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Liquid crystal displays are a subject of intense research interest because of their application to high definition display devices. Recently, polymer stabilized ferroelectric liquid crystals (PSFLCs) have been investigated due to the enhanced electro-optic properties of FLCs. We have utilized thiol-ene photopolymerizations to form a PSFLC system. Thiol-ene photopolymerizations are radical reactions, which proceed via a step growth reaction mechanism. During the polymerization, the polymer network structure is trapped into place due to the rapid transition from low molecular mass monomers and oligomers to high molecular mass polymer. This aspect is evidenced by phase transition data for the FLC, which indicates that the monomer and polymer are not phase separated from the FLC. Infrared dichroism shows that both monomer and polymer are ordered in parallel with the smectic layers of the FLC. Small angle X-ray scattering (SAXS) data show that both monomer and polymer are swelling the smectic layers. Thus, a polymer nanostructure is produced that serves as an ordered, stabilizing host for the FLC.

1. Introduction

Ferroelectric liquid crystals (FLCs) exhibit unique properties enabling their use in a variety of applications, including displays [1–3], telecommunication switching [4, 5], and optical storage [6, 7]. In particular, due to the increasing market for high definition displays, liquid crystal displays (LCDs) have become a prominent area of research in the LC field. LCs enable the production of displays with higher resolution, lighter weight, and reduced thickness.

Currently, nematic LCs are used extensively for LCD applications. However, nematic LCs have several drawbacks that limit their commercial viability for high definition displays, such as reduced viewing angles and slow switching speeds. FLCs have enhanced electro-optical properties relative to conventional nematic LCs, including wider viewing angles, higher contrast and resolution, and faster switching speeds [8, 9]. These properties make them desirable for use in high definition

displays. However, despite the significant benefits of FLCs, a number of difficulties have kept these materials from reaching large scale commercial applications, including defects, alignment, and stability issues [10–12].

One of the more significant drawbacks of FLCs is their susceptibility to mechanical shock [11]. Polymer/liquid crystal composites have been explored extensively to maintain LC properties while adding stabilization from a polymer network. Research in this area includes polymer dispersed LCs [13–20], main chain and side group polymeric LCs [21–24], anisotropic network stabilized FLCs [10, 25–27] and polymer stabilized LCs (PSLCs) [12, 27, 29–36].

The area of interest for this work is polymer stabilized FLCs (PSFLCs), which incorporate a small amount of polymer to form a polymer network in an attempt to stabilize the desired electro-optic and mechanical properties of the FLC while limiting defects [11, 26–28, 30, 37–39]. This work addresses the formation of a PSFLC in which the polymer network is formed *in situ* via a thiol-ene photopolymerization.

Previous investigations have demonstrated that small amounts of certain monomer species will segregate between

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the layers of smectic LC phases [12, 30, 40–42] (figure 1). This segregation increases the smectic layer spacing (d) and depresses the phase transitions [30]. It is also seen that during the formation of PSLCs and PSFLCs from acrylic monomers, the polymer phase separates from the FLC and the phase transition temperatures return to those of the neat FLC [30, 32, 33].

