PHOTOISOMERIZATION- AND PHOTOPOLYMERIZATION-INDUCED PHASE TRANSITIONS IN MIXTURES OF PHOTORESPONSIVE CHROMOPHORES AND REACTIVE MESOGENS

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PHOTOISOMERIZATION- AND PHOTOPOLYMERIZATION-INDUCED PHASE TRANSITIONS IN MIXTURES OF PHOTO RESPONSIVE CHROMOPHORES AND REACTIVE MESOGENS

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Phase diagram of various blend systems containing photochromophores and reactive mesogenic diacrylate monomers has been constructed both experimentally and theoretically. Differential scanning calorimetry was commonly utilized to determine phase transition temperature, and theoretical curve was obtained by solving self-consistently the combined free energy of Flory-Huggins, Maier-Saupe, and phase field theory. Depending on the system, it exhibited various single and coexistence phases including crystal, nematic, crystal + isotropic, nematic + isotropic, crystal + nematic, and crystal + crystal. Guided by the phase diagram, we further investigated (i) self-motion of azobenzene chromophore (AC) in triacrylate (TA) solution, (ii) photoisomerization-induced phase transition of liquid crystalline azobenzene (LCAC) and spiropyran (SP) chromophore in its mixtures with reactive mesogenic diacrylate (RMDA), and (iii) photopolymerization-induced phase separation of RMDA/low molecular weight liquid crystal (LMWLC) blends.

Self-motion of AC single crystal in TA solution was investigated in relation to the solid-liquid phase diagram. Upon thermal quenching from the isotropic melt to the crystal + liquid gap, the concentration gradient that formed as the result of TA expulsion induced convective flows and generated spatial variability of surface tension usually responsible for Marangoni effect. A stationary rhomboidal crystal was also shown to swim upon
irradiation with UV light due to mechanical torque generated by trans-cis isomerization.

The trans-cis photoisomerization of LCAC not only exerted a dramatic effect on the mesophase transitions, but also on the stratification on the crystal morphology. The phase diagram of photoisomerized mixtures displayed a significant depression of nematic ordering. Meanwhile, spiropyran-merocyanine molecular shape change induced the I-N phase transition, which was infusible.

Upon photopolymerization of RMDA/LMWLC blends, the homogeneous mixtures underwent phase separation. As the crystalline and nematic ordering of monomeric unit was frozen, LMWLC was dispersed in the continuum of isotropic or anisotropic networks. Phase diagram exhibited the broad immiscible regions.

The phase diagram of annealed hyperbranched polymer/LMWLC mixtures was an upper azeotrope, exhibiting the coexistence of nematic + isotropic phase above the clearing temperature of neat LMWLC. With decreasing temperature a focal-conic fan shaped texture developed in the composition range of 63–93 wt %, suggestive of induced smectic phase in the mixture.
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CHAPTER I
INTRODUCTION

By virtue of recent emergence of optical devices and display technology, our daily lives have been greatly influenced by the information-oriented society. In order to meet rapid development of the electro-optical devices, the high performance materials that can manage the process fast and precisely are in high demand. Optical materials such as functional organics, liquid crystals, and polymers have numerous advantages over their inorganic counterparts because of their flexibility, light weight, ease of processing, and low cost. Especially, photoresponsive chromophores, reactive mesogens, hyperbranched polymers gain immense interest due to their intrinsic characteristics. The former two molecules are sensitive to UV light, while the latter forms birefringence-free film with adjustable functional terminal groups. They are often chemically attached or blended with polymer or liquid crystal host in order to modify their surface or bulk properties.

The photoresponsive chromophores may undergo reversible molecular shape change depending on the wavelength of light.\cite{1,2} Two isomers differ from each other not only in absorption spectra but also in physical and chemical properties such as refractive indices, dielectric constant, polarity, and geometrical structure. The simple and precise property changes without additional processing step are of particular importance to the creation of optoelectronic, reversible holographic, optical switches, and information
storage. Azobenzene and spiropyran derivatives are among the most widely studied photochromophores. Under UV light, they convert trans-to-cis and spiropyran (SP)-to-merocyanine (MC) isomer.\(^2\) When these molecules are blended with liquid crystals (LCs), isothermal phase transition takes place by molecular shape change and thus the transmittance of the blend can be controlled.\(^3,4\) Although LC materials themselves may control the properties of light effectively, they are intrinsically insensitive to the optical field. Therefore, photochromophores into LC host play has practical importance.

The LC networks prepared from reactive mesogens display anisotropic optical, electrical, and thermo-mechanical properties.\(^5\) Since the orientation and other desired properties of liquid crystal monomers are “frozen in” after polymerization, it is easy to prepare the anisotropic networks over the broader area compared to liquid crystalline polymers.\(^6,7\) The macroscopically-oriented anisotropic film can be utilized as an optical compensator to resolve narrow viewing angle in display and alignment layer of low molecular weight liquid crystal (LMWLC) in polymer-dispersed liquid crystals (PDLC) and polymer-stabilized liquid crystals (PSLC) composites. Photopolymerization is a preferred preparation method because curing parameters such as time and temperature are freely chosen and moreover high conversion can be achieved within short time.

In contrast to anisotropic LC network, hyperbranched polymer can form birefringence-free film due to random orientation of molecular arms or fractal branches. Birefringence degrades the performance of optical devices that require maintaining the polarization state of the incident light. It is well known that the larger the anisotropy, the more severe the optical distortion. These dendrimers can be tailored to create a precise composition and with alteration of the terminal functionality, surface control can be
facilitated. When it was blended LC molecules, the multidomain structures are obtained due to random orientation. These scattered film becomes transparent by applying external mechanical and electric forces.\textsuperscript{8, 9} Therefore, hyperbranched polymer/LMWLC composite is another source of display applications. However, simple mixing of these well-suited materials is not enough to get the required properties. We need detailed information of phase behavior at a given composition and temperature.

In the present dissertation, we dealt with four main topics depending on the potential applications of the blending system: (i) construction of equilibrium phase diagram containing photoresponsive chromophores, photoreactive acrylate monomers, and hyperbranched polymers; (ii) demonstration of nucleation and growth behavior of azobenzene single crystals in triacrylate solution subjected to thermal quenching or UV irradiation; (iii) comparison of phase behavior before and after photoisomerization of liquid crystalline azobenzene chromophore (LCAC)/reactive mesogenic diacrylate monomer (RMDA) and spiropyran (SP)/RMDA mixtures, and photopolymerization of RMDA/LMWLC mixtures; (vi) elucidation of induced smectic phase of hyperbranched polymer/LMWLC mixtures. The DSC technique was commonly used to determine crystal melting and mesophase transition of neat component and their mixtures, and theoretical coexistence curve was calculated by solving self-consistently the combined Flory-Huggins (FH), Maier-Saupe (MS), and phase-field (PF) free energies to describe isotropic mixing, nematic ordering, and crystal solidification. The single and coexistence regions of the constructed phase diagram and crystal growth dynamics was examined using polarized optical microscopy.
2.1. Liquid Crystals

Liquid crystals (LC) possess intermediate properties between those of the crystalline solid and the isotropic liquid. They may flow like liquids, but show anisotropic properties like a crystal. Liquid crystal can largely be classified into thermotropic and lyotropic. The former exhibits temperature dependent LC ordering in the pure state, whereas the LC phases of lyotropic material are induced by solvent and therefore strongly concentration and temperature dependent. The molecules that form thermotropic LC are called mesogens and their shapes are highly anisotropic such as a rod-, a disc-, and bend-like entity with specific functionality. These anisotropic properties of small LC materials have been successfully applied to industrial applications since the 1970s. The LC phases induced by the rod-shaped molecules are calamitic phase, while disc- and bend-shaped molecules generate discotic and banana phases. This chapter only deals with thermotropic calamitic LCs.

2.1.1. Ordering in Liquid Crystals

Various mesophases are defined in accordance with the type of orders. Ordering in thermotropic LCs arises both from steric effects and from intermolecular Van der Waals
forces. The orientational order means that the molecules have a preferential orientation with respect to a specific direction in which the symmetry axes of the ordering objects are on average parallel to a well-defined spatial direction, $n$, known as the director (Figure 2.1a). The degree of orientational order can be represented by order parameter, $s$, which varies with temperature. The orientational order exists not only in a nematic phase but also in other LC phases. The second type of order is positional or translational order which may be attributed to the center-of-mass to center-of-mass ordering of a liquid crystal system. When the system remains invariant under translation by an integer number of lattice translation vectors, positional order may be present. The arrangement of basic units (e.g., monomer molecules) or the mass density exhibits periodicity. The smectic-A and -C phase possess the positional order in a layer form. A third type of order is bond orientational order in which a bond is not a chemical bond but a line in space.
joining two adjacent molecules as shown in Figure 2.1(c). If the orientation of these bonds is preserved over a long range, then LCs may be considered to have bond orientational order. It is encountered in the hexatic smectics. The three main types of order are summarized in Figure 2.1.11

2.1.2. Liquid Crystalline Phases

Figure 2.2 illustrates a simplified scheme for achiral LC phases depending on temperature. The molecules in the nematic phase exhibit only an orientational order in which the rod-shape molecules tend to align parallel to each other with their long axes, pointing roughly in the same direction. The molecules in this phase are free to rotate about their long axes (about $10^{12}$ times per second) and to some degree about their short axes (about $10^6$ times per second). The simplest way of defining the degree of alignment is by the order parameter ($s$), which was introduced by Tsvetkov.12 A zero order parameter implies that the long axes of the molecules are randomly distributed, whereas the value of unity indicates that the long axes of the molecules are perfectly oriented.

The diffraction pattern of an unaligned nematic phase is not much different from that of the isotropic phase. The one dimensional wide angle x-ray powder pattern of the nematic phase has one diffuse peak in the wide angle region, roughly corresponding to the average lateral distance between molecules (Figure 2.3a).1 A relatively broad diffuse peak in the low angle region may give an information about the molecular length. Despite the same features of 1D WAXD powder pattern of the isotropic liquid and the nematic phase, the phase transition can still be distinguishable by identifying a sudden shift of the peak maximum in the wide angle region. Since the isotropic to nematic phase transition is
Figure 2.2 An illustration of phase transition of achiral liquid crystals as a function of temperature. The most ordered and least symmetric phase phase is at the bottom (redrawn from references 10 and 11).

a first order transition, it may be accompanied by a discontinuous change of the average molecular volume.

