Macromolecules **2001,** *34,* 6929−6935

Investigation of Polymer Nanostructure Evolution during the Formation of Polymer/Smectic Liquid Crystal Composites

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Received April 2, 2001; Revised Manuscript Received July 5, 2001

ABSTRACT: Polymer stabilized liquid crystalline systems (PSLCs) have been of considerable research interest due to their great potential in liquid crystal display applications. Of particular importance in the properties of PSLC systems is the evolution of the polymer nanostructure. The unique characteristics of fluorinated monomers not only may provide unique polymer nanostructure but also may enhance desirable properties of PSLC materials. This study focuses on the polymerization and polymer nanostructure of low surface energy fluorinated materials in a liquid crystalline solvent. Enhanced polymerization rates are observed as the order of the liquid crystalline solvent is increased with particularly pronounced acceleration for a fluorinated monoacrylate. This behavior is primarily due to segregation both before and after polymerization. Fluorinated monomers segregate between the smectic layers of the liquid crystal comparable to segregation behavior of analogous aliphatic monomers. The monomer structure has a significant impact on the polymer segregation behavior in these polymer/liquid crystalline composites as well. Network polymer structures, obtained from both aliphatic and fluorinated diacrylate monomers, phase separate from the liquid crystal while linear fluorinated polymer structures remain segregated between the smectic layers of the liquid crystal. Not only does this linear polymer remain between the smectic layers and retain its segregation behavior throughout the polymerization, but the polymer is also ordered to a much greater degree than the monomer. This ordered structure significantly alters the polymer/LC interaction and leads to birefringence at temperatures well above the liquid crystalline isotropic clearing point.

Introduction

Polymer/low molar mass liquid crystal (LC) composite systems comprise a new and interesting class of materials that exhibit physical and chemical properties leading to a variety applications, such as light shutters, flexible displays without polarizers, switchable windows, optical logic gates, and a host of other applications.[1−4] Polymer/LC composites can be divided into a number of categories including polymer dispersed liquid crystals (PDLCs),[5] polymer stabilized cholesteric textures (PSCTs),[6] and polymer stabilized liquid crystals (PSLCs).[7] These systems range from liquid crystal droplets dispersed in a polymer matrix (PDLCs) to a continuous LC phase engulfing a light polymer network (PSLCs and PSCTs) and can involve the use of nematic, cholesteric, and chiral smectic liquid crystals or ferroelectric liquid crystals (FLCs).[8]

Certain PSLC systems have been developed that are formed from the polymerization of small amounts of monomer in FLCs (PSFLCs).[9] The polymer may, in fact, lead to large changes in the electrooptic properties of the FLC.[10] Polymer/FLC systems have been developed that have adjustable gray scales,[11] but the polymer will typically have detrimental effects on electrooptical properties.[12] For most polymer/LC systems, in general, the composite properties are dependent not only on the type of polymer introduced but also on the polymerization conditions, temperature,[13] monomer solubility,[14] and monomer structure.[15]

Each of the aforementioned factors acts to influence the evolution of polymer nanostructure during the polymerization of a monomer in an LC solvent. Research has shown that polymer network architecture is significantly affected by monomer solubility with coarse polymer structures resulting from nonsoluble monomers and soluble monomers yielding more well-defined networks.[14] Due to interaction between the liquid crystal and the polymer, it is important to understand and characterize the factors that affect polymer nanostructure within liquid crystalline media. In fact, for certain PSCT systems, elastic forces between the polymer network and the liquid crystal cause reorientation of the LC at a rate 1000 times faster than the pure LC, a desirable property for display applications.[14] To successfully develop polymer/liquid crystalline composites, including PSFLCs, for display applications, it is important to elucidate the mechanism for controlled polymer nanostructure formation.

For polymer/FLC systems in particular, the order of the LC phase as well as the monomer structure affects the segregation of the monomer species within the FLC solvent.[15] Specifically, long chain aliphatic monomers tend to segregate between the smectic C* layers while mesogenic monomers sequester within the smectic C* layer. In addition, this ordering effect of the FLC on the monomer has a significant impact on the polymerization rate.[16] Polymerizations of long chain aliphatic monomers conducted in the more ordered smectic C* phase have a 3−4-fold increase in rate as compared to those conducted in the isotropic phase. This increase in the polymerization rate was found to be a consequence of a decrease in chain termination. The effect of the FLC solvent on the monomer organization and thus the polymerization rate is an important component to understanding how to control polymer nanostructure in anisotropic media. Monomer organization, a consequence of monomer structure, is the most important factor determining the polymer morphology in an anisotropic solvent. An understanding of how monomer

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10.1021/ma010571r CCC: $20.00

structure and the resulting monomer segregation behavior affect polymer architecture in LC media is crucial to the development of more viable FLC electrooptic devices and to further the knowledge of polymer nanostructure evolution in ordered media.

