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Phase behaviour and electro-optic characteristics of a polymer stabilized ferroelectric liquid crystal

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The effects of adding a diacrylate monomer or its polymerized network to a ferroelectric liquid crystal have been characterized. The monomer lowers the temperatures of transition to the more ordered phases, whereas the polymer network phase separates into polymer rich and LC rich phases and has little effect on the LC phase behaviour. Ferroelectric polarization decreases comparably in both monomer and networked systems. As the network concentration increases, the size of LC domains decreases considerably. With low concentrations of polymer and, thus large LC domains, optical response and tilt angle remain fairly independent of polymer concentration, but as the polymer concentration increases, switching speed and tilt angle decrease dramatically. Polymerization rate maxima increase with monomer concentration until saturation of monomer in the liquid crystal is reached. The rate maxima then decrease as monomer must diffuse from monomer rich droplets. Double bond conversion during the polymerization is comparable for all monomer concentrations below 50 per cent.

1. Introduction

In recent years polymer dispersed liquid crystals (PDLCs) have received considerable attention, particularly because of their great potential for electro-optic applications [1, 2]. The most widely studied systems are thin polymer network sheets containing drops of a nematic liquid crystal [3]. Most of these materials are obtained by *in situ* polymerization of a cross-linking monomer in a liquid crystal solution which produces a polymer network containing LC molecules which are not chemically bound to the network [4]. At higher concentrations, plasticized networks are formed. In such systems the LC domains are small and the LC optical and phase behaviour are dominated by interactions with the polymer. At lower concentrations of polymer, the PDLC behaves more like an anisotropic gel [5]. If appropriately aligned, these PDLC films can be switched between a translucent state and a transparent state by application of an electric field. The gel phase of chiral nematic liquid crystals has recently become of special interest due to the discovery of PSCT switching, which provides switching between a translucent and a coloured state due to selective reflection of light by a cholesteric phase [6, 7].

Numerous studies have been performed on PDLC films to characterize their phase behaviour, and the most studied systems involve nematic liquid crystals. The phase behaviour in such systems changes dramatically upon addition of monomer and subsequent polymerization [4, 8, 9]. For example, monomers reduce the nematic to isotropic (N–I) transition temperature considerably. After the system is polymerized, the transitions return to near normal values of the pure liquid crystal, but the N–I transition enthalpy decreases with increasing network concentration. The decrease in the transition enthalpy is caused by an increasing amount of liquid crystal dissolved in the polymer network. Because of the finite size of the LC domains and the strong interactions between the LC and the polymer network, the liquid crystal inside the network orders continuously with decreasing temperature and does not exhibit discrete phase transitions [10].

Optical and electro-optic properties are also changed when polymer networks are introduced into these LC systems. The birefringence typically is reduced up to 50 per cent in the nematic phase of anisotropic gels [4, 8]. For plasticized networks the birefringence also is reduced, and

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even after heating above the clearing point (N–I transition), birefringence is retained due to the LC molecules that remain aligned by the polymer network and to the anisotropy in the polymer network itself. The decrease in the birefringence is caused by frozen-in disorder within the polymer network [6]. Optical response can also change considerably with incorporation of polymer as response times generally increase while decay times decrease with very small amounts of polymer network [5]. Consequently, the switching threshold voltage also increases as more energy is required to overcome the more restrictive environment.

Recently, it has been shown that some systems have photocontrollable optical properties when groups capable of photoisomerization are incorporated [11]. When isomerized, these groups decrease the order in the system and subsequently decrease the birefringence. The degree of change can be regulated by the length of exposure to the appropriate wavelength of UV light.

Despite the versatility of PDLC films, their usefulness is limited by the relatively slow response times of nematic liquid crystals [12]. Chiral tilted smectic liquid crystals, also known as ferroelectric liquid crystals (FLCs), have shown great promise in applications requiring fast switching. FLCs respond up to 500 000 times faster than systems currently used in high contrast computer displays [13].

FLCs exhibit supermolecular polar order with the polar axis normal to the plane of director tilt. This polar structure gives rise to a macroscopic dipole density, i.e. the ferroelectric polarization [14]. If an electric field is applied to the LC, the molecules will orient to align the ferroelectric polarization along the electric field. These properties prompted the development of the surface stabilized FLC (SSFLC) light valve which enables an FLC cell to be switched from a dark to a light state between crossed polarizers upon reversal of the electric field [15].

To combine the advantage of PDLC films with those of ferroelectric liquid crystals, polymer dispersed ferroelectric liquid crystals (PDFLC) [16] and polymer stabilized ferroelectric liquid crystals (PSFLC) [17] have recently been developed. PDFLCs consist of FLC droplets suspended in a polymer matrix, while PSFLCs contain only small amounts of polymer network dispersed in an FLC matrix. These films are prepared in ways similar to those for PDLC films with monomer being dissolved in an FLC matrix. The monomer is then polymerized to create a PDFLC or PSFLC film. Both of these systems show enhanced resistance to mechanical shock relative to normal SSFLC cells [18] and, when polymerized under small shearing rates, can be made bistable [19].

