Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article McCormick, Demetrius T. , Fordham, Zackary W. and Guymon, C. Allan(2003) 'Polymer nanostructure development of fluorinated and aliphatic monoacrylates in smectic liquid crystals via photopolymerization', Liquid Crystals, 30: 1, 49 — 58

To link to this Article: DOI: 10.1080/0267829021000041468

URL: http://dx.doi.org/10.1080/0267829021000041468

Liquid Crystals, 2003, Vol. 30, No. 1, 49–58

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Polymer nanostructure development of fluorinated and aliphatic monoacrylates in smectic liquid crystals via photopolymerization

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(*Received 24 June 2002; accepted 27 August 2002*)

To develop viable polymer stabilized liquid crystal systems, it is crucial to understand the factors that affect polymer nanostructure evolution. This work examines the influence of the photopolymerization of aliphatic and fluorinated monoacrylate monomer within a room temperature smectic liquid crystal (LC). Additionally, the effect of LC order on polymerization kinetics, monomer and polymer organization, and the effect of the polymer on LC properties have been examined. Through this work, insight has been gained regarding the impact that the introduction of a fluorinated monoacrylate monomer has on polymerization kinetics, LC organization, and monomer/polymer segregation and organization within a polymer/LC system. Fluorinated moieties lower the surface energy of the monomer to enhance segregation between the smectic layers of the LC as compared with an analogous aliphatic monomer. Additionally, the enhanced segregation significantly increases the polymerization rate in the smectic phase and drives the continued segregation of the fluorinated polymer during and after polymerization. Fluorination also leads to the formation of an ordered polymer nanostructure if polymerized in ordered LC phases. This ordering is particularly evident when the fluorinated monomer is polymerized in the smectic phase in which the monomer is organized between the smectic layers of the LC. In addition, the ordered polymer structure found with the fluorinated monomer in the smectic phase leads to continued birefringence above the clearing point of the LC due to surface interactions between the LC and the ordered fluorinated polymer. The continued birefringence offers an exceptional opportunity to examine how factors such as polymer molecular mass and UV light intensity affect the overall polymer morphology of these polymer/LC systems. As the initiator concentration and UV light intensity are decreased, longer polymer chains form lattice-type morphologies; whereas, shorter polymer chains form smoother morphologies that more closely mirror the texture of the LC smectic phase.

1. Introduction

Polymer stabilized liquid crystal (PSLC) systems have been studied extensively for their potential in applications such as privacy windows, high intensity light-shutter valves, and large area flat panel displays [1–4]. PSLC systems are generated by the photopolymerization of small amounts ($<5\%$) of monomer dissolved in a low molar mass liquid crystal. The polymer network in the PSLC may improve mechanical stability, but often also alters the electro-optic properties of the liquid crystal (LC) [5, 6]. Dynamic light scattering studies have shown that the polymer network substantially increases the twist elastic constant and viscosity of the low molar mass LC solvent [7]. It has also been shown that increases in polymer concentration may lead to an increase in the response times in PSLCs [8]. Most of recent research on PSLCs suggests that performance relates directly to the morphology of the polymer network [9–11]. Specifically, 'smoother, more defined' polymer morphologies lead to retention of PSLC electro-optic (EO) properties, whereas 'coarser, less defined' polymer morphologies lead to degradation of PSLC EO properties [9]. In addition, the temperature of photopolymerization for mesogenic monomers, and the consequent effect on polymer morphology and electro-optic properties have been investigated [10].

While the majority of the research examining polymer morphology in PSLCs has focused on the photopolymerization of mesogenic monomers within an LC solvent [12–14], some work has also detailed the polymerization kinetics and the organization of non-mesogenic acrylate monomers in ferroelectric polymer stabilized systems [15–19]. Specifically, certain non-mesogenic acrylate monomers segregate between the smectic layers of a ferroelectric liquid crystal. Understanding the location

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829021000041468

of the monomer within the LC before and after polymerization is critical for an understanding of the interactions between the polymer and the LC and the ultimate properties of the system. The monomer segregation behaviour will ultimately affect the resulting polymer morphology. Control of monomer segregation, and the resulting polymer nanostructure could give great flexibility in designing and developing PSLC systems.

The use of perfluorinated monomers offers a novel platform upon which to study the factors affecting polymer morphological evolution in polymer stabilized systems. Fluorinated compounds are typically characterized as having electrical resistance and low surface energies that lead to a variety of interesting characteristics [20]. In polymer dispersed systems, fluorinated monomers have generated systems with improved optical properties and more defined polymer morphologies than non-fluorinated systems [21]. Previous research has investigated the effect of fluorination, monomer structure and polymer structure on polymerization kinetics and polymer segregation behaviour in a smectic liquid crystal [22]. Interesting behaviour was observed when a fluorinated monoacrylate was compared with a fluorinated diacrylate and an aliphatic diacrylate. The fluorinated monoacrylate exhibited dramatically enhanced polymerization rates over the diacrylate monomers. Interestingly, all of the monomers studied segregated between the smectic layers of the LC, but both the fluorinated and aliphatic diacrylate (crosslinked) polymers phase separated out of the LC matrix. Only the fluorinated monoacrylate remained segregated between the smectic layers during and after polymerization.