Fluorinated monomers, specifically fluorinated acrylates, are an interesting class of materials that may prove promising in the study of polymer nanostructure formation in LC media. The use of fluorinated monomers may also lead to improvements in polymer stabilized liquid crystal systems. The use of fluorinated compounds, specifically fluoropolymers, has increased in recent years due to their unique properties and performance.[18] Fluorinated compounds are characterized by electric resistance, inflammability, and low surface energies. The surface energy effects also induce interesting characteristics on monomeric materials. Long-range liquid crystalline smectic ordering in polymerizable monomers composed of both hydrocarbon and fluorinated segments[19,20] have been demonstrated with retention of this LC order after polymerization.[21] Work has also been performed using fluorinated monomers in polymer dispersed systems with improved optical properties and more defined morphologies over nonfluorinated systems.[22] Little work has been done, however, to investigate the effects of adding small amounts of fluorinated monomer into a low molar mass liquid crystal to form polymer stabilized liquid crystal.

The goal of this work is to understand the effects of adding and polymerizing fluorinated and nonfluorinated monomers into a room temperature smectic liquid crystal and thereby enhance the knowledge of polymer structure evolution during the formation of polymer/smectic LC composites. To achieve this goal, the LC phase characteristics, specifically phase transitions, were examined before and after polymerization. The smectic layer spacing was determined before and after polymerization to determine segregation behavior. This smectic layer spacing was also investigated as a function of polymerization time and temperature. The orientation of the monomeric and polymeric materials within the LC matrix was examined as well. Additionally, the polymerization kinetics were observed as a function of polymerization temperature and LC phase. Through these studies greater knowledge and understanding regarding the role of monomer structure and liquid crystalline order during the formation of polymer/LC composite materials have been obtained. In addition, monomer organization and resulting polymer morphology, as well as the processes involved in the polymerization of monomeric species, have been examined. Through further understanding of polymer nanostructure formation in PSLC systems, the necessary foundation will be developed to produce PSLC systems that have an internally stabilizing polymer network but retain the desired electrooptic properties of FLCs.

Experimental Section

Materials. The fluorinated monomers used in this study were octafluorohexanediol diacrylate (FHDDA) and heptadecafluorodecyl acrylate (HDFA-Monomer-Polymer & Dajac Labs, Feasterville, PA). The nonfluorinated monomer used was hexanediol diacrylate (HDDA-UCB Chemicals Corp., North Augusta, SC). The room-temperature smectic A liquid crystal was 4-cyano-4′-*n*-octylbiphenyl (8CB-BDH, Poole, England). Chemical structures of the monomers and liquid crystal and LC phase behavior of the liquid crystal are shown in Figure 1. Photopolymerizations were initiated using Irgacure I-907 (Ciba Geigy, Hawthorne, NY). All materials were used without further purification. The monomer/LC mixtures were prepared with initiator concentrations approximately 6 mol % of the total monomer double-bond concentration.

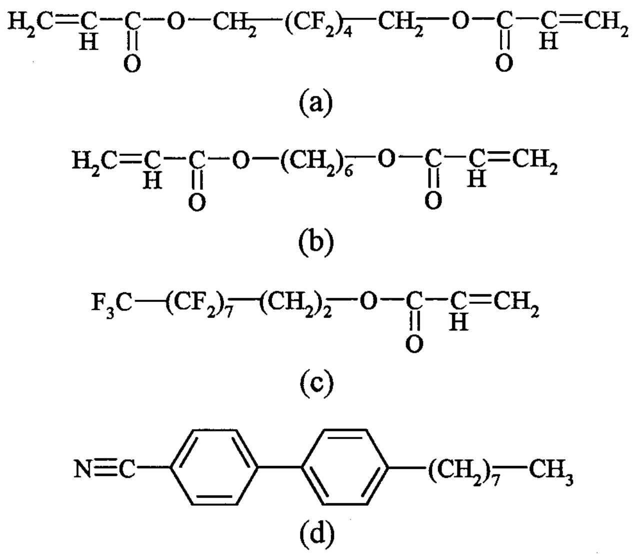


Figure 1. Monomer and liquid crystal structures of (a) octafluorohexanediol diacrylate, (b) hexanediol diacrylate, (c) heptadecafluorodecyl acrylate, and (d) 4-cyano-4′-*n*-octyl-biphenyl (8CB phase sequence: isotropic → 40 °C → nematic → 32 °C → smectic A).

