Polymerization Conditions and Electrooptic Properties of Polymer-Stabilized Ferroelectric Liquid Crystals

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Electrooptic and optical characteristics of polymer-stabilized ferroelectric liquid crystal (PSFLC) materials prepared under different conditions were characterized. Polymerization behavior and segregation properties were also investigated. The rate of polymerization during formation of PSFLCs increases significantly as the order of the LC phase increases and the temperature decreases for the monomers employed. Although the polymerization behavior is similar for these different monomers, trends in electrooptic behavior are considerably different. For C6M and *p*-phenylene diacrylate PSFLCs polymerized in ordered liquid crystalline phases, the temperature of polymerization and the corresponding liquid crystalline phase in which the polymerization occurs have little impact on the ultimate electrooptic and optical properties. The electrooptic properties of 1,6-hexanediol diacrylate (HDDA) PSFLC systems, on the other hand, show a large dependence on the polymerization temperature. Both the ferroelectric polarization and the optical response time increase with polymerization temperature in the ordered phases. Additionally, the optical characteristics of HDDA PSFLCs observed in the smectic C* phase change considerably, as the polymerization temperature is varied within the ordered LC phases. For all of the materials studied, if the polymerization is carried out in the isotropic phase, the polymer has no imparted order and prevents any bulk alignment, thereby detrimentally affecting the electrooptic characteristics. Using these results, the electrooptic and optical properties can be optimized by using appropriate monomer/FLC mixtures and polymerization temperatures.

Introduction

The development of polymer/liquid crystal composites has recently become an area of great interest in liquid crystal (LC) research. To develop novel liquid crystal (LC) phase behavior and properties, a number of different composite materials have been developed. These include systems which employ liquid crystal polymers[1] and others formed by phase separation of LC droplets or polymer-dispersed liquid crystals (PDLCs),[2] which incorporate both nematic[3–5] and ferroelectric liquid crystals.[6–9] Polymer/LC gels, formed by the polymerization of small amounts of monomer solutes in a liquid

crystalline solvent,[10] have also been studied. These polymer/LC gel systems are of particular interest due to a number of desirable properties. Materials have been developed that enable bistability in chiral nematic devices.[11] Additionally, polymer-stabilized ferroelectric liquid crystals (PSFLCs) have been studied[12–16] which combine the fast electrooptic response of ferroelectric liquid crystals (FLCs)[17] with the unique mechanical properties imparted by the polymer.[18] The preparation conditions of these polymer/LC gels have a significant impact on their ultimate properties and performance. A number of studies have examined the polymer struc-

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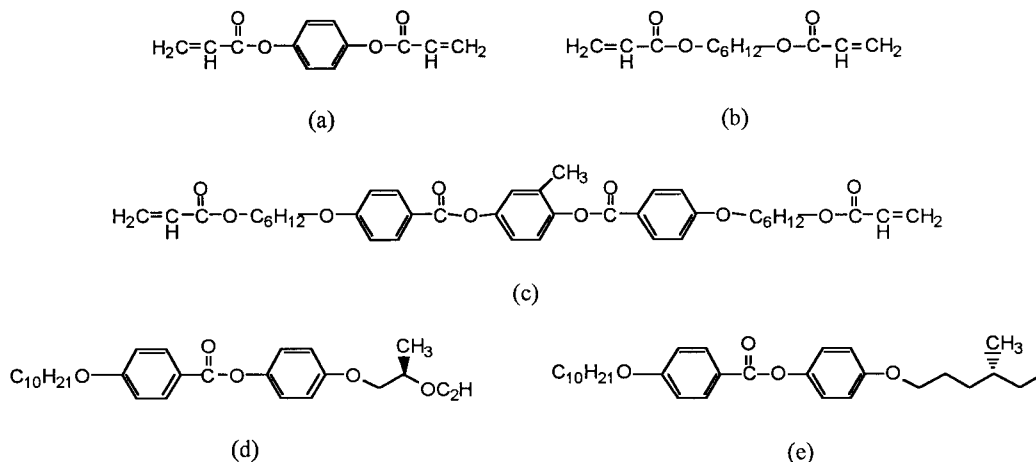
Figure 1. Chemical structures of the acrylate monomers used in this study. Shown are (a) *p*-phenylene diacrylate (PPDA, melting point 89 °C), (b) 1,6-hexanediol diacrylate (HDDA, melting point 5 °C, boiling point 316 °C), and (c) C6M, a liquid crystalline diacrylate (phase sequence: isotropic → 116 °C → nematic → 86 °C → crystalline). Also shown are the ferroelectric liquid crystals (d) W7 and (e) W82 (phase sequence for 1:1 W82,W7 mixture: isotropic → 58 °C → smectic A → 48 °C → smectic C* → 13 °C → more ordered smectic phase).

ture[19] and the electrooptic properties[20] in polymer/nematic LC gels as the LC phase in which the polymer is formed is changed.[21] Little is known, however, about the impact of polymerization conditions on the properties of polymer/smectic LC composites such as PSFLCs.

Interestingly, it has recently been reported that the polymerization conditions during the formation of PS-FLCs have a considerable effect on the polymerization behavior and kinetics. For a variety of different monomers with different chemical structures and LC properties, the polymerization rate increases as the polymerization temperature is decreased into more ordered LC phases.[22] This behavior arises as the monomers segregate in the FLC, increasing the local concentration of double bonds.[23] Not all monomers segregate in the same manner, however. Monomers similar in structure to the FLCs will typically align with the liquid crystals, thereby concentrating the double bonds.[24] Flexible monomers, on the other hand, tend to segregate between the smectic layers, concentrating the entire monomer molecule into a smaller volume.

The variations in both polymerization and segregation behavior have interesting implications in PSFLC systems. If the polymerization and segregation are different, then it is reasonable to assume that the polymer formation is also altered. Such differences may have a significant impact on the ultimate performance of the material. The goal of this work, therefore, is to characterize the influence of polymer species and polymerization temperature on the optical and electrooptic properties of polymer/FLC composites. This behavior is also correlated with the observed segregation behavior of the monomeric species as well as the LC phase in which the polymerization takes place. Not only do these results facilitate the optimization of the properties of PSFLCs, but also further the understanding of the evolution of polymer structure within an ordered LC medium. To accomplish these goals, both optical response time and ferroelectric polarization are determined for composite materials formed with a variety of different polymer network species. The influence of polymerization temperature and LC order on these electrooptic properties is also examined. To understand

further the effects observed, the LC alignment characteristics, as evidenced by textures observed under a polarized light microscope, of these samples prepared for electrooptic measurements are observed. Additionally, the polymerization and segregation of small amounts of monomer in an FLC media is examined, and the influence of the polymerization temperature on the polymerization rate is also investigated. Through these studies, the influence of the polymerization conditions and the presence of the polymer itself on the ultimate performance of PSFLC materials is further understood and methods for the optimization of PSFLC electrooptic properties are developed.

Materials and Methods

The diacrylate monomers chosen for study were two commercially available monomers, *p*-phenylene diacrylate (PPDA) and 1,6-hexanediol diacrylate (HDDA) (Polysciences Inc., Warrington, PA), as well as the liquid crystalline diacrylate 1,4-bis(4-(6-acryloyloxyhexyloxy)benzoyloxy)-2-methylbenzene (C6M, EM Industries, Hawthorne, NY[25]). The FLC used is composed of a 1:1 mixture of W82 and W7 (Displaytech, Longmont, CO). All materials were used without further purification. Chemical structures and pertinent properties of the monomer and liquid crystal components are shown in Figure 1. Photopolymerizations were initiated with Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone, Ciba Geigy, Hawthorne, NY).