Interestingly, preparation strongly influences PDFLC and PSFLC properties. If systems are cured via UV irradiation, polymerization conditions may drastically alter their electro-optic characteristics. Optical response time increases dramatically at lower voltages, and measured polarization decreases when higher UV intensities are used to increase the polymerization rate [18]. Electro-optic characterizations of these systems have also been reported [20, 21].

In this article, investigations of the influence of relatively small concentrations of monomer and a simple polymer network on basic FLC properties are reported. Effects of increasing concentration on phase behaviour are characterized. Changes in optical and electro-optical properties with temperature and concentration are examined as are polymerization rate and double bond conversion for these systems.

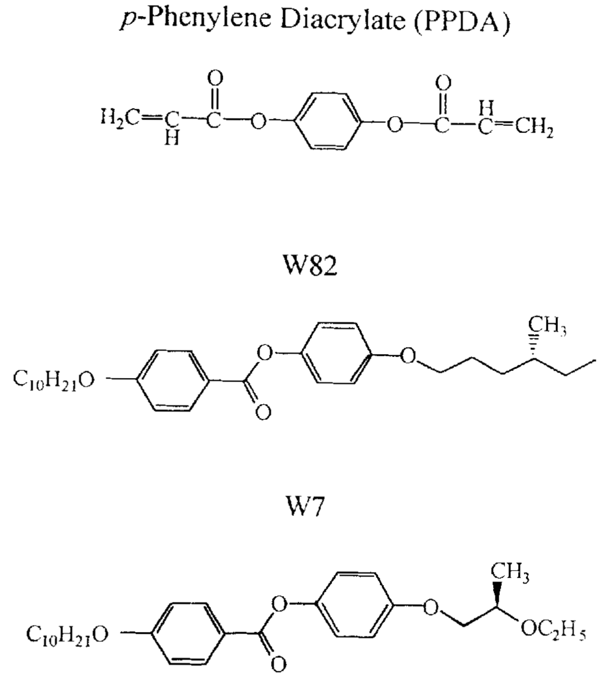
2. Experimental

2.1. *Materials*

The tetrafunctional monomer in these studies was *p*-phenylene diacrylate (Polysciences, Warrington PA). The ferroelectric liquid crystal used was 1 : 1 mixture of W82 and W7 (Displaytech, Boulder, CO). Structures of the monomer and liquid crystal mixture components are seen in figure 1. Photopolymerization was initiated using Irgacure 907 (Ciba-Geigy, Hawthorne, NY).

2.2. *Experimental techniques*

Phase transitions of the ferroelectric liquid crystal systems in the presence of either monomer or the polymer network were measured using both polarizing microscopy


p-Phenylene Diacrylate (PPDA)

W82

W7

Figure 1. The molecular structures of *p*-phenylene diacrylate (PPDA) as well as W82 and W7.

and differential scanning calorimetry. Microscopy was performed using a Nikon polarizing microscope equipped with a rotating, temperature controlled hot stage. Transition temperatures of the systems with monomer and polymer network were found by heating to the isotropic state and then cooling slowly at approximately 1°C min^{-1}. The clearing point, the smectic A → smectic C* transition and the smectic C* → semi-crystalline transition were determined by observing optical changes and switching behaviour. These phase transitions were confirmed by those obtained from differential scanning calorimetry (Perkin–Elmer DSC 7) using a scan rate of 5°C min^{-1}. Enthalpies of transition were also obtained from the DSC experiments.

Tilt angle and switching speed were determined utilizing polarizing microscopy. The tilt angle was determined by halving the angle of rotation between the two points of maximum and minimum transmission during switching. To determine optical response time, samples were placed in a 4 μm rubbed polyimide, indium tin oxide coated cell (Standish, Lake Hills WI). A square wave potential of $8\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ was then applied across the cell. He/Ne laser light (10 mW) was passed through the cell, and its intensity was determined by an optical intensity sensor. The optical response time was then found using a digitizing oscilloscope [22].

Polarization and rotational viscosity were determined utilizing an Automated Polarizations Tester (Displaytech). This instrument measures these quantities utilizing techniques described previously [22, 23]. A $6\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ potential is applied across a 4 μm cell for rotational viscosity measurements and across a 10 μm cell for ferroelectric polarization measurements.