Procedure. Phase transitions of the mixtures were measured using a polarizing optical microscope (Optiphot 2-pol; Nikon, Melville, NY) equipped with a temperature-controlled hotstage (Instec, Boulder, CO). For these measurements, samples were first heated above the isotropic transition and then cooled at approximately 0.3 °C min^{-1}. The phase transitions were confirmed by those obtained from differential scanning calorimetry (DSC 7; Perkin-Elmer, Norwalk, CT) at a scan rate of 5 °C min^{-1}. To prepare polymer/LC samples, the monomer/LC samples were polymerized at temperatures 9 °C below the nematic/smectic A transition of the unpolymerized sample.

Smectic layer *d* spacings of the mixtures were measured using small-angle X-ray scattering (SAXS, Siemens XRD 700 WAXD/SAXS) with a Cu Kα line of 1.5 Å. Bragg's law was used to determine the *d* spacing of the smectic layers. Monomer/LC samples were examined in a SAXS cell designed to achieve isothermal conditions and ensure phase continuity throughout the sample. Polymer/LC samples were prepared by polymerizing monomer/LC samples in the SAXS cell at desired polymerization temperatures.

Sample cells for polarized infrared (IR) absorption measurements were prepared by introducing the monomer/LC sample using capillary action between two rubbed polyimide-coated calcium fluoride plates (Spectral Systems, Hopewell Junction, NY) with 10 μm spacers. To ensure homogeneous alignment, samples were cooled at 0.05 °C min^{-1} from the isotropic to the smectic A phase. The alignment was checked using polarizing microscopy. Polarized IR spectra (32 scans per spectrum) were obtained using an FTIR spectrometer (Protégé 460 E.S.P, Nicolet, Madison, WI) equipped with a ZnSe wire grid polarizer. The dichroic ratios, which are a measure of system order, were also examined. For this study, the dichroic ratio is simply the maximum absorbance over the minimum absorbance.

Polymerization rate profiles were monitored using a differential scanning calorimeter (DSC 7; Perkin-Elmer) modified with a medium-pressure UV arc lamp. Polymerizations were initiated using 365 nm monochromatic light with an intensity of 2.7 mW cm^{-2}. The DSC sample cell was attached to a refrigerated circulating chiller to achieve isothermal reaction conditions. For rate studies, approximately 10 mg of the monomer/LC mixture was placed in an aluminum DSC pan.

Table 1. Phase Transition Temperatures of Various Monomer/8CB Mixtures before and after Polymerization

monomer	transition	before polymerization	after polymerization
8CB	Iso-N/N-Sm	41/33.10	NA
2% HDDA	Iso-N/N-Sm	35/26.9	38.8/31
3.3% FHDDA	Iso-N/N-Sm	35.2/28.1	39.5/32.1
6% HDFA	Iso-N/N-Sm	37.7/32.3	39.3/31.9

The samples were heated above the isotropic transition and cooled to the appropriate polymerization temperature to ensure uniform thickness and sufficient thermal contact. The DSC sample cell was flushed with nitrogen for 10 min prior to polymerization to mitigate oxygen inhibition. The rate of polymerization was determined from the heat flux measured by the DSC as follows:

$$\text{rate} = \frac{(Q/s)M}{n\Delta H_{\text{pol}}\text{mass}} \qquad (1)$$

where Q/s is the 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 mole of double bonds reacted, and the mass is the mass of the monomer in the sample.[16] The polymerization rate in eq 1 is the polymerization rate divided by the initial monomer concentration, giving units of 1/s. This normalized rate allows for a comparison of systems with different monomer concentrations and types of monomer. The theoretical value of 20.6 kcal/mol was used as the heat released per acrylate bond[17] for these calculations. Double-bond conversion was then calculated by integration of the polymerization rate as a function of time.

Results and Discussion

Polymer nanostructure has the potential to affect many of the intrinsic properties of the LC. To fully understand the effect that addition and polymerization of monomers have on liquid crystalline solvents, it is necessary to examine how the monomer and polymer influence the ordering of the LC matrix. A fundamental way to test the effect of monomer and polymer on the LC is to examine the phase transitions of the LC upon addition of monomer and after polymerization. Phase transitions of LC/monomer mixtures are also necessary to establish phase boundaries to ensure that polymerizations are conducted in the proper mesophase.

To determine the impact of polymer nanostructure on certain intrinsic properties, phase transitions for LC/monomer mixtures were determined before and after polymerization by polarized light microscopy as shown in Table 1. All of the monomer/LC mixtures exhibit a transition temperature depression that is a common phenomenon after adding solutes to a LC solvent. However, this depression is not as pronounced in the HDFA/LC mixture as it is for the diacrylate/LC mixtures. This behavior is interesting considering that by weight 6% of the HDFA is incorporated into the LC vs 2% HDDA and 3.3% FHDDA. Typically, the more diluents added to a LC solvent, the more phase depression is observed. After polymerization the diacrylate polymer/LC composites have transition temperatures that are extremely close to that of the pure liquid crystal. The increase in the transition temperatures observed after polymerization for the diacrylate samples may be the result of phase separation.

