

Effect of *trans-cis* photoisomerization on phase equilibria and phase transition of liquid-crystalline azobenzene chromophore and its blends with reactive mesogenic diacrylate

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Photoisomerization-induced phase transition of neat liquid-crystalline azobenzene chromophore (LCAC) and its effect on phase diagrams of its mixtures with reactive mesogenic diacrylate monomer (RM257) have been investigated experimentally and theoretically. Upon irradiation with ultraviolet light, the nematic phase of LCAC transformed to isotropic, while the crystal phase showed corrugated textures on the surface (i.e., ripples). The phase-transition temperatures and corresponding morphologies of the blends have been investigated by means of differential scanning calorimetry and optical microscopy. A theoretical phase diagram of a binary nematic and crystalline system was constructed by self-consistently solving the combined free energies of Flory-Huggins, Maier-Saupe, and phase-field theory. The calculation revealed various coexistence regions such as nematic + liquid ($N_1 + L_2$), crystal + liquid ($Cr_1 + L_2$), crystal + nematic ($Cr_1 + N_2$), and crystal + crystal ($Cr_1 + Cr_2$) over a broad range of compositions including the single-phase nematic (N_1 , N_2) of the corresponding constituents. The calculated liquidus lines were in good accord with the depressed mesophase-isotropic transition points. The present paper demonstrates the effect of *trans-cis* photoisomerization on the mesophase transitions of neat LCAC and the phase diagram of LCAC-RM257 as well as on the ripple formation (i.e., periodic undulation) on the azobenzene crystals.

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I. INTRODUCTION

By virtue of reversible photoswitching capability, azobenzene chromophores have gained considerable attention in various applications, such as optical switching, optical grating, waveguide, and erasable holographic memory storage [1–7]. It is well documented that azobenzene chromophores change their molecular conformations from *trans*- to *cis*-state by selective irradiation with ultraviolet (UV) light and revert back to the *trans*-state upon illumination with visible light. Such *trans-cis* isomerization takes place not only at the molecular level but also at a condensed mesophase from a rodlike assembly to a bent-shaped organization [8–12]. This reversible phase transformation of rod-to-bent assemblies driven by photoisomerization results in reversible photomechanical deformation (i.e., contraction and expansion); the bending moment thus generated during this photomechanical deformation has led to photoactuator applications. Since then, various chemical modifications have been made to the azobenzene chromophores by either attaching with flexible groups or doping in a flexible polymer matrix to impart liquid-crystalline (LC) properties; typical examples include LC elastomers and photoresponsive gels. Of particular importance is that these LC azobenzene polymers can be driven by either photo-optical or electro-optical means through a change of director orientation of the LC mesogens and/or *trans-cis* isomerization of the chromophore [13–17].

In the present paper, we synthesized 4-4' dipentylazobenzene, hereafter called liquid-crystalline azobenzene (LCAC), which exhibits phase transitions from isotropic, nematic, and crystalline phases in descending order of temperature.

As in other azobenzene analogs, neat LCAC is capable of undergoing *trans-cis* isomerization upon UV irradiation. Of particular interest is that the *trans-cis* photoisomerization of the neat LCAC not only exerts a dramatic effect on the mesophase transitions, but also on the surface morphology of their single crystals involving stratification (i.e., periodic undulation). It is a common practice to embed LCAC into the polymer matrix to develop optically controllable polymer composite films for information displays and image-storage applications. In an effort to contain LCAC in matrix resins such as reactive mesogenic diacrylate (i.e., RM257), it is of paramount importance to better understand the individual roles of photopolymerization-induced phase separation and *trans-cis* photoisomerization of LCAC on morphology development that ultimately govern the final properties. To decouple these two effects, we will focus in this paper only on the effect of *trans-cis* photoisomerization of LCAC on the phase diagram and morphology development of the binary nematic-crystalline mixtures of LCAC-RM257 without adding any photoinitiators to prevent photopolymerization.

II. MATERIALS AND EXPERIMENTS

LCAC was synthesized according to a well-established synthesis protocol reported by Barrado *et al.* [18]. Reactive mesogenic diacrylate monomer (RM257, $M_w = 588.6$ g/mol), 4-(3-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenylene ester, was purchased from Merck Ltd. and used without further purification. Various LCAC-RM257 blends were prepared by dissolving in carbon tetrachloride (CCl_4) in a range of 2.5–5 wt.% solute concentrations and mechanically stirred. The homogeneous blend solution was cast on glass slides and then the solvent was evaporated under a fume hood and further dried in a vacuum oven at room

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temperature overnight and again at 40 °C for 24 h. No particular surface treatment was performed on the glass slides.

Phase-transition temperatures of the blend samples were determined using differential scanning calorimetry (DSC) (Q-1000, TA Instruments). During the heating-cooling cycle, the chamber was maintained under nitrogen atmosphere at a flow rate of 50 mL/min. The DSC curves were acquired at a heating rate of 5 °C/min. The morphology change during phase transition was investigated by means of polarized optical microscopy (POM) using an Olympus microscope (BX60) equipped with a digital camera (EOS 300D, Cannon) and a hot stage (TMS93, Linkam). POM pictures were taken during the course of heating at a rate of 1 °C/min. The green-filtered light source was used to prevent potential photoisomerization of the LCAC constituent.