In this work, we have prevented phase separation during polymerization by dramatically changing the polymerization mechanism by utilizing thiol-ene monomers. Thiol-ene polymerizations are reactions utilizing multifunctional vinyl and thiol monomers. The polymerizations are photoinitiated radical reactions, which proceed via a step growth mechanism [43, 44]. During a step growth polymerization, divinyl monomers polymerized with dithiol monomers will form linear polymer chains. When the thiol and vinyl monomer functionality average is greater than two, a crosslinked polymer network is formed. A prominent feature of step growth polymerization, particularly important to this work, is that the molecular mass builds up more slowly and uniformly, with high molecular masses only achieved at relatively high conversions [45]. In contrast, during acrylic chain polymerizations, high molecular mass chains are generated at very low conversions due to the radical centre rapidly propagating through successive acrylate functional groups, leaving a mixture of high molecular mass polymer and unreacted monomer. We theorize that the low to intermediate molecular mass polymer chains, like the reactive monomers that formed them, remain soluble within the FLC layers. In the crosslinking thiol-ene system, the polymer becomes fixed in this configuration upon gelation, during which the transition from low molecular mass monomers and oligomers to a crosslinked network is extremely rapid [45]. This fixed configuration results in a polymer nanostructure containing layers of polymer dispersed between the liquid crystalline layers. A linear thiol-ene system is utilized to demonstrate that a crosslinked system is necessary to prevent phase separation.
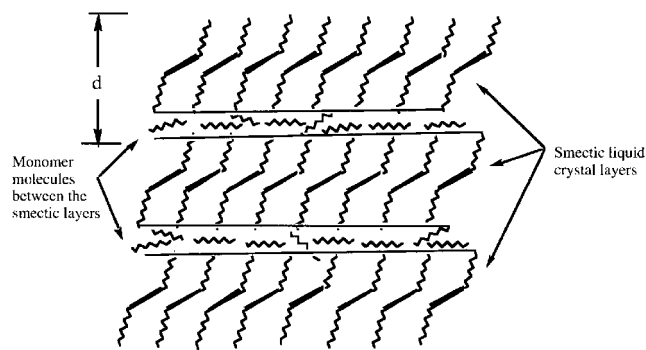
To identify formation of the host polymer nanostructure and measure its effects on an FLC, we have dissolved thiol-ene monomers in a 1/1 mixture of W82/W7. W82/W7 is a FLC, which exhibits isotropic, smectic A (48–58°C), and smectic C* (12–48°C) phases. Organization and orientation of the monomers and polymer between the smectic layers is identified through phase transitions, infrared (IR) dichroism, and small angle X-ray scattering (SAXS) experiments.

2. Experimental
2.1. *Materials*

Synthesis of the W82 and W7 liquid crystals is described elsewhere [46, 47]. All FLC samples are 1/1 mixtures by mass of W82 and W7. C6M liquid crystalline diacrylate was purchased from Merck UK (Poole, England). The crosslinking thiol-ene monomers used in this work are pentaerythritol tetra(3-mercaptopropionate) (the tetrathiol 1) and tri-N-allyltriazine trione (triallyl 2). The linear thiol-ene system comprises 1,6-hexanedithiol (dithiol 3) and trimethylolpropane diallyl ether (diallyl 4). All of the monomers and the photoinitiator, benzophenone, were purchased from Aldrich (Milwaukee, WI) and used as received. The molecular structures of the liquid crystals and monomers used are given in figure 2.

2.2. *Methods*

Optical Microscopy was performed on a Nikon Optiphot2-pol polarizing microscope (Melville, NY) equipped with a temperature controlled hot stage (Instec,

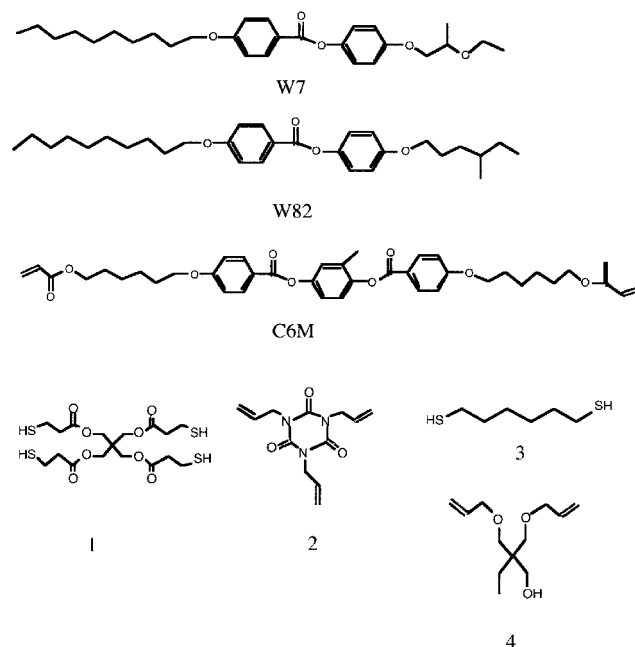Figure 1.   Monomer segregation between the liquid crystalline layers.