Previous research[16] has shown that the order of the LC solvent has a significant effect on the segregation behavior of the monomer and consequently impacts the rate of polymerization. A long chain aliphatic monomer, HDDA, has been studied previously and, when polymerized in a ferroelectric liquid crystalline solvent, exhibited a substantial increase in the polymerization rate with an increase in the order of the anisotropic medium.[16] This increase in the polymerization rate with an increase in solvent order (i.e., lower polymerization temperatures) is in direct contrast with traditional solvent free radical polymerizations. The increased polymerization rate was shown to be a result of enhanced segregation of the monomer between the smectic layers of the liquid crystal.[17]

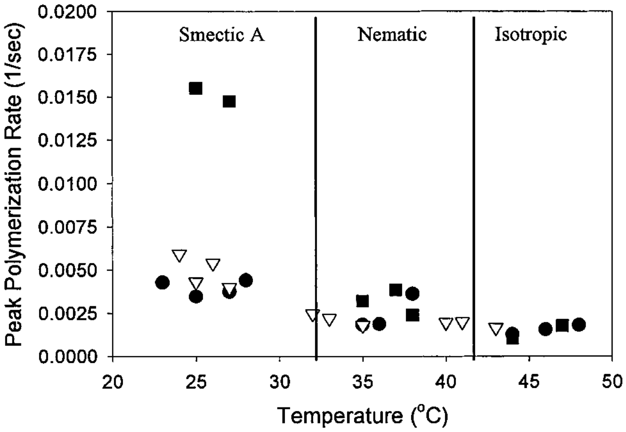


Figure 2. Maximum polymerization rate vs polymerization temperature for 2% HDDA (●), 3.3% FHDDA (▽), and 6% HDFA (■) in 8CB. Monomer concentrations are chosen to achieve equivalent double-bond concentrations.

In an effort to fully understand how monomer structure affects monomer organization in a LC matrix, fluorinated monomers are of interest due to their low surface energies. The low surface energies of the fluorinated monomers FHDDA and HDFA may lead to interesting rate and segregation behavior. Figure 2 is a plot of the maximum polymerization rate for the these two monomers as well as HDDA as a function of polymerization temperature. For DSC experiments the weight percent of each monomer is different so that all monomer/LC mixtures have the same double-bond concentration. This allows for more facile comparison of polymerization rates between monomer/LC samples. All of the monomer samples show a substantial increase in the polymerization rate as the order of the anisotropic medium increases. The fluorinated and nonfluorinated diacrylates show a similar trend of a 3-fold increase in the polymerization rate in the more ordered smectic A phase at lower temperatures as compared to polymerization in the isotropic phase similar to results observed previously.[16] The fluorinated monoacrylate is significantly different, however, and exhibits a 15-fold increase in the polymerization rate in the more ordered smectic A phase. This significant increase in the polymerization rate for the fluorinated monoacrylate is highly unusual. In this case more appears to be occurring than just the ordering effects of the liquid crystal on the monomer species. The monoacrylate has a maximum smectic polymerization rate that is 3 times greater than rates in the smectic phase for the diacrylate monomers.

In an attempt to understand this phenomenon, as well as to understand how the polymer nanostructure evolves within the liquid crystalline matrix, small-angle X-ray scattering was used to investigate the smectic layer spacing as a function of increasing monomer concentration and polymerization time. Figure 3 shows a plot of the smectic layer spacing as a function of monomer

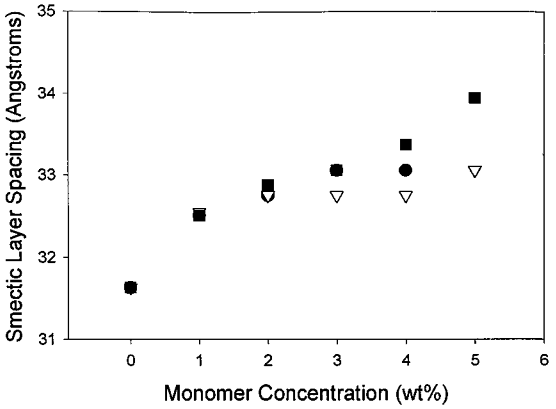


Figure 3. Smectic layer spacing of 8CB with increasing concentration of HDDA (●), FHDDA (▽), and HDFA (■).