The surface morphology of crystalline LCAC was examined with and without UV irradiation using atomic force microscopy (AFM) (MMAFM-2, Digital Instruments). Silicon cantilevers (RTESPW, Veeco Inc.) with a spring constant of 20–80 N/m were used in the tapping mode. The samples were irradiated uniformly on the growing crystal surface using a UV gun (ELC403, Electrolite Corp.) operated at a photointensity of 40 mW/cm² for 1500 s. Photo-DSC (Q-1000, TA Instruments) connected to the photocalorimetric accessory (Novacure, EXFO Photonic Solutions) was employed to determine the phase-transition temperature of photoisomerized mixtures. The samples used in conventional DSC analysis were heated up to the isotropic temperatures (around 100 °C) and cooled down under the continuous UV irradiation. However, the operating temperature of photo-DSC was limited to 80 °C. The phase-transition temperature of photoisomerized mixtures was further evaluated by means of POM using UV fiber optics (LQ UV 1000, LINOS Photonics GmbH & Co.) as a light source. The UV intensity for DSC and POM analysis was maintained at 40 mW/cm².

III. MODEL DESCRIPTION

The total free-energy density of binary crystal and nematic mixtures may be described in terms of a combined Flory-Huggins (f^{FH}), Maier-Saupe (f^{MS}), and phase-field (f^{PF}) theory along with their coupling interaction, viz., $f = f^{\text{FH}} + f^{\text{MS}} + f^{\text{PF}} + f^{\text{coupling}}$. Flory-Huggins (FH) theory is commonly utilized to explain isotropic mixing, which may be expressed as follows [19,20]:

$$f^{\text{FH}} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi_{\text{aa}} \phi_1 \phi_2, \quad (1)$$

where r_1 and r_2 refer to the numbers of statistical segments and ϕ_1 and ϕ_2 are the volume fractions of the respective constituents. The FH interaction parameter representing amorphous-amorphous interaction is evaluated at a given temperature, that is, $\chi_{\text{aa}} = A + B/T$, where A and B are constants.

The free energy of nematic ordering in a binary system may be described in accordance with Maier-Saupe (MS) mean-field

theory [21–23], viz.,

$$f^{\text{MS}} = -\phi_1 \ln Z_1 - \phi_2 \ln Z_2 + \frac{1}{2} v_{11} s_1^2 \phi_1^2 + \frac{1}{2} v_{22} s_2^2 \phi_2^2 + v_{12} s_1 s_2 \phi_1 \phi_2. \quad (2)$$

The s_1 and s_2 represent the orientational order parameters of the RM257 and LCAC, and v_{11} and v_{22} are the nematic interaction parameters, which may be defined as $v_{11} = 4.541(T_{NI,1}/T)$ and $v_{22} = 4.541(T_{NI,2}/T)$. Further, the orientational order parameter, s_j , is defined as

$$s_j = \int f(\cos \theta_j) \frac{1}{2} (3 \cos^2 \theta_j - 1) d \cos \theta_j = \frac{1}{Z_j} \frac{dZ_j}{dm_j}, \quad (3)$$

where m_j is the dimensionless mean-field parameter. The orientation distribution function, $f(\cos \theta_j)$, and the partition function, Z_j , are given as

$$f(\cos \theta_j) = \frac{1}{4\pi Z_j} \exp[-u(\cos \theta_j)/kT], \quad (4)$$

$$Z_j = \int \exp\left[-\frac{u(\cos \theta_j)}{kT}\right] d(\cos \theta_j). \quad (5)$$

The cross-interaction parameter (v_{12}) representing the interspecies (cross) interaction between the dissimilar mesogens depends on the interaction parameter of the individual mesogen in the context of the geometric mean approach, that is, $v_{12} = c_v \sqrt{v_{11} v_{22}}$, where the proportional constant c_v signifies the strength of the cross interaction between the two dissimilar mesogens relative to that in the same species.

Phase-field (PF) model pertaining to a Landau-type asymmetric double well has been employed to explain crystal solidification [24,25],

$$f(\psi_i) = W_i \int_0^{\psi_i} \psi_i (\psi_i - \zeta_i) (\psi_i - 1) d\psi_i = W_i \left[\frac{\zeta_i(T)}{2} \psi_i^2 - \frac{\zeta_i(T) + 1}{3} \psi_i^3 + \frac{1}{4} \psi_i^4 \right]. \quad (6)$$

The crystal order parameter (ψ_i) is defined as the ratio of the lamellar crystal thickness (l) to that of a perfect crystal (l^0), representing the level of crystal perfection. The potential well at $\psi_i = 0$ indicates the metastable melt and $\psi_i = 1$ refers to the crystal order parameter at the solidification potential for crystallization, with ζ_i being the peak position of the free-energy barrier on the ψ axis. The coefficients W_i , relevant to the energy barrier height, may be estimated from the melting point and heat of fusion of crystalline constituent, that is, $W_i = 6\Delta H_i^u / RT(1 - T_{i,m}/T_{i,m}^0)(1/2 - \zeta_i)^{-1}$.

