
[179] Appendix 1.
[180] Appendix 2.
[181] Poly(methyl methacrylate), average M_w ~15000; Aldrich Chemical Co.
[182] Poly(methyl methacrylate), average M_w ~996000; Aldrich Chemical Co.
[183] Dichloromethane, 99.9%; Aldrich Chemical Co.
[184] British Oxygen Company; "white spot".
[185] Smith, G. W. and Vaz, N. A.; *Liq. Crystals*; **3**; 543; (1988).
[186] 1,6-Diisocyanatohexane, 98%; Aldrich Chemical Co.
[187] Polybutadiene, hydroxyl functionalised, average M_w ~2400; Aldrich Chemical Co.
[188] Poly(ethylene glycol), average M_n ~400; Aldrich Chemical Co.
[189] 1,6-Hexanediol, 99+% and 2,5-hexanediol, 99%; Aldrich Chemical Co.
[190] Glycerol, 99+%; Aldrich Chemical Co. Dried by partial distillation before use due to its extremely hygroscopic nature.
[191] Useful for the experimentation was calculation of the relative molecular mass in terms of grammes per mole of hydroxyl function. For the 98.1:1.9 this was 58.552, for the 96.0:4.0 this was 57.954g(mole OH)$^{-1}$ and for the 93.9:6.1 this was 57.350g(mole OH)$^{-1}$.
It is also prudent to note here the remaining values used for the calculations; hexanediol is 59.08465g(mole OH)$^{-1}$, glycerol is 30.69695g(mole OH)$^{-1}$, diisocyanatohexane is 84.0951g(mole NCO)$^{-1}$; the density of diisocyanatohexane is 1.04gml^{-1}.
[192] The 1.74% mixture was calculated as 58.590704g(mole OH)$^{-1}$ and the 0.18% was 59.033552g(mole OH)$^{-1}$.
[193] 1,3-Phenylene diisocyanate, 95%; Aldrich Chemical Co.
[194] For these purposes it is a fair assumption that the aluminium foil is of constant thickness (50μm) and that the glass was perfectly flat thus resulting in a regular thickness throughout the system.
[195] It is practically difficult and perhaps impossible to know the specifics of any thermal gradient in such a system as the layer of the composite is so thin and the heat capacity is likely to change upon cure. See Appendix 2.
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[205] This is a brief overview; more thorough descriptions may of course be gleaned from any number of standard physics textbooks.