Smectic phase has a higher degree of order than nematic phase, possessing positional order. The arrangement of the liquid crystal is layered within which the molecules move freely but they are prohibited to move between the layers. The layered structure allows a partial translational ordering and thus makes more viscous than other phases. The three representative smectic phases are $S_{mA}$, $S_{mC}$, and $S_{nB}$, where the degree of order presented both within and between the layers is different. The $S_{mA}$ phase can be simply described as a stacking of two-dimensional liquid layers with the long axes of the molecules normal to the layer plane on average. Inside each layer, the centers of
Figure 2.3 Molecular structure of liquid crystal phase and its 1D diffraction patterns, representing (a) nematic, (b) smectic-A, (c) smectic-C, and (d) smectic-B phase. $l_o$ is the average length of the molecules and $w_o$ is the average lateral distance between the molecules (redrawn from references 10 and 11).
gravity show no long-range order. This phase may be characterized by short range positional order and short range bond orientational order in the layers. As the tilting is random across the bulk, the $S_mA$ phase is optically uniaxial with the optical axis perpendicular to the layer. The 1D WAXD powder patterns for the $S_mA$ phase is depicted in Figure 2.3b. The broad high angle scattering indicates the liquid-like nature of the lateral molecular packing like nematic phase and the sharp low angle reflection peak reveals the average distance of the layer spacing.

The $S_mC$ phase is different from the $S_mA$ phase in that the director ($n$) shows a constant tilt angle with respect to the layer normal and optically and physically biaxial. Tilt angle ($\alpha$) is a function of temperature and used to describe the transition from the $S_mA$ to the $S_mC$ phase. When temperature decreases lower than $S_mA$-$S_mC$ transition ($T_{AC}$), smectic layer spacing becomes $d(T) = d(T_{AC})\cos\alpha$. The 1D WAXD powder pattern is similar to that of $S_mA$ phase but due to the tilting of molecules the sharp diffraction peak gives a layer spacing smaller than the molecular length. The structural difference between the $S_mC$ and $S_mA$ phase may be more clearly observed in their oriented 2D-WAXD

Figure 2.4 Schematic drawing of 2D WAXD patterns of oriented (a) $S_mA$ and (b) $S_mC$ (redrawn from references 10 and 11).
patterns. In the $S_m^A$ phase, the diffraction spot representing the layer structure appear in the meridian, whereas the molecular tilting of the $S_m^C$ phase makes a pair of diffuse wide angle scattering halos appear in the second and fourth quadrants (Figure 2.4).

Highly ordered smectic phases have long-range bond orientational order. Orthogonal phases include hexatic-B, crystal-B, and crystal-E. In the hexatic-B phase, the molecules are locally hexagonally packed (Figure 2.3d) and the resulting six-fold bond orientational order is maintained for macroscopic distances. Even though these phases are close to three dimensional crystals, the molecules in them have freedom of rotation about their long axis. With a hexagonal arrangement the molecules can also tilt along two distinct directions with respect to the hexagonal lattice. In smectic-I, crystal-J, and crystal-K phase, the molecules tilt towards a corner, whereas in smectic-F, crystal-G, and crystal-H phases the tilt occurs in a direction perpendicular to the sides of the hexagon.

**Chiral Liquid Crystalline Phases**

The classification scheme for chiral rod-shaped LC phases is illustrated in Figure 2.5. Chiral compounds form a similar mesophase structure and phase sequences related to those of non-chiral substances. However, due to configurational chirality the chiral LC sometimes exhibits a new phase. A chiral nematic, often called cholesteric, differs from the nematic phase in that the director varies in direction throughout the medium. The molecules tend to align in a helical manner as depicted in Figure 2.6a. This phase may occur by nematic mesogenic molecules containing a chiral center like cholesterol ester or introducing some quantity of chiral molecules (dopant) to the nematic LC. The length scale of the helical pitch, ranging from 0.1 $\mu$m to infinity, is quite sensitive to temperature,
flow, chemical composition, and applied magnetic or electric field. In the widely used twist nematic LC displays (TN LCDs) the polarizer and analyzer are usually arranged perpendicular. Above the threshold electric field the molecules stand up from the surface to the center. In this case, light will be prohibited to go through the analyzer. When the electric field is removed, molecules are rotated 90° from the polarizer to the analyzer and therefore some light can go through the analyzer. In order to stabilize handedness of the helix, a certain percentage of N* chiral liquid crystal compounds must be added for the practical TN LCDs application.

Figure 2.5 An illustration of phase transition of chiral liquid crystals as a function of temperature. It shows similar phase sequences related to non-chiral mesophase. Figure is redrawn from the reference.¹⁰
Figure 2.6 Molecular structure of chiral liquid crystal and its application, representing (a) twist nematics (TN) and the construction and operation of the TN cells and (b) ferroelectric liquid crystals (FLCs) and simplified picture of surface stabilized ferroelectric liquid crystal (SSFLC) display (redrawn from references 10 and 11).
In a very small temperature region between cholesteric and the isotropic phase, compounds with sufficiently high twist can display four types of “blue” phases (BP), showing the phase sequence of isotropic $\rightarrow$ BPIII $\rightarrow$ BPII $\rightarrow$ BPI $\rightarrow$ smectic-BP. Both BPI and BPII phases have long-range orientational order. Since the lattice periodicity of the blue phase is of the order of 500 nm, it reflects visible light.

Many of the physical properties of a chiral phase are not present in the $S_m$A phase, but all of the smectic phases with tilted structure exhibits ferroelectric properties. In the $S_mC^*$ phase, the director axis tilts away from the layer normal proceeds in successive layers. This phase is ferroelectric as the molecules have a transverse permanent dipole moment. The presence of permanent dipoles alters the nature of the interactions between the molecules themselves and with any cell wall or applied electric field. Recently, the ferroelectric liquid crystalline phases have gained considerable attention for potential applications to fast switching electro-optical displays. The precession of tilt angle from layer to layer is also seen in other chiral smectic and crystalline phases. These materials generally show the same phases sequences as non-chiral phases and possess optical activity and selective reflection of circularly polarized light.

2.1.3. Reactive Mesogens

Liquid crystalline materials with polymerizable end groups are called reactive mesogens. Schematically, they are composed of three parts; (i) central mesogenic groups, (ii) reactive end groups, and (iii) spacers (Figure 2.7). Each group plays an important role in determining phase transition temperature and optical properties of the monomeric states. Polymerization of reactive mesogen containing more than two polymerizable ends
groups leads to the densely crosslinked networks in which the liquid crystalline order is permanently fixed.\textsuperscript{6,7} That is to say, polymerization of the end groups in the LC phase allows the attainment of the optimum mesophase morphology and alignment, followed by the “freezing in” of this structure on creation of the crosslinked network. The formation of large area, monodomain, and aligned morphology during cooling from isotropic point is possible due to the relatively low viscosity of the small molecules in comparison to the analogous liquid crystal polymer systems, which are more viscous in the liquid crystalline phases. The anisotropy of their mechanical, optical, electrical and electronic properties renders liquid crystals of unique interest as the starting materials for anisotropic networks, as well as for anisotropic elastomers and gels.

Anisotropic liquid crystal materials have several attractive applications. Cholesteric polymer networks formed from reactive mesogens are widely used as color flop pigments with a distinct viewing angle dependence of the color.\textsuperscript{15} Moreover, crosslinked cholesteric mesophases may be applicable to broad band polarizers in which such the reflected light is “recycled” and transmission up to 82\% have been achieved. Another advantage of reactive mesogens is that through the use of a shadow mask during the crosslinking process, pattern formation like in a negative photoresist is possible, compensating positive birefringence of LC in displays. Lub et al. produced a color filter
for all three fundamental colors with a pixel size of 100 µm. The three main applications of anisotropic LCs produced by polymerization are summarized below.

**Anisotropic Network**

Although polymerization of monofunctional monomers can lead to a polymer with a higher degree of order on a microscopic scale, the macroscopic order is difficult to sustain because of molecular shrinkage and phase transition during polymerization. Therefore, the uniaxially oriented films may be formed from the reactive mesogens having more than two functional groups (Figure 2.8a). Prior to polymerization, the orientation of monomer may be induced by external mechanical force, orientation layers, electric or magnetic fields, polarized light, etc. Broer and co-workers, Hikmet et al., and Braun et al. reported that highly crosslinked, macroscopically oriented films could be obtained by polymerization of difunctional LC monomers in contact with unidirectionally rubbed thin-film substrates. In addition, amorphous or liquid crystalline side group and/or main chain polymers incorporating additional reactive groups can be transferred onto a macroscopically oriented substrate and then crosslinked. Sometimes crosslinking can lead to the formation of a different mesophase.

**Anisotropic Elastomers**

Liquid crystalline elastomers have been developed as promising functional materials. Even though translational motion of the backbone of LC polymers may be eliminated by adding small amount of crosslinks (< 10 wt %), the chain segments between the crosslinked points can undergo micro-Brownian motion. The resulting product becomes
indefinitely viscous and regains its initial shape upon removal of a distorting force (Figure 2.8b). Prior to the crosslinking reaction, the crosslinking agents can act as a plasticizer at low concentrations, leading to a lowering of \( T_g \) of the polymer as well as slight depressions in other transition temperatures. The phase in which the crosslinking is carried out is stabilized by the chemical junctions. The side groups may lie parallel or perpendicular to the main chain director depending on the spacer length, which subsequently exhibits the properties associated with low molar mass LCs as well as standard elastomers.\(^{27}\) The mechanical and optical properties of such networks are also anisotropic below the clearing point \( (T_{cl}) \) in a manner dependent on the stress/strain fields.

### Anisotropic Gels

Anisotropic gels are obtained by \textit{in-situ} polymerization of reactive LC molecules in the presence of non-reactive LMWLCs (Figure 2.8c) in which the LMWLCs are not chemically bound to the network and free to move. Once three-dimensional network has
been formed, it becomes thermally stable, maintaining the orientated structure at even high temperature and having a profound influence on LC molecules. For instance, strong intermolecular forces between the network and the LC molecules result in a residual orientation even at temperatures significantly above \( T_{cl} \) of the original mixture. At relatively low network concentrations, most of the LC molecules are contained in the domains surrounded by the network with no measurable \( T_{cl} \).

