

# Control of Anchoring of Nematic Fluids at Polymer Surfaces Created by in Situ Photopolymerization

Jian Zhou,<sup>†</sup> David M. Collard,<sup>‡</sup> Jung O. Park,<sup>†,§</sup> and Mohan Srinivasarao<sup>\*,†,‡,§</sup>

School of Polymer, Textile & Fiber Engineering, School of Chemistry and Biochemistry, and Center for Advanced Research in Optical Microscopy (CAROM), Georgia Institute of Technology, Atlanta, Georgia 30332

Received: September 29, 2004; In Final Form: February 18, 2005

In situ photopolymerization of alkyl acrylate monomers in the presence of a nematic fluid provides a cellular matrix of liquid crystalline droplets in which the chemical structure of the encapsulating polymer exerts control over the alignment (anchoring) of the liquid crystalline molecules. Control is obtained by variation of the alkyl side chains and through copolymerization of two dissimilar monofunctional acrylates. For example, among a series of poly(methylheptyl acrylate)s, the 1-methylheptyl analogue prefers planar anchoring of a nematic (TL205) over the temperature range studied. However, the polymers of other methylheptyl side chains display a homeotropic-to-planar anchoring thermal transition temperature similar to that of the *n*-heptyl analogue. Copolymerization of two monofunctional acrylates with opposing tendencies of aligning liquid crystal leads to tunability of anchoring behavior over a wide temperature range. The broad anchoring transitions we observed provide a way of achieving highly tilted anchoring.

## Introduction

A liquid crystalline (LC) phase in contact with an interface exhibits preferential alignment (so-called “anchoring”), in which the director of the LC phase can be parallel (“planar” anchoring, P), perpendicular (“homeotropic” anchoring, H), or tilted at an intermediate angle (tilted anchoring) to the interface.<sup>1</sup> Anchoring plays an important role in determining the electrooptical properties of liquid crystal-based devices.<sup>2</sup> Numerous techniques have been used to modify surfaces to control anchoring in LC devices, such as mechanical rubbing,<sup>3,4</sup> oblique evaporation of inorganic materials (e.g., SiO<sub>x</sub>),<sup>5,6</sup> photoalignment,<sup>7,8</sup> deposition of surfactants<sup>9,10</sup> and self-assembled monolayers,<sup>11–13</sup> grafting of polymer brushes,<sup>14</sup> and use of micropatterned surfaces,<sup>15–17</sup> etc. In most commercial LC display (LCD) devices, mechanical rubbing is used to provide a strong and unidirectional planar anchoring. Most of these techniques require a separate surface treatment step in the fabrication of LC devices. It would be an advantage to develop methods to obtain a desired alignment on a surface produced in situ, for example, by photopolymerization-induced phase separation. This process has been used to prepare LC–polymer composite films with a variety of morphologies: droplets-in-matrix morphology within typical polymer-dispersed liquid crystal (PDLC) films,<sup>18,19</sup> cellular morphology,<sup>20,21</sup> and parallel layer morphology.<sup>22</sup> In addition to their ease of manufacture, these LC–polymer composite films are compatible with methods used to make flexible LC displays.<sup>23,24</sup> However, the relationships between the alignment properties of nematic fluids and the encapsulating polymer surfaces are still poorly understood and need to be systematically explored. We have previously shown that the anchoring behavior of nematic fluids in a PDLC film can be controlled by the length<sup>20</sup> and branching<sup>21</sup> of the side chains attached to the backbone of the polyacrylate

matrix. In this paper, we demonstrate: (i) how the copolymerization of two monomers with opposing tendencies of aligning nematic fluids leads to the ability to tune the homeotropic-to-planar (H-to-P) anchoring transition temperature ( $T_I$ ) over a large range of temperatures, and (ii) why *continuous* H-to-P anchoring transitions occur at some copolymer surfaces, which are in contrast to *sharp* anchoring transition at homopolymer surfaces.<sup>20,21</sup> These results not only provide a convenient way of controlling anchoring in LC-based devices by tailoring polymer surfaces but also contribute to understanding the molecular origins of interfacial properties of nematic fluids.

LC alignment with a high pretilt angle to a substrate is usually desired in many LCD devices (for example, twisted nematic devices) because it prevents the formation of defect by inhibiting the bulk LC director from realigning in two opposite directions during a switching-off process and also helps to reduce threshold voltage.<sup>4,25</sup> However, a highly tilted anchoring is not commonly obtained without special surface treatments.<sup>1</sup> The techniques to achieve a high pretilt angle include tangentially evaporating SiO<sub>x</sub> materials to glass, rubbing polyimides with homeotropic aligning tendency,<sup>26</sup> deposition of two chemicals with competing anchoring tendencies,<sup>27</sup> using inhomogeneous surfaces,<sup>28</sup> or use of a continuous homeotropic-to-planar transition.<sup>29</sup> Here we report a highly tilted anchoring which can be readily obtained in situ by tuning the composition of the copolymer with which the nematic phase is in contact.

## Experimental Section

**Materials.** The nematic fluid we used, TL205 (EM Industries), is a mixture of chlorinated bi- and ter-phenyls with aliphatic tails of 2 to 5 carbons. This fluid displays a nematic phase from –20 to +87 °C, thereby allowing the exploration of the anchoring behavior over a temperature range greater than is possible with a single-component nematic.<sup>20</sup> 2-Ethylhexyl acrylate (2-EHxA), *n*-hexyl acrylate (C6A), *n*-octyl acrylate (C8A), *n*-decyl acrylate (C10A) and 1,1,1-trimethylol propane

\* Corresponding author. E-mail: mohan@ptfe.gatech.edu.

<sup>†</sup> School of Polymer, Textile & Fiber Engineering.