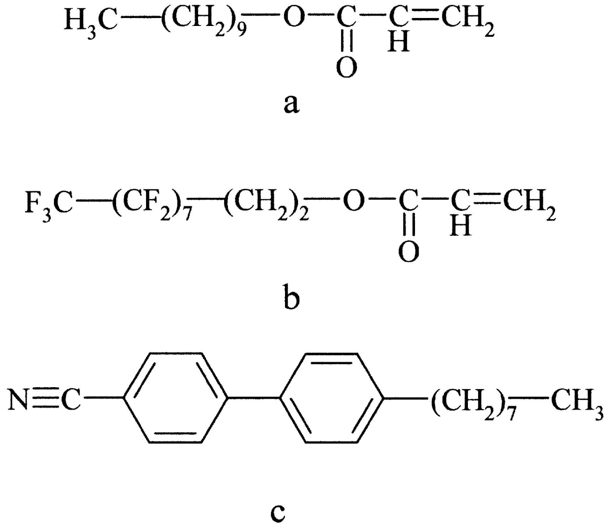
The goal of this work has been to understand the direct impact of incorporating fluorinated moieties into a linear polymer for polymer/smectic LC systems. To this end, the polymerization rate, monomer and polymerization organization, as well as monomer and polymer segregation behaviour were examined for a fluorinated monoacrylate and compared with these same characteristics for an aliphatic monoacrylate system. In addition, the LC phase characteristics were examined upon addition of monomer and after polymerization. The smectic layer spacing was determined before and after polymerization, and as a function of polymerization time, to investigate segregation behaviour. The orientation of monomer and polymer were also examined within the LC host. The polymerization kinetics of both the aliphatic and fluorinated systems were observed as a function of polymerization temperature and subsequent LC phase order.

Through this investigation, a greater understanding has been developed regarding the role that fluorinated moieties play in the segregation behaviour and polymerization kinetics of non-mesogenic monomers within a smectic liquid crystalline host. The role of these factors on polymer organization in a LC solvent was also examined. Further understanding of such aspects that affect the development of polymer nanostructure in PSLC systems is necessary for the further development of systems that successfully incorporate an internally stabilizing polymer without compromising the electro-optic properties.

2. Experimental

The fluorinated monomer used in this study was heptadecafluorodecyl acrylate (HDFA; Monomer-Polymer &/Dajac Labs, Feasterville, PA). The analogous non-fluorinated monoacrylate used was *n*-decyl acrylate (DA; Polysciences, Warrington, PA). The room temperature smectic A liquid crystal was 4-cyano-4′-*n*-octyl-biphenyl (8CB; Aldrich, St. Louis, MO). Chemical structures of the monomers and liquid crystal as well as the LC phase behaviour are given in figure 1. Photopolymerizations were initiated using Irgacure I-907 (Ciba Specialty Chemicals, Hawthorne, NY). All materials were used as received. The monomer/LC mixtures were prepared with initiator concentrations approximately 6 mol % of the total monomer double bond concentration.

The isotropic to nematic and nematic to smectic A phase transitions of the monomer/LC mixtures were measured using a polarized light microscope (Optiphot 2-pol; Nikon, Melville, NY) equipped with a temperature controlled hotstage (Instec, Boulder, CO). The samples were heated above the isotropic transition temperature and cooled at approximately 0.3°C min^{-1}.



$$H_3C{-}(CH_2)_9{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{H}{C}{=}CH_2$$

$$F_3C{-}(CF_2)_7{-}(CH_2)_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{H}{C}{=}CH_2$$

Figure 1. Monomer and liquid crystal structures of (*a*) decyl acrylate (DA), (*b*) heptadecafluorodecyl acrylate (HDFA), and (*c*) 4-cyano-4′-*n*-octylbiphenyl (8CB). Liquid crystal phase sequence of 8CB is isotropic → 40°C → nematic → 32°C → smectic.

Smectic layer *d*-spacings of the mixtures were measured using small angle X-ray scattering (SAXS, Siemans, XRD 700 WAXD/SAXS) with a CuK_α line of 1.5 Å. Bragg's law was used to determine the *d*-spacing for the smectic layers. Changes in SAXS behaviour as a function of polymerization time were examined using a temperature controlled SAXS cell.

Sample cells for polarized infrared (IR) absorption measurements were prepared by introducing the monomer/LC mixture by 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 $0.05^\circ\mathrm{C\,min}^{-1}$ from the isotropic to the smectic A phase. The alignment was checked using polarized light 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 ZeSe wire grid polarizer. The dichroic ratios, which are a measure of system order, were calculated as the ratio of 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 lamp. Polymerizations were initiated using 365 nm monochromatic light (unless otherwise noted) with an intensity of $1.5\,\mathrm{mW\,cm}^{-2}$. The DSC sample cell was attached to a refrigerated circulating chiller to achieve isothermal conditions. For rate studies, approximately 10 mg of the monomer/LC mixture was placed in an aluminium DSC pan. The samples were heated above the isotropic transition temperature of the monomer/LC mixture 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. Polymerization rate was calculated as shown elsewhere [22]. The polymerization rate as shown has units of s^{-1}, giving a normalized rate that allows for facile comparison of systems with different monomer concentration and type.

3. Results and discussion

The use of fluorinated materials has increased substantially over the past three decades due to their ease of synthesis and the fact that fluorine can readily replace hydrogen without gross distortion of molecular geometry [23]. The similarity of molecular geometry allows for facile comparison between the properties of hydrogen-containing compounds and fluorinated materials. Fluorinated compounds have already found a number of different industrial applications because of their interesting physical properties which include high thermal stability and low surface energies, and show great promise in a number of other areas.

The low surface energy of fluorinated materials, due to the electronic nature of the fluorine atom, gives rise to the self-associative nature of perfluorinated molecules. Consequently this self-association can lead to enhanced phase separation in polymer PDLCs [21]. Little research, however, has been dedicated to studying fluorinated monomers in polymer stabilized systems. The low surface energy of fluorine monomers has the potential to advance the formation of well defined polymer architectures within LC hosts that do not interfere with organization and electro-optic properties. Crucial to development of PSLC systems is an understanding of the factors that determine the formation of polymer nanostructure during photopolymerization of non-mesogenic monomers. Factors such as monomer chemical structure, resulting polymer morphology, and polymerization kinetics must be considered in order to develop a comprehensive picture of polymer evolution in these systems.

The mesophase order of a liquid crystalline solvent can significantly affect the polymerization mechanism. Previous research has shown that the order of the LC solvent has a significant impact on the polymerization of aliphatic and fluorinated acrylate and diacrylate monomers when polymerized in a smectic liquid crystal [15, 22]. Specifically, fluorinated and aliphatic acrylate monomers exhibit substantial increases in polymerization rate as the order of the liquid crystalline solvent increases. This increase in polymerization rate is a result of monomer segregation between the smectic layers of the liquid crystal.

