Photochromism and Photopolymerization Induced Mesophase Transitions in Mixtures of Spiropyran and Mesogenic Diacrylate

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A phase diagram of a binary mixture of photochromic molecule (spiropyran) and mesogenic diacrylate monomer has been established by means of differential scanning calorimetry and polarized optical microscopy. Subsequently, a theoretical phase diagram has been calculated by self-consistently solving the combined Flory–Huggins free energy for isotropic mixing, Maier–Saupe free energy for nematic ordering, and phase field free energy for crystal solidification. The phase diagram thus obtained consists of various coexistence regions involving single-phase crystals, pure nematic, crystal + liquid, crystal + nematic, and crystal + crystal coexistence gaps. Under UV irradiation, both SP and SP/RM257 mixtures showed the lowering trend of the melting points, which may be attributed to the plasticization effect by the merocyanine isomers. When UV light is illuminated on the 2/98 SP/RM257 mixture for an extended period, mesogenic diacrylate in the mixtures gets polymerized, showing the permanent fixation of isotropic and nematic structures due to the network formation of RM257 caused by the biradicals in the merocyanine intermediate.

Introduction

Recent advances in optoelectronic devices have focused on development of new materials for fast information processing. Among many potential materials, organic chromophores have received considerable attention because of their photoreversibility and precision controls.¹⁻³ Taking advantage of different optical properties in the bistable isomeric states, such chromophores may be incorporated in a variety of matrixes to produce various functions: specifically, photomechanical response, anisotropic photoalignment, molecular assembly or selforganization, and so forth.4-8 Especially, liquid crystalline chromophores and their mixtures with liquid crystal (LC) counterparts have been investigated extensively because of their potential applications, including image display or recording, in which the molecular ordering/disordering of liquid crystalline system can be manipulated by light-induced preferential alignment.^{9–13} The light-manipulation of molecular architecture of these LC/chromophore systems has practical significance; for example, thin LC films containing photochromic molecules can be easily inscribed by means of photolithographic patterning. Moreover, the coherent light induces surface relief of the structure by mass migration at the surface as well as in the bulk for a variety of volume holographic gratings.^{14–16}

Photochromic spiropyran (SP) and its derivatives are one of the frequently used chromophores because of their photoinduced transformation of molecular geometry (or shape) and bistability. Upon exposure to UV light (320–400 nm), the C–O bond of the SP molecules undergoes heterolytic cleavage by transforming from the colorless closed SP structure to the colored open merocyanine (MC). Merocyanine is capable of returning to the initial SP form by irradiation with visible light or thermal treatment. Various applications using SP chromophores have been reported in the fields of optical switch, image storage, and surface modification by taking advantage of their photoreversible properties.^{17–21}

On the other hand, reactive mesogenic diacrylate monomers have been used to fabricate the macroscopically aligned polymer films. Upon polymerization, the reactive mesogens containing more than two polymerizable terminal groups yield the macroscopically ordered polymeric networks while maintaining their orientations as well as their mesophase structures permanently up to their degradation temperatures.²²⁻²⁴ By virtue of the inherent anisotropy of these mesogenic LC units and the concomitant mesophase ordering, the shrinkage due to polymerization is relatively low as compared with the conventional nonmesogenic networks. The blends of spiropyran (i.e., photoisomerizable chromophore) and mesogenic diacrylate (RM257, photopolymerizable monomer) are therefore of considerable interest because the alignment of polymeric LC network can be controlled by the SP-to-MC transformation. However, phase segregation and crystallization of these photochromic units have often led to deterioration in photophysical properties of these composite films. Therefore, understanding the phase diagram and associated phase transitions of these SP/RM257 mixtures is of paramount importance from the fundamental as well as practical standpoints.