<sup>‡</sup> School of Chemistry and Biochemistry.

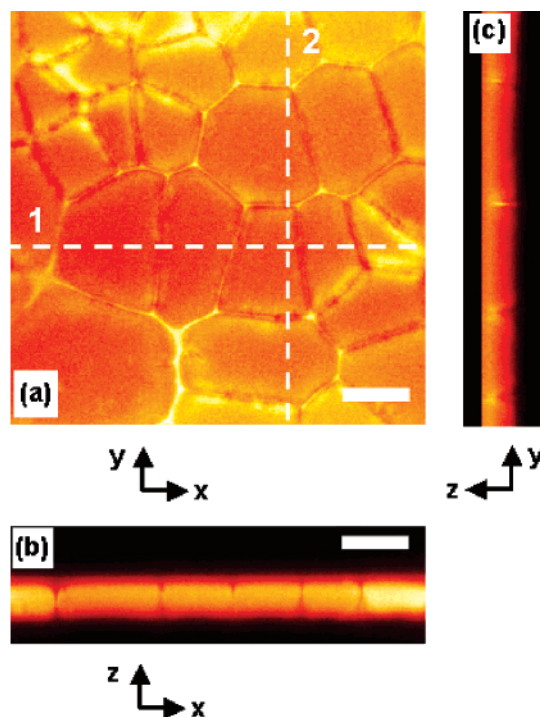
<sup>§</sup> Center for Advanced Research in Optical Microscopy.

triacylate were obtained from Scientific Polymer Products, Inc., and *n*-heptyl acrylate (C7A) was provided by Lancaster, Inc. All the monomers were used without further purification. The nematic fluid, monofunctional acrylate monomers and the triacylate cross-linker were mixed in an 80:18:2 weight ratio. The mixtures are homogeneous and isotropic at room temperature before polymerization. Mixtures consisting of two monofunctional acrylates were used to study the effect of copolymerization on the anchoring of LC phases, where the mole fraction of one monofunctional acrylate among the two was varied from 0 to 100 mol %. The triacylate was added to provide rigidity to the film structure. Approximately 0.5 wt % of Darocur 1173 (Ciba, Inc.) was used as a photoinitiator. Because the anchoring of LC is insensitive to the amount of the triacylate cross-linker within the range studied (less than 15 wt % of the total monomer),<sup>20</sup> we refer to the polymers made from one monofunctional acrylate and the triacylate as “homopolymers” and those made from two monofunctional acrylates and the triacylate as “copolymers” in this paper.

The surfaces of microscope glass slides (75 × 25 mm) and cover slips (22 × 22 mm) were rinsed by acetone, gently scrubbed with a swab, and dried with nitrogen flow before usage. Glass cells were assembled using a microscope glass slide, a cover slip, and 15- $\mu$ m glass microbeads (Duke Scientific) as spacer between the two glass substrates. The boundary of the glass cell was sealed by epoxy glue, but the two ends of the cell were left open before filling liquid samples into the cell.

**Photopolymerization and Film Morphology.** The reactive mixture of the nematic LC, acrylate monomer(s), triacylate cross-linker and photoinitiator was placed in the 15- $\mu$ m gap of a glass cell by capillary action, and exposed to UV irradiation of 360 nm with low intensity (50  $\mu$ W/cm<sup>2</sup>) until a cellular morphology was formed. The film was then cured at much higher UV intensity (16 mW/cm<sup>2</sup>) for 20 min. The resulting film morphology was visualized in three dimensions using a Leica-TCS SP laser scanning confocal microscope. Pyromethene 546 was added to the polymerization mixture to provide imaging contrast, which is known to align parallel with rodlike molecules.<sup>21</sup> The dye was excited with the 488 nm line of an Ar<sup>+</sup> laser, and the fluorescence was collected at 515–580 nm. As shown in Figure 1, a typical cellular morphology consists of one layer of close-packed polygonal LC cells between the two glass substrates. The size of the cellular LC cells was varied from 5 to 70  $\mu$ m by changing the conditions of the polymerization. Each LC cell is completely enclosed by the polymeric matrix, with thin vertical polymer walls extending from the top substrate to the bottom.

**Measurement of Anchoring Transition Temperatures.** The anchoring of nematic LC in the PDLC films was observed using a light microscope equipped with a hot stage (Linkam TMS 90, with an accuracy of  $\pm 0.1$  °C) and crossed polarizers. For the observation of a sharp transition (i.e., anchoring transition occurring within a narrow temperature window, e.g.,  $\leq 1$  °C), the samples were heated at 2 °C/min from room temperature, and then in 0.1 °C steps at temperatures close to the anchoring transition temperature, holding the temperature constant for 5 min between each step. For the observation of a broad transition (i.e., occurring within a temperature window of greater than 1 °C), the samples were heated at 2 °C/min from room temperature initially, and then in 0.3 °C steps through the whole process of the anchoring transition, holding the temperature constant for 5 min between each step. The measurement of  $T_i$  was repeated with at least two films prepared using the same

