RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 58, NUMBER 2 AUGUST 1998

Liquid-crystal-anchoring transitions at surfaces created by polymerization-induced phase separation

Karl R. Amundson and Mohan Srinivasarao*
Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974

(Received 29 May 1998)

A surface anchoring transition of a nematic at polymer surfaces created by polymerization-induced phase separation is presented. This transition is unusual in that it occurs far from bulk nematic phase transitions and it is tunable across nearly the entire nematic temperature range by modification of the polymer side group. Anchoring behavior is qualitatively understood by considerating enthalpic and entropic contributions to surface energy. Interesting behavior of some polymer-dispersed liquid-crystal films is explained, and observations provide a pathway to control properties. [S1063-651X(98)50308-X]

PACS number(s): 64.70.Md, 64.75.+g

Surface energetics of liquid crystals is intriguing and crucial for technologies that use liquid crystals, such as flat-panel displays and optical components. The fact that liquid crystals exhibit preferential orientation at interfaces, a phenomenon called surface anchoring, has been known for over 80 years, but its molecular origins are still elusive. Whether a liquid-crystal material prefers to orient with the director **n** normal to the interface (homeotropic anchoring), in the plane of the interface (homogeneous anchoring), or along a tilted direction or directions depends upon subtle interactions that are not well understood. Unidirectional homogeneous alignment can be produced by rubbing a substrate [20] and homeotropic alignment by treating the bounding surfaces with amphiphilic alkyl compounds such as surfactants [1–4]. The less common tilted anchoring has been seen at a glass surface exposed to smoke soot [19] or coated with a commercial fluorinated surfactant [5].

Transitions between surface anchoring states are particularly exciting because they arise from a competition between opposing components of surface anchoring. A number of nematic surface anchoring transitions have been observed. Most of them occur close (within ~10 K) to *bulk* phase transitions of the nematic to isotropic, smectic, or crystalline phases. Noting the sensitivity of several contributions to surface anchoring on the bulk nematic order parameter S, surface anchoring transitions near the nematic-isotropic transition have been attributed to the rapid decrease in S upon heating close to the nematic-isotropic transition [6]. Near the transition to smectic or crystalline phases, pretransitional layering near surfaces has been cited to explain transitions to homeotropic anchoring [7].

Surface anchoring transitions very far from bulk phase transitions are rare. Volovik and Lavrentovich [8] reported a transition at a surface composed of two fluid components known to induce opposing anchoring tendencies. This could perhaps arise because of a changing surface composition or because of different temperature dependencies of the anchoring strength of the two components. Recently, Drzaic [9] reported a surface anchoring transition far from bulk liquid-crystal transitions at poly(vinyl alcohol) surfaces modified by amphiphilic molecules.

We discovered a set of temperature-driven surface anchoring transitions of a nematic liquid crystal at polymer interfaces *created by phase separation*. Not only are these transitions far from all bulk transitions, but the anchoring transition temperature can be varied across nearly the entire nematic temperature range by subtle changes in the polymer side group and by mixing side groups. This set of anchoring transitions is significant because it provides a different set of data for gaining insight into surface anchoring.

Over the past decade, a variety of polymer/liquid-crystal dispersions have been developed for applications in displays and photonics [10,11], and many are made by phase separation induced by polymerization. One example is the polymer-dispersed liquid crystal (PDLC), which consists of micrometer-scale nematic drops trapped within a polymer matrix. Surface anchoring at interfaces that form during phase separation, like the ones studied here, is a crucial factor in device performance. This study of surface anchoring indicates a pathway for strongly affecting electro-optical properties of polymer/liquid-crystal dispersions by controlling polymer structure.

The liquid crystal chosen for this study, TL205 (EM Industries), is a mixture of halogenated bi- and terphenyls with aliphatic tails of length two to five carbons, averaging between three and four carbons [12]. It was chosen because it exhibits a wide nematic range (<−20 °C–87 °C) and thus permits the exploration over a much wider temperature range than typical single-component nematics.

The liquid crystal was mixed with a mixture of monomers to form a single-phase isotropic solution that is ~80 wt % liquid crystal. The monomer mixture was 85 wt % monofunctional acrylate, 13.5 wt % 1,1,1-trimethylol propane triacrylate, and 1.5 wt % UV photoinitiator (Darocur 1173, Ciba). The chemical variable in these experiments is the side group on the monofunctional acrylate.