Monitored polymerizations of monomer/initiator/FLC mixtures were performed in a differential scanning calorimeter (Perkin–Elmer DSC 7) modified with a photocalorimetry accessory. Polymerizations were carried out in the smectic C* phase, 15°C below the smectic A → smectic C* transition. The heat of polymerization was also measured and used to calculate the relative rate as such:

$$\text{Rate} = \frac{(Q/s)M}{n\Delta H_{\text{pol}}Mass}$$

where Q/s is heat flow per second, M is the molar mass of the monomer, n is the number of double bonds per monomer molecule, ΔH_{pol} is the heat released per mol of double bonds reacted (the accepted value for acrylates of $86{\cdot}2\,\mathrm{kJ\,mol^{-1}}$ [24] was used in this study) and the mass is the mass of monomer in the sample. Double bond conversion is calculated by integrating the rate of polymerization as a function of time.

3. Results and discussion

3.1. *Phase behaviour*

The phase diagram for the monomer (PPDA) and FLC mixture is presented in figure 2. The temperature of the isotropic to smectic A transition decreases almost linearly with concentration as expected for a first order transition. However, the decrease for the smectic A to smectic C* transition is much more pronounced, and this sharp decrease continues until the FLC is saturated with monomer. At this point distinct monomer rich and FLC rich domains are seen in both the smectic A and smectic C* phases. This saturation point is reached at approximately 13 wt% monomer. After saturation, the temperature of both second order transitions, smectic A to smectic C* and smectic C* to a more ordered smectic, remain nearly independent of concentration. The range of temperatures for coexistence of the isotropic and smectic A phases increases until saturation is reached, and a distinct smectic A phase is evident over an ever smaller range until no distinct smectic A phase is observed.

After polymerization, the phase behaviour changes dramatically as shown in figure 3. The interactions which considerably lower the transitions in monomer/FLC systems are not significant in polymer/FLC systems. This factor indicates phase separation of the polymer network during polymerization.

The enthalpies of the isotropic to smectic A transitions (ΔH_{IA}) for polymer and monomer systems are presented in figure 4. This enthalpy decreases monotonically with

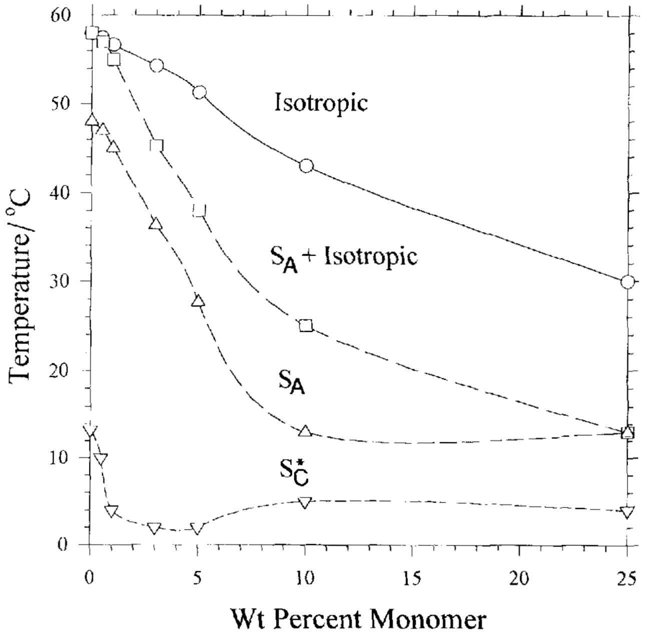


Figure 2. Phase diagram of FLC(W82, W7, 1 : 1) with varying percentages of PPDA monomer. At temperatures below the smectic C* phase, a more ordered smectic phase is present.

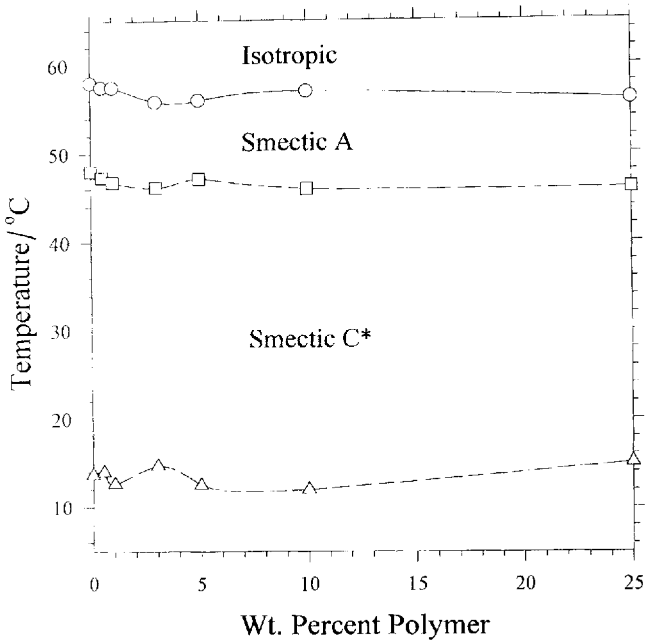


Figure 3. Phase diagram of FLC with varying percentages of PPDA polymer network.

increasing monomer concentration. A small initial decrease is seen for polymer systems, but then ΔH_{IA} plateaus at a value approximately 90 per cent of the value for the pure FLC. Thus, the polymer interacts to some extent with the LC molecules, but this interaction is limited and does not change with increasing amounts of polymer network.