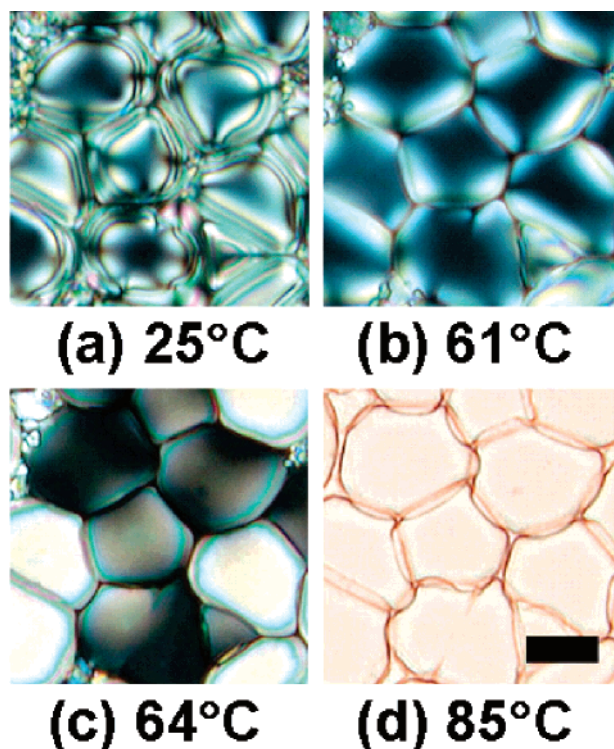


**Figure 1.** Cellular morphology observed by confocal microscopy: (a) *xy* optical section; (b) and (c) *xz* and *yz* optical sections taken along the dotted lines 1 and 2 of (a), respectively. The sample is made from TL205 and comonomer mixture of C8A and 2-EHxA (15/85 molar ratio). The scale bars are 20  $\mu$ m.

monomer composition and photopolymerization procedure. The reproducibility in measuring a sharp transition temperature of a single sample is  $\pm 0.1$  °C. Because the value of  $T_i$  and the nematic-to-isotropic clearing temperature ( $T_{NI}$ ) of the LC phase are sensitive to the composition of the nematic fluid, it is important that the photopolymerization be as complete as possible. On completion of photopolymerization, the  $T_{NI}$  of the resulting PDLC film reaches  $84 \pm 0.5$  °C. We have shown that  $T_{NI}$  drops from that of pure TL205 (87 °C) due to the unreacted monomer dissolved in the LC phase: a 3 °C decrease in  $T_{NI}$  here is caused by  $\sim 1$  wt % unreacted monomer left in the bulk LC phases of the PDLC films. Thus we estimate that the conversion of the total acrylate monomers at the end of the photopolymerization is approximately 95%.

## Results and Discussion

**Homopolymers: Effect of the Side Chain Branching on  $T_i$ .** The cellular structure of a PDLC film prepared from 2,2-dimethylhexyl acrylate is shown in the polarized light micrographs in Figure 2. At temperatures from room temperature up to  $T_i$ , the nematic fluid is homeotropically anchored; that is, the director of the nematogen is perpendicular to the cell wall. This is apparent from observation of the edges of the LC droplets that appear brightest when the projection of the wall is aligned at ca.  $\pm 45^\circ$  to the polarizer or analyzer (Figure 2a,b). The centers of the LC cells remain dark upon rotation of the sample under crossed-polarizers, indicating that the optical axis of the nematogen is along the direction of propagation of the light. The sample undergoes a homeotropic-to-planar anchoring transition at a temperature of 64 °C, displaying a dramatic change in appearance (Figure 2c). Above  $T_i$ , in-plane birefringence dominates the texture. The nematic–isotropic transition is also visible in the polarized light micrographs as the samples are heated above the nematic clearing temperature 84 °C (Figure



**Figure 2.** Polarized light microscopic images of the homeotropic-to-planar transition for a film made from 2,2-dimethylhexyl acrylate: (a)–(c) are taken under crossed polarizers and (d) is taken without polarizers ( $T_i = 64$  °C,  $T_{NI} = 84$  °C). The scale bar is 20  $\mu\text{m}$ .

2d). The  $T_i$  of the films made from methylheptyl or dimethylhexyl acrylates are summarized in Table 1. A sharp H-to-P anchoring transition (transition occurring within 0.1 °C) was observed for the film made from the polyacrylates that have the branches at positions other than C-1, with the anchoring temperature similar to those of the linear side chain analogues.<sup>21</sup> However, only planar anchoring of TL205 was observed for films with a 1-methylheptyl or 1,1-dimethylhexyl side chain (Figure 3), where the methyl branches are closest to the backbone of the polymer.

A thermodynamic model that accounts for enthalpic and entropic contributions to the interfacial energy explains the above H-to-P anchoring transitions.<sup>20,21</sup> We suggest that the unique planar anchoring behavior of the LC in contact with poly-(1-methylheptyl or 1,1-dimethylhexyl acrylate) surface is related to the side chain conformation of these polymers at the interface. These side chains are likely to adopt a “tilted” conformation with respect to the interface normal. The ordered packing of the side chains at the interface<sup>30</sup> becomes impossible and planar anchoring is thus preferred for entropic reasons.<sup>31</sup> This relationship between nematic alignment and side chain conformations is consistent with the observation of the alignment of liquid crystals by a monolayer of surfactant molecules on glass substrates.<sup>9</sup> A similar effect of side chain branching was also found in liquid crystalline molecules bearing a 1-methylheptyl chain as the nonpolar tail, where this tail plays an essential role in determining spatial packing of the molecules in the mesophases.<sup>32,33</sup>

**Effect of Copolymerization.** To further establish a link between the molecular structure of polymer surfaces and anchoring properties of the nematic fluids in the LC–polymer composite films, we have varied the structure of the polymers by copolymerization of branched (2-EHxA) and linear acrylates (C10A, C8A, C7A and C6A). Here we show that the  $T_i$  of