Polymerization rate profiles were monitored with a differential scanning calorimeter equipped with a dual beam photocalorimetric accessory (DSC-DPA 7; Perkin-Elmer, Norwalk, CT). Polymerizations were initiated using monochromatic light of wavelength 365 nm with an intensity of 2 mW/cm². The DSC sample cell was also attached to a refrigerated circulating chiller (RTE−111; NESLAB, Newington, NH) to

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achieve isothermal reaction conditions. For monitored polymerizations, approximately 12 mg of the monomer/LC mixture was placed in an aluminum DSC pan. Samples were also heated above the isotropic transition and then cooled to the appropriate polymerization temperature to ensure uniform thickness and adequate thermal contact. The DSC sample cell was flushed with nitrogen for 10 min prior to polymerization to mitigate oxygen inhibition.[26] Polymerization rate profiles and double bond conversions were determined from the heat flux measured by the DSC. For these studies the theoretical value of 20.6 kcal/mol was used as the heat evolved per acrylate double bond reacted.[27]

Sample cells for infrared absorption measurements were prepared by introducing the sample between two rubbed nylon-coated calcium fluoride substrates spaced 10 μm apart. To ensure proper homogeneous alignment, samples were cooled at 0.05 °C/min from the isotropic to the Smectic C* phase. The alignment was then checked using polarizing microscopy. Polarized IR spectra at a resolution of 2 cm^{-1} (128 scans per spectrum) were obtained using an FTIR spectrometer (Magna IR 750; Nicolet, Madison, WI) equipped with an adjustable ZnSe wire grid polarizer to obtain infrared light polarized at different angles.[28]
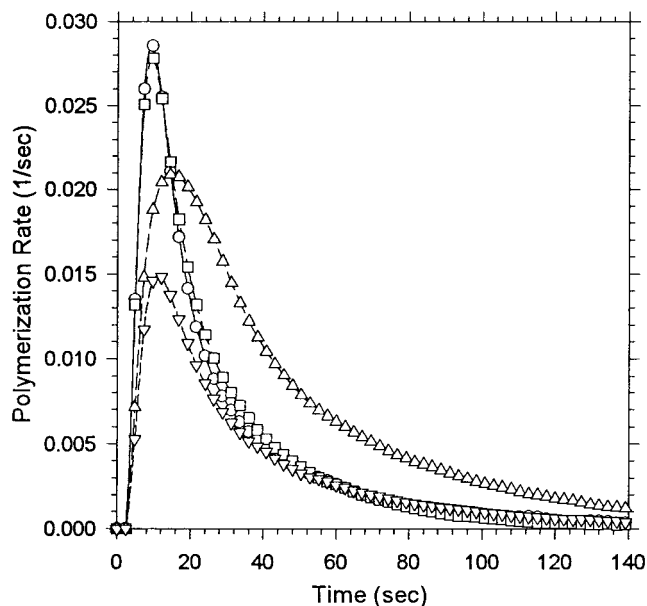
Ferroelectric polarization values were obtained using an automated polarization tester (APT, Displaytech) by applying a 6 V/μm electrical field across a 4 μm rubbed polyimide indium tin oxide cell (Displaytech) and integrating the induced current peak.[29] To determine optical response time, a square wave electric field (6 V/μm) was applied across the same 4 μm cell under a polarizing microscope (Nikon Optiphot 2-pol). Light from the 100 W light source of the microscope was passed through the cell located between crossed polarizers, and the light intensity was determined using an optical sensor. The optical response time was then found utilizing a digitizing oscilloscope and measuring the time required for the intensity to increase from 10 to 90% of the maximum. The rotational viscosity was calculated from the optical response time and ferroelectric polarization by[30]

$$\eta = \frac{\tau_R P E}{1.8} \qquad (1)$$

where η is the rotational viscosity, τ_R is the optical response time, P is the ferroelectric polarization, and E is the applied electric field. All measurements and observations were determined using surface stabilized samples.[31] Additionally, optical micrographs were taken at 200× magnification utilizing the polarizing microscope.

Results and Discussion

Polymerization and Segregation Behavior. Studying the polymerization conditions and the effects that the formation process has on the ultimate performance of PSFLC composite materials is of great interest. The anisotropic reaction media afforded by the liquid crystal may significantly alter the polymerization. This factor may have an impact on the electrooptic properties, especially in polymer/smectic LC composites such as PSFLCs. If the polymerization reaction changes, the polymer structural evolution will also be altered. These changes may, in turn, modify the final polymer structure, particularly the network alignment, which could

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Figure 2. Polymerization rate as a function of time for 2% PPDA in W82,W7 polymerizing in smectic C* at 35 °C (○) and 40 °C (□), in smectic A at 54 °C (△), and in the isotropic phase at 70 °C (▽).

have a significant impact on polymer/LC interactions. Consequently, if the interactions between the two species are different, it would be expected that the electrooptic properties would also be different. Understanding of the polymerization is, therefore, quite important in the understanding of the effects of polymerization conditions on the performance of PSFLCs.

To determine what effects, if any, the order of the liquid crystalline polymerization media has on these polymerizations and to understand the effects that the polymerization might induce in the electrooptic properties, the polymerization rate was determined for PPDA in W82,W7 in various FLC phases. Figure 2 shows the normalized polymerization rate as a function of time for 2% PPDA in W82,W7 at different temperatures. The highest temperature corresponds to a polymerization in the isotropic phase, the next highest to a smectic A polymerization, and the two lowest temperatures to polymerizations in the smectic C* phase. Interestingly, and in contrast to behavior generally found in isotropic solvents, as the temperature decreases, the polymerization rate increases significantly. By simply decreasing the temperature 35 °C from the isotropic phase to the smectic C* phase, the polymerization rate almost doubles. Similar behavior has also been observed for HDDA and C6M, a liquid crystalline diacrylate.[22] Therefore, for different monomers with varying chemical structures, the polymerization is significantly altered when performed in the ordered LC phases. In fact, for all of these polymerizations, as the temperature increases, and thus the order of the FLC/monomer system decreases, the polymerization rate decreases, implying that the formation of the polymer is significantly different for different polymerization temperatures and LC phases.

These results seem to indicate that the liquid crystal somehow acts to segregate the monomer or the monomer double bonds, effectively increasing the local concentration of double bonds. If the monomeric species

is segregated, or ordered, this may change the order of the polymer, which will significantly impact the alignment of the LC and thereby also affect the ultimate properties and performance of the PSFLC. In fact, evidence of such segregation behavior has been given previously for both C6M and HDDA in an FLC solvent. In mixtures of C6M and W82,W7, for example, the C6M molecules align parallel to the FLC molecules, thereby concentrating the double bonds into a smaller volume. Other monomers, like HDDA, exhibit the opposite response in that the molecules align parallel to the smectic layers. Additionally, HDDA molecules swell the smectic layers at levels indicative of complete interlamellar segregation. From these segregation results, two proposed models for monomer segregation and organization in smectic LCs have been presented:[24] one distinguished by monomer molecules aligning with the LC molecules and another with monomer molecules segregating between the smectic layers, thereby aligning parallel to the smectic layers. For both scenarios the monomer double bonds are concentrated into a smaller volume which may result in the observed polymerization rate increase.

Similarly, the segregation behavior of PPDA may provide additional useful information regarding the influence of segregation on polymerization and electrooptic characteristics. The PPDA chemical structure and molecular mass are quite similar to those of HDDA, but the inflexibility of the central phenyl core in PPDA may have a large impact on any segregation characteristics. Although the PPDA polymerization results give indications of segregation, it is also important to obtain direct information on the type of segregation in order to understand both the effects on the polymerization and those that might be induced on the polymer structure. Without this knowledge, it would be difficult to predict the influence of LC order on the ultimate electrooptic and optical properties of these systems.