2.2. Photochromophores

Since first observation of reversible color change of organic compounds in 1899,\textsuperscript{28} extensive studies have been devoted to the photochromophores. Photochromism is referred to as reversible transformation of a chemical species between two states having different absorption spectra by electromagnetic radiation (Figure 2.9a).\textsuperscript{1, 2} The activating radiation is generally in the UV region but could be in the visible. As shown in Figure 2.9b, initially the system contains only the A state of the molecules. The relative concentration of B increases right after exposing light at \( t_1 \) and then reaches the photostationary state for the equilibrium. When the exciting radiation is removed (\( t_2 \)), the original structure (A) is restored at a rate dependent on the dark reaction. Therefore, two bistable molecular structures (A and B) can be interconverted.

Depending on the reaction mechanism, chromophores can typically be divided into \textit{cis-trans} isomerization, bond cleavage, and tautomerism, as shown in Figure 2.10.\textsuperscript{1} Well-known molecules that undergo \textit{cis-trans} isomerization are the azobenzene. When UV light around 365 nm is irradiated, azobenzene chromophore at the ground \textit{trans}-state gets excited and switches its conformation to a higher energy \textit{cis}-state. The irradiation of
blue light (e.g. 420–450 nm) or thermal relaxation causes the cis-isomer to reverse into the trans-isomer. The spiropyran and diarylethene undergo the ring open-closure reaction under UV light. The initial colorless closed forms of spiropyran transforms into the colored open merocyanine structure, whereas the diarylethenes changes to the colored closed form. A major type of photochromic tautomerism is hydrogen transfer (Figure 2.10c). After irradiation with UV light, molecular rearrangement occurs. The keto-form of reddish or brown appears from enol-form which is pale yellow. This keto tautomer appears to exist in two forms: an intramolecular hydrogen bonded cis-keto form and a rotated trans-keto form. Light-driven precise and fast controls provides them to be often incorporated chemically or doped into amorphous polymers, liquid crystals, or other matrices in order to create various types of photofunctions such as photomechanical response, photoalignment of anisotropic materials, photoinduced phase changes, and so forth.

Figure 2.9 (a) The absorption spectra of two isomers, A and B, and (b) typical behavior of a photochromic substance A (redrawn from reference 1).
2.2.1. Azobenzene

In 1937, Hartley was the first to report the effect of light on the configuration of the N=N double bond. Azobenzene and its derivatives exhibit reversible photochromism in both solution and in solid. They have the principal absorption bands ($\pi \rightarrow \pi^*$) in the ultraviolet region and their yellow color is caused by a weak $n \rightarrow \pi^*$ absorption near 450 nm. On conversion to the cis-isomer, there is an increase in the strength of $n \rightarrow \pi^*$ absorption. Even though there has been extensive discussion of the reversible trans-cis
isomerization mechanism such as inversion and rotation, the exact mechanism has not been firmly established. The photochromism of azobenzene molecules is not accompanied by the distinct color change, but they have better photostability and faster response time. A strong interest in these compounds has developed because of their potential application in optical-switch and image storage. Figure 2.11 summarizes the hierarchical applications of azo-containing soft materials, ranging from molecules (sub nanometer size) to materials (micro- and centimeter size).\textsuperscript{30} Polymer films containing azobenzene moieties may undergo photomechanical deformation, i.e., contraction and expansion, for photoactuator and surface relief grating (SRG), while block copolymers form mesoscopic phase separated structures by self-assembly. In the case of liquid crystalline azobenzene chromophore, the orientation of rod shaped LC molecules can be affected by changing the direction of LC director (alignment) and phase transition.

The liquid crystalline azobenzene chromophore (LCAC) itself and its blend with other liquid crystalline molecules are capable of inducing the isothermal order-disorder mesophase transition by molecular shape. The rod-shaped \textit{trans}-form stabilizes the nematic (N), whereas bent-shaped \textit{cis}-form reduces the order of mesogenic molecules (Figure 2.12a).\textsuperscript{31-34} Therefore, the $T_{NI}$ of the mixtures with \textit{cis}-form is much lower than that with \textit{trans}-from. In contrast to temperature controlled transition, the instant and precise modulation is feasible for the photon-mode ferroelectric LC in displays. As described earlier, the macroscopically oriented networks can be prepared by the photopolymerization of reactive mesogenic diacrylate monomer (RMDA). When LCAC is incorporated into RMDA, the alignment of anisotropic networks and transmittance of light through the composite films can be manipulated. Under the linearly polarized light,
the LCAC monolayers on substrate are generally oriented to an unexcitable direction, namely, perpendicular to the electric vector of the polarization direction (Figure 2.13b). Since the monomeric RMDA molecules can be aligned along with LCAC, the anisotropic networks are easily fabricated by photopolymerization. Such active surface layers are called “command surface”. The composite films consisting of slightly-crosslinked anisotropic networks and LCAC can control the transmittance of light on the basis of the distribution of incident light. The trans-cis isomerization is induced in bright area of the interference patterns. These properties are the basis for the phase-mode holographic gratings, i.e., periodic nematic and isotropic phases (Figure 2.13c).\textsuperscript{35-37} They form fast and repeatable recording with high resolution. With low molecular weight liquid crystals (LMWLC), it is difficult to obtain stable holographic gratings because of high mobility.
Figure 2.12 Effect of UV light on (a) molecular shape, (b) alignment of anisotropic networks, and (c) phase-mode holographic gratings.
2.2.2. Spiropyran

Since the first observation of the photochromism of spiropyrans (SP) in 1952 by Fischer et al.,\textsuperscript{38} the SP and its derivatives are one of the most frequently used chromophores because of their geometrical isomerization. Upon exposure to UV light (320-400 nm), the Csp-O bond undergo heterolytic cleavage which transform the colorless closed spiropyran structure (SP) to the colored open merocyanine (MC). The MC itself is an equilibrium mixture of highly zwitterionic and non-ionic ortho-quinoidal structure (Figure 2.10b). Merocyanine returns back to the initial SP form thermally or photochemically. Spironaphthopyrans, piperidinospiropyran, and spirooxazines behave similarly. Molecular rearrangement from twist to planar structure formed by rotation of one half at approximately 90° is responsible for reversible color change. It is known that closed SP form is relatively hydrophobic, whereas open MC form is highly polar as a consequence of zwitterionic resonance form.\textsuperscript{23}

When the SP is dissolved in solvents with low polarity, a colorless solution is obtained. Upon increasing solvent polarity, the solution becomes colored, indicating that in polar solvents certain SPs are in equilibrium with MC-form, so-called solvatochromism.\textsuperscript{39, 40} Many spiropyran derivatives also exhibit temperature-dependent color change (thermochromism).\textsuperscript{41, 42} The light yellowish spiropyran leads to deep color on melting, generally red, purple, or blue. Moreover, heating of the colorless solution also causes coloration. The thermochromic mechanism in these classes has been assumed to be a thermally sensitive equilibrium between the spiropyran form and open merocyanine-like structure. The thermal produced colored materials appear to be spectrally and kinetically identical with that produced photochemically.
Among various kinds of spiropyrans, 1’-3’-3’-trimethyl-6-nitrospiro[2\(H\)-1-benzopyran-2,2’-indoline] has been extensively studied. Introduction of a nitro group at the 6-position of the benzopyran moiety shifts the equilibrium toward the open form, enhancing the quantum yield and colorability. However, one of major deficiencies for the potential applications is its short life cycle because of the thermal and photochemical decomposition. The polarity of solvent affects the photodegradation. It had a half-life of 1 min in hexane and longer than 100 min in acetonitrile. In nonpolar solvents strong intermolecular interactions would accelerate photodegradation process and moreover increasing the concentration affects photodegradation more severely.

Using different chemical and physical properties of each isomer including dipole moment, surface energy, refractive index, and volume, the spiropyran in a various matrixes or solution is employed for photonics and surface modification. Figure 2.13a illustrates the surface relief structures of SP-doped polymer films produced through a photomask.\(^{43}\) When light is shaded completely only a flat surface is observed. Upon irradiation of patterned light, the surface modulation is by inscribed by material migrations. Since it is a one-step process, it is advantageous for image storage and LC alignment. The control of ionic conductance using different polarity is suitable for optical valve (Figure 2.13b).\(^{44}\) Transport of ion or non-volatile neutral molecules across the membrane cannot occur until the membrane has been wet. The switching from SP to MC form opens membrane and lets the molecules through. The surface modification based on photochemical isomerization may control the hydrophobicity and hydrophilicity, leading to the reversible wetting change of solid substrate (e.g. glass) and aggregation and dispersion of colloidal silica.\(^{45, 46}\)
Figure 2.13 Applications of spiropyran chromophores; (a) surface relief grating, (b) light valve, and (c) surface modification (redrawn from references 43-46).
2.3. Hyperbranched Polymer

Dendritic molecules are typically composed of six subclasses: (a) dendrons and dendrimers, (b) linear-dendritic hybrids, (c) dendrigrafts or dendronized polymers, (d) hyperbranched polymers, (e) multi-arm star polymers, (f) hypergrafted polymers (Figure 2.14). Even though dendrimers exhibit perfect structures with a degree of branching (DB) of 1.0 compared to hyperbranched polymer exhibiting random branched structure, the synthesis scheme of hyperbranched polymers is known to be simpler than that of dendrimers, which require an additional step such as protection/deprotection. Up to now the hyperbranched polymers have been synthesized by using (i) A\textsubscript{x}B monomers in the presence of a catalyst or (ii) a core molecule and A\textsubscript{x}B monomers. The lower cost of synthesizing hyperbranched polymers allows them to be produced on a large scale, giving them an advantage over dendrimers in applications.