To determine whether similar trends are observed in the polymerization of HDFA and DA in a smectic liquid crystal, polymerization rates were examined as a function of temperature. Figure 2 shows a plot of the maximum polymerization rate as a function of polymerization temperature for 3.4% DA and 6% HDFA in 8CB. The monomer percentages are such that each monomer/LC sample has the same total double bond concentration. Both monomer/LC systems show an increase in the polymerization rate as the polymerization temperature decreases or as the order in the anisotropic solvent increases, over the range of 15 to 45°C. The polymerization temperatures were chosen to sample each of the LC phases for the monomer/LC samples. Interestingly, the polymerization rate increase is appreciably higher for the HDFA system. The maximum polymerization rate of HDFA when polymerized in the smectic phase displays an almost ten-fold increase in the rate from polymerization conducted in the isotropic phase. In contrast, DA exhibits a more modest two-fold

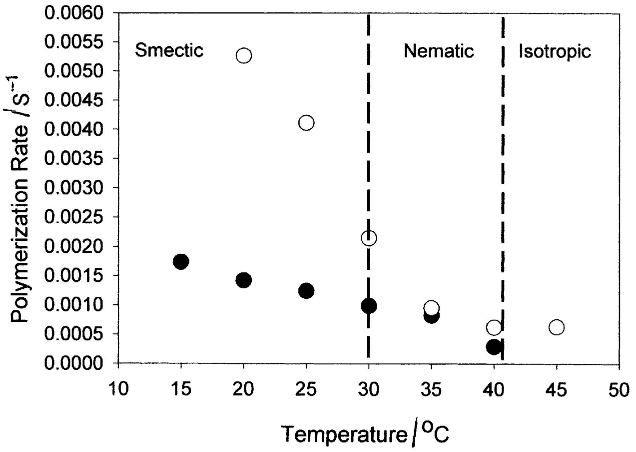


Figure 2. Maximum polymerization rate versus temperature for (○) 6% HDFA and (●) 3.4% DA in 8CB. Monomer concentrations were calculated to ensure equivalent double bond concentrations.

acceleration in polymerization rate in the smectic phase when compared with the isotropic phase. It is interesting to note that the maximum polymerization rate of HDFA in the smectic phase is almost four times greater than that of DA in the same phase. For both monomers, the LC appears to have an ordering effect on the monomers and thereby enhances the polymerization rate. This effect appears significantly enhanced in the fluorinated acrylate system. The dramatically enhanced polymerization rate may be due not only to the ordering effect of the LC, but also to enhanced segregation of the fluorinated monomer.

In an effort to understand the polymerization behaviour as well as to elucidate how the monomer/polymer affects the LC, the phase transition temperatures were examined for each of the monomer/LC mixtures. The table shows the isotropic–nematic and nematic–smectic phase transition temperatures for 6% HDFA and 3.4% DA in 8CB, after addition of monomer and after polymerization in the smectic A, nematic and isotropic phases. After addition of monomer, depression of transition temperatures is observed, common with addition of diluents to anisotropic solvents. However, it is interesting to note that the transition temperature depression of the smectic to nematic transition is much less in the HDFA (2.3°C) sample compared with the DA (5.5°C) sample. Similar behaviour is also observed in the isotropic to nematic transition for both monomer samples. The reason behind this disparity in transition temperature depression is probably due to the association of the aliphatic monomer with the oily aliphatic tails of 8CB. The low surface energy of the fluorinated monomer would prohibit interaction of the heavily fluorinated tails of HDFA with 8CB.

Interestingly, when the 6% HDFA/LC sample was polymerized in the ordered smectic phase, no increase was observed in the phase transition temperatures over those before polymerization. The 3.4% DA/LC sample, however, showed a marked increase in phase transition temperatures after polymerization in the smectic phase against the unpolymerized composite: approximately 4°C increase for the I–N transition and more than 7°C for the N–Sm transition. Both HDFA/LC and DA/LC systems exhibit an increase in the phase transition temperatures after polymerization in the nematic and isotropic phases. However, the increase is much less for the HDFA/LC samples than for the DA/LC samples. The phase transition temperatures of the composites polymerized in the less ordered nematic and isotropic phases actually approach the transition temperatures of the neat LC. The overall causes for this shift in the phase transition temperatures after polymerization in the less ordered phases may result from phase separation between the polymer and the LC. The DA/LC samples show larger increases in the LC phase transition temperatures after polymerization in the less ordered LC phases than do the HDFA/LC systems; the DA/LC samples also show a large increase in the phase transition temperatures when polymerized in the ordered smectic phase, whereas virtually no increase is observed when HDFA is polymerized in the smectic phase. This behaviour indicates that the aliphatic polymer may phase separate from the anisotropic solvent to a greater extent than the fluorinated polymer.

To illuminate further the unique polymerization and phase transition behaviour of HDFA, it is important to understand the segregation behaviour before, during, and after polymerization. Small angle X-ray scattering (SAXS) was used to investigate the smectic layer spacing as a function of increasing monomer concentration and polymerization time. Figure 3 is a plot of the smectic

Table. Phase transition temperatures of monomer/LC mixtures before and after polymerization in various LC mesophases.