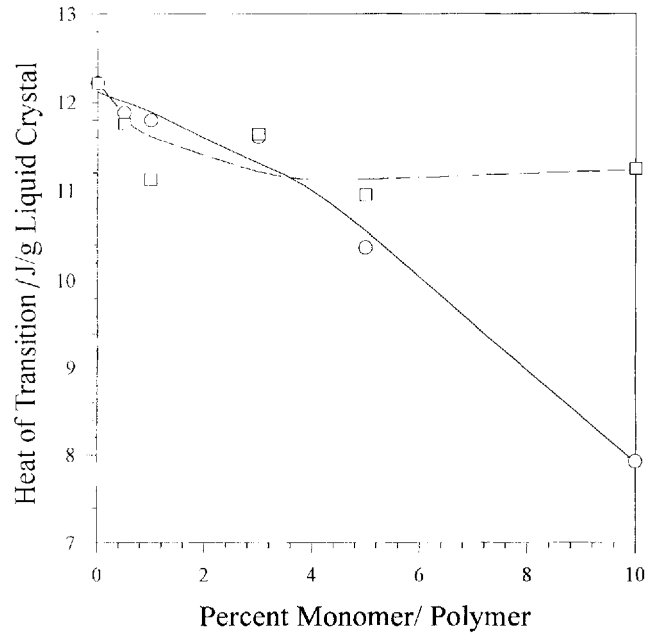


Figure 4. The heat of the nematic–isotropic transition (per gram of liquid crystal) for monomer (○) and polymer (□) systems.

This evidence also supports the view that the polymer network phase separates.

3.2. *Electro-optical characteristics*

In order to investigate the effects of the monomer or the polymer network on the FLC mixture, the ferroelectric polarization density, *P*, of the samples was measured using an Automated Polarization Tester. The value of *P* decreases considerably after addition of monomer and remains nearly constant after polymerization, as indicated for one weight per cent monomer and polymer as shown in figure 5. This decrease continues until more than 70 per cent of the net dipole is lost in systems with five per cent polymer network (see figure 6). Polarization decreases to some extent simply due to the dilution of the FLC by monomer and presence of the polymer. The decrease, however, is greater than would be predicted simply by the decrease in amount of liquid crystal. This indicates that increased disorder is generated within the liquid crystal matrix due to additional freedom around the axis normal to the smectic layers. By contrast, the decrease in the net dipole after the polymer network is formed is due to the network-hindering of liquid crystal molecules adjacent to the network structure. The polymer network also decreases the magnitude of the temperature dependence on polar order, particularly at temperatures approaching the smectic C* to semi-crystalline transition.

As seen in figure 7, the rotational viscosity shows decreases similar to that seen for the net macroscopic

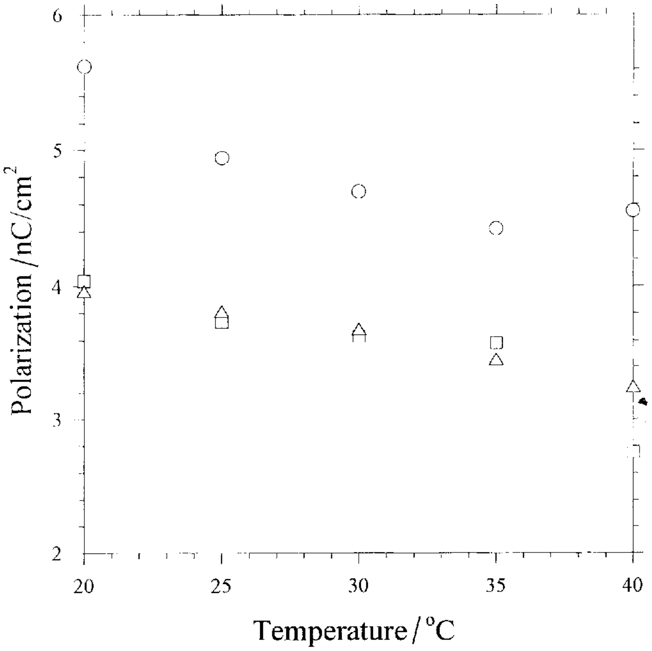


Figure 5. Polarization as a function of temperature for pure W82, W7 (1 : 1) (○), 1 per cent PPDA monomer (□), and 1 per cent PPDA polymer (△).