The free energy of the coupling interaction may be described as

$$f^{\text{coupling}} = (\chi_{\text{ca}} \psi_1^2 - 2\chi_{\text{cc}} \psi_1 \psi_2 + \chi_{\text{ac}} \psi_2^2 + \alpha s_1^2 \psi_1 \psi_2 + \beta s_2^2 \psi_1 \psi_2 + \gamma s_1 s_2 \psi_1 \psi_2) \phi_1 \phi_2. \quad (7)$$

The crystal-amorphous (χ_{ca}) and amorphous-crystal (χ_{ac}) interaction parameters are proportional to the ratio of heat of fusion and absolute temperature, that is, $\chi_{\text{ca}} \sim \Delta H_1^u / RT$ and $\chi_{\text{ac}} \sim \Delta H_2^u / RT$, in which the proportional constant can be determined from the slope of the $(1 - T_{i,m}/T_{i,m}^0)$ versus $(1 - \phi_{\text{cr}})$ plot [26]. The crystal-crystal interaction parameters (χ_{cc}) may also be related to χ_{ca} and χ_{ac} by the geometric mean approach. α , β , and γ are the coupling coefficients. Since

the crystal (ψ_1 , ψ_2), nematic (s_1 , s_2), and compositional order parameters (ϕ_1 , ϕ_2) of each constituent are less than unity, their multiplication, that is, $(\alpha s_1^2 \psi_1 \psi_2 + \beta s_2^2 \psi_1 \psi_2 + \gamma s_1 s_2 \psi_1 \psi_2) \phi_1 \phi_2$ terms in Eq. (7), makes their coupling interactions be much smaller relative to the quadruple interaction terms $(\chi_{ca} \psi_1^2 - 2\chi_{cc} \psi_1 \psi_2 + \chi_{ac} \psi_2^2) \phi_1 \phi_2$, and thus the above higher-order terms were ignored in the calculation. Combining Eqs. (1), (2), (6), and (7), the total free energy is given as follows:

$$\begin{aligned} f(\phi, \psi, s) = & \phi_1 f(\psi_1) + \phi_2 f(\psi_2) + \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \\ & - \phi_1 \ln Z_1 - \phi_2 \ln Z_2 + \frac{1}{2} \nu_{11} s_1^2 \phi_1^2 \\ & + \frac{1}{2} \nu_{22} s_2^2 \phi_2^2 + (\chi_{aa} + \chi_{ca} \psi_1^2 - 2\chi_{cc} \psi_1 \psi_2 \\ & + \chi_{ac} \psi_2^2 + \nu_{12} s_1 s_2) \phi_1 \phi_2. \end{aligned} \quad (8)$$

The nematic-isotropic transition may be determined by minimizing the total free energy with respect to the nematic order parameters (s_1 , s_2) in the following:

$$\frac{\partial f(\phi, \psi, s)}{\partial s_1} = 0, \quad \frac{\partial f(\phi, \psi, s)}{\partial s_2} = 0. \quad (9)$$

By the same token, the crystal-nematic transition can be obtained through minimization with respect to the crystal order parameters (ψ_1 , ψ_2), that is,

$$\frac{\partial f(\phi, \psi, s)}{\partial \psi_1} = 0, \quad \frac{\partial f(\phi, \psi, s)}{\partial \psi_2} = 0. \quad (10)$$

Furthermore, the coexistence lines may be determined by balancing the chemical potentials for each phase, viz., $(\partial f / \partial n_i)|_{\varphi_i^\alpha} = (\partial f / \partial n_i)|_{\varphi_i^\beta}$, in conjunction with a common tangent method described elsewhere [27].

IV. RESULTS AND DISCUSSION

The photoisomerization of azobenzene chromophore in solution has been explored extensively on the basis of UV-Vis spectra [28–30]. The *trans* form shows a strong absorption peak from the π - π^* electronic transition, which decreases upon UV irradiation. Concurrently, the peak corresponding to the n - π^* transition appears due to the formation of the *cis* isomer (> 400 nm). Although the photoinduced *trans-cis* transition of the azobenzene molecule is well documented in the literature, it is interesting to determine how the photoresponsive property of azobenzene will occur in the condensed solid state or influence the phase behavior of the RM257-LCAC mixture upon irradiating UV irradiation, that is, the effect of *trans-cis* isomerization on the phase diagrams of the RM257-LCAC.

We first examined the phase-transition temperatures of the as-synthesized LCAC using DSC. As shown in Fig. 1, the heating and cooling DSC runs exhibit three distinct endothermic or exothermic peaks at indicated temperatures. By virtue of the nonequilibrium nature of the cooling run, the optical microscopy experiment was carried out for the heating cycle. The optical micrographs, taken at 10 and 27 °C, show some resemblance to each other, but one can notice different crystal modifications under close examination. However, the pictures clearly show the nematic disclinations at 35 °C

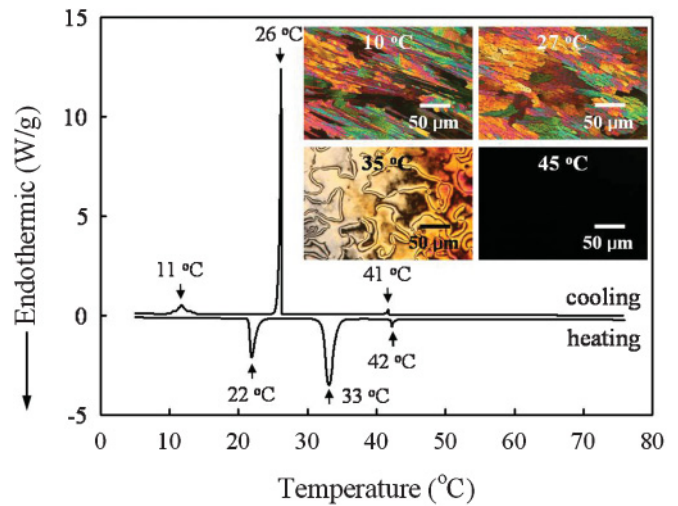


FIG. 1. (Color online) DSC thermograms of neat LCAC, showing various phase transitions and the polarized optical micrographs taken at the specified temperatures of 10, 27, 35, and 45 °C corresponding to various mesophase regions. The heating-cooling rates of DSC runs were 5 °C/min.

and the isotropic phase at 45 °C, respectively. These POM observations suggest that the two strong DSC endothermic peaks at around 22 and 33 °C correspond to the crystal-crystal and crystal-nematic transitions, and a weak broad peak near 42 °C may be attributed to the nematic-isotropic phase transition.