Numerous applications have been suggested for hyperbranched polymers because they are unique in that their properties are easily tailored by changing the nature of end group. Modification of the number or type of functional groups is crucial to control their solubility, compatibility, reactivity, adhesion to various surfaces, self-assembly, chemical recognition, and electrochemical and luminescence properties. A large number of functional groups allows for the tailoring of their thermal, rheological, and solution properties, and thus provides a powerful tool to design for a wide variety of applications. The combination of hyperbranched polymer and liquid crystals has demonstrated their potentials in information technology, most prominently in liquid crystal displays and in electro-optic and photonic devices.
At present, liquid crystal displays based on the light scattering methods of hyperbranched polymers have been an interesting research area due to possible applications in large-area display technology. The scattering originates from either i) solid particles, e.g., inorganic aerosol or rigid polymeric particles, dispersed in a filled nematic LC matrix, so-called polymer-filled nematics (PFN), or ii) small droplets of nematics dispersed in a continuous polymer matrix, polymer-dispersed liquid crystals (PDLC). Although these composites may show efficient contrast ratios, the high switching voltages requirement and the presence of hysteresis effects are pointed out as drawbacks for the above applications. Instead, when the hyperbranched polymers are used as a replacement the highly branched structures may provide a better scatterer due to their secondary interaction.
2.4. Thermodynamic Models

Prior to investigating the dynamics of phase separation and morphology evolution, it is prerequisite to understand how the equilibrium thermodynamics influences the phase behavior of the mixtures. The respective theoretical model describing isotropic mixing, nematic ordering, and crystal solidification will be employed. The total free energy density can be written in terms of the combined Flory-Huggins ($f_{FH}$), Maier-Saupe ($f_{MS}$), phase field ($f_{PF}$), and its coupling free energies, viz., $f = f_{FH} + f_{MS} + f_{PF} + f_{coupling}$.

2.4.1. Isotropic Mixing

Flory-Huggins (FH) theory is commonly employed for describing liquid-liquid demixing of a polymer blend. Gibbs free energy of mixing ($\Delta F_m$) of polymer solution can be defined by a combination of entropic mixing ($\Delta S_m$) and enthalpic mixing ($\Delta H_m$)

\[
\Delta F_m = \Delta H_m - T\Delta S_m.
\]  

(2.1)

The entropy and enthalpy change on mixing can be described in the context of the statistical lattice model$^{62-64}$

\[
\Delta S_m = -Nk_B \left( \frac{\phi_1}{r_1} \ln \phi + \frac{1-\phi_1}{r_2} \ln(1-\phi) \right),
\]  

(2.2)

\[
\Delta H_m = Nk_B T \phi(1-\phi) \chi_{FH},
\]  

(2.3)

where $N$ is total number of segments defined as $N = r_1N_1 + r_2N_2$ and $r_1$ and $r_2$ represent the numbers of statistical segments or sites occupied by component 1 and 2, respectively. The volume fraction of respective component, $\phi_1$ and $\phi_2$, can be given as $\phi_1 = r_1N_1/(r_1N_1 + r_2N_2)$ and $\phi_2 = r_2N_2/(r_1N_1 + r_2N_2)$. The lattice model for small
molecular mixture (solvent-solvent), a polymer solution, and a polymer blend is illustrated in Figure 2.15. The combination of arranging the molecules follows: small molecules $\gg$ polymer solution $\gg$ polymer blend. Therefore, the combinatorial entropy of mixing in first two systems makes an important contribution to the free energy of mixing. With high molecular weight polymers, the $T\Delta S_m$ term is small and thus the enthalpy of mixing determines the phase behavior of the polymer blend. The dimensionless FH interaction parameter $\chi_{FH}$ representing amorphous-amorphous interaction between the pair is generally assumed to be inversely proportional to absolute temperature, i.e., $\chi_{FH} = A + B/T$, where $A$ is related to athermal entropic correction and $B$ represents enthalpic contribution. The UCST and LCST phase behavior can be determined by choosing negative or positive value of interaction parameter. By inserting Eqn.(2.2) and Eqn.(2.3) into Eqn.(2.1), the free energy density can be rewritten as

$$f_m = \frac{\Delta F_m}{Nk_B T} = \phi \ln \phi + \frac{(1-\phi)}{r_1} \ln (1-\phi) + \chi_{FH} \phi (1-\phi). \quad (2.4)$$

Figure 2.15 Two-dimensional representation of the possible arrangement in (a) a small molecule mixture, (b) a polymer solution, and (c) a polymer mixture (redrawn from reference 65).
In order to determine the stability at a given temperature and pressure the following conditions should be satisfied\textsuperscript{65, 66}

\[ \Delta F_m < 0, \quad (2.5) \]

\[ \left( \frac{\partial^2 \Delta F_m}{\partial \phi^2} \right)_{T_P} > 0. \quad (2.6) \]

The coexistence of different phases under equilibrium state can be determined by equating the chemical potential of the constituent in each phase by taking the first order partial derivative of free energy of mixing with respect to the \( N_1 \) and \( N_2 \), respectively

\[ \Delta \mu_1 = k_B T \left[ \ln \phi + \left( 1 - \frac{r_1}{r_2} \right) (1 - \phi) + \chi_{\mu_1} r_1 (1 - \phi)^2 \right], \quad (2.7) \]

\[ \Delta \mu_2 = k_B T \left[ \ln (1 - \phi) + \left( 1 - \frac{r_2}{r_1} \right) \phi + \chi_{\mu_2} r_2 \phi^2 \right]. \quad (2.8) \]

By stipulating equality of the chemical potentials at each phase (\( \alpha, \beta \)), the binodal points can be determined

\[ \mu_1^\alpha = \mu_1^\beta \quad \text{and} \quad \mu_2^\alpha = \mu_2^\beta. \quad (2.9) \]

The spinodal points can be calculated by taking into account the second order partial derivative of the free energy of mixing with respect to \( \phi \) and making it equal to zero, viz.,

\[ \left( \frac{\partial^2 F_m}{\partial \phi^2} \right)_{p,T} = \frac{1}{r_1 \phi} - \frac{1}{r_2 (1 - \phi)} - 2 \chi_{\phi_1} = 0. \quad (2.10) \]

The binodal and spinodal points coincide at the critical temperature (\( T_c \)), which satisfies the following equality for the third derivative of the Gibbs free energy

\[ \left( \frac{\partial^3 F_m}{\partial \phi^3} \right)_{p,T} = 0. \quad (2.11) \]
Figure 2.16 Schematic phase diagram and corresponding free energy and its derivative at a given temperature. It shows how to determine the binodal curve based on double tangent method. 67
The critical volume fraction \( \phi_c \) and critical interaction parameter \( \chi_c \) can be determined.

\[
\phi_c = \frac{\sqrt{r_1} + \sqrt{r_2}}{\sqrt{r_1} + \sqrt{r_2}}, \quad (2.12)
\]

\[
\chi_c = \frac{(\sqrt{r_1} + \sqrt{r_2})^2}{2r_1r_2}. \quad (2.13)
\]

Figure 2.16 plots the free energy and its derivative curves at a given temperature and the phase diagram. The binodal points can be calculated using a double-tangent method.\(^67\)

### 2.4.2. Nematic Ordering

Maier-Saupe theory is based on a mean field approximation in which the energy of a molecule is independent of its particular environment. Rigid-rod molecules are assumed to have an attractive, orientation-dependent van der Waals interaction and the director of one rod can be represented by a unit vector \( \hat{a} \) with polar angle \( \theta \) and azimuthal angle \( \phi \).

The rod is symmetric about \( \hat{a} \), which can be defined by the polar angle \( \theta \) and \( \phi \) as

\[
a_x = \sin \theta \cdot \cos \phi, \quad (2.14)
\]

\[
a_y = \sin \theta \cdot \sin \phi, \quad (2.15)
\]

\[
a_z = \cos \theta. \quad (2.16)
\]

The orientation of the rods at an angle of \( \theta \), the angle between the liquid crystal director and the reference axis, can be represented by a distribution function \( f(\theta, \phi) \, d\Omega \), which is defined as the fraction of LC molecules in solid angle \( \, d\Omega = \sin \theta \, d\theta \, d\phi \) around the director. The summation of all solid angles is equal to unity, i.e., \( \int f(\theta, \phi) \, d\Omega = 1 \). In the case of random orientation, the distribution function is independent of the director \( \hat{a} \) and
therefore \( f(\theta, \phi) d\Omega = 1/4\pi \) where for a more ordered system the function becomes more pronounced around the angles 0 and \( \pi \). The distribution function for conventional rod-like nematics is considered to have a cylindrical symmetry around the reference axis \( \hat{n} \) so that it is independent of \( \phi \). If the director is non-polar, \( \hat{n} \) is equal to \(-\hat{n}\), the polar angle lie in the range of zero to \( \pi/2 \). From the symmetry and non-polar assumptions, the orientational order parameter, \( s \), can be defined as

\[
s = \frac{1}{2} \left\langle 3\cos^2 \theta \right\rangle - 1, \quad (2.17)
\]

where \( \left\langle \right\rangle \) denotes the ensemble average which is represented as

\[
\left\langle \cos^2 \theta \right\rangle = \int f(\theta) \cos^2 \theta d\Omega. \quad (2.18)
\]

The orientational distribution function \( f(\theta) \) is given as follows

\[
f(\theta) = \frac{1}{4\pi Z} \exp \left( -\frac{u(\cos \theta)}{k_bT} \right), \quad (2.19)
\]

in which the nematic interaction potential \( u(\cos \theta) \) is described as

\[
\frac{u(\cos \theta)}{k_bT} = -\nu s \left( \frac{3\cos^2 \theta - 1}{2} \right). \quad (2.20)
\]

The nematic interaction parameter, \( \nu \), can be expressed

\[
\nu = \frac{C}{V_c^2 k_b T}, \quad (2.21)
\]

in which \( C \) is a constant and assumed to be independent of pressure, volume, and pressure. \( V_c \) is the molar volume of liquid crystal. The partition function is basically a statistical ensemble average of liquid crystal directors which relates the microscopic orientation of molecules to the macroscopic bulk average orientation of the system.
\[
Z = \int \exp \left( -\frac{u(\cos \theta)}{k_B T} \right) d(\cos \theta). 
\]

(2.22)

The internal energy per mole of the system can be determined as

\[
U = \frac{N}{2} \langle u \rangle = \frac{N}{2} \int u f(\cos \theta) d\cos \theta = -\frac{1}{2} N k_B T \nu s^2. 
\]

(2.23)

The entropy term leads to

\[
S = N \left( \frac{\langle u \rangle}{T} + k_B \ln Z \right) = -N k_B \left( \nu s^2 - \ln Z \right). 
\]

(2.24)

The Helmholtz free energy of the system becomes

\[
F = U - TS = N k_B T \left( \frac{1}{2} \nu s^2 - \ln Z \right). 
\]

(2.25)

For a stable equilibrium of the ordered system

\[
\left( \frac{\partial F}{\partial s} \right)_{V,T} = 0 \quad \text{and} \quad \left( \frac{\partial^2 F}{\partial s^2} \right)_{V,T} < 0. 
\]

(2.26)

Figure 2.17 illustrates that the free energy is minimum under these conditions. At \( T = T_{NI} \), the free energy corresponding to two minima appearing at \( s = 0 \) (isotropic melt) and \( s = s_c \) (nematic phase) are equivalent, i.e., the isotropic phase and nematic phase are at equilibrium. Depending on the temperature, whether \( T \) is higher than \( T_{NI} \) or not, the stability of nematic phase or isotropic melt is determined.