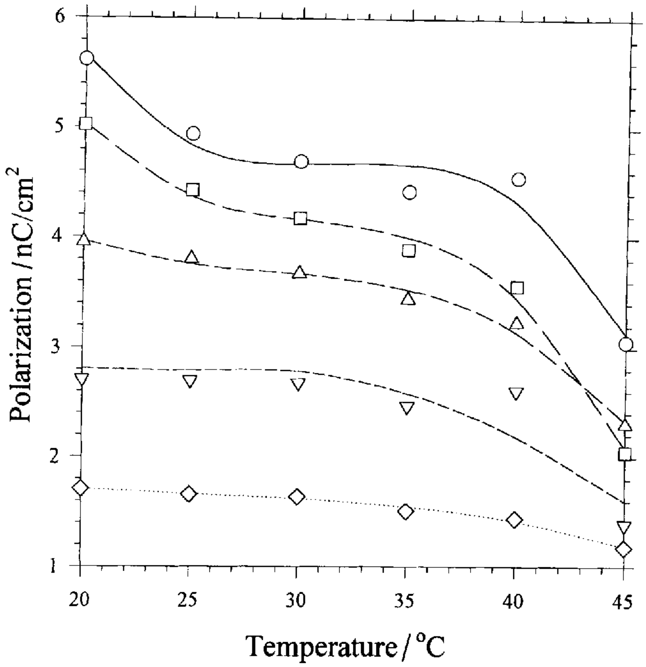


Figure 6. Polarization as a function of temperature for W82, W7 (1 : 1) with 0 per cent (○), 0·5 per cent (□), 1 per cent (△), 3 per cent (▽), and 5 per cent (◇) PPDA polymer.

dipole. The measure of rotational viscosity is highly dependent on this measured polarization, and the measured polarization values for samples before and after polymerization are approximately equal. The optical response for these same samples is approximately the same (see figure 9); thus the rotational viscosity decrease can be attributed to the decrease in ferroelectric polarization.

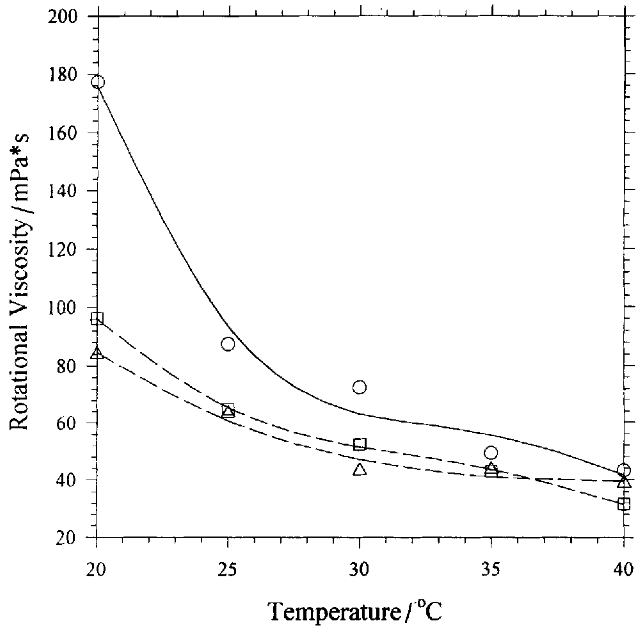


Figure 7. Rotational viscosity as a function of temperature for pure FLC (○), 1 per cent PPDA monomer (□), and 1 per cent PPDA polymer (△).