Figure 2.   Molecular structures of liquid crystals and monomers used in this work.

Boulder, CO). Liquid crystal cells were assembled using indium tin oxide (ITO) coated glass with a rubbed nylon alignment layer and $2\,\mu m$ spherical spacers in Norland optical adhesive 61 (Norland Ind., Cranbury, NJ). Phase transition temperatures were determined by observing optical changes in the samples while the sample cell was heated at a rate of $0.3^{\circ}C\,min^{-1}$.

IR dichroism was performed by placing a ZnSe wire grid polarizer in the chamber of a Magna IR 760 Nicolet FTIR spectrometer to obtain spectra from linearly polarized infrared radiation. Spectra were obtained at a resolution of $2\,cm^{-1}$. The absorption peaks monitored were the S–H vibration of the thiol peak at $2570\,cm^{-1}$, the urea carbonyl peak of the triallyl monomer and thiol-ene polymer at $1690\,cm^{-1}$, and the carbonyl peak of the FLC at $1730\,cm^{-1}$. Polar plots were generated by plotting the normalized peak area of the functional groups versus the polarization angle of the infrared radiation.

Smectic layer spacings were measured using a Kratky compact small angle X-ray scattering (SAXS) system on a Rigaku RU-200 X-ray generator with a CuK_{α} rotating anode source. Samples were placed in 1 mm quartz capillary tubes (Charles Supper Co., Natick, MA).

Polymerizations were performed with a B100 AP long wave ultraviolet Blak-Ray, (UVP, San Gabriel, CA), using a light intensity of approximately $10\,mW\,cm^{-2}$ measured with a Cole-Parmer Instruments Co. Series 9811 Radiometer.

3. Results and discussion

Monomers dissolved in an FLC act as impurities in the sample, reducing the phase transition temperatures of the FLC and producing a coexistence region between the smectic A and isotropic phases. An indication that phase separation occurs upon polymerization is that the phase transition temperatures return to those of the pure liquid crystal, as occurs when multiacrylates are used in PSFLCs [30]. We have observed in crosslinked thiol-ene systems that the phase transition temperatures remain depressed when the polymer does not phase separate (i.e. the polymer remains soluble between the smectic layers). We illustrate this effect using two different thiol-ene systems: the crosslinked thiol-ene system that suppresses phase separation, and the linear thiol-ene system which phase separates during polymerization.