A ~15 μm gap between indium-tin-oxide coated glass plates was filled with the mixture of liquid crystal and acrylate, then irradiated with a mercury arc lamp (365 nm of UV light) at a low intensity, ~50 μW/cm^2. As polymerization proceeded, the solution supersaturated and drops of liquid crystal formed. The slow polymerization allowed time for the drops to coalesce into large structures before solidifica-

---

*Present address: North Carolina State University, College of Textiles, 2401 Research Dr., Raleigh, NC 27695-8301.

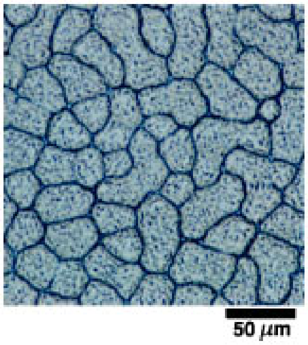


FIG. 1. (Color) Bright field image of the cellular film at 84 °C.

tion of the matrix. The resulting films, here called ‘‘cellular films,’’ are comprised of liquid-crystal cells that span the cell gap and are typically 20–50 μm wide. The cells are separated by thin polymer walls extending vertically from one substrate to the other, as was verified by confocal fluorescence microscopy. Anchoring behavior indicates that the substrates are coated with the polymer as well. Surface anchoring behavior was determined from polarized light microscopy. The cells were heated and cooled during microscopy in a Mettler FP82 hot stage with cold nitrogen gas flow.

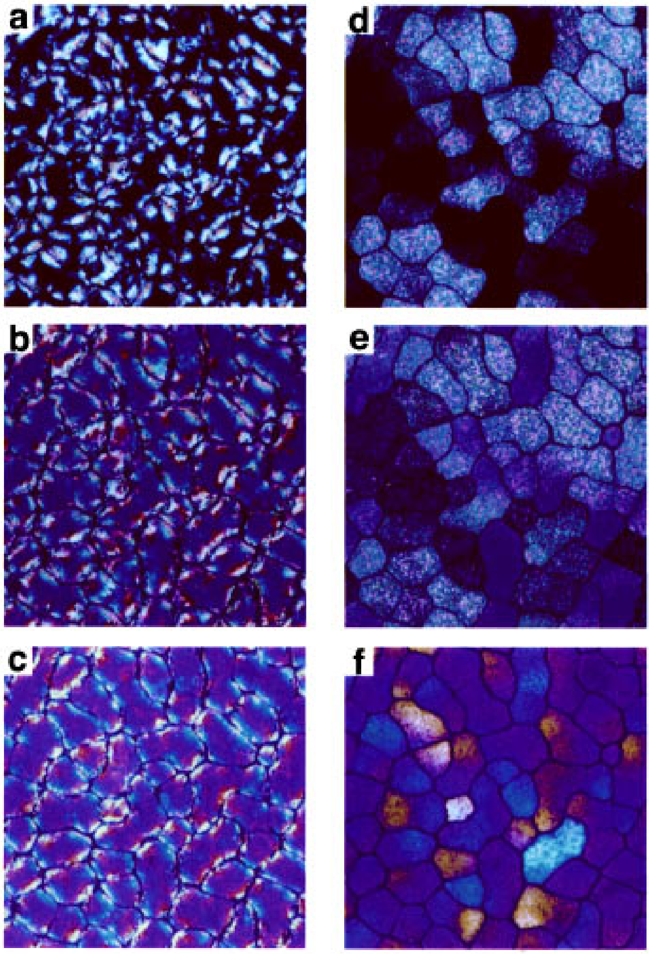


FIG. 2. (Color) Image of the same region as in Fig. 1 at 75 °C [(a)–(c)] and 77 °C [(d)–(f)] between crossed polarizers. The polarizer is horizontal and the analyzer is vertical. In (b) and (e), the tint plate has been inserted, with its slow axis along the upper-right to lower-left diagonal. An electric field is applied in (c) and (f) with rms amplitude of 0.14 and 0.05 V/μm, respectively.