Monomer/LC mixture	Before polymerization (I–N : N–Sm)/°C	Smectic phase polymerization at 23°C	Nematic phase polymerization at 34°C	Isotropic phase polymerization at 45°C
6% HDFA	37.7 : 27.3	37.6 : 27.3	38.7 : 29.8	39.5 : 31.4
3.4% DA	34.5 : 23.2	38.2 : 30.5	38.8 : 31.6	39.3 : 32.1
8CB Neat	40 : 32	NA	NA	NA

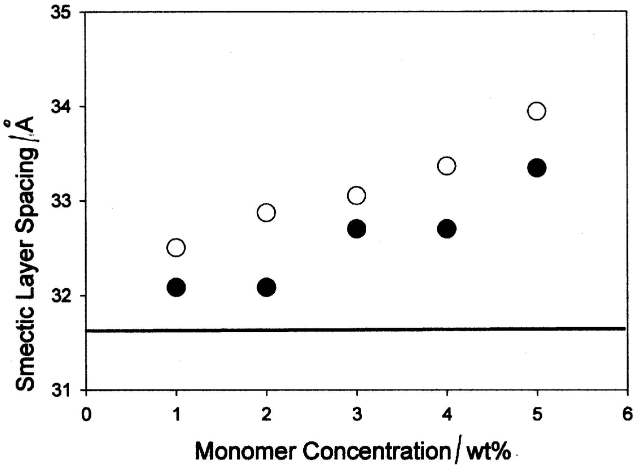


Figure 3. Smectic layer spacing of monomer/LC mixtures as a function of monomer concentration for (○) 6% HDFA and (●) 3.4% DA. The smectic layer spacing of 8CB neat is 31.6 Å and is denoted by the black line. The smectic layer spacing after polymerization for DA is 31.6 Å, which is indicative of phase separation of the aliphatic polymer from the LC matrix. The smectic layer spacing of HDFA after polymerization is 33.5 Å. This retention of the smectic layer spacing increase is evidence that the fluorinated polymer remains segregated between the smectic layers of the LC.

layer spacing of 8CB as a function of monomer concentration. As the monomer concentration is increased, a monotonic increase in the smectic layer spacing of the monomer/LC composite is observed. If the monomers phase separate from the LC, or if the monomer partitions within the smectic layers, an increase in smectic layer spacing with increasing monomer concentration would not be seen. This increase in the smectic layer spacing for both systems is clear evidence that the monomers are segregated between the smectic layers of the liquid crystal [16, 22].

While both monomers segregate between the liquid crystal smectic layers after their addition, the situation changes after polymerization. For a 3.4% DA/LC sample, the smectic layer spacing decreases to the smectic layer spacing of the pure liquid crystal (31.6 Å) after 5 min of polymerization. This behaviour indicates phase separation of the aliphatic polymer from the anisotropic solvent during the course of the polymerization. The HDFA/LC sample behaves differently. The smectic layer spacing increase observed upon addition of monomer (33.5 Å) is retained in a 6% HDFA/LC sample even after 10 min of polymerization. Therefore while the aliphatic polymer phase separates from the LC matrix, the fluorinated polymer remains sequestered between the smectic layers of the liquid crystal. Given that both of the polymers formed are linear, it is reasonable to assume that the fluorination of HDFA is at least partly responsible for continued segregation of the fluorinated linear polymer between the smectic layers of the liquid crystal.

As demonstrated, the polymerization of a monomer in the LC can affect inherent LC properties such as phase transition temperatures. The addition of monomer and its subsequent polymerization can also affect LC molecule organization in the liquid crystalline mesophase. An understanding of the effect that monomer and polymer have on the overall LC order is of great importance for controlling detrimental interactions between the polymer and LC. Any disruption in the LC order, in this case smectic order, can potentially affect electro-optic properties. A successful polymer stabilized system would minimize LC order disruption. A useful characterization method for the study of liquid crystalline order is polarized IR spectroscopy. This characterization technique allows for facile examination of the organization of the monomer and polymer structures within the anisotropic solvent. It is necessary to examine the organization of the monomer and the resulting polymer structures to understand controlled polymer nanostructure formation.

Figure 4 shows the IR absorption of the cyano functional group of 8CB before and after polymerization of 5% HDFA and 5% DA. The orientation of the cyano group is along the long axis of the LC molecule. Therefore, the cyano functional group order is also a good measure of LC order. The dichroic ratios give a more quantitative indication of the effect of the monomer on the LC solvent. The dichroic ratio of neat 8CB is 3.1. However,

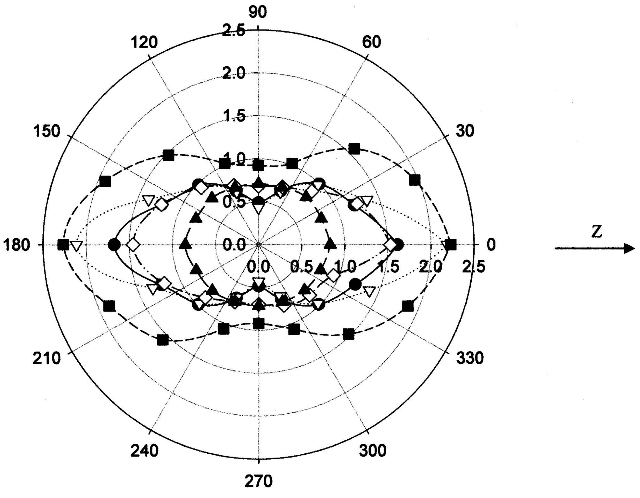


Figure 4. Polar plot of the cyano functional group stretch (2223 cm^{-1}) of 8CB as observed by polarized light IR for (●) 8CB neat, (▽) 5% HDFA before polymerization, (■) 5% HDFA after polymerization, (◇) 5% DA before polymerization and (▲) 5% DA after polymerization. Dichroic ratios are 3.2, 5.4, 2.1, 2.2 and 1.14, respectively. The director *Z* denotes the long axis of the LC molecule.

upon addition of DA the ratio decreases to 2.2. This decrease indicates that the aliphatic monomer disrupts the LC order to some degree, but the LC molecules still retain their overall order. Upon addition of the fluorinated monomer, the dichroic ratio increases to 5.4, a dramatic increase as compared with the aliphatic monomer. Such a large increase in the dichroic ratio suggests that the fluorinated monomer may actually enhance the orientation of the LC molecules in the system. The monomer could be ordering the liquid crystal through the formation of a more discreet monomer layer in between the smectic layers of the liquid crystal.