In the present paper, phase behavior of spiropyran and mesogenic diacrylate (RM257) mixture has been investigated by means of differential scanning calorimetry (DSC) and optical microscopy. A theoretical phase diagram was calculated by selfconsistently solving the combined free energies of Flory–Huggins (FH), Maier–Saupe (MS), and phase field (PF) models. From the nematic and crystal phase order parameters of each constituent, the phase transition temperatures were determined, and the coexistence points were evaluated in the context of a double tangent method via balancing the chemical potentials of each phase. Thermal quenching experiments were performed to identify the single and coexistence regions in comparison with the theoretical phase diagram. Finally, the photochromism and photopolymerization-induced mesophase transition has been

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examined by irradiating UV light at the single-phase nematic and isotropic phases, and the effect of UV induced SP-to-MC chromism on the phase diagram of the SP/RM257 blend has been explored.

Experiments

Materials and Methods. The spiropyran chromophore (SP, $M_w = 322.4$ g/mol) and reactive mesogenic diacrylate monomer (RM257, $M_w = 588.6$ g/mol) were purchased from Aldrich and Merck Ltd. respectively, and used without further purification. Spiropyran transforms to merocyanine upon exposure to UV light and reverts back to its ground state by thermal treatment or irradiation with visible light. The mesogenic diacrylate monomer possesses acrylate double bonds at both ends of the backbone, capable of undergoing photoinitiated radical reaction (or photo-cross-linking). The blend samples containing different SP contents were prepared at room temperature by dissolving in a common solvent, carbon tetrachloride (CCl₄). These mixtures were mechanically stirred and homogenized and then cast onto slide glasses. The residual solvent was further removed by drying in a vacuum oven at 40 °C for 24 h.

The closed SP/open MC molecular shape transformation was monitored by means of a UV/vis spectrophotometer (model 8453, Hewlett-Packard). The spiropyran/n-hexane solution was piped into a quartz cell, and then absorption spectra were recorded as a function of UV wavelength. Phase transition temperatures of pure and mixed samples were determined using differential scanning calorimetry (DSC, model Q-1000, TA Instruments). The DSC scan rate was 5 °C/min unless indicated otherwise. Only the first DSC scan was analyzed because neat RM257 can undergo self-polymerization during annealing at 150 °C if the annealing time exceeds 1 h. The cell was purged with nitrogen gas at a flow rate of 40 mL/min. For optical microscopy (BX60, Olympus) analysis, the pictures of various coexistence phases were taken using a digital camera (EOS 300D, Cannon) following several thermal quenches. The UV unit (ELC403, Electrolite Corporation) having an intensity of 40 mW/cm² at a wavelength of 350-380 nm was utilized to trigger photochromism.

Thermodynamics Description. To describe the phenomena of liquid–liquid demixing, nematic ordering, and crystal solidification, we combined free energies of Flory–Huggins (f^{EH}), Maier–Saupe (f^{MS}), and phase field (f^{PF}) model along with their coupling interaction (f^{coupling}) energy. The free energy density of liquid–liquid demixing can be generally described according to the Flory–Huggins (FH) theory,^{25,26}

$$f^{\rm FH} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi_{\rm aa} \phi_1 \phi_2 \tag{1}$$

where r_1 and r_2 represent the numbers of lattice sites occupied by constituent molecules 1 and 2, which may be taken as unity for a small molecular system. ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. χ_{aa} is the Flory-Huggins interaction parameter representing the amorphous-amorphous interaction given empirically by $\chi_{aa} = A + B/T$, where A and B are constants.

Maier–Saupe (MS) mean-field theory is employed to account for the nematic ordering of liquid crystal molecules through the orientational order parameter, s_2 , in what follows:^{27–29}

$$f^{\rm MS} = \frac{\phi_2}{r_2} \left(-\ln Z + \frac{1}{2}\nu\phi_2 s_2^2 \right) \tag{2}$$