Figure 2 depicts the DSC thermograms of RM257-LCAC mixtures obtained at a heating rate of 5 °C/min. The neat RM257 exhibits a crystal-nematic transition (T_{Cr-N}) at around 66 °C and a nematic-isotropic transition (T_{NI}) at 128 °C. In addition, a minor endothermic peak can be discerned at ~58 °C, which may be a consequence of the melting of

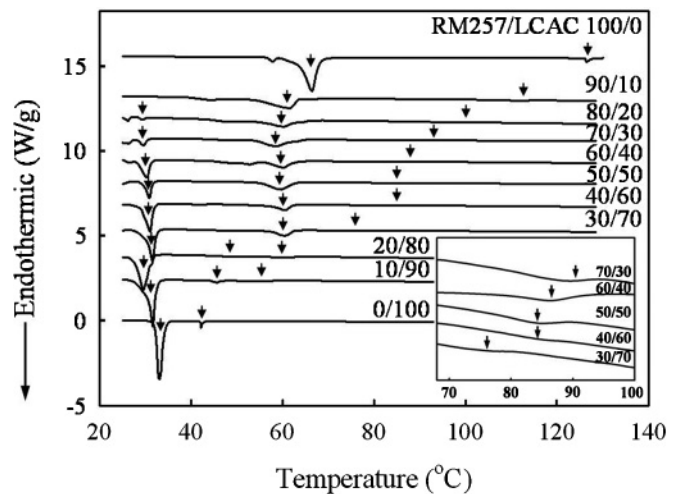


FIG. 2. DSC thermograms of RM257-LCAC mixtures obtained at a heating rate of 5 °C/min, showing the systematic shifts of the crystal-nematic and nematic-isotropic transitions with blend composition. The inset shows the enlarged *N-I* transition endotherms of the intermediate compositions. The DSC thermograms of pure RM257 and its blend samples were shifted from the baseline for clarity.

nonequilibrium crystals that formed during cold crystallization or a different type of crystal modification. Since this minor peak of neat RM257 is no longer discernable in the RM257-LCAC blends, we shall focus only on the major T_{Cr-N} peaks. The endothermic peak corresponding to T_{Cr-N} of both RM257 and LCAC are depressed only slightly in their mixtures. The lack of movement in the T_{Cr-N} implies that the pair is not miscible in the crystalline state and forms separate crystals. On the other hand, the T_{NI} of RM257 decreases drastically with the addition of LCAC; such movement of T_{NI} is more apparent in the enlarged scale of some RM257 compositions, especially in 70–30 wt.% RM257. Since these DSC data alone would be inadequate to identify all coexistence phases, we turn our attention to establishing a theoretical phase diagram in conjunction with the morphology examination by optical microscopy.

In Fig. 3, we show the plot of phase-transition temperature versus composition phase diagram obtained by DSC (indicated by open circles) in comparison with the liquidus and solidus lines calculated self-consistently by solving Eq. (8) (represented by the solid line). The model and material parameters used in the phase diagram determination were $r_1 = r_2 = 2$ [i.e., representing two coupled mesogenic (aromatic) units] with $A = 0.6$ ($\chi_{aa} = A + B/T$), $T_{crit} = -50$ °C, $\Delta H_1^u = 33.3$ kJ/mol at $T_{m,1} = 66$ °C, $\Delta H_2^u = 16.9$ kJ/mol at $T_{m,2} = 33$ °C, $\chi_{ca} = 0.7$ at $T_{Cr-N,1}$, $\chi_{ac} = 0.4$ at $T_{Cr-N,2}$, $c_v = 0.9$, and $c_w = 0.01$.