Table 2. Smectic Layer Spacing (in Å) as a Function of Polymerization Time for Various Monomer/8CB[a] Mixtures

polymerization time (min)	smectic spacing of 2.1% HDDA	smectic spacing of 3.3% FHDDA	smectic spacing of 6.1% HDFA
0	32.3	33.0	33.9
0.5	32.3	33.0	33.9
1	31.9	33.0	33.9
3	31.6	32.3	33.5
10	31.6	31.6	33.5

[a] Smectic layer spacing neat 8CB is 31.6 Å.

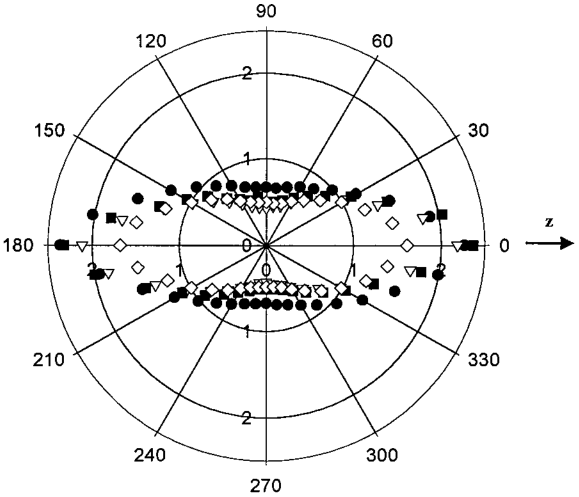
concentration for the fluorinated monoacrylate, the fluorinated diacrylate, and the aliphatic diacrylate. Each of the monomer samples shows the general trend of a monotonic increase in smectic layer spacing with increasing monomer concentration. This is evidence that each of the monomer species segregates between the smectic layers of the liquid crystal. If the monomers were phase separated or if the monomers were within the smectic layers, then no corresponding increase in the smectic layer spacing would be observed.[15]

The low surface energy of the fluorinated monomers may provide an enthalpic driving force for the continued segregation of the fluorinated monomers between the smectic layers of the LC matrix after polymerization. Knowing how the monomer concentration and thus how the amount of polymer in the polymer/LC composite affects the segregation of the polymer in the LC is an important component to understanding how to develop controlled polymer nanostructure formation in liquid crystalline media. The next step in understanding polymer nanostructure evolution is to study how the polymer segregation behavior changes over the course of polymerization by examining the smectic layer spacing as a function of polymerization time. Table 2 shows the smectic layer spacing as a function of polymerization time for each of the monomer samples with concentrations that are approximately the same as those used for the polymerization rate studies. Not only will these data give a great deal of information regarding the evolution of polymer structure, but the mechanism behind the pronounced polymerization rate increase for the fluorinated monoacrylate in the smectic phase may also be elucidated.

The nonfluorinated diacrylate, HDDA, exhibits interesting behavior as the polymerization proceeds. Initially, after 30 s of polymerization, the layer spacing has not changed significantly. After 1 min of polymerization time a significant decrease in the smectic layer spacing is seen. The observed spacing then drops to the original smectic layer spacing of 8CB at 31.6 Å after 3 min of polymerization. The fluorinated diacrylate, FHDDA, exhibits a behavior similar to that of HDDA but does not show a significant decrease in the smectic layer spacing until after 1 min of polymerization and then a more substantial decrease after 10 min to that of 8CB. For both the FHDDA and HDDA polymer/LC samples this decrease in the smectic layer spacing may be due to the gradual phase separation of the polymer from the liquid crystal as the polymerization proceeds. The situation is a markedly different for the fluorinated acrylate, HDFA. For this sample a slight decrease in the smectic layer spacing occurs during the 3 min of polymerization, but then the spacing appears to remain the same for the duration of the polymerization. Although a decrease in the smectic layer spacing is observed for the HDFA polymer/LC composite, the smectic layer spacing does not approach that of the original 8CB. This slight decrease in the smectic layer spacing may be attributed to volume shrinkage that is common in radical polymeriztions. Some correlation between the polymer structure and the segregation behavior appears to be evident. Network polymer structures, both aliphatic and fluorinated, phase separate while the linear fluorinated polymer structure, formed with HDFA, stays between the smectic layers.