At \( T_{NI} \), a discontinuous transition takes place in the order parameter without any change of volume. Putting \( F = 0 \) at transition, one can obtain

\[
\frac{C}{V_c^2 k_B T_{NI}} = 4.541. 
\]

(2.27)

The value of order parameter at the transition
Figure 2.17 Anisotropic free energy calculated from Maier-Saupe theory versus order parameter for various temperatures. The Figure is redrawn from reference 70.

\[ s_c = 0.429. \] (2.28)

Therefore, we can simplify nematic interaction parameter \( \nu \) as a function of temperature

\[ \nu = 4.541 \frac{T_{NI}}{T}. \] (2.29)

The orientational order parameter can be measured experimentally by a number of ways on the basis of optical and magnetic anisotropy such as UV spectroscopy, nuclear magnetic resonance (NMR), and X-ray Diffraction (XRD) techniques.

A liquid crystal mixture in which both materials show nematic phase can also be described by Maier-Saupe theory but the interaction between these mesogens should be considered. The free energy density of nematic ordering in binary LC system can be given by\(^{71,72}\)
The first two terms indicate the decrease of entropy and the last three terms represent enthalpic contributions. $s_1$ and $s_2$ are orientational order parameters and $\nu_{11}$ and $\nu_{22}$ represent the nematic interaction parameters of the first and second constituents. These parameters can be expressed as

$$f^{MS} = -\sum_1 \phi - \sum_2 \phi_2 \frac{1}{2} V_{11} s^2_1 \phi^2_1 - \frac{1}{2} V_{22} s^2_2 \phi^2_2 - V_{12} s_1 s_2 \phi_1 \phi_2.$$  \hspace{1cm} (2.30)

The cross-interaction parameter $\nu_{12}$ is evaluated in the context of the geometric mean approach

$$\nu_{12} = c_{\nu} \sqrt{V_{11} V_{22}},$$  \hspace{1cm} (2.34)

where the proportional constant ($c_{\nu}$) signifies the departure from the ideal geometric mean, characterizing the relative strength of the cross interaction between the two constituents.
dissimilar mesogens relative to that in the same species. If it is higher than unity, the nematic interaction between the dissimilar mesogens is stronger than that of the same mesogen.

2.4.3. Crystal Solidification and Coupling Interaction

Regarding the free energy of crystal solidification, a phase field model pertaining to Landau-type asymmetric potential may be utilized\textsuperscript{73,74}

\[
f(\psi) = W \int_0^\psi (\psi - \zeta)(\psi - \zeta_0) \, d\psi = W \left[ \frac{\zeta(T) \zeta_0(T_m)}{2} \psi^2 - \frac{\zeta(T) + \zeta_0(T_m)}{3} \psi^3 + \frac{1}{4} \psi^4 \right]. \tag{2.35}
\]

where crystal-phase order parameter (\(\psi\)) signifies the orderness of the crystal phase, i.e., \(\psi = 1\) for a perfect crystal, otherwise imperfect. In polymer crystals, it may be related to the ratio of the lamellar thickness (\(l\)) to the lamellar thickness of a perfect crystal (\(l^0\)), viz., \(\psi = l/l^0\). In small molecule systems, it is possible that the crystal can reach the equilibrium solidification potential, viz., at \(\psi = 1\). The coefficients \(\zeta\) and \(W\), representing the unstable hump for the crystal nucleation to overcome the energy barrier and the penalty for the nucleation process, can be directly evaluated from the material parameters. The order parameter at the stable solidification potential is taken as \(\zeta_0 = \frac{l}{l^0} = \frac{T_m^0 - T_m}{T_m^0 - T}\), where \(T_m^0\) is the equilibrium melting temperature and \(T_m\) is the melting temperature. The free energy of crystallization is an asymmetric double well potential for crystal ordering with respect to a crystal order parameter (\(\psi\)) as shown in Figure 2.18. When \(T < T_m\), the free energy density of the crystal ordering has a global minimum and thus the solid
crystal phase is a stable phase and the melt is metastable.

![Diagram with labels](image)

Figure 2.18 Schematic plot of local free energy density and crystal order parameter for various temperatures.

The free energy of coupling interaction of binary nematic and crystalline system can be described as

\[
f_{\text{coupling}} = (\chi_{ca} \psi_1^2 - 2\chi_{cc} \psi_1 \psi_2 + \chi_{ac} \psi_2^2 + \alpha \psi_1 \psi_2^2 + \beta \psi_2 \psi_1 \psi_2 + \gamma \psi_1 \psi_2 \psi_1 \psi_2) \phi_1 \phi_2
\]

(2.36)

The crystal-amorphous (\(\chi_{ca}\)) and amorphous-crystal (\(\chi_{ac}\)) interaction parameters are proportional to the ratio of heat of fusion and absolute temperature, i.e., \(\chi_{ca} \sim \Delta H^c_f / RT\) and \(\chi_{ac} \sim \Delta H^c_a / RT\), in which the proportional constant can be determined from the slope of the composition versus melting point curve.\(^{26}\) The crystal-crystal interaction parameters (\(\chi_{cc}\)) may also be related to \(\chi_{ca}\) and \(\chi_{ac}\) by geometric mean approach. The contribution of last three terms in eq 6 representing crystal-nematic
interaction is very small relative to other terms, and thus they are neglected in calculation.

The nematic-isotropic and crystal-nematic transitions may be determined by minimizing the total free energy with respect to the nematic \((s_1, s_2)\) and crystal \((\psi_1, \psi_2)\) order parameters in what follows:

\[
\frac{\partial f(\phi, \psi, s)}{\partial s_1} = 0; \quad \frac{\partial f(\phi, \psi, s)}{\partial s_2} = 0; \quad \frac{\partial f(\phi, \psi, s)}{\partial \psi_1} = 0; \quad \frac{\partial f(\phi, \psi, s)}{\partial \psi_2} = 0 \quad (2.37)
\]

Furthermore, the coexistence line may be determined by balancing the pseudo chemical potentials for each phase, viz., \(\left.\frac{\partial f}{\partial \phi}\right|_{\psi_1} = \left.\frac{\partial f}{\partial \psi}\right|_{\psi_1}\) \(^{56}\).

2.4.4. Elasticity of Polymer Networks

Once diacrylate monomers are photopolymerized to form crosslinking networks, we have to consider the free energy contribution from network elasticity because of volumetric shrinkage. Total free energy density of isotropic networks/LMWLC mixtures can be decomposed into three terms, \(f = f_{FH} + f_{MS} + f_{\text{elasticity}}\), in which \(f_{FH}\), \(f_{MS}\), and \(f_{\text{elasticity}}\) represent free energy of isotropic, nematic, and elasticity. Polymerization is undertaken at isotropic phase of monomer and thus FH free energy should be modified. If polymer networks are assumed to have infinite molecular weight \((r_p = \infty)\), it can be written as, \(^{77}\)

\[
f_{FH} = \frac{\phi}{r_i} \ln \phi + \chi_{aa} \phi \phi , \quad (2.38)
\]

If this network chain obeys ideal Gaussian statistics, the elastic free energy for a crosslinked polymer chain may be described according to the Dusek’s approach. \(^{78-80}\)

\[
f_{\text{elasticity}} = \frac{3\alpha}{2r_c} \Phi_0^{2/3} \left(\phi_p^{2/3} - \phi_p\right) + \frac{\beta}{r_c} \phi \ln \phi . \quad (2.39)
\]
\( \alpha_e \) and \( \beta_e \) are the network constants. These parameters are expressed as, \( \alpha_e = 1 \) and \( \beta_e = 2/f \). The parameter \( f \) indicates the network functionality. \( r_c \) is the segment length between crosslinked points. The parameter \( \Phi_0 \) represents the volume fraction of the network in the unswollen state (\( \Phi_0 = 0 \) for bulk polymerization).

2.5. Dynamics of Phase Separation

The liquid-liquid phase separation from a homogeneous polymer mixture can take place by variations in temperature, pressure, and compositions. Depending on the thermodynamic stability, nucleation and growth (NG) or spinodal decomposition (SD) can occur in metastable and unstable region, respectively.\(^{81, 82}\) According to phase diagram, the metastable region lies between the stable and unstable gaps. If a homogeneous solution is cooled into this region, the large composition fluctuations are needed before phase separation. Figure 2.19 shows a schematic illustration of concentration fluctuation in spatial arrangement during various stages of NG and SD and the resulting structures. During NG, there is a sharp interface between the mother crystals and the surrounding melt and the precipitate at all stages has the required equilibrium composition. Once nuclei are formed at \( C' \) from the solution of composition \( C_0 \), the composition of the mother phase near that nuclei becomes \( C'' \) but the concentration remains at \( C_0 \) when it is a little distance from the nuclei. The growth will occur locally at these nucleation sites and subsequently lead to isolated spherical domains. SD originates from small periodic compositional fluctuations with wavelength \( \Lambda \) inside the spinodal envelope. The amplitude increases with time with continuing sinusoidal composition.
modulation. The wavelength $\Lambda$ is influenced by “quench depth” but the amplitudes vary with elapsed time in reaching asymptotic equilibration of the growth dynamics. Spinodal decomposition involves uphill diffusion, whereas diffusion is always downward for nucleation and growth.

2.5.1. Nucleation and Growth

A nucleus possesses an excess of surface energy that produces aggregation process and consequently forms a new stable phase. The activation energy $\Delta G^*$ required to take place the NG process can be expressed in terms of volume and surface contributions,

$$\Delta G^* = -\frac{4}{3} \pi r^3 \Delta G_t + 4 \pi r^2 \sigma,$$

(2.40)
where the first term represents the free energy contribution due to the volume, bulk property, created by the nucleus and the second term is the free energy contribution of the interface, surface property. \( \Delta G_t \) indicates the free energy difference of the mother phase and the nucleus. \( \sigma \) is the interface energy per unit area and \( r \) is a radius of the nucleus. By minimizing free energy with respect to \( r \), \( d\Delta G^*/dr = 0 \), the critical radius for nuclei, \( r_c = 2\sigma/\Delta G_t \), can be obtained. Upon the formation of nuclei, the system decomposes with a decrease in the free energy and causes the growth of nuclei and eventually the formation of droplet domains.