After polymerization, the resultant polymer has a definitive impact on the order of the LC molecules. The aliphatic polymer severely disrupts the order of the LC, driving the dichroic ratio of the cyano group down to 1.14 and a circular shape develops in the polar plot curve (figure 4). This behaviour suggests that the polymer causes an almost complete disruption of the LC order. The fluorinated polymer has a less dramatic effect. The dichroic ratio of the HDFA/LC polymer sample is 2.1. This reduction in the dichroic ratio does mean that some disruption of the overall LC order occurs, but the dichroic ratio is still well above one. It is interesting that the aliphatic polymer phase separates out of the LC matrix, and causes LC order disruption, but the fluorinated polymer remains segregated between the smectic layers of the LC and causes only limited reduction in LC order.

In order fully to understand the polymer nanostructure formation in these systems, it is necessary to understand the polymer organization within the LC and the role that fluorination may play in polymer organization. Figure 5 is a polar plot of the carbonyl group of 4% DA and 6% HDFA in 8CB before and after polymerization in the smectic phase. Before polymerization, the carbonyl stretches of both monomers display circular polar plot curves, which is indicative of no preferential ordering of the carbonyl functional group. In contrast to these results, the vinyl groups of similar systems exhibit preferential ordering [22]. The absence of ordering for the carbonyls is reasonable given the free rotation of the carbonyl bond. Though the molecules themselves are constrained within the LC matrix, the carbonyl has sufficient mobility to prevent the distinct ordering that is observed with the vinyl functional groups.

After polymerization, the situation changes dramatically. The carbonyl groups of the linear aliphatic (DA) polymer exhibit no preferential ordering; on the other hand, the linear fluorinated (HDFA) polymer shows a significant increase in carbonyl ordering (figure 5). This increase in carbonyl ordering can be directly seen when the dichroic ratios are considered. Before polymerization, the HDFA carbonyls of the monomer have a dichroic ratio around 1, whereas upon polymerizing the monomer, the dichroic ratio increases to approximately 2. This near doubling of the dichroic ratio, and the shape anisotropy of the polar plot curve, are clear evidence of induced ordering of the carbonyls and consequently of the fluorinated polymer itself. The decyl acrylate carbonyl dichroic ratios for the monomer and polymer stay at the same value of 1.

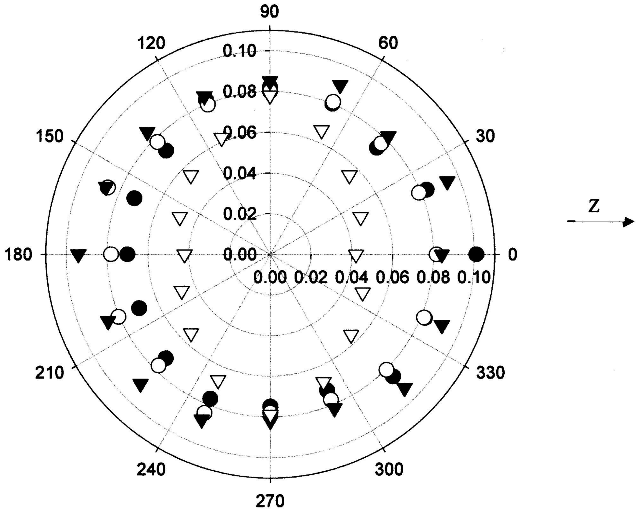


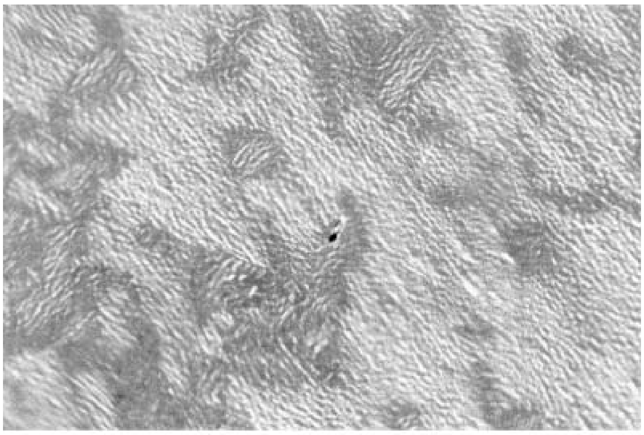
Figure 5. Polar plot of carbonyl functional group stretch as observed by polarized light IR ($1740\,\mathrm{cm}^{-1}$) of (●) 4% DA before polymerization, (○) 4% DA after polymerization, (▼) 6% HDFA before polymerization and (▽) 6% HDFA after polymerization. Dichroic ratios are 1.02, 1.04, 1.02 and 1.98, respectively.

As stated previously, the aliphatic polymer phase separates from the LC medium during the course of the polymerization. The lack of ordering of the carbonyls in the linear aliphatic homo-polymer is due to the random arrangement of the polymer in the phase separated domains. The linear fluorinated polymer, however, stays segregated between the smectic layers of the LC throughout the polymerization, and it is this sequestering effect that serves to drive the formation of the ordered polymer structure. This sequestering effect is two-fold. First, the fluorination of HDFA leads to the enhanced segregation of the monomer between the smectic layers of the LC. This enhanced segregation leads to accelerated polymerization rates in the smectic phase. The low surface energy of the fluorination also drives the continued segregation of the newly formed linear fluorinated polymer between the smectic layers of the LC, during and after polymerization and the formation of the ordered polymer structure.

Interesting and unique optical behaviour of the poly-HDFA PSLC system is observed after the formation of the ordered fluorinated polymer between the smectic layers of the LC. When the PSLC sample is heated above the isotropic clearing point of the LC (40°C), continued birefringence is observed that persists to temperatures as high as 90°C. This continued birefringence is a result of polymer–LC surface interactions that cause LC molecules to become 'anchored' to the polymer surface, as well as of the ordering of the polymer itself. It is interesting to note that neither the DA system, nor any other non-mesogenic monomer studied previously [22], displays this continued birefringence. This situation is unique to the linear fluorinated monomer and has only been previously observed with crosslinkable mesogenic monomers.