3.3. *Optical properties*

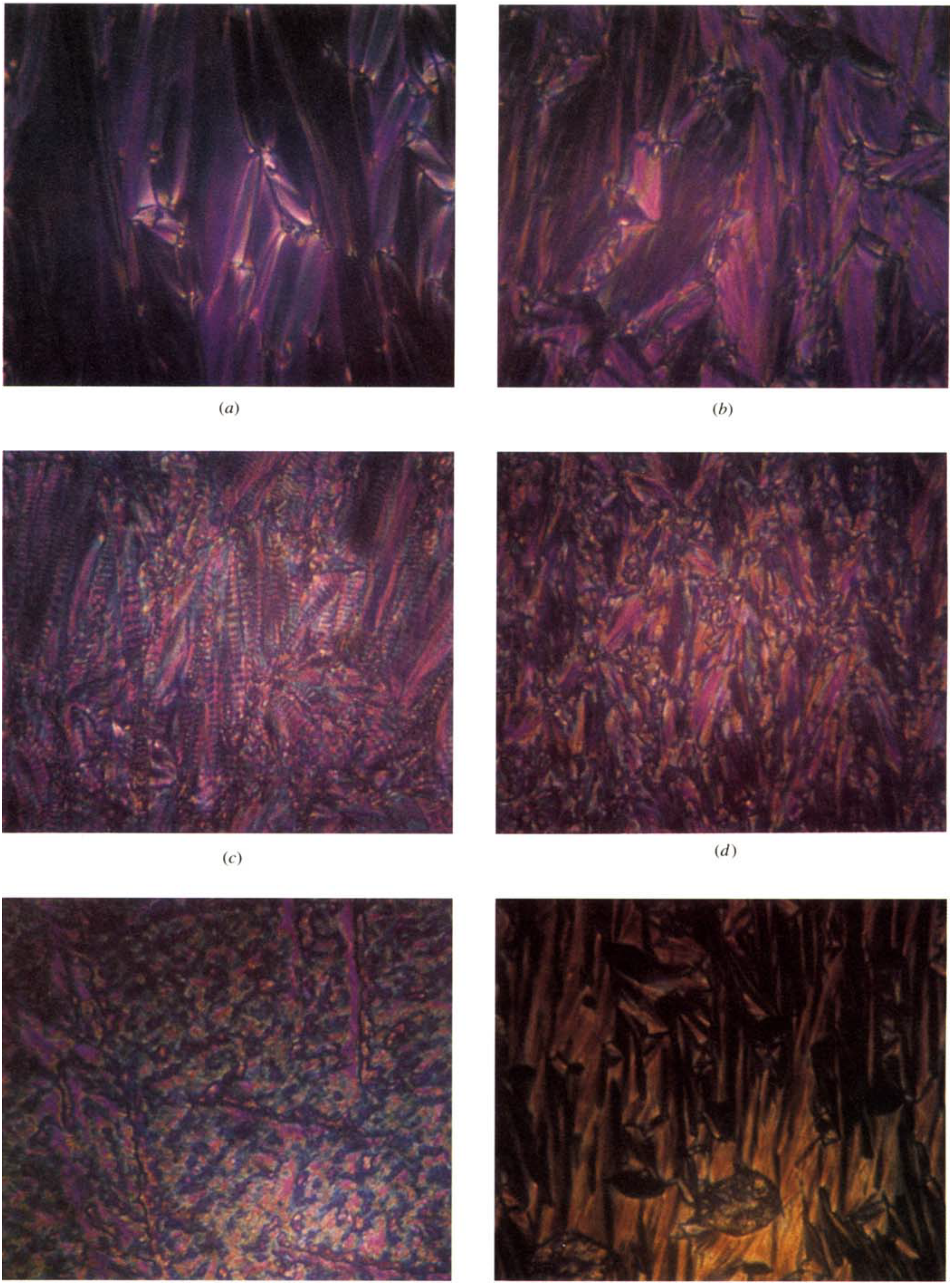
The presence of a polymer network considerably alters the optical properties in PDFLC and PSFLC systems. Optical micrographs of selected samples are shown in figure 8. After addition of monomer, the number of defects increases slightly, but the sample appears similar to pure FLC below monomer concentrations close to the saturation point. As described previously, once the saturation point is reached monomer rich and FLC rich domains are observed in all liquid crystal phases. Interestingly, both domains switch upon application of an electric field.

Polymerized samples at any concentration of polymer network, however, have much different characteristics from pure W82, W7 or the monomer/W82, W7 mixtures. In contrast to the monomer/W82, W7 mixtures, which show distinct isotropic monomer (see figure 8 (*f*)), the polymer/W82, W7 mixtures show no distinct polymer rich and FLC rich domains. The isotropic monomer rich drops are depleted during polymerization and the polymer network is continuous throughout the FLC. The monomer is a solid at the temperatures at which the polymerization proceeds and thus the monomer rich droplets do not polymerize and the monomer must diffuse into the FLC rich phase to become part of the polymer network. In the polymer case, defects are numerous even at very low concentrations, and as concentration is increased the FLC domains decrease considerably in size. At higher concentrations, little, if any, alignment is observed and macroscopic polymer networks are observed (see linear objects in figure 8 (*e*)). These results indicate that polymerization creates small pockets of liquid crystal confined within the polymer network structure. In saturated samples, once the monomer is depleted by polymerization within the liquid crystal, monomer diffuses from the monomer rich domains and reacts to become part of the network.

Considerable changes are also seen in optical response time upon polymerization as shown in figure 9. Response time changes little when monomer or a small amount of polymer is added. Once polymer concentrations as low as three per cent are reached, however, a considerable increase in response time is observed. At this point the size of FLC domains is decreased enough to constrain the reorientation of the liquid crystal molecules. The energy barriers resisting rotation and thus response time increase. The tilt angle is independent of monomer concentration, but decreases after polymerization (see figure 10).