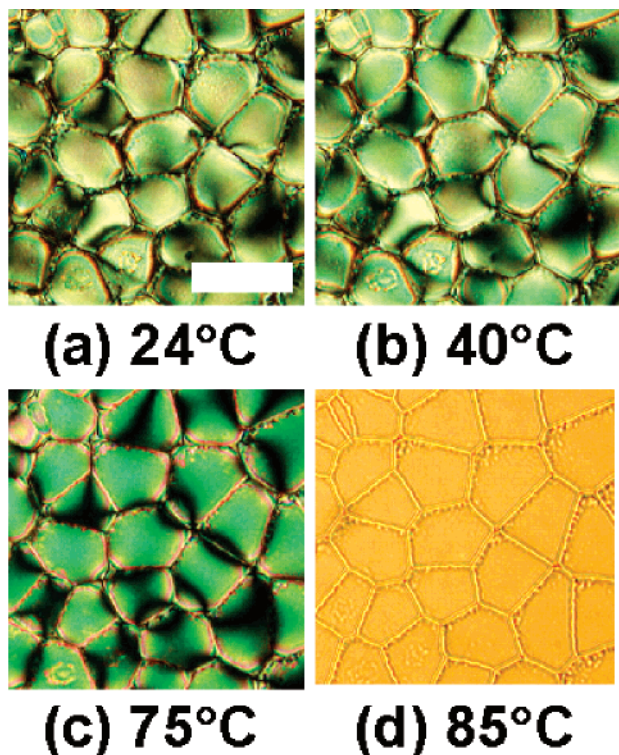
**TABLE 1: Anchoring Transition Temperatures ( $T_i$ ) of TL205 in PDLC Made from One Monofunctional Acrylate<sup>a</sup>**

Acrylate side chain	Monomer structure	$T_i$ (°C)
n-heptyl (C7A)		78
1-methylheptyl (1-MHA)		— <sup>b</sup>
2-methylheptyl (2-MHA)		78
n-hexyl (C6A)		65
1,1-dimethylhexyl (11-DMHxA)		— <sup>b</sup>
2,2-dimethylhexyl (22-DMHxA)		64
2-ethylhexyl (2-EHxA)		23
n-decyl (C10A)		81
n-octyl (C8A)		79

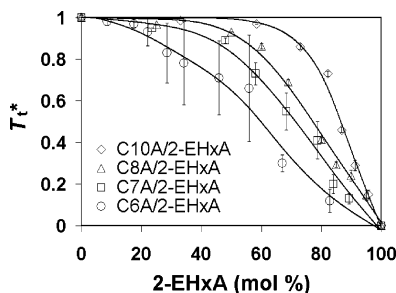
<sup>a</sup>  $T_{NI}$  of the nematic phases in all PDLC films is  $\sim 84$  °C. On the basis of the phase diagram of the binary mixture of monomer and TL205, this corresponds to  $\sim 1\%$  residual monomer in the LC-rich phase at the end of the photopolymerization. <sup>b</sup> Only planar anchoring was observed.

TL205 at a copolymer surface can be adjusted over the temperature range between the anchoring transition temperatures at the individual homopolymer surfaces.

Values of  $T_i$  at the copolymer surfaces are normalized such that  $T_i^* = (T_i - T_{i2}) / (T_{i1} - T_{i2})$ , where  $T_{i1}$  and  $T_{i2}$  are the anchoring transition temperatures of TL205 at the surfaces of individual homopolymers (the values of  $T_i$  at these homopolymer surfaces are listed in Table 1). The normalization offers good comparison of  $T_i$  between different monomer pairs. Figure 4 is a plot of  $T_i^*$  against the mole percentage of 2-EHxA in copolymerization mixtures with C10A, C8A, C7A, and C6A, respectively. All of the curves are nonlinear, and there is a strong dependence on the length of the linear alkyl side chain on the appearance of the curve. In the case of the PDLC films prepared by copolymerization of 2-EHxA with either C10A or C8A (case I), when the mole percentage of 2-EHxA is below 60 or 40 mol %, respectively, a sharp anchoring transition was observed with a value of  $T_i^*$  close to 1.0 (i.e.,  $T_i^*$  is similar to the film made by homopolymerization of the linear acrylate).  $T_i$  drops substantially only when the fraction of 2-EHxA exceeds 60 or 40 mol %. However, in the case of the films prepared from 2-EHxA and C6A (case II), the shortest linear homologue studied, even a small amount of 2-EHxA results in a lower  $T_i$ . The anchoring transitions of the films in case II were also found



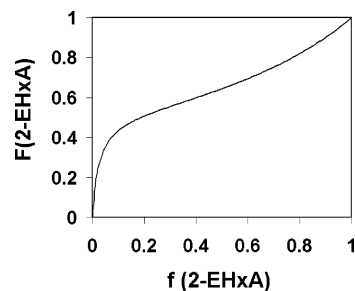
**Figure 3.** Polarized light microscopic images showing planar anchoring of the film made from 1-methylheptyl acrylate: (a)–(c) taken under crossed polarizers; (d) taken without polarizers. The scale bar is 30  $\mu\text{m}$ .



**Figure 4.** Plot of normalized anchoring transition temperature,  $T_t^* = (T_t - T_{t2}) / (T_{t1} - T_{t2})$ , against the molar composition of the comonomer mixtures. The monomer mixtures consist of 2-EHxA and one of the acrylates with linear alkyl side chain, C10A, C8A, C7A and C6A. Key: ( $\diamond$ ) the C10A/2-EHxA pair; ( $\triangle$ ) the C8A/2-EHxA pair; ( $\square$ ) the C7A/2-EHxA pair; ( $\circ$ ) the C6A/2-EHxA pair. The vertical bar on each data point represents the range of temperature over which the anchoring transition occurs.