2.5.2. Spinodal Decomposition

The spinodal decomposition (SD) is a diffusion process caused by concentration fluctuations and a spontaneous and continuous growth of another phase from mother phase.\(^{83-86}\) Compared to nucleation and growth, the decomposed structure at some point has a high level of interconnectivity. However, since such interconnected structure can also be observed as a result of shearing during NG mechanism, the observation of continuous growth of amplitude is important to elucidate SD mechanism. It occurs via three steps; early, intermediate, and late stages. In the early stage of SD, the growth rate of small concentration fluctuations can be explained by the linearized diffusion equation.\(^{87-91}\) For the intermediate and late stages, a scaling law is operative but there is no exact analytical solution available so far.

Spinodal decomposition from homogeneous system can be approximately described by Cahn and Hilliard equation. The continuity equation for \( \phi \) is given as

42
\[
\frac{\partial \phi(r,t)}{\partial t} + \text{div} J = 0, \quad (2.41)
\]

where \( J \) is the diffusion or mass flux of binary blend component, having expression of

\[
J = -M \nabla \mu. \quad (2.42)
\]

\( M \) is the mobility coefficient and related to Onsager kinetic coefficient \( \Lambda \) via

\[
M = \frac{\Lambda}{k_B T}, \quad (2.43)
\]

in which Onsager kinetic coefficient \( \Lambda \) satisfies the Onsager reciprocity given by

\[
\Lambda = \phi \Lambda_1 + \phi_2 \Lambda_2, \quad (2.44)
\]

\[
\Lambda_1 = \phi^2 N_1 D_1, \quad (2.45)
\]

\[
\Lambda_2 = (1 - \phi_1)^2 N_2 D_2. \quad (2.46)
\]

\( D_1 \) and \( D_2 \) are the self-diffusion coefficient of 1st and 2nd component, respectively. The local chemical potential, \( \mu \), is functional derivative of free energy density, \( \mu = \delta F / \delta \phi \), and therefore Eqn.(2.48) becomes

\[
\frac{\partial \phi(r,t)}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \phi}. \quad (2.47)
\]

Eqn. (2.45) is the time-dependent Ginzburg-Landau (TDGL) equation for a conserved system. A thermal noise, i.e., the thermal fluctuations due to Brownian motion, should be added in order to trigger the time-evolution process

\[
\frac{\partial \phi(r,t)}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \phi} + \eta(r,t) \quad (2.48)
\]

where \( \eta(r,t) \) can be related to the mobility \( M \) via a fluctuation-dissipation relationship.
\[ \langle \eta(t',t) \rangle = -2Mk_bT\nabla^2 \delta(r-r') \delta(t-t') \] (2.49)

The governing equation is analogous to that of time-dependent Ginzburg-Landau theory except the definition of free energy given by

\[ F = \int \left[ f(r,t) + k(\nabla \phi)^2 \right] dV. \] (2.50)

The first term, \( f(r,t) \), accounts for the local free energy density of a homogeneous system and second term is the interfacial gradient in composition explaining the local effect due to the existence of interface in the mixtures. \( k \) may be regarded as a constant for a regular mixture.

Cahn-Hilliard theory was modified by de Gennes in which the constant \( k \) for the asymmetric binary blends was simply expressed as

\[ k = \frac{1}{36} \left( \frac{\sigma_1^2}{\phi} + \frac{\sigma_2^2}{1-\phi} \right) = \frac{a^2}{36\phi(1-\phi)} \] (2.51)

The Kuhn’s segmental length \( \sigma_1 \) and \( \sigma_2 \) are assumed to be independent of \( \phi \) and \( a \) is the characteristic length. The relationship, \( \sigma_1 = \sigma_2 = a \), is valid when the constituent polymers have a comparable size.

The modified Cahn-Hilliard theory can be written as

\[ \frac{\partial \phi(r,t)}{\partial t} = M \nabla^2 \left\{ 2(\chi_s - \chi) + \frac{2}{9} \nabla^2 \right\} \phi(r,t) \] (2.52)

where the subscript \( s \) refers to the spinodal condition.

2.6. Photopolymerization

Photopolymerization is defined as the reaction of monomers or macromers to
produce polymeric structures by light-induced initiation (excitation of a photoinitiator) and subsequent propagation followed by termination. The main advantage is the high polymerization rates that can be reached instantaneously under intense illumination such that the liquid to solid phase change takes place within a fraction of a second. Photopolymerization requires three essential elements, i.e., electromagnetic radiation ($h\nu$), chromophore-containing photoinitiators (PI), and mono/macromers with unsaturated moieties such as a vinyl group and its derivatives. Ultraviolet (UV: 190~400 nm) and visible light (Vis: 400~800 nm) are commonly used for light sources in which maximal absorption wavelength of initiator is concentrated in the relatively high energetic UV or near UV visible range.

2.6.1. Photopolymerization Kinetics

The irradiated photons with proper frequency are absorbed by the $\pi$-electron conjugates of initiators that are simultaneously promoted to a higher energy orbital (PI$^\ddagger$). This excited quantum state has a half-life of less than a $\mu$-second. Numerous PI$^\ddagger$ may chemically decompose into reactive fragments, such as radicals [I$-$] or ions [I$^+$/I$-$]. As reactive intermediates, these fragments are more stable and serve as direct initiators for radical polymerization or anionic/cationic polymerization.$^{96-98}$

$$\text{PI} + h\nu \rightarrow \text{PI}^\ddagger \rightarrow \text{PI} \text{ (decay)}$$

$$\text{PI} + h\nu \rightarrow \text{PI}^\ddagger \rightarrow \text{[I$-$] or [I$^+$/I$-$] + mono/macromer}$$

$$+ \ h\nu \rightarrow \text{higher MW polymer or crosslinked network}$$

Most of the practical applications of photopolymerization use a free radical mechanism to initiate addition polymerization of vinyl group-containing
mono/macromers. Free radical polymerization usually occurs via three reaction steps; initiation, propagation, and termination. It may be described by the simple kinetic equations below\textsuperscript{99, 100}

\textbf{Initiation}

\[ \frac{d[R^*]}{dt} = \Phi I_a - k_i [R^*][M] , \] (2.53)

\textbf{Propagation}

\[ \frac{d[P^*]}{dt} = k_p [R^*][M] - k_p [P^*]^2 , \] (2.54)

\textbf{Termination}

\[ \frac{d[M]}{dt} = -k_t [R^*][M] - k_t [M][P^*] , \] (2.55)

where \([R^*]\) is the radical concentration activated from photoinitiator. \([P^*]\) is the total concentration of polymer radicals and \([M]\) is the monomer concentration. Moreover, \(k_i, k_p,\) and \(k_t\) are the reaction kinetic constants of initiation, propagation, and termination, respectively.

The rate of photochemical initiation is given by

\[ R_i = \Phi I_a^z , \] (2.56)

in which, the \(R_i\) is the rate of initiation. \(\Phi\) is the number of propagating chains initiated per light photo absorbed. \(I_a\) is the intensity of absorbed light in moles, which is in unit of Einsteins in photochemistry. The exponent values \(z\) varies from 1/2 to 1; 1/2 implies that two radicals are produced per molecule undergoing photoinitiation.

For thin films through the thickness of which the incident light intensity does not vary appreciably or for films in which the absorption of light is very low, \(I_a\) may be conventionally expressed as

\[ I_a = \varepsilon I_o [D]b , \] (2.57)

where \(I_0\) is the incident light intensity, \(\varepsilon\) is the molar absorptivity (extinction coefficient)
of the photoinitiator at a particular frequency of radiation absorbed, and \([D]\) is the initial concentration of photoinitiator and \(b\) is sample thickness.

For thick films where \(I_a\) varies with the thickness or for films in which the absorption of light is quite high, the expression of \(I_a\) can be obtained from the Lambert-Beer’s Law

\[
I_a = I_0 e^{-\epsilon[D]b}. 
\] (2.58)

To a first approximation, the rate of propagation is considered much faster than that of initiation so that the polymerization rate is simply given by the rate of propagation

\[
R_p = -\frac{d[M]}{dt} = k_p [M][P^*]. 
\] (2.59)

The monomer fractional conversion is defined as

\[
\alpha = \frac{[M]_0 - [M]}{[M]_0}, 
\] (2.60)

with \([M]_0\) the initial monomer concentration. The polymerization rate can be written as

\[
R_p = k_p (1 - \alpha)[M]_0[P^*]. 
\] (2.61)

Customarily, photopolymerization can be analyzed by the pseudo-steady state kinetics, which assumes that all radical concentrations reach the steady state very quickly so that

\[
\frac{d[R^*]}{dt} = 0 \text{ and } \frac{d[P^*]}{dt} = 0. 
\] (2.62)

The polymerization rate can be rewritten as

\[
R_p = \frac{k_p}{k_t^{1/2}} (\Phi I_a) (1 - \alpha)[M]_0, 
\] (2.63)

\[
-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} (\Phi I_a) (1 - \alpha)[M]_0. 
\] (2.64)
\[
\frac{d\alpha}{dt} = \frac{k_p}{k_i^{1/2}} (\Phi I_a)^{1/2} (1 - \alpha).
\] (2.65)

2.6.2. Acrylic Monomers and Its Mixtures with Liquid Crystals

Acrylate analogues are one of the most reactive and widely used monomers, polymerized by a free radical mechanism. The produced polymers exhibit remarkable chemical, optical, and mechanical properties and thus account for a great commercial success of acrylate-based UV-curable resins. For this reason, the photoinitiated polymerization of multifunctional acrylate monomers and oligomers have been thoroughly investigated, mainly from the kinetic and mechanistic points of view.\textsuperscript{101-106}

For a diacrylate monomer irradiated in the presence of a photocleavable aromatic ketone, the basic chemical scheme is given in Figure 2.20. The high viscosity of the prepolymer often necessitates the addition of low molecular weight monomers, which will act as reactive diluents. Depending on the length and chemical structure of the crosslink segments, the photocured polymers exhibit a great resistance to chemicals, heat and radiation, show well-designed physical properties.