Since the liquid crystal molecules are anchored to the polymer surface, the continued birefringence, as observed through polarized light microscopy, may give clues as to the nature of the polymer morphology. Specifically, changes in the polymer morphology may be observed based on the LC phase in which the monomer is polymerized [4]. Figures 6(*a*) and 6(*b*) show optical photomicrographs of 5.2% poly-HDFA in 8CB observed at 60°C after polymerizing in the smectic and nematic phases, respectively. This temperature is more than 20°C above the clearing point of the neat LC. From the micrographs, large differences in the observed polymer morphology are seen as the order of the polymerization medium is altered. Finer 'honeycomb'-type structures form in the smectic phase polymerization whereas less defined polymer structures develop when the polymerization is conducted in the nematic phase. Interestingly, no continued birefringence is observed when the polymerization is performed in the isotropic phase. This behaviour implies that not only is the fluorination important in the formation of the ordered polymer structure, but that LC order during polymerization also plays a significant role. The ordered LC molecules serve to organize the HDFA monomer and aid in the formation of this unique polymer nanostructure.

The continued birefringence observed in the poly-HDFA/LC composites offers an interesting opportunity to investigate how issues such as initiator concentration and UV light intensity affect the observed polymer morphology in these polymer/LC composites. The UV light intensity and photopolymerization time were kept constant (8.2 mW cm^{-2}). Higher initiator concentrations should produce shorter polymer chains due to an increase in the number of radical chains being initiated; each sample was polymerized in the smectic phase. Figure 7 shows optical photomicrographs of 6% HDFA in 8CB with increasing initiator concentrations at 60°C. Significant changes in the polymer morphology are observed as the initiator concentration is increased and long polymer chains are generated. At the lowest initiator concentration of 0.1 wt %, figure 7(*a*), a defined, honeycomb polymer morphology develops. At the next higher initiator concentration, a smoother, finer polymer morphology and one more indicative of a smectic phase develops. The polymer morphology continues to become finer and at the highest initiator concentration, an extremely smooth polymer morphology is observed which is almost an exact image of the focal-conic textures in the smectic A phase. It is interesting to note that, as the polymer molecular weight decreases or as initiator concentrations increase, the birefringence of the polymer/LC composites increases. This increase indicates that more of the LC is anchored to the polymer surface of the lower molecular mass polymer. Apparently the polymer adopts the LC morphology to a greater degree at lower molecular mass. An optimum molecular mass should therefore exist that allows continued birefringence with maximum LC structure retention.



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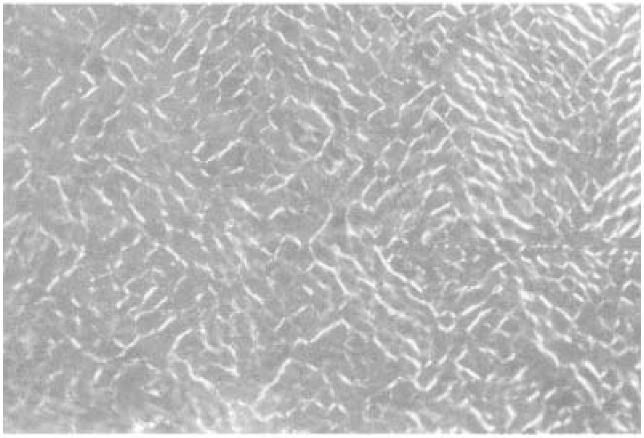

(*b*)

Figure 6. Optical photomicrographs at 60°C demonstrating continued birefringence of 5.2% HDFA polymerized in the (*a*) smectic phase at 25°C and (*b*) nematic phase at 35°C of 8CB. The clearing temperature of neat 8CB is at 40°C. No continued birefringence was observed after polymerization in the isotropic phase.