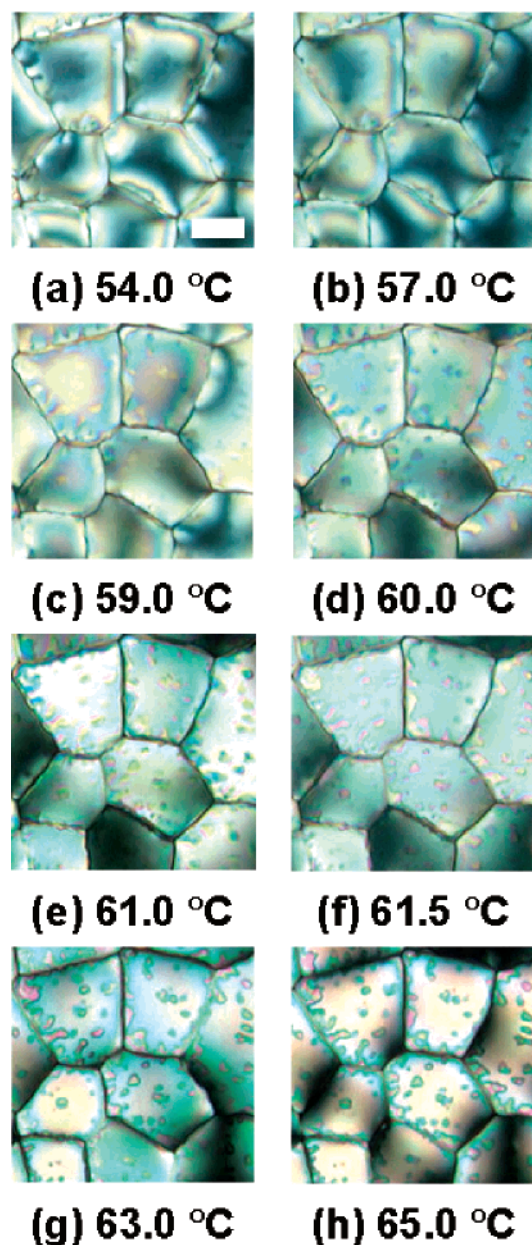
to occur over a broad temperature range (3–22  $^{\circ}\text{C}$ ), as indicated by the vertical bars on the data points in Figure 4. The films prepared by copolymerization of 2-EHxA with C7A is an intermediate case between case I and II.

Here the influence of copolymerization of acrylates on  $T_t$  can be understood in terms of the interfacial model for nematic alignment as suggested above and the kinetics of copolymerization. In the present system, the long linear alkyl chains at the interface may be considered to form ordered domains at low temperatures that favor homeotropic packing of nematic molecules. The incorporation of 2-EHxA into the interface through the random copolymerization presumably disturbs the order of these domains, due to the different side chain conformation of the branched side chain with respect to that of linear one.<sup>20,21</sup> This reduces the tendency of the nematic molecules to align homeotropically, and hence lowers  $T_t$ .



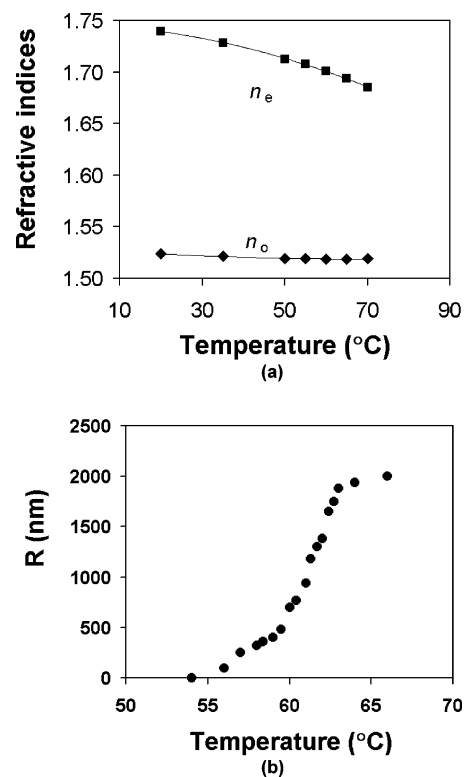
**Figure 5.** Plot of the calculated mole fraction of 2-EHxA in copolymers ( $F(2\text{-EHxA})$ ) versus the mole fraction of 2-EHxA in the starting monomer mixtures ( $f(2\text{-EHxA})$ ) for free radical copolymerization of *n*-octyl acrylate and 2-ethylhexyl acrylate (2-EHxA).

On the other hand, the composition of the monomer mixture in the copolymerization does not necessarily represent the composition of the copolymer at the LC–polymer interface. Because the anchoring of the LC is determined by the interactions between the nematic molecules and the side chains of the polymer at the LC–polymer interface, the value of  $T_t$  must reflect the copolymer composition at the interface. In case I, if the comonomer mixture contains 40–60 mol % or less of 2-EHxA, the anchoring behavior of the LC/copolymer interface is very similar to that of the LC/homopolymer of the linear alkyl acrylate, in terms of both  $T_t$  value and sharp transition characteristics (i.e., the H-to-P transition occurs over a narrow temperature range of  $\leq 0.1$   $^{\circ}\text{C}$ ), Figure 4. The chemical composition at these copolymer interfaces is presumably rich in the linear alkyl acrylate unit. That is, there is a nonuniform distribution of the copolymer composition in the polymer matrix of the PDLC film, which can be understood by considering the kinetics of copolymerization. On the basis of the Q–e scheme<sup>34</sup> for free radical copolymerization, the reactivity ratios of the monomer pair C8A ( $M_1$ ) and 2-EHxA ( $M_2$ ) are calculated to be 0.05 ( $r_1$ ) and 0.90 ( $r_2$ ), respectively. The relationship between the mole fraction of 2-EHxA in 2-EHxA/C8A monomer mixtures ( $f$ ) and that in the resultant copolymers ( $F$ ) is thus calculated and shown in Figure 5. During the process of polymerization-induced phase separation, 2-EHxA reacts faster and is depleted from the comonomer mixture during the early stages of the polymerization. The mixture becomes enriched in the less reactive monomer, C8A. As the polymerization is continued to high conversion, the less reactive monomer is over-represented in the interfacial region that is formed at the end of polymerization. A concentration gradient of comonomers in the polymer wall must be established in which the amount of 2-EHxA decreases upon proceeding from the interior of the wall out to the interface with the LC. Thus, the linear alkyl side chains still predominate at the interface even if the fraction of 2-EHxA in the comonomer mixture is as large as 40 mol % in this case. The same argument may be applied for all of the copolymers. As the side chain length decreases from C10A to C6A, the reactivity ratio difference between the two comonomers also decreases, and hence the polymer wall has a less steep concentration gradient, which results in a shorter plateau of  $T_t^*$ . Due to the similarity in reactivity ratio for the C6A/2-EHxA pair (i.e., case II), the corresponding copolymer interfaces possess appreciable amounts of both side chains as long as the composition of comonomer mixture is within an intermediate range. Therefore the broad anchoring transitions observed in this case can be explained by the coexistence of, and the competition between, the two opposite aligning tendencies for the nematic, arising from the two types of side chains at the LC/copolymer interface.