One method that has proven very useful in examining the organization of specific bonds, such as monomeric double bonds, utilizes polarized infrared spectroscopy.[28] In acrylate/W82,W7 mixtures, two bands, one at 1635 cm^{-1} (C=C stretch) and another at 1408 cm^{-1} (C–H wag), unique to the acrylic C=C groups, can be isolated in the infrared spectrum. Figure 3 shows a polar plot for the absorbance of these two bands in a 5% PPDA/W82,W7 mixture as a function of the polarization angle. If the acrylate double bonds are randomly distributed throughout the LC media, the absorbance at all different polarization angles should be the same. As is obvious from the figure, in PPDA/W82,W7 systems this scenario is not the case. The maximum absorbance for both acrylic bands occurs at 0°, corresponding to light polarized parallel to the layer normal (**z**), or perpendicular to the smectic layers. In fact, the maxima for both the 1635 and 1408 cm^{-1} bands is approximately 3.5 times the minimum absorbance observed for light polarized parallel to these same smectic layers, suggesting a very high degree of orientational order. These data also indicate that the PPDA double bonds orient preferentially along the director, implying that the double bonds and thereby the complete molecule are aligning in the
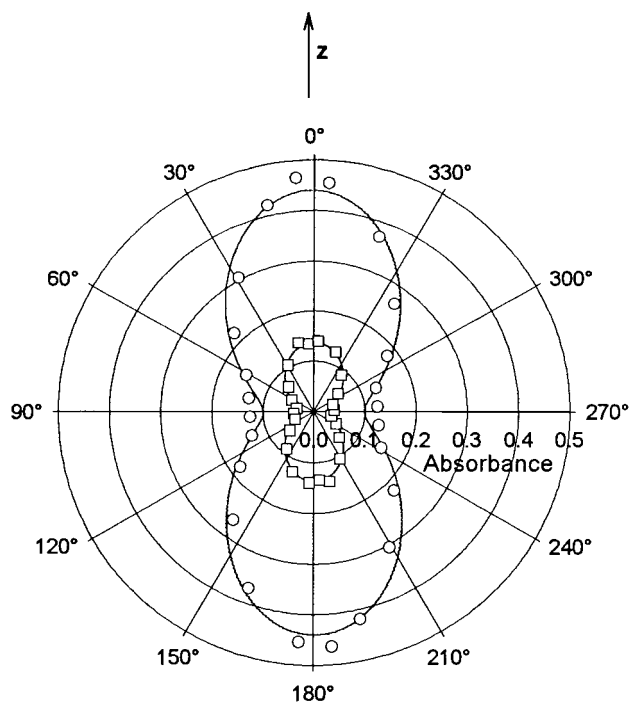
Figure 3. Polar plot of the absorbance, $A(\Psi)$, of the IR bands for the acrylate C=C stretch at 1635 cm^{-1} (□) and the C–H wag at 1408 cm^{-1} (○) for 5% PPDA in W7,W82 showing the high degree of orientational order in the double bonds in the direction of the layer normal (**z**).

same direction as the LC molecules. Therefore, despite the similarity in structure to HDDA, the segregation behavior is much more like that exhibited in LC monomers, such as C6M. The central phenyl ring in the PPDA molecular structure apparently acts similar in some aspects to the central mesogenic cores of the LC molecules and allows the PPDA molecules to align parallel to them.

The segregation of PPDA and C6M within the layers and HDDA between the layers may also have an interesting impact on the ultimate performance of the composite material. By using various monomers with different segregation properties, the polymer evolution and structure may be significantly altered, thereby changing the optical and electrooptic properties of the polymer-stabilized ferroelectric liquid crystal (PSFLC). Additionally, by changing the LC phase in which the polymerization occurs, the polymer structure may be modified to an even greater extent, thus having further effects on electrooptic performance. These effects are of great import in understanding and optimizing the properties of these fascinating materials.

Optical Response. One important characteristic of all display materials, and liquid crystals in particular, is the time required to switch between states. In LCs, this switching involves reorientation of molecules which changes the transmission of light through the material. Typically, an electric field is used to switch between a "dark" and a "bright" state. As mentioned earlier, one attractive feature of ferroelectric liquid crystals is that this optical response time is quite fast, on the order of microseconds and typically more than 100 times faster than other contemporary LC technologies.[17]

Therefore, if the mechanical stability of FLCs is to be improved by using polymeric materials, it is obviously

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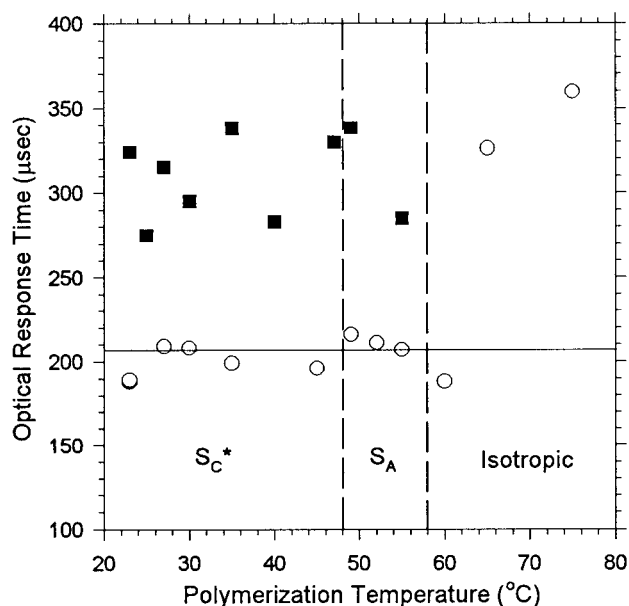
Figure 4. Optical response time observed at 35 °C for 2% PPDA (○) and 6.3% C6M (■) in W82,W7 polymerized at different temperatures. Phase transitions and the optical respsonse time at 35 °C for neat W82,W7 are also shown.

desirable to minimize the impact that the polymer has on the electrooptic properties such as the optical response characteristics. To elucidate the effects that the polymer induces in the switching dynamics, the optical response time was determined for a variety of different polymer/FLC composites, incorporating polymers with different chemical structure and different segregation characteristics before polymerization. Additionally, to understand the LC ordering and segregation effects during polymerization on the switching and to optimize the response characteristics, samples were polymerized at several temperatures corresponding to different LC phases.

The segregation of both *p*-phenylene diacrylate (PPDA) and C6M, a liquid crystalline diacrylate, are quite similar, as indicated previously. To investigate not only the effects and similarities of these two polymerizations, but also the role that the polymerization temperature plays, the optical response time was observed at various temperatures in the smectic C* phase for both PPDA and C6M polymerized at a number of different temperatures corresponding to the smectic C*, smectic A, and isotropic phases. Figure 4 shows the optical response time observed at 35 °C for 2% PPDA and 6.3% C6M in W82,W7 for samples polymerized at various temperatures. The response time for pure W82,W7 at 35 °C is shown as a solid line and the phase transitions for the neat FLC are also given.

As is evident from the figure, the type of polymer used may have a dramatic impact on the optical response. For PPDA samples polymerized in the ordered smectic phases, the optical response is very close to that exhibited in the FLC. On the other hand, the properties of C6M samples are significantly more scattered and show dramatically increased response times, typically more than a 50% increase over W82,W7 or the PPDA composites. This behavior may, in part, be due to the amount of polymer introduced. The C6M samples have a much higher weight percent (6.3%) than do the PPDA

samples (2%). These percentages, however, do correspond to the same molar concentration of double bonds, thereby producing a polymer network of approximately the same cross-linking density upon polymerization. The switching time, therefore, appears to be more dependent on the bulk amount and type of polymer.