To understand how the polymer structure is affected by and is affecting the liquid crystalline matrix, polarized IR spectroscopy was used to determine the functional group orientation from the monomer, polymer, and liquid crystal. While the previous results demonstrate the effect of the monomer and polymer on the smectic layer spacing, they do not describe the effect of the monomer and polymer on the order of the LC solvent. To use polymer stabilized composite systems for display applications, it is important that the monomer and polymer do not significantly disrupt the order of the liquid crystal. Polarized IR examines the orientation of the functional group with respect to polarization angle of the infrared light. If the sample being examined has a completely isotropic molecular arrangement, then as the polarization angle is varied, there would not be a change in the absorbance value of a given functional group. However, if the sample has an anisotropic arrangement, then, as the polarization angle is varied, there will be a change in the absorbance value as the light interacts with the molecules that are aligned in a preferential direction.

Figure 4a shows a polar plot of the 8CB cyano functional group absorbance as a function of polarization angle both before and after the addition of the monomer. Before the addition of monomer, the cyano functional group displays a characteristic dumbbell shape, indicating the anisotropic alignment of the LC molecules. From the direction of rubbing on the CaF_2 cells, the long axis of the molecule corresponds to 0° and 180°. In other words, the maximum absorbance is achieved when the light is polarized parallel to the molecule or interacts with the long axis, and the minimum is achieved when the light is polarized perpendicular to the molecule or interacts with the short axis of the molecule (90° and 270°). After the addition of monomer, this shape anisotropy is retained. The monomer does not appear to be altering the ordering of the liquid crystal. In fact, when the dichroic ratios are examined, an increase in



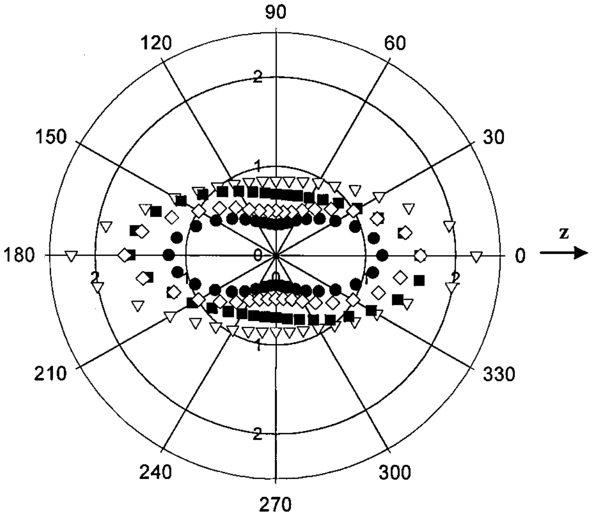


Figure 4. (a, top) Polar plot of CN stretch (2224 cm^{-1}) before polymerization for 5% HDDA (●), 5% HDFA (▽), and 5% FHDDA (■) in 8CB and for neat 8CB (◇). Dichroic ratios are 3.4, 5.1, 4.7, and 3.2, respectively. (b, bottom) Polar plot of CN stretch (2224 cm^{-1}) after polymerization for 5% HDDA (●), 5% HDFA (▽), and 5% FHDDA (■) in 8CB and for neat 8CB (◇). Dichroic ratios are 2.3, 3.5, 2.6, and 3.2, respectively.

the ratio is actually observed upon incorporation of monomer. Specifically, the dichroic ratio increases from 3.22 for pure 8CB to 5.09 for a 5% HDFA LC mixture. It appears that the monomer may actually be increasing the order of the LC to an extent.

After polymerization the distinct potential exists that the resulting polymer may have detrimental effects on the order of the liquid crystal. After polymerization of each of the monomer samples, however, the shape anisotropy is retained as shown in Figure 4b, a polar plot of the absorbance of the cyano group vs polarization angle after polymerization. The polymer, therefore, does not appear to be significantly affecting the order of the LC. These results fit well with the SAXS data presented in the previous section. For the diacrylate monomers, the polymer phase separates from the liquid crystal so that after polymerization the LC phase can adopt an orientation that is more like that of the pure liquid crystal. The fluorinated monoacrylate, however, stays segregated between the smectic layers, but the liquid crystal still retains its order. Though some disruption of the LC order is inevitable, this disruption is not significant and does not affect the overall orientation and order of the LC phase. This point is illustrated in Figure 4b, when looking at the dichroic ratios for the various polymer/LC composites. The dichroic ratios fall slightly below that of pure 8CB for 5% HDDA and 5% HDFA but are still well above 1.

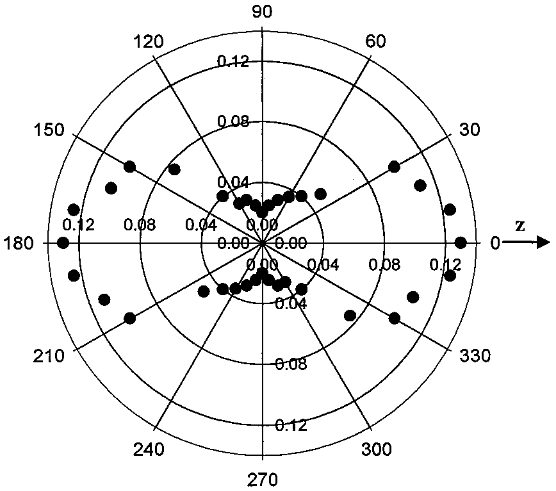


Figure 5. Polar plot of vinyl stretch (1631 cm^{-1}) of 8.3% HDFA in 8CB showing preferred orientation of vinyl groups.