**Figure 6.** Polarized light microscopic images under crossed polarizers, showing broad homeotropic-to-planar transition. The film is made from C6A and 2-EHxA (C6A/2-EHxA = 72/28 mol/mol,  $T_i = 54\text{--}65\text{ }^\circ\text{C}$ ). The scale bar is  $20\text{ }\mu\text{m}$ . The thickness of the LC layer is  $11.5\text{ }\mu\text{m}$ , measured by laser scanning confocal microscopy.

**Variation of Tilt Angle during a Broad Anchoring Transition.** The temperature range over which a broad H-to-P anchoring transition occurs varies from 3 to  $22\text{ }^\circ\text{C}$ . The change in tilt angle of the nematic director as a function of temperature during such a broad transition can be estimated by the change in birefringence color of the LC cells under crossed polarizers.<sup>35</sup> As shown in Figure 6, the color in the central regions of each LC cell is sensitive to the temperature, changing gradually upon heating from low-order white to the fourth- or fifth-order in accordance with the Michel–Levy chart.<sup>36</sup> The tilt angle  $\theta$  ( $\theta$  is  $0^\circ$  if the nematic director is parallel to the substrate normal) was estimated using eqs 1 and 2, where the optical retardation,  $R$  (i.e., the effective birefringence ( $n_{\text{eff}} - n_o$ ) times the sample thickness  $d$ ), was obtained by referring the observed birefringence color to the Michel–Levy chart (Table 2). The refractive indices of LC,  $n_e$  and  $n_o$ , were measured by polarized Abbe



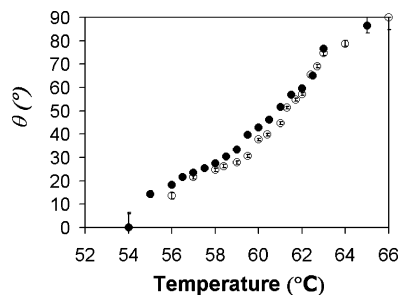
**Figure 7.** (a) Refractive indices and (b) retardation as a function of temperature for the calculation of the tilt angle of the nematics. The values of retardation were measured by referring the birefringence colors of the LC film at various temperatures in Figure 6 to Michel–Levy chart, for the film thickness of  $11.5\text{ }\mu\text{m}$ .

refractometry<sup>37</sup> (Figure 7a), and  $d$  was measured by laser scanning confocal microscopy.

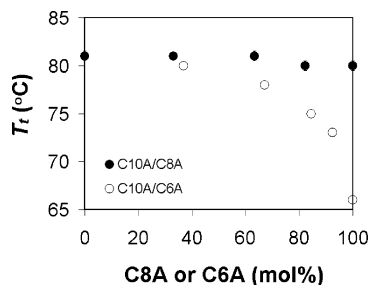
$$\cos^2 \theta = \frac{n_o^2 \left( \frac{n_e^2}{n_{\text{eff}}^2} - 1 \right)}{(n_e^2 - n_o^2)} \quad (1)$$

$$n_{\text{eff}} = n_o + R/d \quad (2)$$

For the above estimation,  $\theta$  was assumed to be constant through the thickness of the film (i.e.,  $\partial\theta/\partial z = 0$ ), which is reasonable due to the weak anchoring condition existing around the anchoring transition temperature.<sup>20,21</sup> The retardation versus temperature during the broad H-to-P transition in Figure 6 is given in Figure 7b, and the plot of  $\theta$  against temperature is shown in Figure 8. A detailed discussion of the mechanism for broad anchoring transitions based on the  $\theta(T)$  data is beyond the scope of this paper and will be addressed elsewhere. Nevertheless, Figure 8 is reminiscent of the continuous anchoring transitions previously reported,<sup>29,35</sup> during which the tilt angle of the LC phase changes gradually upon heating or cooling. The origins of the continuous anchoring transitions are not clear in these previous studies. Here, however, we attribute the nature of the broad anchoring transition to the competition between two anchoring forces arising from the two different side chains at the LC–polymer interface: one favors homeotropic anchoring and the other planar anchoring. It is also apparent in Figure 4 that the broad anchoring transition is more obvious in the films made by the copolymerization of C6A and 2-EHxA than in the other cases, which is consistent with the suggestion that C6A and 2-EHxA have similar reactivity ratios. In other words, the pair of C6A and 2-EHxA, having similar



**Figure 8.** Tilt angle  $\theta$  as a function of temperature during the broad homeotropic-to-planar transition shown in Figure 6. Solid circles and open circles represent the data obtained from two samples made from the same PDLC solution. The error bar of each data point is given by the error in estimation of retardation from birefringence color, ca.  $\pm 20$  nm.