where ν is the anisotropic interaction parameter, and Z is the partition function. Equation 2 can be understood by dividing the total free energy density of MS theory into the entropic and enthalpic terms; that is, $f^{MS} = -(1/2)\nu\phi_2^2 s_2^2 - \phi_2(\ln Z - \nu\phi_2 s_2^2)$, where the entropy is dominant initially, contributing to an increase in the total free energy. With increasing director alignment, the enthalpic contribution due to the attractive interaction (i.e., the first term) becomes more negative, offsetting the entropic contribution (i.e., the second term). Consequently, the total free energy density exhibits a complex trend, giving rise to an unstable free energy hump at some intermediate value of s. However, with further increase in the director alignment, it decreases to a large negative value and exhibits a potential well for a nematic phase to stabilize. The detailed explanation of the variation of the free energy density with orientational order parameter pertaining to eq 2 can be found elsewhere.²⁹ The orientational order parameter (s_2) is defined as follows:

$$s_2 = \int f(\cos\theta) \frac{1}{2} (3\cos^2\theta - 1) \,\mathrm{d}\Omega \tag{3}$$

where θ is the angle between the director of LC molecules and the reference axis and $u(\theta)$ represents the nematic potential of the LC director orientation. The orientation distribution function, $f(\cos \theta)$, and the partition function, Z, are defined as

$$f(\cos \theta) = \frac{1}{4\pi Z} \exp[-u(\cos \theta)/kT]$$
(4)

$$Z = \int \exp\left[-\frac{u(\cos\theta)}{kT}\right] d(\cos\theta)$$
(5)

The anisotropic interaction parameter is given as $\nu = 4.541 T_{\text{NI}}/T$.

The free energy density of crystal solidification may be described in the context of the phase field model in which the free energy of pure crystal has the Landau-type asymmetric double-well form; namely,^{30,31}

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

The coefficient of the third-order term in eq 6 should be finite to describe the first-order phase transition. ψ_1 and ψ_2 are the crystal order parameters of each constituent. The coefficient W_i is related to the energy to overcome the unstable energy hump (ξ_i) , which may be estimated experimentally from the melting point $(T_{i,m})$ and heat of fusion (ΔH_i^u) ; that is,

$$W_i = 6\Delta H_i^{\rm u}/RT(1 - T/T_{i,{\rm m}}^0)(1/2 - \zeta_i)^{-1}$$

In addition, the coupling interaction term may be expressed in terms of crystal-amorphous (noncrystal), amorphous-crystal, and crystal-crystal interactions; that is,

SP, SP/RM257 Mixtures Mesophase Transitions

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

The last term in eq 7, indicating the nematic-crystal higherorder coupling interaction, is very small relative to the lower order coupling terms, and thus, it can be ignored. Hence, the total free energy of the binary crystalline and single component nematic system becomes

$$f(\phi, \psi, s) = \phi_1 f(\psi_1) + \phi_2 f(\psi_2) + \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + (\chi_{aa} + \chi_{ca} \psi_1^2 - 2\chi_{cc} \psi_1 \psi_2 + \chi_{ac} \psi_2^2) \phi_1 \phi_2 + \frac{\phi_2}{r_2} \left(-\ln Z + \frac{\nu \phi_2 s_2^2}{2} \right)$$
(8)

where $\chi_{ca} \equiv \chi_{c_1 a_2}$ is the crystal—amorphous interaction and $\chi_{ac} \equiv \chi_{a_1 c_2}$ represents the amorphous—crystal interaction. These interaction parameters are taken to be proportional to the heat of fusion of crystalline component; that is, $\chi_{ca} \sim \Delta H^u_1/RT$; $\chi_{ac} \sim \Delta H^u_2/RT$, and the crystal—crystal interaction parameters can be expressed by their geometric mean; that is, $\chi_{cc} = c_w(\chi_{ca} \cdot \chi_{ac})^{1/2}$, where c_w signifies the departure from the ideality (i.e., $c_w = 1$ for the ideal solid solution). The crystalline—amorphous interaction parameter, χ_{ca} , of a crystalline—amorphous blend can be determined experimentally from the liquidus front (i.e., the melting point depression approach), as reported by Rathi et al.³² The phase transitions from nematic—isotropic and crystal—nematic may be obtained by minimizing the total free energy with respect to the respective order parameters as follows:

$$\frac{\partial f(\phi, \psi, s)}{\partial s_2} = 0 \quad \frac{\partial f(\phi, \psi, s)}{\partial \psi_1} = 0 \quad \frac{\partial f(\phi, \psi, s)}{\partial \psi_2} = 0$$
(9)