When a crosslinking thiol-ene system is polymerized in the FLC, the phase transition temperatures remain depressed (figure 3), indicating that the polymer is not phase separating. In contrast, when the linear thiol-ene system is polymerized, the lack of crosslinks in the polymer network allows the polymer to phase separate macroscopically from the FLC host, allowing the smectic spacing and phase transitions to return to that of the
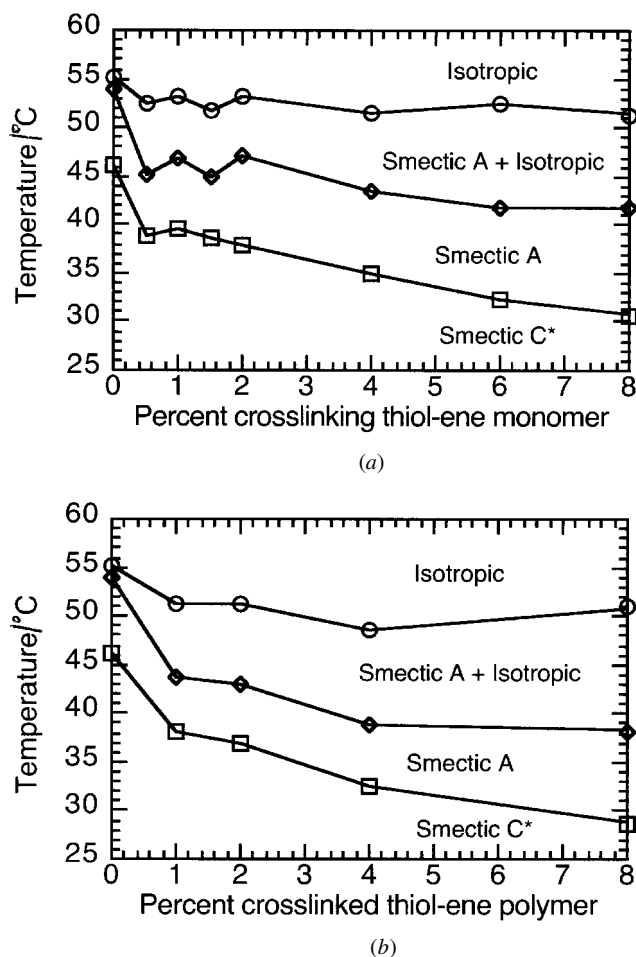

(*a*)

(*b*)

Figure 3. Phase diagrams for the triallyl and tetrathiol crosslinked thiol-ene system in W82/W7: (*a*) crosslinking thiol-ene monomers, (*b*) crosslinked thiol-ene polymer.

neat FLC. Incomplete return of the phase transition temperatures to those of the neat FLC is due to lower molecular mass polymer fragments that remain soluble in the FLC.

When a small amount of a liquid crystalline diacrylate (C6M) is incorporated into the thiol-ene/FLC systems, the C6M aligns in the smectic phases with the FLC [40, 42]. The acrylate functional groups at either end of the molecule are in the layer spacings with the thiol-ene monomers and are capable of copolymerizing with the thiol-ene monomers [44]. When C6M is used in conjunction with the linear thiol-ene system, it acts both as a crosslinking agent leading to the formation of a crosslinked polymer network and to form bridges between the polymer layers. Both of these phenomena serve to trap the polymer network between the smectic layers. The phase transition temperatures of the FLC are unaffected by the linear polymer, but show slightly depressed transitions with the addition of small amounts of C6M (figure 4).
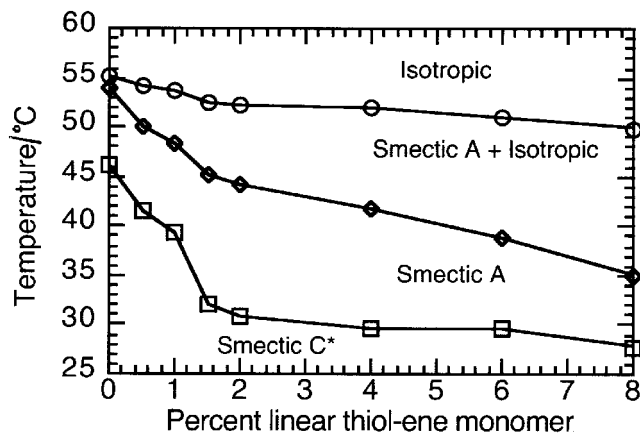
(a)
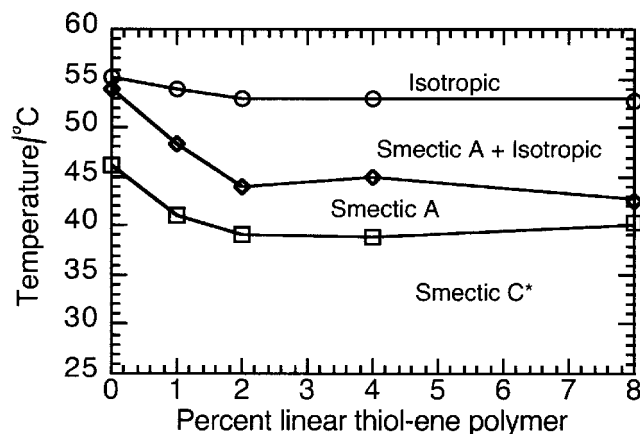
(b)
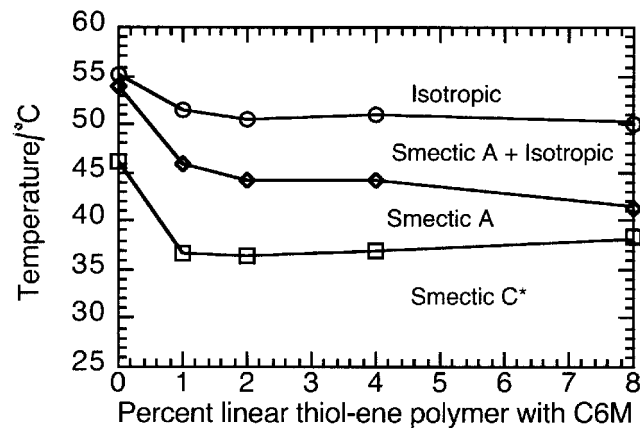
(c)