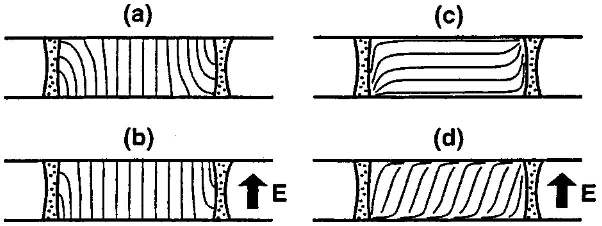


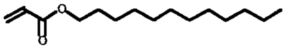
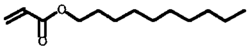
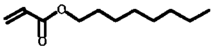
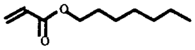
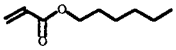
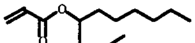
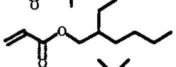
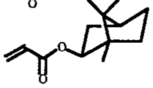
FIG. 3. Cross section of a liquid crystal cell showing the director field inferred from microscopy for (a) homeotropic and (c) homogeneous anchoring. The polymeric walls are stippled and lines indicate the nematic director field. The boundary layer of transverse alignment is made smaller by an electric field in (b) and the homogeneous alignment is tilted by the field in (d).

Figures 1 and 2 show microscopic images of a cellular film made using *n*-octyl acrylate. Heating the film above the nematic-to-isotropic transition temperature ($T_{\mathrm{NI}} \sim 82\ ^\circ\mathrm{C}$) affords a clear view of the cellular structure (Fig. 1). The polymer walls appear dark because they scatter light. Besides the polymer walls, there are polymeric fibrillar features and surface modulations inside the cells, giving them a mottled appearance.

Upon cooling below 82 °C the nematic phase forms. With further cooling an anchoring transition is crossed at 76 °C. Figure 2(a) shows an image of the film at 75 °C, just below the anchoring transition temperature, between crossed polarizers. The centers of the cells remain dark as the sample is rotated, indicating no in-plane birefringence and a director field that is perpendicular to the film substrates. Tilted anchoring is ruled out because even a slight tilt would make the center of the cells appear bright. The boundaries near the vertical walls are bright because of an in-plane director component. The orientation of this component was determined by inserting a tint plate into the optical train [Fig. 2(b)] and interpreting the interference colors using a Michel-Lévy color chart [13]. Applying an electric field reduces the width of the boundary region near the polymer walls [Fig. 2(c)] and simplifies interpretation of the interference colors. Cyan near walls running predominantly from the upper left to the lower right and yellow near walls running from the upper right to the lower left [Fig. 2(c)] show that the director is orthogonal to the walls, indicating homeotropic anchoring [Figs. 3(a) and 3(b)].

The microscopic observations change very little between room temperature and 76 °C. However, upon heating the film through 76 °C, the director field rearranges suddenly and dramatically. Figure 2(d) shows a view between crossed polarizers at 77 °C; adding a tint plate gives the image of Fig. 2(e). Except for some fine structure, the variations within a single drop are very gradual. Individual cells pass between extinction and pastel colors through every 90° rotation, indicating high, uniform in-plane birefringence. This and the gradual, uniform decrease in the in-plane birefringence with increasing electric field indicates homogeneous anchoring, as illustrated in Figs. 3(c) and 3(d). Tilted anchoring is ruled out here by the absence of a boundary layer of misalignment near the vertical walls during field alignment. Instead, the alignment toward vertical occurs at a lower field near the

TABLE I. Anchoring transition temperature for films made using various monofunctional acrylates. The asterisk means that anchoring was homogeneous and no transition was observed.

acrylate	monomer structure	T_t (°C)
lauryl		80
n-decyl		79
n-octyl		76
n-heptyl		76
n-hexyl		65
2-octyl		48
2-ethyl hexyl		23
isobornyl		<-15*

vertical walls than in the center of the cells, although this detail is not resolvable in the photographs of Fig. 2.

Similar behavior was observed when other monofunctional alkyl acrylates were used in the construction. Homeotropic anchoring was seen below an anchoring transition temperature T_t and homogeneous anchoring above. The anchoring transition temperature, while insensitive to the choice and amount of *polyfunctional* acrylate, varied with choice of monofunctional acrylate. Values are tabulated in Table I.

PDLC films for electro-optic studies were made from the same mixtures used to make the cellular films, but with a much higher irradiation intensity (~ 17 mW/cm^2). The rapid photopolymerization prevented much coalescence of the drops, which were typically 1–3 μm in diameter. Electro-optic properties of the PDLC film were determined from time-resolved, forward-transmittance measurements of a HeNe laser beam (632.8 nm) passing through the film, while applying 1-kHz sinusoidal voltage pulses across the film.