To further understand how the monomer is organized before polymerization as well as to understand how the polymer is organized after polymerization, the orientation of the functional groups of the monomer and polymer was examined using polarized IR spectroscopy. The functional groups of interest are the vinyl and carbonyl groups of the monomer and the carbonyl groups of the polymer. The vinyl groups allow facile characterization of the orientation of the monomer before polymerization, while the carbonyl groups allow for characterization of the monomer as well as the polymer orientation after polymerization. Figure 5, a representative polar plot of the absorbance of the vinyl group of FHDDA vs polarization angle, shows the orientation of the vinyl group. Both HDDA and HDFA display similar shape anisotropies. The long axis of the functional group is the long axis of the dumbbell curve. The orientation of the vinyl group indicates that the functional group is aligned perpendicular to the smectic layer with the molecule having an orientation that is parallel to the smectic layer.

Figure 6a, a polar plot of the absorbance of the carbonyl group as a function of polarization angle for 7.25% FHDDA, shows the carbonyl group orientation before and after polymerization. In this case a characteristic shape anisotropy before polymerization does not exist, and at first, this appears to conflict with the results shown from the vinyl group, which does show a preferential orientation. This behavior is understood when the free rotation of the C═O bond is considered. Because of this free rotation at any point in time, the bonds are randomly oriented throughout the sample. Thus, at any polarization angle there will be the same absorbance for the carbonyl functional group. After polymerization the resulting polymer network has carbonyls that are distributed randomly throughout the network also. The situation is considerably different for the fluorinated monoacrylate, however.

The fluorinated monoacrylate, HDFA, has exhibited enhanced polymerization rates with respect to the diacrylate monomers in ordered smectic phases. HDFA also shows continued polymer segregation between the

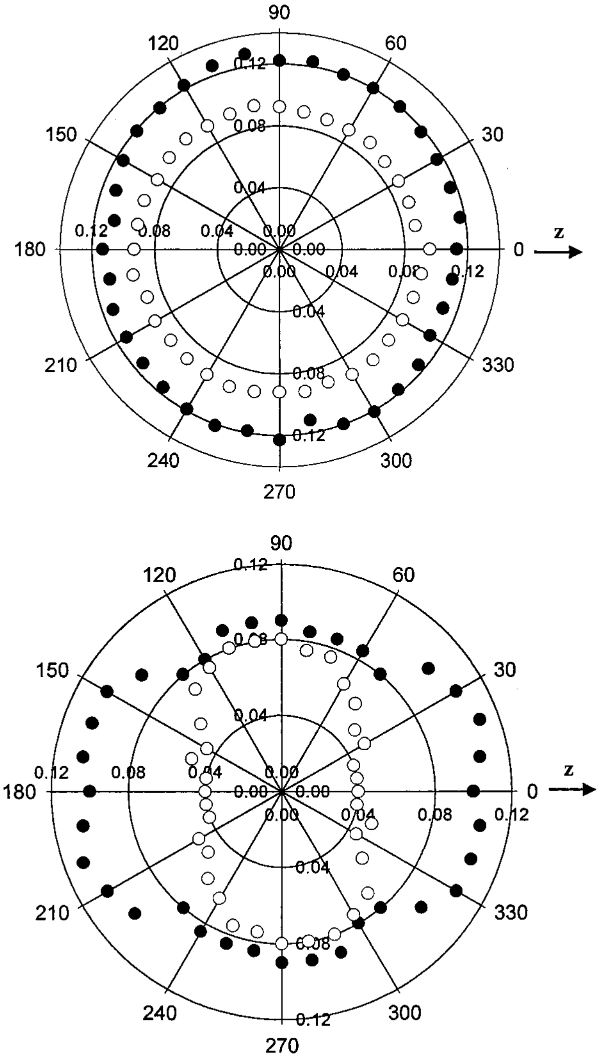


Figure 6. (a, top) Polar plot of carbonyl stretch (1740 cm^{-1}) of 7.2% FHDDA in 8CB before (●) and after (○) polymerization. (b, bottom) Polar plot of carbonyl stretch (1740 cm^{-1}) of 8.3% HDFA in 8CB before (●) and after (○) polymerization. Dichroic ratios are approximately 1 before polymerization and 1.8 after polymerization.