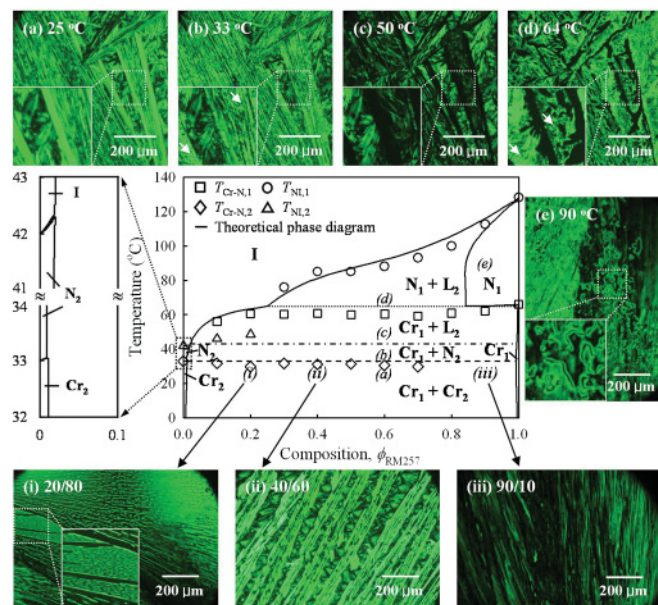


FIG. 3. (Color online) Comparison between theoretical and experimental phase diagrams of RM257-LCAC mixtures. The symbols represent DSC data and the solid lines representing the coexistence lines were calculated self-consistently. Polarized optical micrographs were taken at various coexistence regions of the 60-40 composition indicated by (a)–(d) and the 90-10 RM257-LCAC mixtures indicated by (e). The phase diagram consists of crystal + crystal ($Cr_1 + Cr_2$), crystal + nematic ($Cr_1 + N_2$), crystal + liquid ($Cr_1 + L_2$), and nematic + liquid ($N_1 + L_2$) phase, and the single-phase nematic (N_1). The two separate crystals develop at (ii) 40 wt.% RM257, but the individual crystal of each component dominates at (i) 20 and (iii) 90 wt.% RM257.

The enlarged view of T_{Cr-N} and T_{NI} at LCAC-rich composition is shown on the left-hand side. The calculated liquidus line accords well the lowering trends of the T_{NI} of the DSC study. In descending order of temperature, various coexistence regions can be identified, including nematic + liquid ($N_1 + L_2$), crystal + liquid ($Cr_1 + L_2$), crystal + nematic ($Cr_1 + N_2$), and crystal + crystal ($Cr_1 + Cr_2$) coexistence regions. The single-phase N_1 and N_2 regions are observed at the extreme compositions >80 or <5 wt.% RM257, respectively. The predicted solidus lines of the $Cr_1 + Cr_2$ region are close to the axis of the pure constituent and thus most impurities are presumably rejected from these emerged RM257 and LCAC crystals.

The morphologies at various coexistence regions are investigated further by means of polarized optical microscopy. Figures 3(a)–3(e) exhibit the polarized optical micrographs of the 60-40 and 90-10 RM257-LCAC blends. The coexistence regions are labeled on the phase diagram. Upon heating the 60-40 RM257-LCAC mixture to 33 °C, the LCAC crystals melt into the nematic phase as manifested by the appearance of line disclinations (as indicated by the arrows) in the enlarged view [Fig. 3(b)]. But RM257 remains in the crystalline phase and thus their coexistence phases correspond to the $Cr_1 + N_2$ coexistence region. When the temperature reaches 50 °C, the nematic LCAC further transforms completely to the isotropic phase, and therefore their RM257-LCAC mixture belongs to the $Cr_1 + L_2$ coexistence phase [Fig. 3(c)]. Upon further heating to 64 °C, the RM257 crystals melt to a nematic phase, showing the Schlieren textures in the magnified view [Fig. 3(d)]. At high concentrations of RM257 (e.g., 90 wt.% at 90 °C), the Schlieren texture covers the entire view of the enlarged inset, indicative of a single nematic phase (N_1) [Fig. 3(e)]. These emerged morphologies at each composition and each temperature gap are in good agreement with the coexistence regions as manifested by our theoretical calculation. At ambient temperature below the $Cr_1 + Cr_2$ coexistence line, the formation of separate RM257 and LCAC crystals can be confirmed clearly in the intermediate composition of 40-60 RM257-LCAC [Fig. 3, picture (ii)]. However, at a high concentration, the crystalline morphology is dominated by the majority component (i.e., LCAC crystal) with the minority crystal (RM257) being entrapped in the interlamellar regions [Fig. 3, picture (i)]. In the opposite case, the RM257 crystals dominate the crystalline morphology, as depicted in picture (iii) of Fig. 4. More importantly, these POM investigations confirm the formation of separate crystals in this $Cr_1 + Cr_2$ coexistence gap.

Figure 4 shows the effect of irradiation by green, white, and UV light on mesophase transitions of neat LCAC in the nematic state at 34 °C, which is significantly lower than its T_{NI} of 42 °C. The change in the Schlieren texture of the LCAC was monitored using different lights, such as green, white, and UV. The intensity of green and white light was 90 $\mu\text{W}/\text{cm}^2$, whereas the intensity of UV irradiation was 40 mW/cm^2 . The time for completion of the *trans-cis* transition of azobenzene in carbon tetrachloride is about 20 s, but all pictures were taken at 10-s intervals at indicated temperatures. As demonstrated in Fig. 4(a), the nematic phase of neat LCAC remains unchanged under the illumination by green light for a prolonged period of 600 s, indicating the lack of any reactivity. However, upon

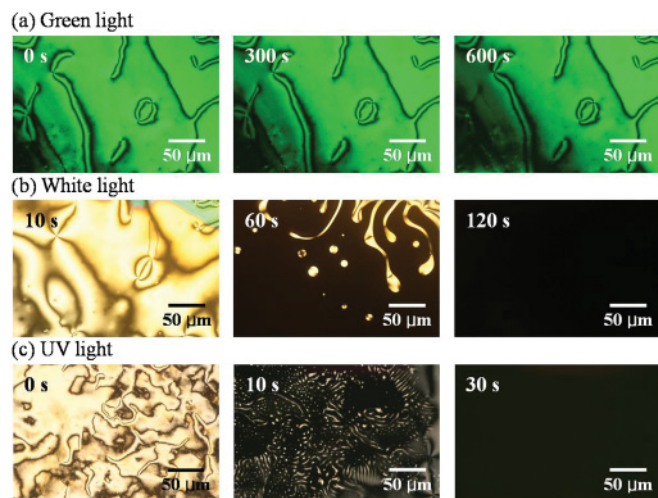


FIG. 4. (Color online) Optical micrographs of neat LCAC at 34 °C, showing transformation of nematic phase to isotropic phase upon irradiation with (a) green-filtered light, (b) white light, and (c) UV light for the specified exposure times. The 0 s implies no exposure to UV light.