These minimized values of *s* and ψ_i thus obtained may be subsequently substituted in the free energy expression (eq 8), and then the coexistence points may be calculated by balancing the pseudo chemical potentials for each phase along with the double tangent method; namely, $(\partial f/\partial \phi_i)|_{\phi_i^{\alpha}} = (\partial f/\partial \phi_i)|_{\phi_i^{\beta}}$. The detailed procedures for seeking the self-consistent solution by a double tangent algorithm can be found elsewhere.³³

Results and Discussion

Phase Diagram of SP/RM257 Mixtures. The initial SP/nhexane solution is transparent and colorless, showing no discernible UV/vis absorption peak (Figure 1). Upon UV irradiation, the transparent SP/n-hexane solution turned to a dark blue merocyanine (MC), which may be attributed to the cleavage of a C–O bond. When the UV light is turned off, the solution gradually returns to the transparent state, implying a reversible nature of the SP-MC transformation. With the UV illumination, a broad absorption peak develops at around 590 nm and a minor shoulder appears at 420 nm, which are ascribed to excited state absorptions from merocyanine isomers.³⁴ The pathway of SPto-MC transition is shown in Figure 1, where the C-O bond cleavage has led to the generation of the biradicals in the intermediate that eventually transform to a more stable Zwitterion form of the MC molecule.35 The intensity of both peaks progressively increases with irradiation time, indicative of the forward SP-to-MC conversion. After 3 min, the peak intensities



Figure 1. UV/vis absorption spectra of spiropyran in *n*-hexane solution as a function of UV light irradiation time. The intensity of the UV source was 40 mW/cm.²



Figure 2. Comparison of DSC thermograms and optical micrographs of neat RM257 before and after photopolymerization. (a) Optical micrographs of monomeric RM257, corresponding to the crystal + nematic, nematic + isotropic coexistence regions, and the isotropic phase. (b) Upon photopolymerization of RM257/photocurative system, the crystal, nematic, and isotropic morphologies got permanently fixed, showing no signs of degradation up to the maximum temperature of the experiment (i.e., 250 °C).

show a tendency of leveling off as the SP-to-MC conversion reaches asymptotic equilibrium in hexane solution.

The DSC thermogram of neat RM257 exhibits two major endothermic peaks at ~71 and 128 °C, along with a weak minor peak at around 43 °C. The weakest broad peak at 43 °C may be a consequence of the melting of nonequilibrium crystals formed during the cold crystallization. As manifested by the optical micrographs in Figure 2a, the crystalline, nematic, and isotropic phases can be identified at 26, 100, and 130 °C respectively. This observation suggests that the low-temperature DSC peak at 71 °C corresponds to the crystal-nematic (T_{Cr-N}) transition, whereas the highest peak at 128 °C is due to nematic-isotropic $(T_{\rm NI})$ transition. When photopolymerization was carried out on the RM257/photocurative (Irgacure 651) system at various reaction temperatures corresponding to the isotropic, nematic, and crystalline regions of neat RM257, these hierarchical morphologies got permanently fixed due to the formation of the diacrylate networks. More importantly, these structures persisted up to the highest experimental temperature of 250 °C without any sign of degradation (Figure 2b).