Another interesting aspect in the figure is the change in behavior as the polymerization temperature is increased. Despite the extra scatter for the C6M data, it appears that the polymerization temperature in the ordered phases has little influence on the switching behavior for both PPDA and C6M systems. When polymerization temperatures exceed the clearing point, this behavior changes. For PPDA the optical response increases greatly for samples prepared in the unordered isotropic phase. Conspicuously absent from the figure, however, is data for C6M polymer samples prepared in the isotropic phase. The primary reason for this omission is the fact that the optical response is impossible to measure using the described apparatus. The formation of polymer in the isotropic phase dramatically alters the optical texture (see Figure 11) and prevents any visual bulk alignment. It is quite apparent that the disorder of the polymerization system has a tremendous impact on the switching characteristics. For PPDA, the switching time increases, and for C6M, it becomes impossible to measure. In summary, it appears that the optical response characteristics have very little dependence on polymerization temperature until temperatures above the clearing point are utilized for both polymer systems.

Therefore, in both PPDA and C6M systems, which exhibit similar segregation characteristics before polymerization, the polymerization temperature in the ordered phases does not appear to have a significant impact on the optical response time. To investigate the effects that might be induced by using a monomer with different segregation characteristics, the optical response was also determined at temperatures in the smectic C* phase for composites formed with HDDA. Figure 5 shows this response at both 30 and 35 °C for 2% HDDA in W82,W7 polymerized at various temperatures. The optical response in the figure is normalized by the response time for the neat FLC. The LC phase behavior of W82,W7 is again denoted.

These data are significantly different from those discussed earlier. For samples polymerized at lower temperatures, response times are very similar to those in the FLC. As the polymerization temperature is increased within the smectic C* phase, a small increase is observed. This increase is somewhat larger in the smectic A polymerizations, and when samples polymerized in the isotropic phase are examined, the optical response slows considerably. In fact, the isotropically polymerized samples exhibit response times more than double those of materials polymerized at lower temperatures in the smectic C* phase. This increase for isotropically polymerized samples is comparable to that observed in Figure 4 for C6M and PPDA systems. The trend appears to be similar for both observation temperatures. It is quite evident, therefore, that in HDDA/W82,W7 composites the polymerization temperature and corresponding LC phase have a dramatic impact
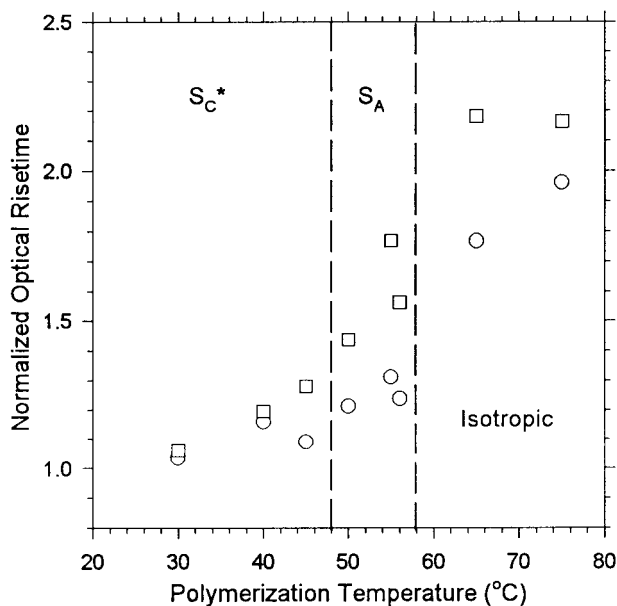
Figure 5. Optical response time normalized by the corresponding response time of W82,W7 for 2% HDDA in W82,W7 observed at 30 °C (○) and 35 °C (□) polymerized at different temperatures. Phase transitions for neat W82,W7 are also given.
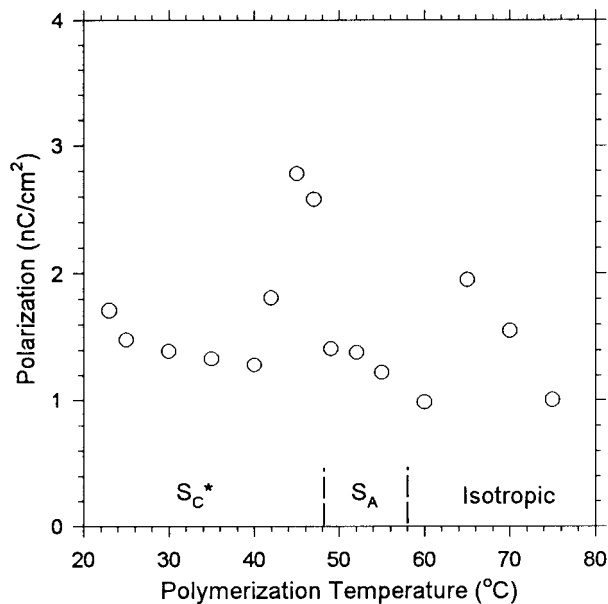

Figure 6. Ferroelectric polarization for 2% PPDA in W82,W7 observed at 30 °C (■) and 35 °C (○) polymerized at different temperatures. Phase transitions and polarization values at the two observation temperatures for neat W82,W7 are also shown.

on the optical response of the PSFLC and that the monomer segregation characteristics have an effect on the observed trends.

Ferroelectric Polarization. The polymerization conditions as well as the polymeric species also seem to have a significant effect on the switching characteristics of PSFLCs. Another inherent property of these chiral smectic C materials that might be affected by the polymerization conditions is the net macroscopic dipole, or spontaneous polarization. One unique quality of this polarization in W82,W7 systems is that it is quite sensitive to changes in the environment of the FLC, and small changes in the system, such as addition of a polymer network, may induce large differences in the polarization. This factor may help in understanding the implications of the polymer network on the ultimate electrooptic properties of these composite materials.

Previous results[12] have indicated that a large decrease in this spontaneous, or ferroelectric, polarization may be observed by introducing only a small amount of PPDA polymer network in W82,W7. To determine what effects, if any, the polymerization temperature has on these changes, the ferroelectric polarization was observed at temperatures in the smectic C* phase for samples polymerized at temperatures corresponding to different LC phases. Figure 6 shows the polarization results observed at 30 and 35 °C as a function of the polymerization temperature for 2% PPDA in W82,W7. The phase transitions for W82,W7 are denoted by dashed lines and the polarization values for the FLC at the two observation temperatures are given by solid lines. As would be expected, the polarization drops as the observation temperature is increased for both W82,W7 and the PPDA composite samples. Also consistent with previous results,[12] the values are significantly lower in the composite samples than in the neat FLC. The magnitude of this difference, however, changes considerably as the polymerization temperature is
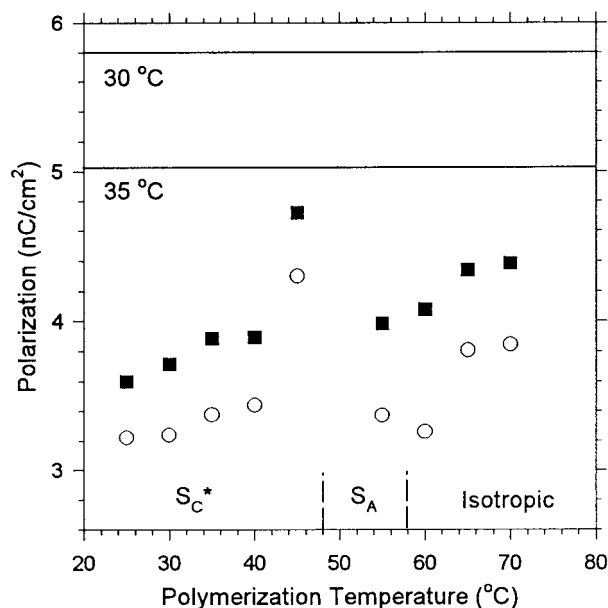
altered. By increasing the polymerization temperature 45 °C from the smectic C* phase to the isotropic phase, the polarization at both observation temperatures increases almost 20%. With the exception of a few points, this increase is monotonic with increasing polymerization temperature and appears to be somewhat independent of the LC phase. As a result of the observed increase, the polarization values of the PPDA/W82,W7 composite come significantly closer to those exhibited in the FLC when polymerized at higher temperatures.