The photopolymerization technique has been customarily applied to reactive liquid crystal systems. Among them, polymer dispersed liquid crystals (PDLCs) and polymer stabilized liquid crystals (PSLCs) have gained considerable interest for their applications for switchable windows and reflective displays. The former contains less than 50 % LC, whereas the latter is composed of > 95 % LC concentration in the polymer matrix. PDLC is made up of micron-sized liquid crystal droplets that are dispersed in an isotropic polymer matrix.\textsuperscript{107, 108} PDLC films are generally prepared via polymerization-induced
phase separation (PIPS) because the curing parameters can be chosen independently, controlling the final morphology. It is well documented the performance of PDLCs such as switching voltage, response time, brightness, and contrast of PDLCs displays is mostly influenced by the morphology. In addition, it permits tailoring of liquid crystal dispersions and ultimately electro-optic properties through control of the competition between phase separation dynamics and the rate of polymerization.\(^{109}\)

![Chemical structure](image)

Figure 2.20 Photoinitiated crosslinking of a diacrylate monomer (redrawn from reference 101).
3.1. Materials

The materials selected in the dissertation are mainly classified into photoresponsive chromophores and photopolymerizable monomers. Regarding photochromophores, three different molecules were used; crystalline azobenzene, liquid crystalline azobenzene, and crystalline spiropyran. They were blended with photopolymerizable triacrylate or mesogenic diacrylate monomers to investigate dynamics of crystallization after thermal quenching and photoisomerization-induced mesophase transition under the UV light. Reactive mesogens and hyperbranched polymers have been mixed with low molecular weight liquid crystal molecules to prepare the polymer/LC composites films.

3.1.1. Photochromophores

Azobenzene with a reported molecular weight of $M_w = 182.2$ g/mol bought from Aldrich Chemical Co., were used without further purification. The azobenzene crystal exhibits a melting transition ($T_m$) at $\sim 68 \, ^\circ$C. 4-4’Dipentylazobenzene, i.e., liquid crystalline azobenzene chromophore (LCAC,) was synthesized according to a synthesis protocol of Barrado et al. by mixing 4-pentylaniline with copper(I) chloride and pyridine (Aldrich) in circulating air for 24 hrs. The resulting residue was placed on alumina supported columns and eluted for 4 hrs using distilled n-hexane. The 4-4’
The dipentylazobenzene solution thus obtained from column chromatography was dried under vacuum. The yield of 4-4’dipentylazobenzene crystals was ~70 % having a molecular weight of 322.5 g/mole. It exhibits the crystal melting transition at around 33 °C, and nematic phase becomes isotropic ($T_{NI}$) at around 42 °C. Spiropyran (SP) purchased from Aldrich undergoes photoisomerization to merocyanine (MC) upon exposure to UV light and reverts back to its ground state by thermal treatment or irradiation with a blue light. It exhibits a single melting peak (Tm) around 178 °C. The chemical structure of chromophores and their isomerization reaction are shown in Figure 3.1.

Figure 3.1 Chemical structures of photoresponsive chromophores and their isomers of (a) azobenzene, (b) liquid crystalline azobenzene, and (c) spiropyran.
3.1.2. Monomers

The reactive monomers containing acrylate group have been added to LCAC or SP photochromophores and low molecular weight liquid crystals (LMWLC), respectively. Trimethylolpropane triacrylate (TA, $M_w = 296.3$ g/mol) purchased from Aldrich Chemical Co. is a nonvolatile viscous liquid. The density is around 1.1 g/mL at 25 °C and the flash point is above 130 °C.

The reactive mesogenic diacrylate monomer (RMDA, $M_w = 588.6$ g/mol) was supplied by Merck Ltd. It contains acrylate double bonds at the ends of the backbone capable of undergoing photo-initiated radical reaction (or crosslinking). Moreover, this telechelic acrylate LC material reveals crystal melting ($T_m$) and nematic-isotropic ($T_{NI}$) transitions at 66 °C and 128 °C, respectively. The density of crystalline RMDA is around 1.22 g/mL at 25 °C.

The hyperbranched polyester (HBPEAc-COOH) was synthesized from polyaddition of bisphenol-A diglycidyl ether (BPGE) with trimesic acid (TMA) and methacrylic acid (MA), followed by cis-1,2,3,6-tetrahydrophthalic anhydride (THPA), triphenylphosphine (TPP), and hydroquinone (HQ) having pendent methacryloyl and carboxyl groups. The number-average molecular weight and polydispersity of the HBPEAc-COOH, as measured by GPC (Model 1515, Waters) using tetrahydrofuran (THF) with a polystyrene standard, were $M_n = 6,800$ and $M_w/M_n = 1.42$, respectively. The uniqueness of this HB polyester is its photo-curability through radical photopolymerization of the acrylate doubles bonds and carboxylic acid functionality that affords ionic or dipolar interactions with its counterpart.
3.1.3. Low Molecular Weight Liquid Crystals

Eutectic liquid crystal mixtures E7 exhibiting a positive dielectric anisotropy presents a single nematic-isotropic transition at around 59 °C. Many favorable properties such as broad range of nematic phase (-60~59 °C), chemical stability, no absorption in the visible range, and low viscosity, make it popular for the calculator, display, and switchable windows. It contains 51 wt % of 4’-n-pentyl-4-cyanobiphenyl (5CB, $T_m = 24$ °C, $T_{NI} = 35$ °C), 25 wt % 4’-n-heptyl-4-cyanobiphenyl (7CB, $T_m = 30$ °C, $T_{NI} = 42$ °C), 16 wt % 4’-n-octoxy-4-cyanobiphenyl (8OCB, $T_m = 54$ °C, $T_{SmAN} = 67$ °C, $T_{NI} = 80$ °C).

Figure 3.2 Chemical structures of photoreactive monomers including (a) trimethylolpropane triacrylate, (b) reactive mesogenic diacrylate, (c) hyperbranched polymer.
Figure 3.3 Composition of eutectic E7 mixtures, consisting of 5CB (51 wt%), 7CB (25 wt%), 8OCB (16 wt%), and 8 wt% 4'-n-pentyl-4-cyanoterphenyl (5CT, $T_m = 130 \, ^\circ\text{C}$, $T_{NI} = 239 \, ^\circ\text{C}$). It is important to determine the exact composition of the mixture because the mixtures deviated from the eutectic point may gradually phase separate as a solid.

3.2. Characterization Techniques

Phase transition temperatures of various crystalline and liquid crystalline blends have been determined using differential scanning calorimetric (DSC). The point where the endothermic peak appeared was selected as transition temperature. The various single and coexistence regions in phase diagram were confirmed by means of optical microscopy (OM) and wide angle x-ray diffraction (WAXD) techniques. The UV-triggered photoisomerization of azobenzene and spiropyran molecules was examined using UV/Vis spectroscopy, while photopolymerization of acrylate monomers were monitored using FT-IR and photo-DSC.

3.2.1. DSC and Photo-DSC

Crystal melting and nematic-isotropic transition of photochromophores and liquid
crystalline molecules, and glass transition temperature of hyperbranched polymers were determined using differential scanning calorimetric (Q-1000, TA Instruments). Before scanning the samples, the temperature was calibrated with indium standard having a melting point of 165.5 °C. The pure or blended samples weighing around 3~5 mg were sealed in aluminum hermetic cell and scanned a constant heating/cooling rate. During the heating/cooling process, the chamber was maintained under nitrogen atmosphere (N$_2$) at a flow rate of 50 ml/min to maintain an inert atmosphere.

The photo-DSC (Q-1000, TA Instruments) connected to the photo calorimetric accessory (NovaCare, EXFO Photonic Solutions) was used to record heat evolution during photo-induced polymerization and phase transition of photoisomerized LCAC/RMDA mixtures. Since the exothermic peak area at isothermal condition is proportional to polymerization rate, the conversion of the monomers can be calculated. Both reference and sample cell were not covered with lid and thus UV light is directly exposed. The UV intensity was maintained at approximately 40 mW/cm$^2$ under N$_2$ atmosphere. The heating and cooling scan of isomerized mixtures was carried out at the same rate as that of regular-DSC. However, the maximum operational temperature was limited to 80 °C. Schematic diagram of Photo-DSC is given in Figure 3.4.\textsuperscript{110}

3.2.2. Optical Microscopy

Using optical microscopy (BX60, Olympus), the morphological textures of crystalline and liquid crystalline phases of nematic (N) and smectic-A ($S_m$A) were captured during heating/cooling or thermal quenches using a digital camera (EOS 300D, Cannon) under the cross polarizer. The samples located between two cover glasses were
put on the Linkam Scientific Instruments hot stage (TMS93, Linkam) to control the temperature, which was calibrated with thermocouple before using it.

Spatio-temporal growth dynamics of azobenzene crystals in triacrylate solution was video-taped following thermal quenches from 70 °C to room temperature using polarized optical microscope (POM) (PZMTIV, World Precision Instruments Inc.). Concave circular cell (16 mm in diameter and 0.5 mm in depth at the deepest point) and flat rectangular cell (37 mm × 8 mm in cross-section and 1 mm in depth) were used as a container of solution in order to remove uncertain effect of container cell geometry.

3.2.3. Fourier Transform Infrared Spectroscopy

FT-IR technique was employed to examine conversion of acrylic monomer upon photopolymerization and identify the liquid crystalline constituent of eutectic E7 mixtures. In general, the extent of polymerization of acrylic monomer is monitored by
measuring the decay of absorption band at around 1630 (corresponding to C=C stretching) and 810 cm\(^{-1}\) (=C-H out of plane). The LC molecules were characterized by annotating the characteristic functional group such as nitrile group of E7 at around 2230 cm\(^{-1}\). It should be noted that the IR spectrum and its intensity significantly depends on the phase (crystal vs nematic vs isotropic) and alignment (homogeneous vs homeotropic). The spectra were acquired using a Nicolet 380 (Thermo Scientific Instrument) spectrometer by 32 scans with a resolution of 4 cm\(^{-1}\). The samples cast on potassium bromide (KBr) disk were scanned at room or elevated temperature between the frequency ranges of 4000 to 400 cm\(^{-1}\).