Figure 3 depicts the DSC thermograms of the SP/RM257 blends obtained at a heating rate of 5 °C/min. The crystal melting point ($T_{m,1} = 178$ °C) of neat SP and crystal-nematic ($T_{Cr-N,2} = 71$ °C) and nematic-isotropic ($T_{NL2} = 128$ °C) transition



Figure 3. DSC thermograms of SP/RM257 mixtures, showing the systematic shift of phase transitions as a function of blend ratio. The inset shows the enlarged DSC melting transitions of SP at intermediate compositions. The heating rate was 5 °C/min.

temperature of neat RM257 decline in their blends, as indicated by the arrows. The enlarged view of $T_{m,1}$ at 40–20 wt % SP is shown in the inset. Compared with $T_{m,1}$, the depression of $T_{Cr-N,2}$ of RM257 in mixtures is not significant because of the limited plasticizing effect by SP. On the other hand, the T_{NI} of RM257 decreases drastically from 128 to 88 °C with addition of 10 wt % of SP, and thereafter, it levels off. To identify the single and coexistence phases bound by the liquidus and solidus lines, the theoretical calculation has been carried out and compared with the experimental phase diagram as well as with the morphology development in the thermal quench experiments.

In the theoretical calculation, we examined the variation of crystal and nematic order parameters of each constituent in neat constituents as well as their blends. As can be seen in Figure 4a, the order parameter of pure SP crystal (ψ_1) drops discretely at 178 °C. Upon adding RM257, a similar discontinuous transition takes place at a lower temperature, and concurrently, its value decreases with concentration. The lower value of crystal order parameter suggests that the emerged SP crystal is solvated and becomes less perfect. A similar trend is observed for RM257 crystal (ψ_2) in Figure 4b, in which the crystal-nematic phase transition of pure RM257 declines from 71 to 62 °C with increasing SP (to 15 wt %) with its value around 0.99 and an additional discontinuous change occurring at a higher temperature arising from the nematic-isotropic phase transition (Figure 4b). The isotropization temperature of RM257 drops from 128 to 68 °C as the SP content is increased from 0 to 15%. By inserting these values into the respective PF and MS free energies and combining together, the total free energy curve can be constructed for each temperature, and the coexistence points can be determined in accordance with the common tangent. Subsequently, the liquidus and solidus lines were obtained by connecting the loci.

The predictive capability of self-consistently calculated phase diagram is further compared with the experimental observations. In Figure 5, the calculated lines represented by the solid lines are in good accord with the DSC melting transition points denoted by the open circles. The model parameters utilized in the self-consistent calculation were $r_1 = r_2 = 1$, A = 0, $B (= \chi_c T_c) = 346$ K at $T_c = -100$ °C, and $c_w = 0.01$, along with the experimentally accessible material parameters: $\Delta H_1^u = 20.3$ kJ/mol at $T_{m,1} = 178$ °C, $\Delta H_2^u = 30.7$ kJ/mol at $T_{Cr-N,2} = 71$ °C, and $T_{NI,2} = 128$ °C. Of particular interest is that the calculated liquidus line captures the experimental trend of the depressed melting points, whereas the crystal solidus line is virtually



Figure 4. Temperature dependence of crystal and nematic order parameters of SP and RM257 in their neat and blend concentrations: (a) crystal order parameter of SP (ψ_1) and (b) crystal and nematic order parameters of RM257 (ψ_2 , s_2).



Figure 5. The calculated liquidus and solidus lines in comparison with the experimental phase diagram of SP/RM257 mixture. The circular symbol represents the phase transition points determined by DSC, and the solid line denotes the theoretical curves.

coincided with the pure axes of the constituents. In a descending order of temperature, the crystal + liquid (Cr₁ + L₂), crystal + nematic (Cr₁ + N₂), and crystal + crystal (Cr₁ + Cr₂) coexistence regions are discernible over the broad compositions. At extreme RM257 compositions (e.g., <10 wt % SP), the single-phase nematic (N₂) appears below the T_{NI} of RM257. With descending temperature, the isotropic phase transforms to a single-phase nematic (N₂) by passing through the narrow liquid + nematic (L₁ + N₂) coexistence gap. The single-phase crystal of respective constituent (Cr₁, Cr₂) is hard to identify in the phase diagram because the solidus lines of Cr₁ + Cr₂ coexistence region are virtually overlapped with the pure axes,



Figure 6. Polarized optical micrographs of 5/95 and 60/40 SP/RM257 mixtures taken after 5 h following several temperature quenches into various coexistence regions corresponding to (a) single nematic (N₂), (b) crystal + liquid (Cr₁ + L₂), (c) crystal + nematic (Cr₁ + N₂), and (d) crystal + crystal (Cr₁ + Cr₂) coexistence regions.

implying that the SP and RM257 molecular crystals prefer to grow within their own species, forming separate crystals.