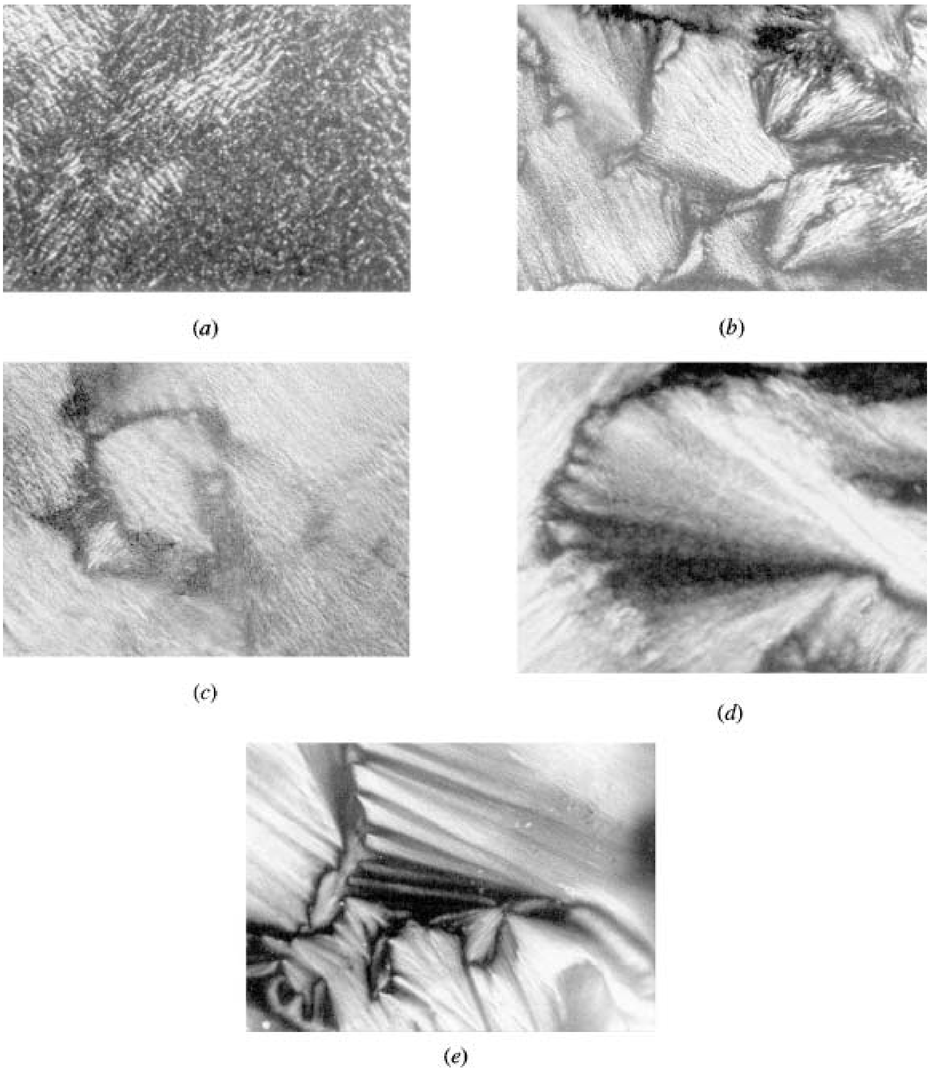

Figure 7. Optical photomicrographs of 6% HDFA polymerized at 25°C in the smectic phase with (*a*) 0.1, (*b*) 0.2, (*c*) 0.5, (*d*) and (*e*) 2 wt % I-907 at 25°C and shown at 60°C. The UV light intensity is 8.2 $\mathrm{mW\,cm^{-2}}$.

These structures may also be enhanced due to the increased rate of polymerization with increasing initiator concentration.

Further differences in polymer morphology are observed when the intensity of UV light is modulated. The UV initiation light intensity has a direct impact on the polymerization rate and molecular mass in UV curable systems. Lower polymerization rates are expected with lower UV light intensity while the rate increases with higher light intensity. Furthermore, lower UV light intensities lead to slower photopolymerization initiation rates and the generation of longer polymer chains in a given PSLC system. Conversely, high UV light intensities can potentially lead to higher initiation rates giving shorter polymer chains.

Figure 8 shows optical photomicrographs shown at 60°C of 6% HDFA in 8CB polymerized at various UV light intensities in the smectic phase at 25°C with 0.2 wt % photoinitiator. At the highest UV light intensity studied (1.2 $\mathrm{mW\,cm^{-2}}$), a lattice-type polymer structure is formed similar to the morphology exhibited by the poly-HDFA composites with lower initiator concentrations. When the UV light intensity is decreased a less coarse polymer morphology develops. Further reduction of the UV light intensity results in an even smoother morphology similar to that developed at 244 $\mathrm{\mu m\,cm^{-2}}$. No observable polymerization occurred at UV light intensities lower than 150 $\mathrm{\mu m\,cm^{-2}}$. It is curious that the polymer morphology that evolves at lower UV light intensities is very similar to those generated in higher initiator-containing poly-HDFA systems. Apparently, the shorter polymer chains allow greater degrees of continued birefringence and continued LC morphology. While the morphologies produced at lower UV light intensities are smoother than those at higher intensities, they are still considerably more defined than shorter chain polymer morphologies exhibited by higher initiator systems. These results indicate that lower molecular

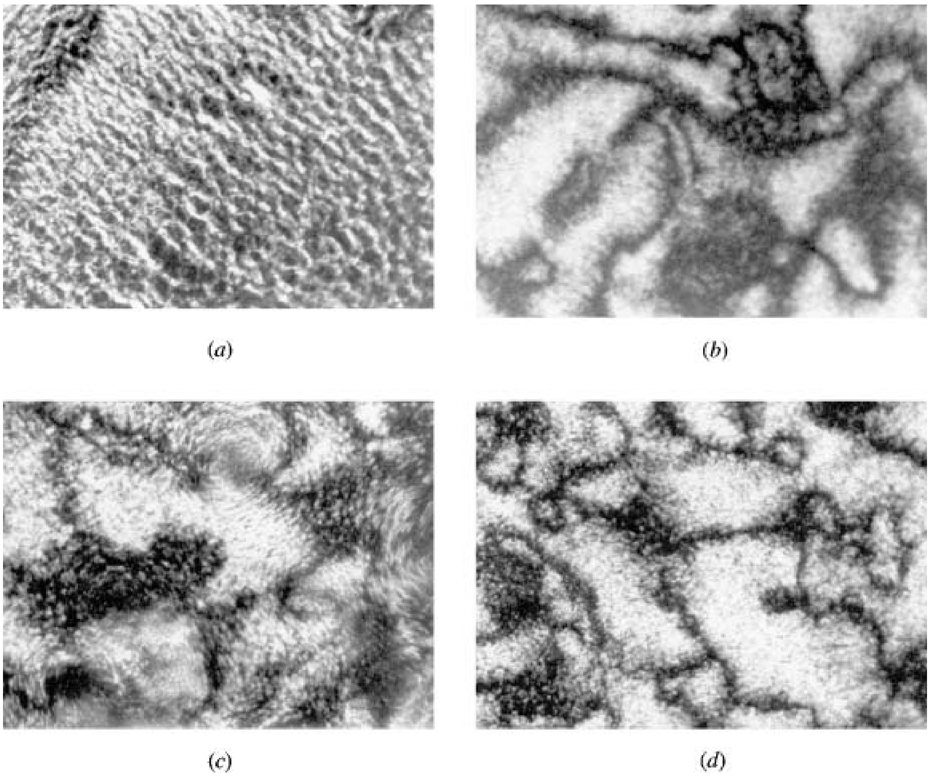

Figure 8. Optical photomicrographs of 6% HDFA (0.2 wt % I-907) polymerized at 25°C in the smectic phase with UV light intensities of (*a*) 1200, (*b*) 570, (*c*) 244 and (*d*) 150 $\mu W\,cm^{-2}$ shown at 60°C. Observable polymerization did not occur below 150 $\mu W\,cm^{-2}$.

masses allow optical structure retention and stabilization. On the other hand, polymerization must proceed to some extent to allow any continued birefringence, implying that perhaps an optimal molecular mass can be achieved to induce the desired polymer morphology and optical texture.