3.4. *Polymerization behaviour*

To examine the effects of the FLC on polymerization, both polymerization rate (see figure 11) and double



(*a*)

(*b*)

(*c*)

(*d*)

(*e*)

(*f*)

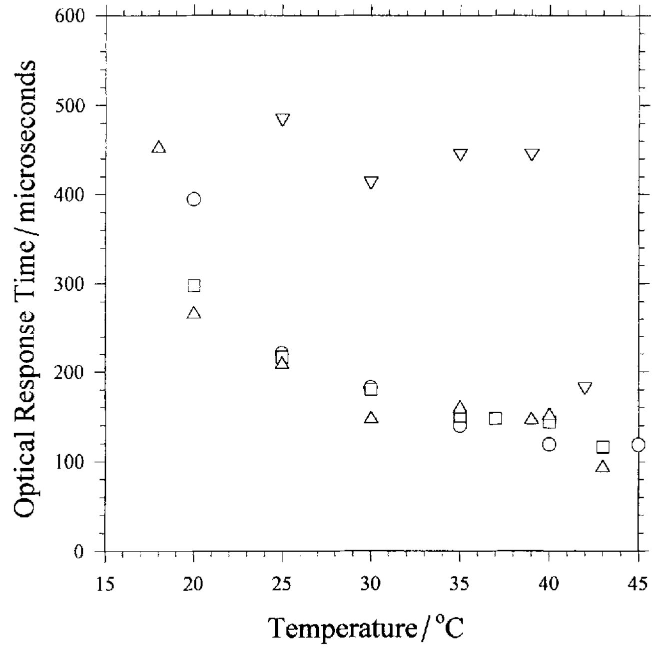


Figure 9. Optical response time at various temperatures for W82, W7 (1 : 1) with 0 per cent PPDA monomer (○), 1 per cent PPDA monomer (□), 1 per cent PPDA polymer network (△), and 3 per cent PPDA polymer network (▽).

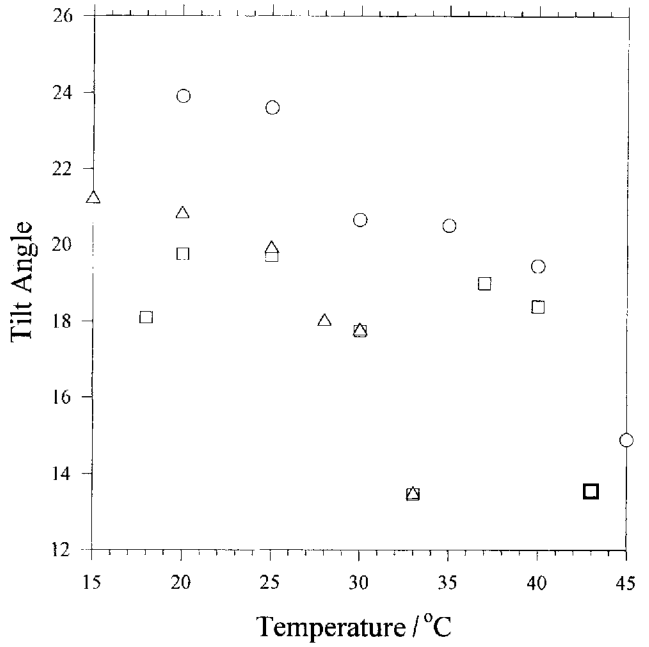


Figure 10. Tilt angle as a function of temperature for W82, W7 (1 : 1) with 0 per cent PPDA monomer (○), 1 per cent PPDA monomer (□), and 1 per cent PPDA polymer network (△).

conversion (see figure 12) were monitored. In figure 11, the rate of polymerization is presented as a normalized rate in which the absolute rate is divided by the initial monomer concentration. In this manner the comparison of rates at different monomer concentrations is facilitated. For concentrations lower than one per cent monomer, the normalized polymerization rate is relatively low. For these monomer concentrations the monomer and polymer are extremely dilute in the liquid crystal, and the presence of this large amount of solvent (i.e. liquid crystal) prevents auto-acceleration from occurring. It is also probable that the rate is reduced because the dilution reduces the initiator efficiency.

Above three per cent monomer, different samples reach the maximum rate at approximately the same time after polymerization begins. The maximum normalized rate increases with concentration until saturation is reached. The increase in the normalized rate is caused by more pronounced auto-acceleration in the presence of a network with higher crosslink density. Beyond the point at which monomer saturation is the LC occurs, the maximum rate then begins to decrease.

Similar effects are also seen when double bond conversion is examined as seen in figure 12. Double bond

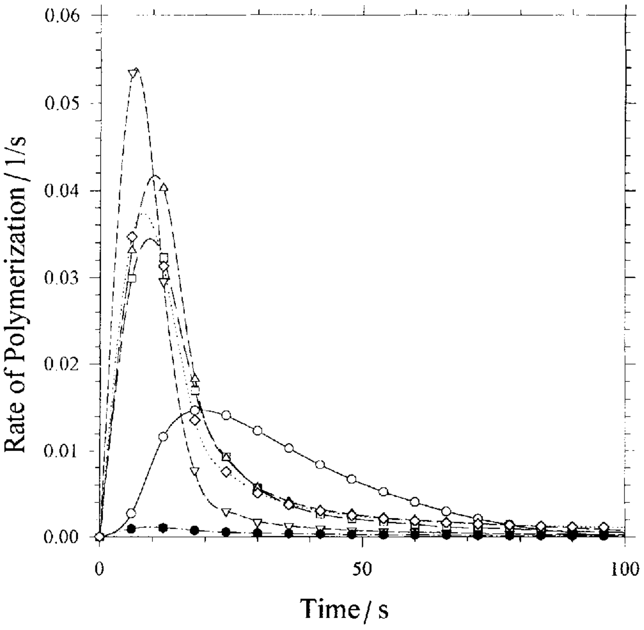


Figure 11. Rate of polymerization as a function of time for polarizing samples of 0·5 per cent (○), 3 per cent (□), 5 per cent (△), 10 per cent (▽), 25 per cent (◇), and 90 per cent (◆) PPDA in W82, W7 (1 : 1).