The thermal quenching experiments are further undertaken to test the validity of the calculated phase diagram. Figure 6a-d shows the polarized optical micrographs of 5/95 and 60/40 SP/ RM257 mixtures taken after 5 h following various temperature quenches to the single and coexistence regions (marked on the phase diagram). At 5 wt % SP (Figure 6a), the Schlieren textures with two and four brushes representing the strength of line disclination of $\pm 1/2$ and ± 1 are fully developed at 90 °C, indicative of the single-phase nematic (N_2) (Figure 6a). The presence of $Cr_1 + L_2$, $Cr_1 + N_2$, and $Cr_1 + Cr_2$ coexistence regions has been confirmed by changing the quench depth of 60/40 SP/RM257 mixture. The sample was heated to the isotropic state (170 °C) and then quenched to the corresponding coexistence regions. When the sample was quenched to 110 °C, the numerous needle-like crystals were found to disperse in the continuum of surrounding isotropic liquid (Figure 6b). Since the morphology shows no structural change after 5 h, it may be inferred that $Cr_1 + L_2$ coexistence region reaches asymptotically a stable state. Upon thermal quenching from 170 to 75 °C (Figure 6c), the bright area with dark brushes develops at the edge of the crystals, since the isotropic RM257 transforms to the nematic phase (please see the enlarged view). However, the dark region still persists, the origin of which is presently unclear. One possible conjecture is that it may be associated with the homeotropic alignment of RM257 mesogens. Figure 6d shows the optical micrograph taken after a temperature quench to 28 °C, in which the whole microscopic view area is covered by both constituent crystals, confirming the $Cr_1 + Cr_2$ coexistence region.

Effect of Photochromism on Phase Behavior of SP/ RM257 Mixtures

The effect of SP–MC photochromism on phase transition behavior of pure SP was examined by irradiating with UV light for 5 min in the isotropic state, that is, 4 °C above the isotropization temperature. After cooling the sample to ambient temperature, DSC scans were acquired at a rate of 5 °C/min. Since the SP-to-MC chromism can hardly reach full conversion, the residual SP may undergo crystallization during cooling. As shown in Figure 7, the crystal melting temperature of the UVexposed neat SP was found to be depressed from 178 to 174 °C. The observed lowering of T_m of neat SP may be due to the plasticizing effect by the UV irradiated noncrystalline merocyanine or its intermediate.



Temperature (⁰C)

Figure 7. DSC thermograms of pure SP and its blends with RM257 after UV irradiation at the isotropic region, displaying a slight depression of crystal melting point of SP. No transition peak was observed above 80 wt % RM257. DSC scans were conducted at a heating rate of 5 °C/min.



Figure 8. Comparison of DSC thermograms of the 2/98 SP/RM257 mixture before and after UV irradiation, showing the complete disappearance of the crystal-nematic and nematic-isotropic transitions of RM257 upon UV irradiation.

The same study was extended to various SP/RM257 blends, in which the melting temperature ($T_{m,1}$) of SP was systematically reduced with increasing RM257 content (Figure 7). There are two possible scenarios for the reduction of $T_{m,1}$ in the SP-MC/ RM257 mixtures: the plasticization effect by RM257 (provided that there is no cross-linking) or the formation of MC during UV irradiation, or combination of both. At higher RM257 loading levels above 80%, the DSC thermograms show no melting peaks, suggesting that the original eutectic melting behavior of SP/RM257 blend is no longer discernible upon UV irradiation.