**Figure 9.** Plots of anchoring transition temperature,  $T_t$ , against the composition of the comonomer mixtures for two monomer pairs with linear side chains: (solid circles) C10A with C8A; (open circles) C10A with C6A.

reactivity, forms an interfacial structure with comparable amount of both linear and branched side chains, thus showing broad transitions over a wide range of the composition of the comonomer mixture.

**Effect of Copolymerization of the Acrylates with Only Linear Side Chains.** The variations of  $T_t^*$  as a function of the composition of the comonomer mixtures consisting of two linear acrylates were also investigated. The result is shown in Figure 9. For copolymers of C10A and C6A, having a large difference in side chain length (and hence a large difference in reactivity ratio and individual anchoring temperatures), the  $T_t$  shows a similar behavior as in Figure 4. However, for the case of the two comonomers having similar side chain lengths (e.g., C10A and C8A, which have similar reactivity ratios and anchoring transition temperatures),  $T_t$  is almost constant across the entire composition range.

**Additional Comments on the Anchoring Mechanism.** The consistency we found in the relation between the anchoring of the nematic phase and the copolymer composition strongly suggest the mechanism of anchoring in such a system is due to molecular interactions between nematic phase and the side chains of the polymer. The mechanism based on the morphology or topography of the polymer surface is unlikely here. We have observed that for a LC-homopolymer composite system, the anchoring condition of a growing nematic droplet in the coarsening stage of the phase separation process during the PDLC film formation is exactly the same as that within the final film. Because the final morphology of the polymer surface is not formed yet for a growing nematic domain, this observation supports the above anchoring mechanism on the basis of molecular interactions. In fact, the final polymer surface morphology was formed in the presence of the nematic phase. The preexisting anchoring condition of the nematic phase may be imprinted into the morphology of the polymer surface, which

in turn should enhance such an anchoring.<sup>38</sup> The fact that the anchoring conditions and anchoring transition temperatures are reproducible for given acrylate systems also supports that the molecular interaction is indeed the driving force of the anchoring.

## Conclusions

We have demonstrated that three types of anchoring (planar, homeotropic and highly tilted) can be achieved in nematic LC-polymer composite films made by in situ photopolymerization of acrylates. The anchoring of the nematic fluid at a given poly-(alkyl acrylate) is controlled by both the temperature and the surface interactions between the alkyl side chains of the polymer and the nematic molecules. Planar anchoring is achieved on the polymer surfaces having branched alkyl side chains with methyl branches closest to the polymer backbone. Tuning the composition of copolymers of two dissimilar acrylate monomers allows for adjustment of the H-to-P anchoring transition temperature across a wide temperature range. The broad anchoring transitions observed at the copolymer surfaces are explained by the competition between two opposing anchoring forces arising from two different alkyl side chains at the interface. If a monomer with a branched side chain which provides a H-to-P transition temperature lower than room temperature (e.g., for the PDLC made from TL205 and isobornyl acrylate,  $T_t < -15$  °C)<sup>20</sup> is used for copolymerization with another appropriate linear acrylate (e.g., C6A), such a broad anchoring transition can be obtained around room temperature, which will be useful for the highly tilted anchoring desirable in many LC displays.

**Acknowledgment.** This work was supported by the National Science Foundation (CAREER award for M.S.) under Grant No. 0096240. We thank Dr. Karl Amundson for helpful discussions and Dr. Qingbing Wang for measurement of the refractive indices of TL205 as a function of temperature.

**Supporting Information Available:** Synthetic details and <sup>1</sup>H and <sup>13</sup>C NMR spectral data for methylheptyl acrylates and dimethylhexyl acrylates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Jerome, B. Surface effects and anchoring in liquid crystals. *Rep. Prog. Phys.* **1991**, *54*, 391 and references within.
- (2) Uchida, T.; Seki, H. In *Liquid Crystals: Applications and Uses*; Bahadur B., Ed.; World Scientific: Singapore, 1992; Vol. 3, pp 1-63.
- (3) Geary, J. M.; Goodby, J. M.; Kmetz, A. R.; Patel, J. S. The mechanism of polymer alignment of liquid-crystal materials. *J. Appl. Phys.* **1987**, *62*, 4100.
- (4) Ge, J. J.; Li, C. Y.; Xue, G.; Mann, I. K.; Zhang, D.; Wang, S. Y.; Harris, F. W.; Cheng, S. Z. D.; Hong, S.-C.; Zhuang, X.; Shen, Y. R. Rubbing-induced molecular reorientation on an alignment surface of an aromatic polyimide containing cyanobiphenyl side chains. *J. Am. Chem. Soc.* **2001**, *123*, 5768.
- (5) Armitage, D. Alignment of liquid-crystal on obliquely evaporated silicon-oxide films. *J. Appl. Phys.* **1980**, *51*, 2552-5.
- (6) Jerome, B.; Pieranski, P.; Boix M. Bistable anchoring of nematis on SiO films. *Europhys. Lett.* **1988**, *5*, 693.
- (7) Schadt, M.; Schmitt, K.; Kozinkov, V. Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers. *Jpn. J. Appl. Phys. Lett.* **1992**, *31*, 2155.
- (8) Ichimura, K. Photoalignment of Liquid-Crystal Systems. *Chem. Rev.* **2000**, *100*, 1847-73 and references within.
- (9) Proust, J. E.; Ter-Minassian-Saraga, L.; Guyon, E. Orientation of a nematic liquid crystal by suitable boundary surfaces. *Solid State Commun.* **1972**, *11*, 1227.
- (10) Porte, G. Tilted alignment of MBBA induced by short-chain surfactants. *J. Phys. (Fr.)* **1976**, *37*, 1245.