As mentioned previously, the LC monomer, C6M, exhibits similar segregation behavior to PPDA in W82,W7. Interestingly, the dependence of the polarization on polymerization temperature is somewhat different. The polarization observed at 30 °C as a function of polymerization temperature for 6.3% C6M in W82,W7 is given in Figure 7. The LC phases of W82,W7 are also indicated. As seen in the figure, the values for the polarization are much lower than observed at comparable polymerization temperatures in Figure 6. In fact, the polarization is typically less than 50% of that in the PPDA composites and only around 30% of the polarization of the FLC. Interestingly, the values also do not seem to be as dependent on polymerization temperature, as seen earlier. By increasing the polymerization temperature, little change in polarization is seen. It does appear that LC phase may influence the polarization slightly but not significantly.

One aspect of the polarization behavior seen in Figure 7 is quite interesting and deserving of further discussion. For samples polymerized at temperatures slightly below the smectic C* → smectic A transition of the FLC, the polarization values are substantially larger than those at other polymerization temperatures. In fact, the polarization is almost doubled for certain samples. The explanation may lie in the phase behavior before polymerization. Typically, by adding small amounts of monomer to an LC, the phase transitions are somewhat
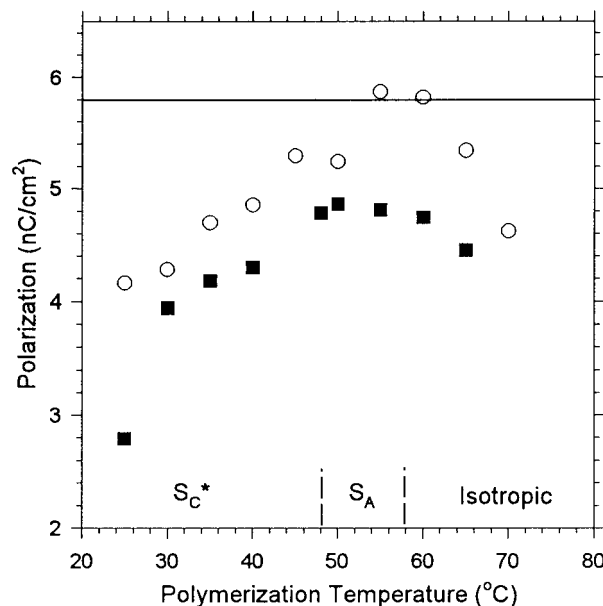
Figure 7. Ferroelectric polarization for 6.3% C6M in W82,W7 observed at 30 °C (○) polymerized at different temperatures. Phase transitions for neat W82,W7 are also shown.

Figure 8. Ferroelectric polarization for 2% (○) and 5% (■) HDDA in W82,W7 observed at 30 °C and polymerized at different temperatures. Phase transitions and polarization values at the observation temperature for neat W82,W7 are also shown.

depressed.[12] At the concentrations of C6M used in this study, the smectic C* → smectic A transition decreases almost 6 °C. After polymerization, however, these transitions return to temperatures very close to those exhibited in the FLC. So, at appropriate temperatures a sample may be in the smectic A phase initially, but during polymerization may change to the smectic C* phase. A similar situation would also happen with PPDA at temperatures slightly below the transition. These polymerization-driven phase transitions[32] likely affect the three samples polymerized between 42 and 48 °C in Figure 6 as well as the sample polymerized at 45 °C in Figure 5. Interestingly, these samples exhibit the elevated polarization values as compared to samples polymerized at other temperatures, indicating that the polymerization-driven phase transitions strongly influence the electrooptic behavior of the resulting composite.

To determine if this behavior changes when the polymer network is formed by the flexible diacrylate HDDA, the spontaneous polarization as a function of polymerization temperature was investigated at different temperatures in the smectic C* phase and for different concentrations of HDDA. As discussed earlier, the segregation behavior for this monomer is much different from that of PPDA and C6M and also seems to play a significant role in the characteristics of the ferroelectric polarization. Figure 8 shows the ferroelectric polarization in the smectic C* phase at 30 °C with changing polymerization temperature for both 2 and 5% HDDA. The transition temperatures of W82,W7 are also designated and the polarization at 30 °C is given as a solid line.

In contrast to the results for both C6M and PPDA, both the temperature and the LC phase of polymerization appear to have a large impact on the polarization. At lower polymerization temperatures for the 2% samples, the polarization is relatively small but, interestingly, much higher than that observed at comparable temperatures in PPDA or C6M systems. As the polymerization temperature in smectic C* increases, so does

the polarization. With only an increase of 20 °C in the polymerization temperature, the polarization increases over 25%. This increase continues until temperatures close to the smectic C* → smectic A transition are reached. By this point, the polarization has increased significantly and comes very close to that observed in W82,W7. The values appear to stop increasing at this point and level out somewhat in the smectic A phase. However, at the polymerization temperature, where these characteristics are observed, the polarization values of the samples are almost identical to that of W82,W7. Therefore, by changing the polymerization temperature, the polarization can be optimized to achieve polarization characteristics very near those of the liquid crystal. After polymerization temperatures above the clearing point are reached, the polarization decreases quite significantly.

To elucidate if these effects are also observed at higher concentrations of HDDA, polarization data for 5% HDDA in W82,W7 are also presented. As would be expected, the values for 5% are lower than those for 2% HDDA, but the decrease with increasing concentration is relatively small. The same basic trend is seen in the 5% samples, with an increase in polarization with polymerization temperature to the smectic C* → smectic A transition. Little change is also observed within the smectic A phase and values begin to decrease with samples prepared above the clearing point. Although the polarization does decrease somewhat with increasing concentration, quite large polarizations are still achievable, and for 5% HDDA polymer prepared under appropriate conditions, over 80% of the polarization is retained. Interestingly, with this large of a concentration of HDDA polymer, the polarization is consistently larger than observed in the 2% PPDA samples and much larger than that seen in 6.3% C6M.

In summary, the polymerization temperature does not seem to have a significant effect on electrooptic proper-

ties for C6M composites unless temperatures above the clearing point are used for polymerization. Additionally, the polarization and the switching speed are much smaller than for other composites and the pure FLC. PPDA samples, on the other hand, show a slight increase in polarization in the ordered phases with increasing polymerization temperature, but little dependence in the optical response is detected until samples are polymerized at elevated temperatures in the isotropic phase. The polarization for these samples is still substantially lower than for W82,W7, but the optical response for preparations in the ordered phases is quite similar. HDDA composites show a large dependence for both parameters on the polymerization temperature, and at appropriate polymerization temperatures, characteristics very close to that exhibited by the FLC can be achieved.

Another parameter that may provide further insight into these differences in electrooptic behavior and its dependence on the polymerization temperature is the rotational viscosity. These values can be calculated from the optical response time and the ferroelectric polarization, as shown in eq 1. Although many of the assumptions required to derive this equation may not be valid after a polymer is introduced, the calculations provide another interesting method to compare different samples to determine reasons for particular behavior.