Figure 8. Optical micrographs (×200) of W82, W7 (1 : 1) with (*a*) no monomer in the smectic C* at 30°C, (*b*) 1 per cent PPDA polymer in the smectic C* at 30°C, (*c*) 3 per cent PPDA polymer in the smectic C* at 30°C, (*d*) 5 per cent PPDA polymer in the smectic C* at 30°C, (*e*) 25 per cent PPDA polymer in the smectic C* at 30°C, and (*f*) 10 per cent PPDA monomer with smectic A and isotropic phases at 40°C.

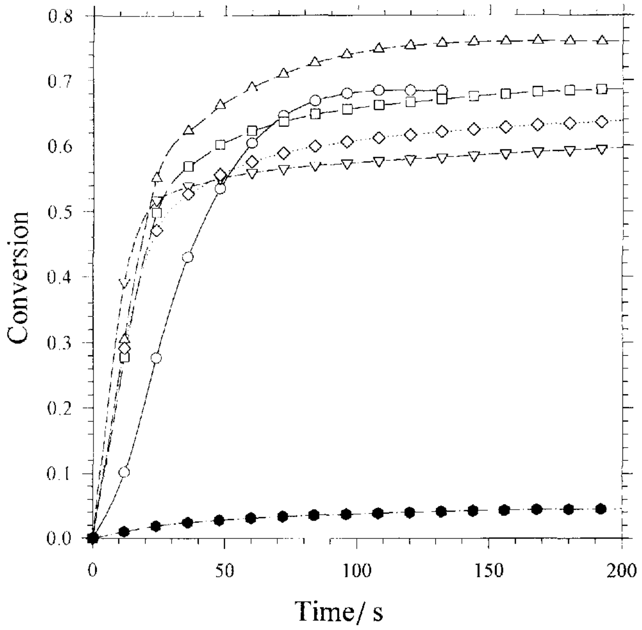


Figure 12. Double bond conversion as a function of time for polymerizing samples of 0·5 per cent (○), 3 per cent (□), 5 per cent (△), 10 per cent (▽), 25 per cent (◇), and 90 per cent (◆) PPDA in W82, W7 (1 : 1).

conversion is slightly higher for lower monomer concentrations. For such samples the amount of network is small, and thus the network is more flexible and fewer double bonds are trapped and unable to react. As concentration of monomer is increased, the density of the network also increases. This effect limits the mobility of double bonds which are then less able to react, and the conversion decreases correspondingly. Despite this small decrease, double bond conversion is fairly comparable for samples with less than 75 per cent monomer. This indicates that the amount of unreacted monomer and pendant double bonds is relatively independent of concentration. Above 75 per cent monomer, solidification of the monomer phase plays a significant role and only low double bond conversions are achieved.

4. Conclusions

Addition of a low molar mass diacrylate monomer to a ferroelectric liquid crystal matrix dramatically affects phase behaviour, as well as optical and electro-optical properties. The monomer lowers the temperatures of transition to the more ordered phases and decreases the percentage of liquid crystal that exhibits typical phase behaviour. The net ferroelectric dipole also decreases considerably upon addition of monomer as the monomer molecules allow for greater freedom around the long axis. The creation of polymer networks within these systems via photopolymerization induces different effects. The polymer network causes only small changes to the phase and transition behaviour which indicates phase separation of the polymer network. As the concentration of network increases, the liquid crystal domain size decreases. Upon generation of small concentrations of network and thus large LC domains, the optical response does not change. As the LC domains are reduced in size with increasing network concentration, the optical response time increases. Such adverse effects are small at low percentages of polymer network, less than 3 per cent, and characteristics are not significantly changed as compared to the pure FLC.

Polymerization behaviour is strongly dependent on the amount of monomer. The polymerization is relatively slow for very low and for very high concentrations due to plasticization and solidification effects, respectively. The polymerizations for intermediate concentrations occur on a much faster time scale, with the maximum rate increasing with concentration until the saturation point of monomer in the liquid crystal is reached. Once saturation is exceeded, the maximum rate decreases as increasing amounts of monomer must also diffuse from the monomer rich phase. Double bond conversion and thus network density are comparable for most concentrations.

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