illumination with the white light in the same area, the nematic disclinations transform to an isotropic state within 120 s [Fig. 4(b)], implying the light sensitivity of photoisomerization of the LCAC. With UV light (40 mW/cm²), the isotropization time is shortened to 30 s [Fig. 4(c)] as the nematic phase is destabilized by the *trans-cis* photoisomerization of LCAC and/or by the heat generated by the UV light. The change of temperature due to UV irradiation was about 2 °C and thus the *trans-cis* photoisomerization is the major contributor to this expedited isotropization.

Although the effect of isomerization on the nematic-isotropic phase transition of neat LCAC is profound, its effect on the crystalline phase has yet to be explored. A natural question is whether the mechanical torque generated by the *trans-cis* photoisomerization of azobenzene can cause any volume change (or deformation) in the condensed solid crystalline phase. The LCAC was crystallized by slowly cooling at 1 °C/min from the nematic phase (34 °C) to 28 °C under the green filtered light to prevent isomerization of azobenzene. When the temperature reaches 28 °C, the green filter was removed from the optical path of the microscope and thus the sample was exposed to the white light. As expected, the exposure to the white light did not cause any morphological change in the crystalline state [see the picture at 1 s, Fig. 5(a)]. This crystalline texture remains the same even after 24 h.

However, when the same crystallization is conducted under continuous irradiation using the UV light (40 mW/cm²) at 28 °C and held isothermally, the LCAC crystals grow in size with time. When a specific area of optical micrograph at 1500 s, indicated by a white dashed box, is magnified five times, one can clearly notice multiple striations on the crystal surface [Fig. 5(b), (i) upper right picture]. Upon increasing temperature to 30 °C under the UV irradiation, the striations persist for some time [see Fig. 5(b), picture (ii) at 60 s] while the isotropic dark region expands, and finally the crystals melt away. Upon recrystallization from the melt of 30–28 °C by natural cooling, numerous rhomboidal single crystals develop

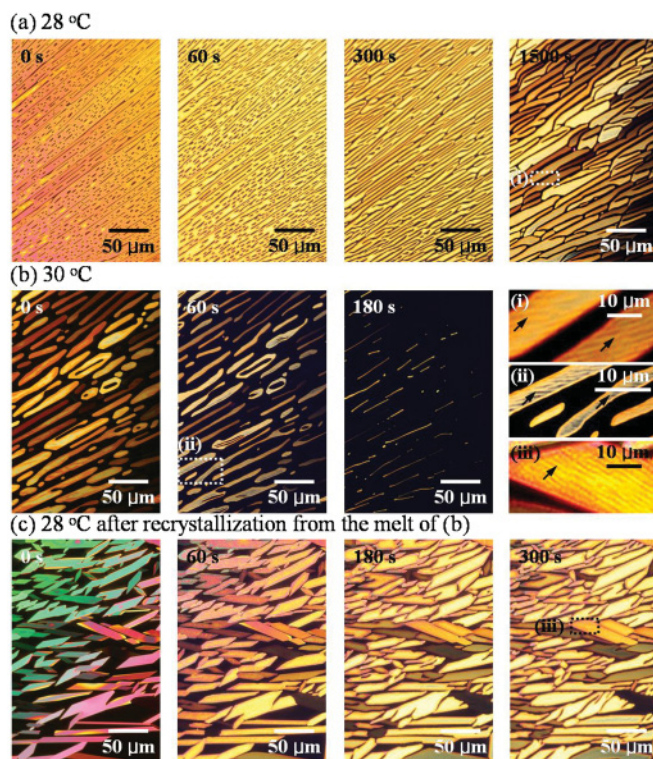


FIG. 5. (Color online) Morphology evolution of the LCAC crystal subjected to continuous irradiation of UV light showing (a) the growth of LCAC crystal at 28 °C, exhibiting stratification in the enlarged picture, and (b) melting of the fragmented crystals at 30 °C. (c) Upon recrystallization by natural cooling, the stratified stripes developed on the crystal surface under UV exposure for 300 s similar to that of (a). The 0 s implies no exposure to UV light.

[Fig. 5(c)]. Under the continuous UV irradiation, these crystals grow while the stratified stripes develop on the crystal surface, as illustrated in Fig. 5(b), picture (iii).

The POM and AFM images at 1500 s further confirm the ripple formation on the crystal surface with an average periodicity of 6–7 μm and an average height of 2–3 μm [Figs. 6(a) and 6(b)]. A similar occurrence of periodic undulations on rectangular single crystals of syndiotactic polypropylene (sPP) was found to occur during thermal quenching from the melt [31]. This ripple formation has been attributed to the volumetric shrinkage driven by a sudden change of density at the solid-melt interface during sPP