From the equation it appears that increases in either the optical response time or in the ferroelectric polarization could drive increases in the rotational viscosity. Very small changes, if any, were observed in either of these parameters for both C6M and PPDA samples. Therefore, little change would be expected in the rotational viscosity until polymerization temperatures in the isotropic phase are used. A large change is observed in both the polarization and response time for HDDA composites, with the value of both increasing as a function of polymerization temperature in the ordered phases. It is conceivable that the rotational viscosity of a given sample would be constant at different temperatures as both the polarization and response time increase with temperature. Given the behavior of HDDA samples, it may, therefore, be possible that the increase in polarization observed with increasing polymerization temperature may be offset by the increase in response time. If this scenario bears true, the calculated rotational viscosity would remain constant for the given polymerization temperatures, which would imply that the energy barrier for rotation is likely the same for all different polymerizations. To determine if this behavior is observed, the rotational viscosity was calculated and is shown at 30 °C in Figure 9 for different polymerization temperatures of 2% HDDA in W82,W7. Values are also shown for 2% PPDA for comparison. Analogous to previous figures, the transition behavior of W82,W7 is indicated, as is the rotational viscosity of the FLC at 30 °C.

As anticipated, the rotational viscosity for PPDA samples increases slightly with polymerization temperature due to the small increase observed in the polarization. Additionally, the values escalate sharply in the isotropic phase as both the polarization and response time increase dramatically. Interestingly, for HDDA composites the behavior is quite different. It appears
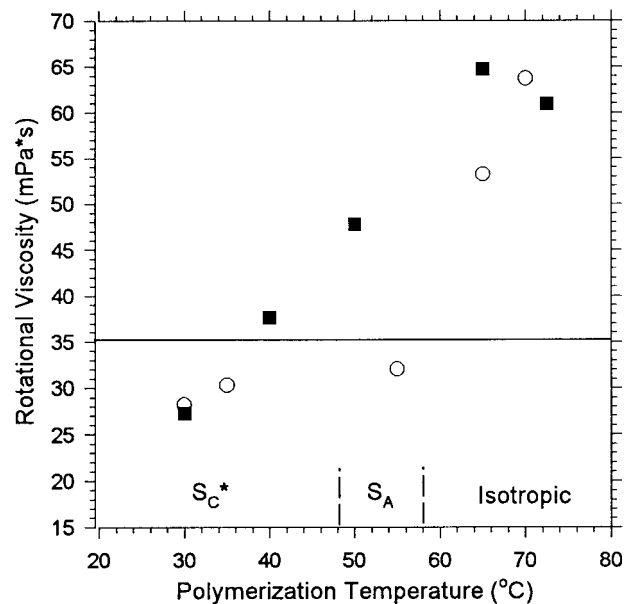
Figure 9. Rotational viscosity at 30 °C for 2% PPDA (○) and 2% HDDA (■) polymerized at different temperatures. Phase transitions and rotational viscosity values at the observation temperature for neat W82,W7 are also shown.

that the rotational viscosity increases monotonically and almost linearly with polymerization temperature, implying that the energy barrier for rotation increases significantly.

Optical Properties. The results given to this point show the interesting effects of the polymerization conditions and polymer type on the electrooptic properties of PSFLCs, but little can be directly elucidated about how the monomer segregation affects these final characteristics and what role the polymerization conditions play. The optical appearance, as observed microscopically, provides a means to understand further these polymer-stabilized materials and allows for a better grasp on the mechanisms driving the observed electrooptic behavior. To determine the effects of introducing a polymer on the optical textures of the FLC, optical micrographs were taken in the smectic C* phase for the various polymer/FLC composites. Analogous to the experiments described earlier, the influence of polymerization temperature and order of the system were also examined by preparing materials at different temperatures.

Figure 10 shows optical micrographs at 25 °C in the smectic C* phase for 2% PPDA in W82,W7 polymerized at temperatures in the smectic C* phase (a), in the smectic A phase (b), and in the isotropic phase (c). For comparison, a micrograph of neat W82,W7 (d) is also shown. Interestingly, the optical texture appears to depend not only on the polymerization temperature but also on the LC phase in which the polymerization was performed. For the samples polymerized in smectic C*, the bulk alignment direction is quite visible. The polymer does induce a number of defects which are more prevalent than seen in the neat FLC. These defects would decrease the optical clarity, but the bulk alignment appears to be controlled primarily by the alignment layer and not the polymer network. A very similar texture is also observed for the smectic A polymerization. Bulk alignment is still quite evident, although not as distinct as that seen in the sample prepared in
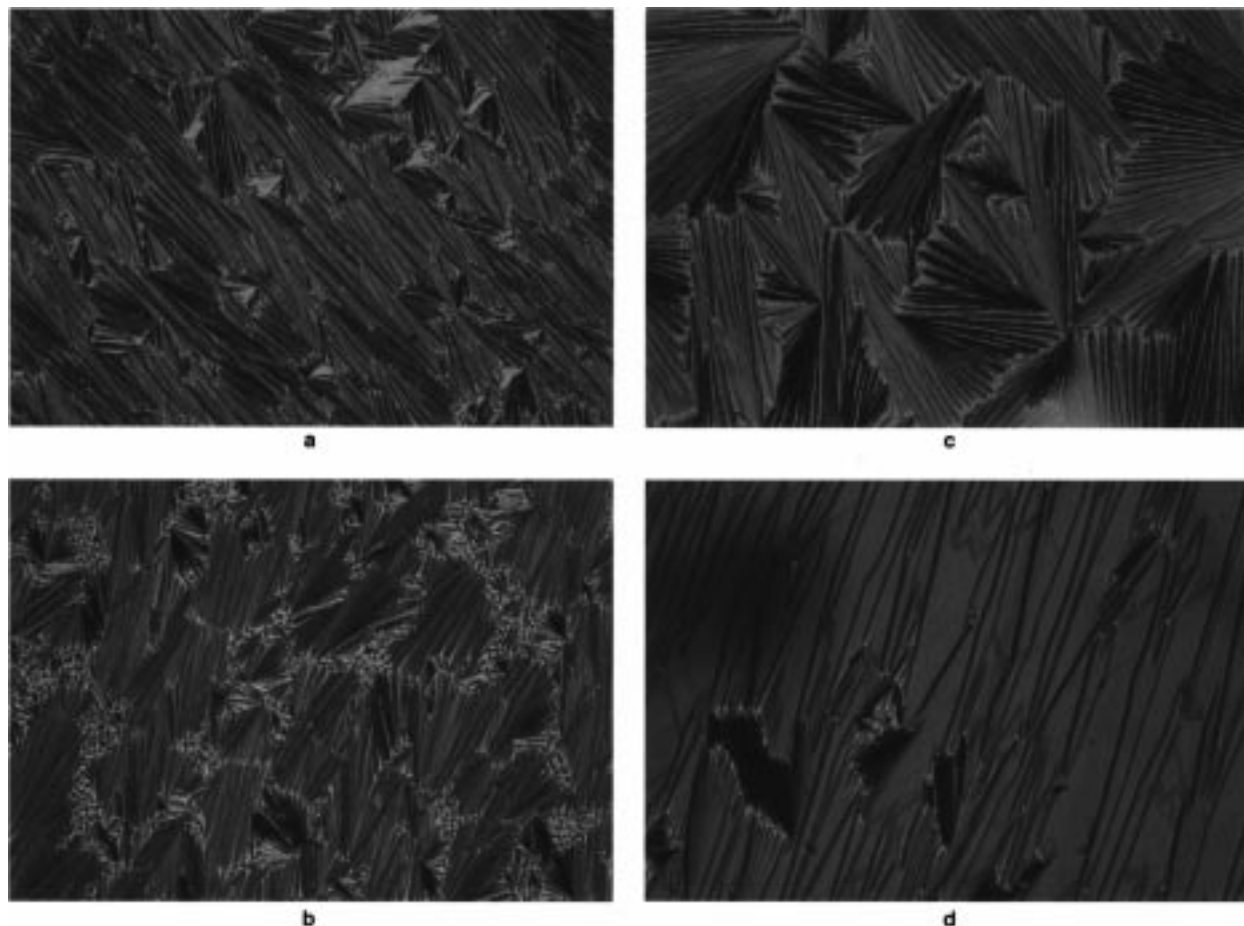
Figure 10. Optical micrographs (200×) at 25 °C for 2% PPDA in W82,W7 polymerized (a) at 27 °C in the smectic C* phase, (b) at 52 °C in smectic A, and (c) at 65 °C in the isotropic phase.

smectic C*. The defects may also be slightly smaller, and a number of very small defects not observed in the previous sample also seem to be present, but as a whole both samples are quite similar.