The temperature-induced anchoring transition is apparent from several electro-optic measurements. A lucid example is afforded by a plot of the switching voltage and the relaxation time as a function of temperature for a PDLC film made with *n*-hexyl acrylate (Fig. 4). There is a minimum in the switching voltage and a peak in the relaxation time at 65 °C. Both of these reflect a passage from homeotropic anchoring below T_t to homogeneous anchoring above. Near T_t anchoring weakens and the elastic distortion in the drops relaxes [11,14]. Since the electric-field energy must overcome elastic distortion energy to achieve alignment, the switching voltage dips at T_t. Also, the relaxation time peaks at T_t because the nematoelastic restoring force is small in weak anchoring.

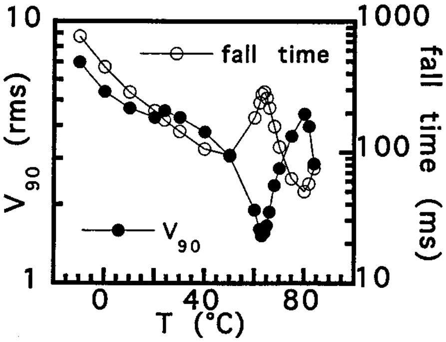


FIG. 4. V_{90} and fall time. V_{90} is the voltage required to achieve 90% of maximum transmittance, and the fall time is the relaxation time upon cessation of the voltage.

Similar signatures of anchoring transitions were seen for films made using other alkyl acrylates. In all cases, T_t determined from PDLC electro-optics corresponds to the transition temperature seen in the corresponding cellular film. We also found that T_t varies monotonically when a mixture of two monofunctional acrylates was used instead of just one. This way intermediate T_t values could be attained.

Most anchoring transitions are reported to be close (within ~ 10 °C) to bulk ordering transitions from nematic to isotropic, smectic, or crystalline phases [5,6,15]. Theoretical explanations for these anchoring transitions typically involve the rapidly changing bulk order near these transitions; for example, pretransitional layering near a nematic-smectic phase transition [7,16] or rapidly changing dipolar and quadrupolar contributions to the surface energy [6,17].

In contrast, the anchoring transitions we observe are unique in that the transition temperature T_t can be readily adjusted across most of the nematic temperature range by modifying the polymer side group and by mixing side groups, and so they are seen very far from bulk transition temperatures. An appealing starting point for understanding the basis of this transition is to consider a competition between an enthalpic drive for homeotropic anchoring and an entropic drive for homogeneous anchoring. For example, Sharlow and Gelbart [18] showed that due to excluded volume between isolated rigid rods and a surface there is an entropic drive for homogeneous anchoring, as rods lying parallel to a surface can explore space closer to the surface than those perpendicular to the surface. An enthalpic drive for homeotropic anchoring could arise from the presence of the alkyl polymer side chains, as described below. The transition from low-temperature homeotropic to high-temperature homogeneous anchoring would then occur at a temperature at which the enthalpic and entropic contributions balance. A complete model must include additional factors such as intermolecular interactions between the densely packed mesogens. This model is useful as a starting point because it shows how an anchoring transition from low-temperature homeotropic to high-temperature homogeneous can occur far from bulk transitions, and it explains several trends.

The importance of the polymer alkyl side group on anchoring is clear. T_t is very sensitive to subtleties in the side chain configuration, as can be seen from Table I, while it is very insensitive to other factors such as drop size, the nature and number density of cross-links in the polymer network, and the addition of a methyl group to the polymer backbone (through substitution of the acrylate by the equivalent methacrylate). Also, it has been repeatedly demonstrated that a high density of alkyl chains attached to an interface induces homeotropic anchoring in a wide variety of liquid crystals. Previous work on alkyl brush surfaces, created by treating substrates with amphiphilic compounds [1–4], such as surfactants, lecithins, and fatty acids, have generally shown homeotropic anchoring when the alkyl chain is long, typically greater than about 7–10 carbons [2,4]. It is thought that the alkyl brush surface forms a ‘‘seaweed-bed-like’’ arrangement for portions of the mesogens to interdigitate, and this interdigitation is best achieved when the mesogens are perpendicular to the surface [1]. Attractions between alkyl ends of mesogens and the alkyl brush can give an enthalpic preference for homeotropic anchoring.