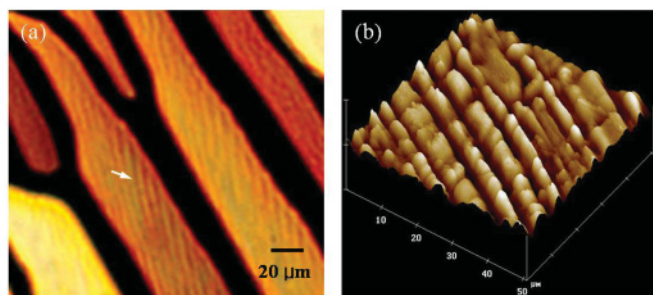


FIG. 6. (Color online) (a) POM and (b) AFM morphology of LCAC crystal after UV exposure for 1500 s, showing the corrugated structures.

crystallization. In the present case, the mechanical torque (or the bending moment) driven by *trans*-to-*cis* isomerization of LCAC may have caused the differential volume shrinkage at the crystal-melt interface under the UV illumination [32,33]. As a matter of fact, the distance (i.e., length) between 4- and 4'-positions of the azobenzene rings, where the flexible pentyl groups (C_5H_{11}) were appended, is approximately 9.0 Å in the *trans* configuration, whereas it is 5.5 Å in the *cis* state [34]. Hence, the volume of the *cis* form would be appreciably smaller than that of the *trans* form; therefore, the volume can shrink upon UV irradiation. It is this volume shrinkage that drives the surface undulation of the azobenzene single crystals as manifested by the AFM topology [Fig. 6(b)].

Alternatively, one can obtain the striations on the surface when azobenzene polymer is exposed to two coherent laser beams [35,36]. The surface relief structures are known to form on the polymer surface by the mass transport; however, a plausible mechanism was not reported in the literature. Although the present work does not require two interference waves to obtain the striations or undulations, one cannot rule out the possibility of a surface release mechanism leading to buckling on the crystal surface, which is a commonly observed phenomenon in azobenzene-based polymer systems [35,36].

Figure 7 displays the photo-DSC thermograms measured under the continuous irradiation of UV light at 40 mW/cm². The neat LCAC exhibits a single endothermic peak at about 31 °C in contrast to two peaks observed in regular DSC at around 33 and 42 °C. Considering its intensity and position, it may be related to the crystal-isotropic transition (T_m). Therefore, the isotropization of LCAC crystal at 30 °C in Fig. 5(b) may result from the depressed T_m in which the transition starts from about 28 °C. In blends, the crystal melting point of each constituent declines from 66 to 60 °C in mixtures of <70 wt.% RM257, but a lesser extent from 31 to 30 °C at <80 wt.% LCAC, respectively (indicated by the arrows). Of particular importance is that LCAC melts directly to the isotropic phase under UV irradiation

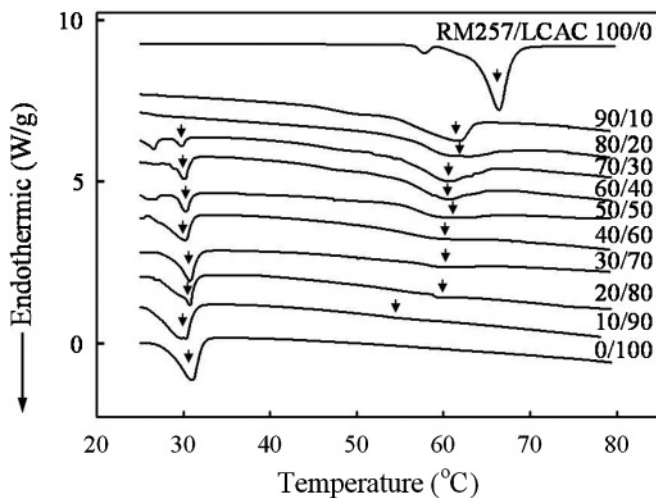


FIG. 7. Photo-DSC thermograms of RM257-LCAC mixtures under the continuous UV irradiation at 40 mW/cm². The thermograms were obtained at a heating rate of 5 °C/min. The photo-DSC thermograms of pure RM257 and its blend samples were shifted from the baseline for clarity.

without transiting through a nematic phase. We further analyze the DSC trends of the crystal-nematic and nematic-isotropic transitions by numerical calculation and optical microscopy.

To establish the theoretical phase diagram, the free energy of nematic ordering from the second component is inconsequential because LCAC did not form a nematic phase under UV light. Therefore, the total free energy in Eq. (8) is simplified to

$$f(\phi, \psi, s) = \phi_1 f(\psi_1) + \phi_2 f(\psi_2) + \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 - \phi_1 \ln Z_1 + \frac{1}{2} v_{11} s_1^2 \phi_1^2 + (\chi_{aa} + \chi_{ca} \psi_1^2 - 2\chi_{cc} \psi_1 \psi_2 + \chi_{ac} \psi_2^2) \phi_1 \phi_2 \quad (11)$$

in which the crystal-isotropic transition point and the corresponding heat of fusion (ΔH_2^u) of the photoisomerized LCAC were determined from the photo-DSC experiments. The parameters used in the self-consistent calculation are $r_1 = r_2 = 2$, $A = 0.6$, $T_c = -50$ °C, $\Delta H_1^u = 33.3$ kJ/mol/at $T_{Cr-N,1} = 66$ °C, $\Delta H_2^u = 12.7$ kJ/mol at $T_{m,2} = 31$ °C, $\chi_{ca} = 0.7$ at $T_{Cr-N,1}$, $\chi_{ac} = 0.3$ at $T_{m,2}$, and $c_w = 0.01$. As plotted in Fig. 8, the phase diagram consists of nematic + liquid ($N_1 + L_2$), crystal + liquid ($Cr_1 + L_2$), and crystal + crystal ($Cr_1 + Cr_2$) coexistence regions, and the single-phase nematic (N_1) and the crystalline phase (Cr_1 , Cr_2) in a manner depending on composition and temperature. Upon photoisomerization, the nematic phase (N_2) of neat LCAC completely disappears (enlarged view) and consequently the $Cr_1 + Cr_2$ coexistence region directly transforms to $Cr_1 + L_2$