Figure 4. Phase diagrams for the diallyl and dithiol linear thiol-ene system in W82/W7: (a) linear monomers, (b) linear polymer, (c) linear polymer with 10 wt % C6M.

IR dichroism is utilized to probe the orientation of the monomer and polymer organized between the smectic layers of the FLC. A polar plot of the IR absorption bands of the carbonyl of the FLC, which aligns parallel

to the smectic layers, the S–H stretch of the thiol monomer, and the urea carbonyl of both the triallyl monomer and the polymer is presented in figure 5. Since the urea carbonyl of the triallyl monomer is preserved during polymerization, it is used to probe the orientation of both monomer (before polymerization) and polymer. As seen in figure 5, all of the functional groups exhibit strong dichroism, indicating anisotropic orientation of both monomer and polymer in parallel with the smectic layers.

Monomers and polymer segregated between the smectic layers will increase the overall smectic layer spacing while monomers or polymer that do not segregate between the smectic layers, or are phase separated, will have no effect on the smectic layer spacing. As indicated in table 1, when both linear and crosslinking thiol-ene monomers are dissolved in the FLC, the FLC exhibits increased layer spacing. Upon polymerization of the
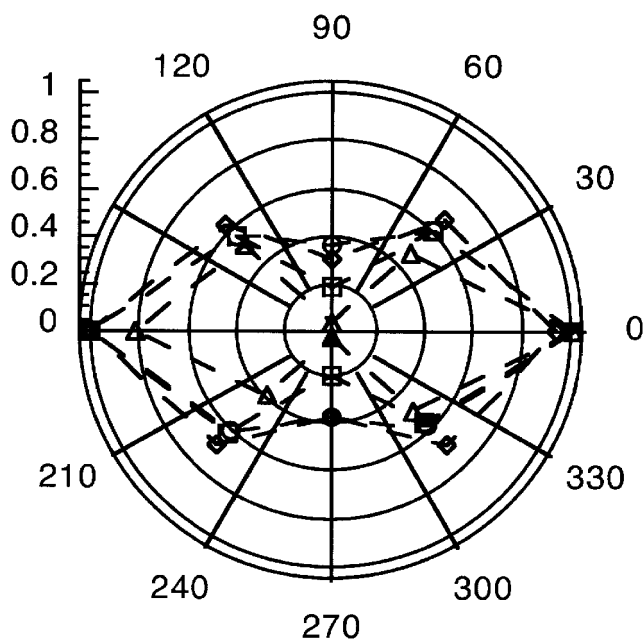
Figure 5. Polar plot of normalized absorbance for the functional group peak of the S–H stretch of the tetrathiol monomer □, the triallyl monomer carbonyl ◇, the triallyl carbonyl in the crosslinked polymer △, and the FLC carbonyl ○.