The analogy between the polymer side chains at the interface and alkyl brush surfaces is strengthened by a couple of trends. First, for linear side chains, the tendency for normal anchoring increases with side chain length, as shown by an increase in T_t with an increasing number of carbons. This is consonant with the observations of Porte [2] and Crawford *et al.* [4], the anchoring evolved toward homeotropic or jumped from homogeneous to homeotropic when the number of carbons increased to above about 7–10 carbons. Second, branching of the alkyl side group reduces the tendency for normal anchoring, presumably by frustrating the seaweed-bedlike packing of the side groups. In changing the side group from the linear (*n*-octyl) to the secondary (2-octyl) and branched (2-ethyl hexyl) eight-carbon isomers, T_t drops from 78 °C down to 23 °C.

By appropriate choice of polymer side group, one can exercise significant control over the electro-optics of devices such as PDLC films without the introduction of additives or changes in morphology. For example, choosing an acrylate that weakens anchoring at a desired operating temperature results in a lower switching voltage and a larger relaxation time, while choosing an acrylate that strengthens anchoring has the opposite effect. One can also choose strong or weak temperature sensitivity of a PDLC film by judicious placement of the anchoring transition temperature.

The authors thank Paul Drzaic for helpful discussions.

[1] J. E. Proust, L. Ter-Minassian-Saraga, and E. Guyon, Solid State Commun. **11**, 1227 (1972).

[2] G. Porte, J. Phys. (France) **37**, 1245 (1976).

[3] K. Hiltrop and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. **82**, 884 (1978); K. Hiltrop, J. Hasse, and H. Stegemeyer, *ibid.* **98**, 209 (1994).

[4] G. P. Crawford, R. J. Ondris-Crawford, J. W. Doane, and S. Zumer, Phys. Rev. E **53**, 3647 (1996).

[5] J. S. Patel and H. Yokoyama, Nature (London) **362**, 525 (1993).

[6] K. Flatischler, L. Komitov, S. T. Lagerwall, and B. Stebler, Mol. Cryst. Liq. Cryst. **198**, 119 (1991).

[7] J. Als-Nielsen, F. Christensen, and P. S. Pershan, Phys. Rev. Lett. **48**, 1107 (1982); C. Rosenblatt and D. Ronis, Phys. Rev. A **23**, 305 (1981); A. A. Sonin, A. Yethiraj, J. Bechoefer, and B. J. Frisken, Phys. Rev. E **52**, 6260 (1995); A. A. Sonin, *The Surface Physics of Liquid Crystals* (Gordon and Breach, Amsterdam, 1995).

[8] G. E. Volovik and O. D. Lavrentovich, Zh. Eksp. Teor. Fiz. **85**, 1997 (1983) [Sov. Phys. JETP **58**, 1159 (1983)].

[9] P. S. Drzaic, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **37**, 198 (1996); **38**, 362 (1997); (private communication).

[10] D. K. Yang, L.-C. Chien, and J. W. Doane, Appl. Phys. Lett. **60**, 3102 (1992).

[11] P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Teaneck, NJ, 1995).

[12] D. Coates (private communication).

[13] N. H. Hartshorne and A. Stuart, *Practical Optical Crystallography* (American Elsevier, New York, 1964), p. 172.

[14] K. Amundson, Phys. Rev. E **53**, 2412 (1996); Y. Ji, J. R. Kelly, and J. R. West, Liq. Cryst. **14**, 1885 (1993).

[15] A. A. Sonin, A. Yethiraj, J. Bechoefer, and B. J. Frisken, Phys. Rev. E **52**, 6260 (1995); G. A. diLisi, C. Rosenblatt, A. C. Griffin, and U. Hari, Liq. Cryst. **7**, 353 (1990); V. G. Nazarenko and O. D. Lavrentovich, Phys. Rev. E **49**, R990 (1994).

[16] B. Jerome, Rep. Prog. Phys. **54**, 391 (1991).

[17] J. D. Parsons, Phys. Rev. Lett. **41**, 877 (1978).

[18] M. F. Sharlow and W. M. Gelbart, Liq. Cryst. **11**, 25 (1992).

[19] G. Ryschenkow and M. Kleman, J. Chem Phys. **64**, 404 (1976).

[20] H. E. W. Zocher and K. Coper, Z. Phys. Chem. (Munich) **132**, 295 (1928); P. Chatelain, Bull. Soc. Chim. Fr. **60**, 300 (1937); X. Zhuang, L. Marrucci, and Y. R. Shen, Phys. Rev. Lett. **73**, 1513 (1994).