A very large change occurs, however, when the polymerization is performed in the isotropic phase. The picture shows a focal conic structure indicative of a system with surface treatment for planar alignment, but without a rubbing direction. In this case the fact that the polymer was formed in the isotropic phase implies that no specific order is imparted to the polymer during polymerization. This disordered polymer changes the alignment to an extent that the rubbing direction has no real effect on the bulk orientation of the LC molecules. These results also have implications on the effects of the polymer when polymerized in the ordered phases. If the polymer can change the alignment to such a large degree for isotropic polymerizations, the polymer formed in smectic C* and smectic A will also significantly affect the alignment. This behavior is observed through the propagation of defects, but the bulk alignment remains intact, implying that some of the original orientational order of the monomer is retained in the polymeric species.

Interesting effects are also seen in textures produced by polymerization of 6.3% C6M in W82,W7, as shown in Figure 11. Optical micrographs taken at 25 °C are given for polymerizations in smectic C* (a), smectic A (b), and the isotropic phase (c), as well for a polymerization that begins in the smectic A phase and transizaition that begins in the smectic A phase and transitions to the smectic C* phase during polymerization (d). Although the bulk alignment is not as uniform as in the PPDA composites, similar behavior for the ordered polymerizations is observed. In both smectic C* and smectic A polymerizations, a number of relatively large defects are induced, but the bulk alignment is still in the expected direction. Interestingly, the polymer formed in the smectic A polymerization also induces apparent homeotropic domains, indicating a considerable anchoring effect by the polymer. If the polymerization occurs in the isotropic phase, then virtually no azimuthal or longitudinal alignment is observed. Domains are very small, creating a pebbled texture which prevents measurement of the optical response and also makes it difficult to see visually the switching under a microscope (see the discussion of Figure 7). Intriguing behavior is also observed when the phase changes during polymerization. For the sample which begins in smectic A and during polymerization transitions into the smectic C* phase, distinctly different oriented focal conic textures are observed. Defects do not appear to be as prevalent, and although the domains are oriented differently, some longitudinal orientation is observed. This behavior is likely responsible for the fairly dramatic increases in polarization seen for samples that undergo this polymerization-driven phase transition (see Figure 8).

Therefore, for both PPDA and C6M, similar optical behavior is observed for materials polymerized in the ordered phases. Both polymers induce a significant
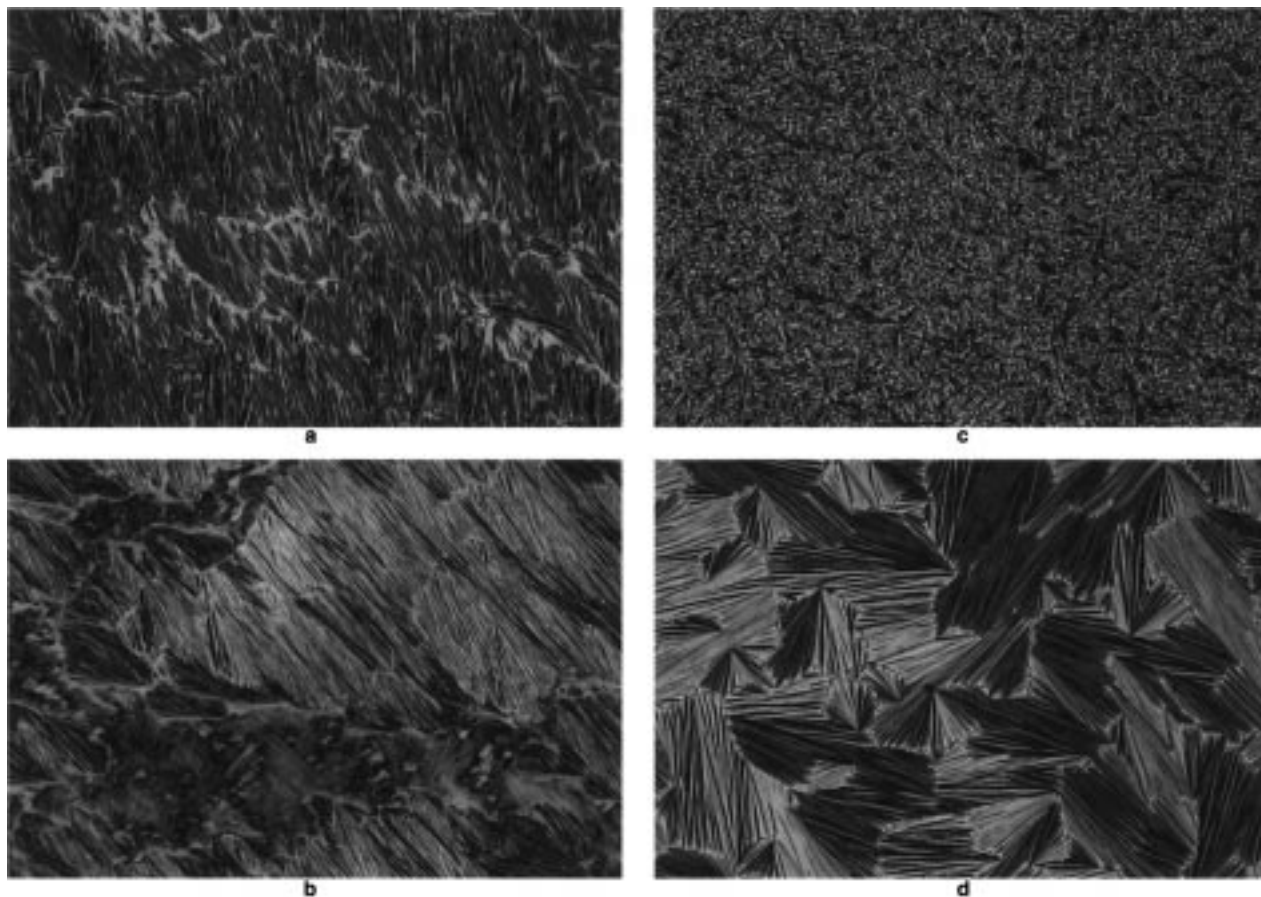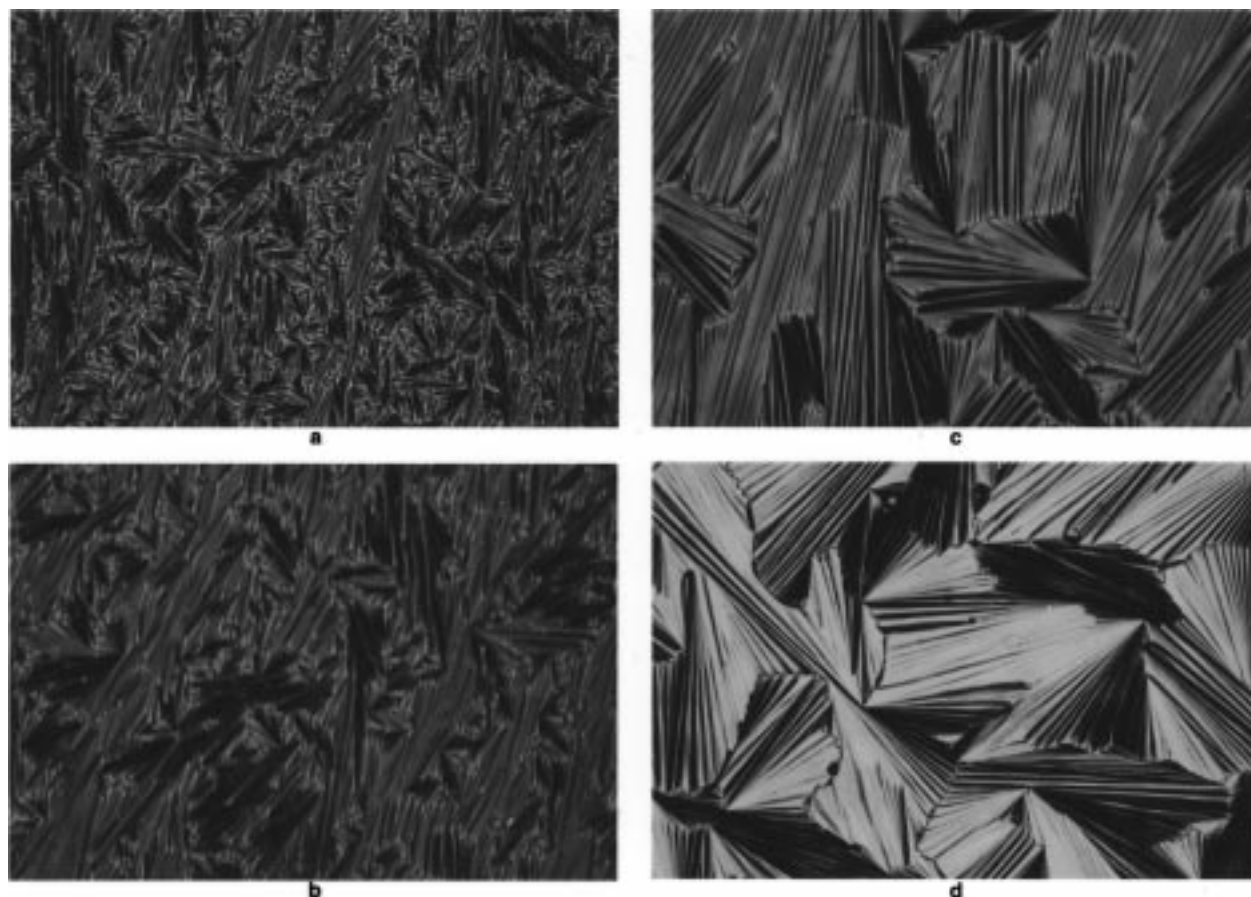
Figure 11. Optical micrographs (200×) at 25 °C for 6.3% C6M in W82,W7 polymerized (a) at 27 °C in the smectic C* phase, (b) at 55 °C in smectic A, (c) at 70 °C in the isotropic phase, and (d) at 45 °C.