Table 1. SAXS layer spacing (Å) for 6 wt % linear and crosslinking thiol-ene monomer, polymer, and polymer with C6M in W82/W7[a]. Polymer with C6M contains 10 wt % C6M.

Sample	Monomer	Polymer	Polymer/C6M
6% Linear	33.3	31.1	32.1
6% Crosslinked	31.6	31.9	32.2

[a] Pure W82/W7 has a layer spacing of 30.6 Å.

linear thiol-ene system, the polymer phase separates from the FLC host and the swelling of the layers is significantly reduced. When C6M is incorporated into the linear system, reduction in swelling upon polymerization is less, due to the formation of a crosslinked polymer. These results are in agreement with the phase transition results of figure 3. In contrast to the linear system, when the crosslinking system is polymerized, the layer spacing is not reduced, but may be slightly increased (table 1). When C6M is added to the crosslinking system, the increase in layer spacing upon polymerization is more pronounced.

The presence of monomer or polymer leads to a reduction of the tilt angle in the smectic C* phase, which results in an additional increase of the layer spacing. This increase must be corrected to isolate the spacing increase due to layer swelling by the monomers or polymer. Table 2 gives the calculated layer swelling attributed only to monomer or polymer segregated between the smectic layers. Sub-angstrom layer spacing indicates that the monomer is not completely covering the layer interface.

The information presented in figures 2–4 and tables 1 and 2 indicates that the crosslinked thiol-ene polymer network is segregated between the smectic layers forming a host nanostructure for the FLC (figure 6). The polymer structure swells the layers by approximately 1.5 Å when small amounts of C6M are used to crosslink across the smectic layers.

Table 2. Calculated layer spacing swelling (Å) attributed only to monomer and polymer segregated between the smectic C* layers in W82/W7.

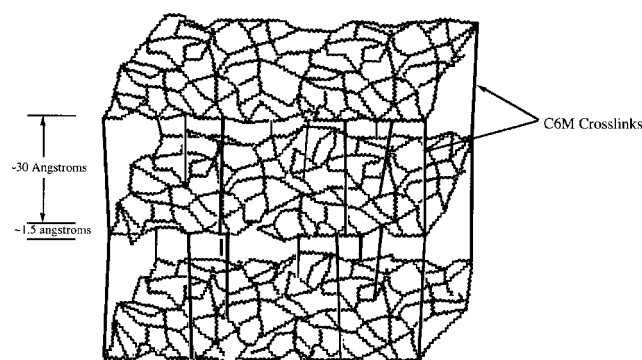| Sample	Monomer	Polymer	Polymer/C6M
6% Linear	2.6	0.3	1.1
6% Crosslinked	0.9	1.4	1.6

Figure 6. The crosslinked thiol-ene polymer network forms a nanostructure comprising layers of polymer approximately 1.5 Å thick interconnected with C6M, which serves as a host for the FLC.

4. Conclusions

Thiol-ene monomers that form both linear and crosslinked polymer are shown to segregate between the layers of an FLC. Upon polymerization, the linear polymer phase separated from the FLC, due to a lack of crosslinks. However, when the crosslinking thiol-ene systems are polymerized, forming a crosslinked polymer, they become locked into place between the smectic layers due to the extremely rapid gelation. Monomer and polymer that are segregated between the smectic layers exhibit strong dichroism as a result of anisotropic orientation. The FLC phase transitions are depressed by both monomer and crosslinked polymer, indicating that the polymer is not phase separating from the FLC. The SAXS data indicates that the crosslinked polymer layers are, on average, approximately 1.5 Å thick, and thus do not completely cover the smectic layers. The crosslinked polymer layers form a nanostructure, which serves as a host for the FLC.

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