- (11) Gupta, V. K.; Abbott, N. L. Design of surfaces for patterned alignment of liquid crystals on planar and curved substrates. *Science* **1997**, *276*, 1533.
- (12) Miller, W. J.; Gupta, V. K.; Abbott, N. L.; Tsao, M. W.; Rabolt, J. F. Comparison of the anchoring of nematic liquid crystals on self-assembled monolayers formed from semifluorinated thiols and alkanethiols. *Liq. Cryst.* **1997**, *23*, 175.
- (13) Fang, J. Y.; Gehlert, U.; Shashidar, R.; Knobler, C. M. Imaging the azimuthal tilt order in monolayers by liquid crystal optical amplification. *Langmuir* **1999**, *15*, 297.
- (14) Ramdane, O. O.; Auroy, P.; Forget, S.; Raspaud, E.; Martinot-Lagarde, P.; Dozov, I. Memory-free conic anchoring of liquid crystals on a solid substrate. *Phys. Rev. Lett.* **2000**, *84*, 3871.
- (15) Lee, B. W.; Clark, N. A. Alignment of liquid crystals with patterned isotropic surfaces. *Science* **2001**, *291*, 2576.
- (16) Kitson, S.; Geisow, A. Controllable alignment of nematic liquid crystals around microscopic posts: Stabilization of multiple states. *Appl. Phys. Lett.* **2002**, *80*, 3635.
- (17) Kim, J. H.; Yoneya, M.; Yokoyama, H. Tristable nematic liquid-crystal device using micropatterned surface alignment. *Nature* **2002**, *420*, 159.
- (18) Doane, J. W.; Golemme, A.; West, J. L.; Whitehead, J. B.; Wu, B. G. Polymer dispersed liquid-crystals for display application. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511.
- (19) Drzaic, P. S. *Liquid Crystal Dispersions*; World Scientific: Singapore, 1995; Chapter 1.
- (20) Amundson, K. R.; Srinivasarao, M. Liquid-crystal-anchoring transitions at surfaces created by polymerization-induced phase separation. *Phys. Rev. E* **1998**, *58*, R1211-4.
- (21) Zhou, J.; Collard, D. M.; Park, J. O.; Srinivasarao, M. Control of the anchoring behavior of polymer-dispersed liquid crystals: Effect of branching in the side chains of polyacrylates. *J. Am. Chem. Soc.* **2002**, *124*, 9980.
- (22) Vorflusev, V.; Kumar, S. Phase-separated composite films for liquid crystal displays. *Science* **1999**, *283*, 1903.
- (23) Penterman, R.; Klink, S. I.; de Koning, H.; Nisato, G.; Broer, D. J. Single-substrate liquid-crystal displays by photoenforced stratification. *Nature* **2002**, *417*, 55.
- (24) Huitema, H. E. A.; Gelinck, G. H.; van der Putten, J. B.; Kuijk, K. E.; Hart, C. M.; Cantatore, E.; Herwig, P. T.; van Breemen, A. J.; de Leeuw, D. M. Plastic transistors in active-matrix displays – The handling of gray levels by these large displays paves the way for electronic paper. *Nature* **2001**, *414*, 599.
- (25) Bos, P. J.; Fredley, D.; Li, J.; Rahman, J. In *Liquid Crystals in Complex Geometries*; Crawford, G. P., Zumer, S., Eds.; Taylor and Francis: Great Britain, 1996; pp 281–9.
- (26) Sinha, G. P.; Wen, B.; Rosenblatt, C. Large, continuously controllable nematic pretilt from vertical orientation. *Appl. Phys. Lett.* **2001**, *79*, 2543.
- (27) Filas, R. W.; Patel, J. S. Chemically induced high-tilt surfaces for liquid crystals. *Appl. Phys. Lett.* **1987**, *50*, 1426.
- (28) Ong, H. L.; Hurd, A. J.; Meyer, R. B. Alignment of nematic liquid crystals by inhomogeneous surfaces. *J. Appl. Phys.* **1985**, *57*, 186.
- (29) Patel, J. S.; Yokoyama, H. Continuous anchoring transition in liquid crystals. *Nature* **1993**, *362*, 525.
- (30) Roussel, F.; Canlet, C.; Fung, B. M. Morphology and orientational order of nematic liquid crystal droplets confined in a polymer matrix. *Phys. Rev. E* **2002**, *65*, Art. No. 021701.
- (31) Sharlow, M. F.; Gelbart, W. M. On the parallel perpendicular transition for a nematic phase at a wall. *Liq. Cryst.* **1992**, *11*, 25.
- (32) Walba, D. M.; Korblova, E.; Shao, R.; MacLennan, J. E.; Link, D. R.; Glaser, M. A.; Clark, N. A. A ferroelectric liquid crystal conglomerate composed of racemic molecules. *Science* **2000**, *288*, 2181.
- (33) Collard, D. M.; Lillya, C. P. Structure–property relationships for the thermal phase behavior of discotic liquid crystals: the effect of branching and unsaturation in the side chains of disklike molecules. *J. Am. Chem. Soc.* **1991**, *113*, 8577.
- (34) Greenley, R. Z. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley and Sons: New York, 1999; p II-268.
- (35) Ryschenkow, G.; Kleman, M. Surface defects and structural transitions in very low anchoring energy nematic thin films. *J. Chem. Phys.* **1976**, *64*, 404.
- (36) Bloss, F. D. *Optical Crystallography*; Mineralogical Society of America: Washington, DC, 1999; Chapters 6 and 8.
- (37) George, A. K. Optical anisotropy of nematic liquid crystals. *Phys. Chem. Liq.* **1998**, *37*, 65.
- (38) Amundson K. R. Imprinting of nematic order at polymer network surfaces as a function of cross-link density. *Phys. Rev. E* **1999**, *59*, 1808.