amount of defects and prevent any real alignment in the rubbing direction if polymerized in the isotropic phase. As discussed earlier, both monomers segregate in the smectic layers and mimic the orientation of the LC. Thus, the formation of the polymer species initially takes place within the layers which may result in the formation of a number of defects. The defects are quite substantial by the time polymerization is completed. The defects appear to dramatically reduce the polarization and, in the case of C6M, the response speed as well.

The electrooptic properties for HDDA composites showed substantially different behavior from the PPDA and C6M materials, however. This behavior might imply that the optical characteristics are also different. Such is the case as shown in Figure 12 for micrographs of 2% HDDA in W82,W7 polymerized at two temperatures in the smectic C* phase (a and b), one temperature in the smectic A phase (c), and one in the isotropic phase (d). Analogous to previous observations, all micrographs were taken at 25 °C in the smectic C* phase. Interestingly, and in contrast to previous results, the sample polymerized at the lower smectic C* temperature shows relatively small oriented domains. Despite the large number of defects that do influence the orientation to some extent, the bulk orientation seems to remain fairly intact. As the polymerization temperature is increased in the smectic C* phase, the domains increase in size, but the defects appear to begin to change the orientation slightly. This trend continues as the polymerization temperature is increased to the smectic A phase. For this sample the domains are quite large and the bulk

orientation is evident, but the domains are not oriented quite as well as in the W82,W7 sample. Despite these small changes, the texture observed here is far and away the most similar to the neat FLC. This optical behavior appears to be consistent with the electrooptic results as the electrooptic properties for smectic A polymerized samples of HDDA are also very similar to those exhibited in W82,W7. As the polymerization temperature exceeds the clearing point, characteristics comparable to PPDA and C6M are observed. The polymer formed in the isotropic medium apparently changes the alignment of the domains to an extent that the rubbing direction has little control of the bulk alignment.

These results are quite intriguing and present some interesting paradigms that help clarify some of the trends in electrooptic characteristics. First of all, and similar to the electrooptic results, the optical characteristics of HDDA PSFLCs appear to be much more dependent on the temperature as well as the LC phase in which the polymerization is performed. As the texture changes from small, relatively well-oriented domains to larger domains with fewer defects at higher polymerization temperatures, the polarization increases significantly until large well-oriented domains are observed for smectic A polymerizations. Interestingly, at this point the polarization is very similar to that exhibited in the FLC. The optical response time is slightly higher, but all in all, the sample is comparable in virtually all aspects to the neat FLC. Therefore, by changing the polymerization temperature in HDDA

Figure 12. Optical micrographs (200×) at 25 °C for 2% HDDA in W82,W7 polymerized (a) at 27 °C and (b) at 40 °C both in the smectic C* phase, (c) at 50 °C in smectic A, and (d) at 65 °C in the isotropic phase.

systems, a number of properties can be optimized to improve the performance of the material. This overall behavior may, in part, be due to the segregation characteristics of the monomer. HDDA segregates between the smectic layers which is much different than the segregation of PPDA and C6M. Therefore, the polymerization begins between these layers that may allow the electrooptic properties to be less affected after the polymerization is completed.

Conclusions

The electrooptic and optical properties of a variety of PSFLC materials prepared under different conditions are described. Both the type of polymer and the polymerization conditions have a dramatic impact on the properties of the PSFLC. The polymerization behavior, the electrooptic properties, and the optical characteristics change considerably with the temperature of polymerization. The polymerization rate for the monomers studied actually increases with decreasing polymerization temperature and increasing order of the LC phase. Although the polymerization results are comparable for the various monomers, the segregation is different. Certain monomers such as PPDA and C6M segregate in the smectic layers, whereas others like HDDA segregate between the smectic layers.

Interestingly, PPDA and C6M systems, in addition to similar segregation properties, exhibit comparable trends in electrooptic and optical behavior after polymerization. The temperature of polymerization has little impact on the optical response time for either PSFLC material. Only when polymerization temperatures above the clearing point are utilized are significant changes in the optical response observed. PPDA composites exhibit response times close to those in the FLC while C6M composites switch more slowly. Additionally, the ferroelectric polarization does not change much with polymerization temperature for either system. For materials with comparable cross-linking density, however, PPDA materials exhibit a much higher polarization than C6M systems, but both still exhibit polarization values considerably less than W82,W7. Optical characteristics are also much the same for both of these systems polymerized in the ordered phases. On the other hand, the characteristics of HDDA systems show a large dependence on the polymerization temperature. Both optical response time and ferroelectric polarization increase with polymerization temperature in the ordered phases. In fact, the electrooptic properties and optical characteristics can be optimized by choosing appropriate preparation conditions. By polymerizing at particular temperatures, characteristics of the PSFLC approach those exhibited by the neat FLC.