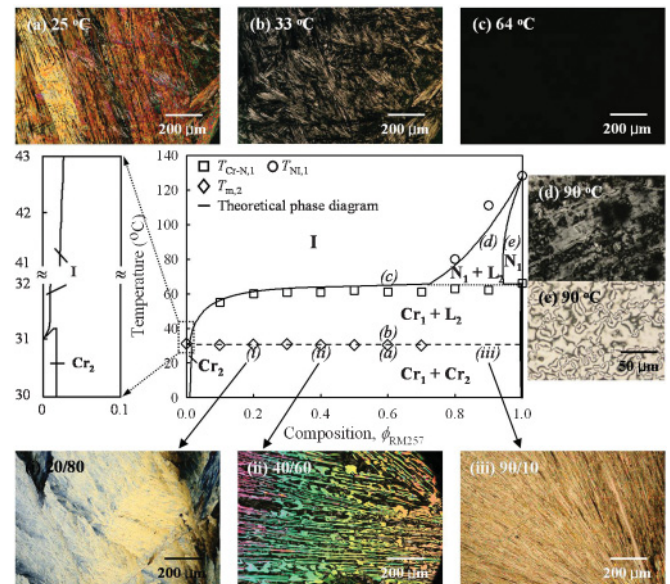


FIG. 8. (Color online) Comparison between theoretical and experimental phase diagrams of RM257-LCAC mixtures. To confirm the coexistence regions, the polarized optical micrographs were taken under the UV light for the 60-40 composition at (a) 25, (b) 33, and (c) 64 °C, and for the 90-10 and 95-5 blends at (d) and (e) 90 °C. Noticed that nematic phase (N_2) of LCAC disappeared due to *trans*-*cis* photoisomerization. The crystalline structures in (i) and (iii) are dominated by the majority constituent, whereas the mixture of separate individual crystals can be seen in (ii).

without passing through the $Cr_1 + N_2$ coexistence region. It should be noted that the liquidus and solidus line of nematic + liquid ($N_1 + L_2$) coexistence region shifts to higher RM257 compositions, implying that the photoisomerization of LCAC also suppresses the nematic ordering of RM257. However, the $Cr_1 + L_2$ gap is not significantly affected by *trans-cis* isomerization.

Figures 8(a)–8(e) show the morphological evolution of 60-40, 90-10, and 95-5 RM257-LCAC mixtures taken at a heating rate of 1 °C/min under continuous UV irradiation. At 60 wt.% RM257, the LCAC crystals become isotropic phase at 33 °C, at which the RM257 crystals are interspersed in a dark background [Fig. 8(b)]. Upon further heating to 64 °C, the crystalline RM257 directly transforms to the isotropic state. At 90 °C, the 90 wt.% RM257 shows the nematic disclinations dispersed in the isotropic liquid (dark), suggesting the nematic + liquid ($N_1 + L_2$) region [Fig. 8(d)]. At 95 wt.% RM257, the Schlieren texture develops, suggestive of the single-phase nematic (N_1) [Fig. 8(e)]. Pictures (i)–(iii) of Fig. 8 show the crystalline morphologies of the 20, 40, and 90 wt.% RM257 at 25 °C, respectively. The crystalline structures in pictures (i) and (iii) are seemingly dominated by the majority component, where the crystals of the minority component are trapped within the interlamellar regions of the majority component. In picture (ii), the mixture of separate individual crystals can be seen, characteristic of the $Cr_1 + Cr_2$ coexistence region.

V. CONCLUSIONS

The effect of photoisomerization on phase behavior of RM257-LCAC mixtures has been demonstrated experimentally and theoretically. The calculated liquidus lines were in

good accord with the depressed trends of the nematic-isotropic transitions. The phase diagram, thus obtained, consisted of the single-phase nematic (N_1, N_2) and crystal (Cr_1, Cr_2), and nematic + liquid ($N_1 + L_2$), crystal + liquid ($Cr_1 + L_2$), crystal + nematic ($Cr_1 + N_2$), and crystal + crystal ($Cr_1 + Cr_2$) coexistence regions. Upon irradiating with the UV light, the nematic phase of LCAC disappeared completely as the crystal transformed directly to the isotropic melt and, therefore, the phase diagram exhibited only the $Cr_1 + L_2$ coexistence regions. Moreover, the photoisomerization of LCAC induced the suppression of nematic-isotropic transition of its counterpart (RM257). The undulation on the LCAC crystal surface during the course of UV irradiation implied that the photoisomerization can take place even in the condensed phase, which may be attributed to the disparity of crystal density (or volume) of *trans*- and *cis*-isomeric states. This phenomenon is commonly found in other systems, such as the buckling phenomenon of syndiotactic polypropylene single crystals caused by a sudden volume change at the crystal-melt interface [31]. It should be emphasized that the present paper demonstrates the effect of *trans-cis* photoisomerization on the mesophase transitions of neat LCAC and the phase diagram of LCAC-RM257 as well as on the ripple formation (i.e., periodic undulation) on the azobenzene crystals.

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