smectic layers after polymerization. Further differences are observed when examining the orientational behavior of the carbonyl group. Similar to the diacrylate monomers, no shape anisotropy of the carbonyl group is observed before polymerization due to the free rotation of the carbonyl bond. The situation is different when the carbonyl is examined after polymerization. The rapid polymerization and continued segregation of HDFA polymer leads to interesting characteristics in the LC. A large increase of the dichroic ratio from around one before polymerization to 1.81 after polymerization is observed as shown in Figure 6b, a polar plot of the absorbance of the carbonyl group from 8.3% HDFA in 8CB as a function of polarization angle before and after polymerization. This increase in the ratio suggests significant ordering of the polymer. After polymerization, a clear shape anisotropy exists for the carbonyl group of HDFA. This shape anisotropy, and the corresponding increase in the dichroic ratio, provides useful information about what is occurring during the polymerization. The monoacrylate forms a linear polymer in contrast to the diacrylate monomers that form network morphologies. Long chain fluorinated materials are known to be liquid crystalline,[18] and after polymerization the resulting HDFA polymer may order within the liquid crystal smectic phase. A possible explanation behind the shape anisotropy of the carbonyl of the polymer is that the carbonyls are locked into a fixed position due to the close packing of the side groups of the polymer chain. The ordered phase that is formed by the polymer, as well as the linearity of the polymer, may be one of the favorable driving forces behind the continued segregation of the HDFA polymer between the smectic layers.

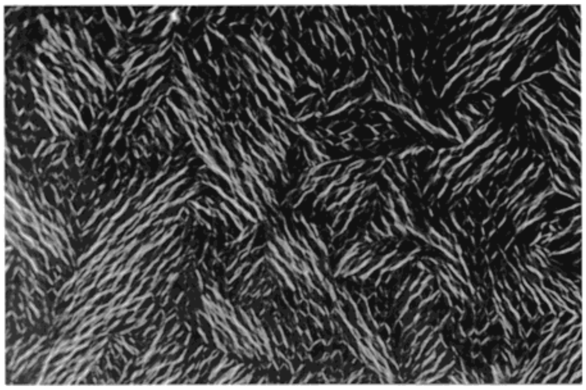


Figure 7. Optical texture (200×) of 4.9% poly-HDFA in 8CB obtained at 60 °C using a polarized microscope, demonstrating continued birefringence past the isotropic transition temperature (40 °C) of the liquid crystal.

Evidence of the effect of polymer anisotropy on the LC can be seen in Figure 7 which shows an optical micrograph of an 4.9% HDFA sample in 8CB at 60 °C. After polymerization, the poly-HDFA/LC sample can be heated well above the isotropic point of the LC (40 °C) with continued birefringence. While continued birefringence has been observed in anisotropic PSLC networks at temperatures above the clearing temperature of the LC formed from mesogenic diacrylates[23] in an LC solvent due to surface interactions, to obtain this same behavior from a linear polymer is unique. The ordering induced in the perfluorinated polymer during polymerization is retained at temperatures well above the clearing point of the LC up to temperatures as high as 90 °C. The ordered polymer will induce birefringence, but the observed degree of birefringence is much larger than would be produced from the percentages of polymer alone. The LC molecules also interact with the ordered polymer and thereby retain order and induce a high degree of birefringence at such elevated temperatures. This situation is unique to PSLC systems with HDFA and is not observed with the other LC/polymer systems studied.

Conclusions

The polymerization of fluorinated and aliphatic mono- and diacrylate monomers within a smectic liquid crystalline matrix affords a unique platform to study the evolution of polymer nanostructure within an LC matrix. Particularly interesting behavior is observed with a fluorinated monoacrylate (HDFA), especially when compared to a fluorinated diacrylate (FHDDA) and an aliphatic diacrylate (HDDA). While all three monomers segregate between the smectic layers before polymerization, only the fluorinated monoacrylate remains segregated between the smectic layers during and after the polymerization. In fact, once polymerized, the fluorinated acrylate exhibits dramatically enhanced order, whereas virtually no polymeric order is observed for the diacrylate monomers. This ordering induces polymer/LC interactions that allow LC ordering, and consequent birefringence, at temperatures well above the LC clearing point temperature. As the polymer chain grows, the segregation of the monomer and the ordering effect of the newly formed fluorinated polymer serve to drive the dramatically enhanced polymerization rate.

Acknowledgment. The authors thank the Southern Regional Education Board for their support of this work through a fellowship to DTM. The financial support of the National Science Foundation through a CAREER grant (CTS-0093911) is also gratefully acknowledged.

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MA010571R