4. Conclusions

To allow development of desirable properties in polymer/smectic LC composites it is critical to understand the factors that affect the evolution of polymer nanostructure within the LC matrix. Factors including polymerization kinetics, monomer and polymer organization, as well as the impact of polymerization on the properties of the LC must all be understood, to control polymer nanostructure formation in these systems. Though the polymerization of an aliphatic and fluorinated monoacrylate, valuable insight has been obtained on the role of chemical structure, especially that of fluorinated materials, on polymerization in PSLCs.

Specifically, the fluorinated monoacrylate HDFA exhibits a significantly enhanced smectic phase polymerization rate over a comparable polymerization in the isotropic phase. Also, HDFA has a smectic phase polymerization rate that is three times faster than the smectic phase polymerization rate of the aliphatic monoacrylate DA. In addition, continued segregation between the smectic layers of the LC is observed during and after polymerization for poly-HDFA, while the aliphatic polymer phase separates from the LC matrix. A significant difference in resulting polymer structure is also obtained between poly-HDFA and poly-DA. After polymerization in the smectic phase, an ordered polymer structure is observed for HDFA, whereas no such order is observed for the aliphatic polymer. This formation of the ordered poly-HDFA is remarkable in that no such order is present in the monomer before polymerization. In addition, the induced polymeric order leads to a continued birefringence of the poly-HDFA composite at temperatures up to 50°C above the isotropic clearing point of the LC.

The formation of this ordered structure is dependent on the phase in which the polymerization is initiated, with dramatic changes occurring when the polymerization occurs in the smectic versus nematic mesophases, while no polymeric order is observed when the polymerization is conducted in the isotropic phase. This behaviour indicates that not only is the fluorinated nature of HDFA important to the formation of the ordered polymer structure, but that LC order also plays a critical role. Considerable changes in polymer morphology, as observed by the birefringence at elevated temperatures, occur as the molecular weight of the polymer is decreased, via changes in initiator concentration and UV light intensity. Longer polymer chains form lattice-type morphologies whereas shorter polymer chains form smoother structures more indicative of a smectic phase.

The authors would like to thank the National Science Foundation for financial support through a PECASE grant (CTS-0093911) and Eastman Company for support of D.T.M. through a fellowship.

References

[1] Hikmet, R. A. M., and Michielsen, M., 1995, *Adv. Mater.*, **7,** 300.

[2] Gu, D. F., Jameieson, A. M., and Chein, L. C., 1994, *Tech. Rep. ALCOM Symp.*, 101.

[3] Fung, Y. K., Sun, Y., Pfeiffer, M. T. P., Yang, D. K., and Doane, J. W., 1994, *Tech. Reports ALCOM Symp.*, 52.

[4] Rajaram, C. V., Hudson, S. D., and Chien, L. C., 1996, *Chem. Mater.*, **8,** 2451.

[5] Hikmet, R. A. M., 1991, *Liq. Cryst.*, **9,** 405.

[6] Hikmet, R. A. M., 1991, *Mol. Cryst.*, **198,** 357.

[7] Hikmet, R. A. M., and Higgins, J. A., 1992, *Liq. Cryst.*, **12,** 831.

[8] Hikmet, R. A. M., 1990, *J. appl. Phys.*, **68,** 4406.

[9] Muzic, D. S., Rajaram, C. V., Chien, L. C., and Hudson, S. D., 1995, *Poly. adv. Techn.*, **7,** 737.

[10] Dierking, I., Kosbar, L. L., Lowe, C., and Held, G. A., 1998, *Liq. Cryst.*, **24,** 387.

[11] Lee, S., Sprunt, S., and Chien, L. C., 2001, *Liq. Cryst.*, **28,** 637.

[12] Broer, D. J., Finkelmann, H., and Kondon, K., 1988, *Makromol. Chem.*, **189,** 185.

[13] Zhao, Y., Chénard, Y., and Paiement, N., 2000, *Macromolecules*, **33,** 1049.

[14] Fung, Y. K., Yang, D.-K., Ying, S., Chein, L.-C., Zumer, S., and Doane, J. W., 1995, *Liq. Cryst.*, **19,** 797.

[15] Guymon, C. A., and Bowman, C. N., 1997, *Macromolecules*, **30,** 1594.

[16] Guymon, C. A., and Bowman, C. N., 1997, *Macromolecules*, **30,** 5271.

[17] Guymon, C. A., Hoggan, E. N., Walba, D. M., Clark, N. A., and Bowman, C. N., 1995, *Liq. Cryst.*, **19,** 719.

[18] Guymon, C. A., Dougan, L. A., Martens, P. J., Clark, N. A., Walba, D. M., and Bowman, C. N., 1998, *Chem. Mater.*, **10,** 2378.

[19] Hikmet, R. A. M., Boots, H. M. J., and Michielsen, M., 1995, *Liq. Cryst.*, **19,** 65.

[20] Gangal, S. V., 1989, *Encyclopedia of Polymer Science*, Vol. 16, edited by H. F. Mark, N. M. Bilkales, C. G. Overberger, and Menges (New York: Wiley-Interscience), p. 557.

[21] Bunning, T. J., Schulte, M. D., Clarson, S. J., Natarajan, L. V., and Tomlin, D. W., 2000, *Liq. Cryst.*, **29,** 3182.

[22] McCormick, D. T., Chavers, R., and Guymon, C. A., 2001, *Macromolecules*, **34,** 6929.

[23] Chambers, R. D., 1973, *Fluorine in Organic Chemistry*, edited by G. A. Olah (New York: Wiley-Interscience), xxx.