To illustrate further, the DSC thermograms of the 2/98 SP/ RM257 mixture before and after UV irradiation at the isotropic state (125 °C) were compared in Figure 8. Prior to irradiation, the 2/98 SP/RM257 mixture shows two endothermic peaks corresponding to the crystal-nematic (69 °C) and the nematicisotropic (121 °C) transitions, but are a few degrees lowered than those of neat RM257 (see Figure 2), which is simply due to the plasticization by SP. However, upon UV irradiation, these peaks completely disappear, implying that the photoinduced SP-MC transformation might have prevented the crystallization of RM257. Even though Zwitterion is a major product of photoisomerized MC, the biradicals are found in the MC intermediates.³⁵ It may be hypothesized that the biradicals resulting from the cleavage of the C–O bonds of SP during the SP-to-MC



Figure 9. Morphology development of the 2/98 SP/RM257 mixture subjected to photochromism at (a) isotropic (i.e., at 125 °C), showing the appearance of infusible birefringence entities; and (b) nematic phase (i.e., at 100 °C), showing the fixation of the nematic Schlieren texture upon UV irradiation in the nematic gap.

chromism have triggered the photo-cross-linking of RM257 in the presence of MC intermediates.

To elucidate possible photopolymerization of RM257 in the presence of SP, the morphological investigation of the 2/98 SP/ RM257 mixture during the course of photochromism was carried out without adding any curatives. When UV light is illuminated on the above mixture at the isotropic state (i.e., 125 °C), numerous birefringence droplets appear and persist up to 200 °C (Figure 9a), which is consistent with the DSC result showing no phase change. Similarly, when photopolymerization was taken at the single-phase nematic temperature of 100 °C (Figure 9b), the Schlieren texture was permanently fixed, that is, infusible up to the maximum experimental temperature of 200 °C. The fixation of the nematic Schlieren texture is one of the signatures of the RM257 reactive mesogen undergoing photopolymerization.²² As seen in Figure 2, the anisotropic polymer network prepared from the neat RM257 sustained its crystalline and nematic structures up to 250 °C. As pointed out earlier, the product of photoisomerized MC intermediates is the biradicals, which may be responsible for the structural vitrification phenomenon of the present SP/RM257 system.

As pointed out above, there are two opposing effects of the UV irradiation on phase transitions of the SP/RM257 blends: (1) the formation of MC that can lower the SP melting associated with the plasticization effect, and (2) the biradicals thus generated in the merocyanine intermediates trigger the curing reaction of RM257 such that the resulting network will raise the melting transition temperature of SP, that is, polymerizationinduced crystallization. Since the melting point depression was found to be prevalent in the UV irradiated SP in its blends with RM257 (Figure 7), it is reasonable to conclude that the plasticization effect predominates over the polymerizationinduced crystallization of SP. The above finding implies that the free radical curing reaction of RM257 in the presence of biradicals of MC intermediates must be slow, and the conversion may be low, but it is just enough to fix the underlying mesophase or crystalline structures permanently in the SP/RM257 system.

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Conclusions

We have demonstrated the eutectic behavior of SP/RM257 blends that consisted of single component mesophases (N2) and $Cr_1 + L_2$, $Cr_1 + N_2$, and $Cr_1 + Cr_2$ coexistence regions in the temperature versus composition phase diagram. The corresponding single and coexistence regions have been further confirmed by the emerged morphologies following thermal quenching. The photochromism of SP to MC was found to lower the melting transition temperatures of neat SP as well as those in the SP/ RM257 mixtures. Moreover, the UV irradiation of the SP/ RM257 blend in the isotropic state has led to the formation of infusible nematic phase over the broad temperature range investigated, which may be attributed to the photopolymerization of RM257 triggered by biradicals of the merocyanine intermediates. These observations imply that either the radical curing reaction of RM257 must be slow, the conversion may be low, or both. However, it is still sufficient to anchor the underlying mesophase or crystalline structures permanently in the present SP/RM257 system.

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