3.2.4. Wide Angle x-ray Diffraction

Phase transformation from crystalline to nematic or isotropic phase has been monitored by 1D WAXD reflection mode in a 12-kW Rigaku rotating-anode x-ray (CuK\(\alpha\) radiation) generator operated at 40 mA and 40 kV. The wavelength of the x-ray source was 1.54 Å. The sample on hot stage was ramped at a heating rate of 10 °C/min to set temperature and then remained for 5 min until the temperature became stabilized. After then, a 2\(\theta\) scan was conducted over an angular range from 2.5 to 35° at a scanning rate of 1 °/min. In the case of two-dimensional x-ray diffraction, wide angle x-ray (AXS D8, Bruker) generator was operated at 40 kV and 40 mA using Cu-K\(\alpha\) radiation with a wavelength of 1.54 Å. A 2-D detector (HI-STAR, Bruker) was used to identify the ordered mesophase structure at room temperature.
3.2.5. UV/Vis Spectroscopy

The chromophores containing π electrons can absorb energy in the UV/Visible region. Molecular shape change of azobenzene and spiropyran chromophores has been verified using UV/Vis spectrophotometer (Model 8453, Hewlett-Packard). The dilute chromophore solution, i.e., liquid crystalline azobenzene in methanol and spiropyran in carbon tetrachloride, has been filled into quartz cuvet (10 mm × 10 mm in cross section and 45 mm in height) and then scanned from 200 nm to 800 nm at ambient temperature. The photoisomerization was triggered by irradiating UV light (ELC403, Electrolite Corporation) at an intensity of 40 mW/cm². The spectra were recorded with respect to exposure time until photostationary state was reached.

3.2.6. Atomic Force Microscopy

Atomic force microscopy (AFM) was chosen to investigate the effect of photoisomerization of neat LCAC on crystalline surface microstructure. The AFM (MMAFM-2, Digital Instruments) image of melt crystallized LCAC surface was collected before and after UV irradiation, respectively. Silicon cantilevers (RTESPW, Veeco Inc.) having a spring constant of 20-80 N/m were used in the tapping mode. The probe can be vibrated at its resonant frequency to make intermittent contact with the sample. UV light was irradiated uniformly for 1500 s.
CHAPTER IV

SHOOTING AND SWIMMING AZOBENZENE SINGLE CRYSTALS IN TRIACRYLATE SOLUTION

4.1. Introduction

Various topologies of polymer single crystals hitherto reported, ranging from rectangular, square, hexagonal, diamond shapes to curved single crystals, were grown primarily from polymer solutions.\textsuperscript{111-113} Occasionally single crystals of pyramidal shape were found to develop on the bottom substrate - some with and some without a terrace pattern. A natural question is whether the pyramidal shaped crystal grow downward (e.g., from the solution-air interface) or upward (e.g., from the substrate, like a man-made pyramid). Similar polymer single crystals can be grown from the melt by thermal quenching or slow cooling below the crystallization temperature. Although the final morphologies between the melt-grown and solution-grown single crystals might be similar, the crystallization pathways traversed by these systems are quite different.

To elucidate the structural evolution dynamics of solution-grown crystals, a non-destructive time-resolved characterization approach is essential. Recently, real-time studies on growth of polymer single crystals from the melt state became possible due to rapid advances of atomic force microscopy (AFM).\textsuperscript{114,115} In melt-grown single crystals, a considerable difference in the hardness of the solid crystal and that of the surrounding
melt surfaces makes the real time AFM investigations possible. In contrast, the time-resolved AFM investigation of polymer crystallization in a binary solution remains impractical because the polymer crystals in solution are fragile and lack the sufficient mechanical strength. Moreover, the initial polymer crystals (i.e., size of nuclei) thus formed are too small to be seen by most non-destructive in-situ techniques. Therefore, it is customary to study crystallization of small molecule systems in order to provide important clues for better understanding of polymer crystallization. This is one of the sources of our motivation for selecting small molecule azobenzene crystal that has interesting photo-reversible phase transition.

A reversible conformational transition from trans- to cis-isomeric states with fast switching time makes azobenzene and its derivatives very attractive, especially for applications such as photo-actuator, shape memory, and optical switching. These photo-switchable polymer films are generally prepared by photopolymerization of azobenzene chromophores/reactive monomer mixtures. While investigating the effect of photoisomerization on the photopolymerization-induced phase separation of azobenzene chromophore/triacrylate (TA) monomer solution, the development of a gigantic pyramidal shaped single crystal of azobenzene was noticed in a manner dependent on the phase diagram of the constituent pair and the supercooling depth. On the basis of non-destructive time-resolved video photography, the azobenzene/TA mixture uniquely affords an in-situ investigation of crystal growth phenomena because of the gigantic size of azobenzene chromophore crystal and non-volatile nature of the triacrylate solvent.

In this article, the swimming and sinking behavior of the growing single crystal of azobenzene chromophore in triacrylate solution is examined in relation to the solid-liquid
phase diagram bound by the solidus and liquidus lines. Plausible mechanisms of the self-propelling crystals are discussed. In addition, the crystal swimming driven by trans-cis photoisomerization of azobenzene in triacrylate solution is explored.

4.2. Experimental Section

Azobenzene with a reported molecular weight of $M_w = 182.2$ g/mol and trimethylolpropane triacrylate (TA) having $M_w = 296.3$ g/mol, were bought from Aldrich Chemical Co., and used without further purification. The azobenzene crystal exhibits a melting transition ($T_m$) at ~68 °C, whereas TA is non-crystalline. Various concentrations of azobenzene/TA solutions were prepared at 70 °C by stirring mechanically until the solution became completely homogeneous. The mixture was sealed in aluminum hermetic pans and used in differential scanning calorimetry (DSC 2920, TA Instruments) measurements. The heating rate was 5 °C/min unless indicated otherwise.

The samples for optical studies were prepared by depositing the solution onto a glass slide having a concave circular well with a dimension of 16 mm in diameter and 0.5 mm in depth at the deepest point. For the purpose of comparison, a flat rectangular cell with a dimension of 37 mm x 8 mm in cross-section and 1 mm in depth was used. Spatio-temporal growth of azobenzene crystals at various concentrations was recorded following thermal quenches to room temperature using polarized optical microscope (POM) (PZMTIV, World Precision Instruments Inc.). The effect of trans-cis isomerization on crystal growth was examined by illuminating the UV light from one end of the cell and the crystal motion was monitored. The UV curing unit (ELC403, Electrolite Corporation) was utilized with the intensity of 40 mW/cm$^2$ at the wavelength of 350–380 nm.
4.3. Results and Discussion

In this section, we showed the phase behavior of crystal + amorphous system and subsequently mechanism of nucleation and crystal growth of azobenzene single crystal in triacrylate solution subjected to thermal quenching or UV light has been suggested.

4.3.1. Phase Behavior of Azobenzene/Triacrylate Mixtures

Prior to investigating crystal growth dynamics following thermal quenches, it is essential to construct the phase diagram of azobenzene/TA mixtures in order to provide guidance to kinetic pathway. That is to say, the emerged crystalline structure and growth dynamics strongly depend on thermal quenched depth and concentrations of the phase diagram. Figure 4.1 exhibits the differential scanning calorimetry (DSC) scans at various blend compositions. The $T_m$ of the pure azobenzene is located at about 68 °C that shifted systematically to lower temperatures with increasing TA content. The trend of melting point depression can be seen more clearly in the plot of $T_m$ versus composition (Figure 4.2). This experimental solid-liquid phase diagram is compared with the self-consistently calculated phase diagram using the combined FH/PF free energy density. The calculated liquidus line is in good accord with the depressed melting points, while the solidus line virtually overlaps with the axis of the pure crystalline constituent with an extremely small crystalline solid gap. The calculated phase diagram is therefore consisted of the isotropic liquid (I) and the crystal + liquid ($\text{Cr}_1 + \text{I}_2$) coexistence region bound by the liquidus and solidus lines.

To confirm the crystal + liquid coexistence region, several thermal quenches were undertaken at various concentrations from the melt state of 70 °C to ambient temperature.
The crystal thus emerged is of a pyramid, diamond, and distorted single crystal surrounded by triacrylate rich solution (Figure 4.2a-d). Since azobenzene is a small organic molecule, its single crystal grows to a gigantic size (over 8 mm) that is visible to naked eyes; the final size is only limited by the solution cell dimension of 16 mm in diameter $\times$ 0.5 mm in depth. At 25 wt% azobenzene concentration, pyramid shape single

![Figure 4.1 DSC thermograms of azobenzene/triacrylate solutions as a function of concentration. The heating rate was 5 °C/min.](image)

Figure 4.1 DSC thermograms of azobenzene/triacrylate solutions as a function of concentration. The heating rate was 5 °C/min.
Figure 4.2 The self-consistently solved coexistence lines in comparison with the experimental phase diagram and polarized optical micrographs of various single crystal structures after thermal quenching of 25, 30, 35, and 40 wt % azobenzene solutions to indicated points, i.e., (a)-(d). The diameter of the concave circular cell is 16 mm and the depth is 0.5 mm at the center.
crystal with a terrace structure is developed. With increasing concentration, the single crystals can stack due to multiple nucleation events (Figure 4.2b). When the single crystal approaches the container cell wall, the shape gets distorted (e.g., see 35 wt %). At 40 wt %, the whole solution cell is filled with multiple single crystals jamming together, thereby loosing the original diamond shape. These observed single crystal structures are non-equilibrium that depends on the supercooling, i.e., the temperature difference between the concentration-dependent phase transition points and the quenched temperature as marked by (a)-(d) in the phase diagram for each concentration. As typical for the crystal + liquid coexistence region, all single crystals were surrounded by isotropic solvent.

Under the optical microscope at a magnification of 50×, the terrace structure can be discerned more clearly (Figure 4.3), exhibiting the multiple terrains with an acute angle of 57°. However, the terrace structure at the core, showing the remnants of the distorted sectorized borders, appears to deplete with the progression of the crystallization
(Figure 4.3b), which is drastically different from that of the polymer single crystal, where the crystal core remained immobile. The stationary core of polymer single crystals and spiral spherulites has been demonstrated by our group both experimentally and theoretically using the time-dependent Ginzburg-Landau equations (model C) with the combined phase-field free energy and Flory-Huggins free energy of liquid-liquid demixing.\textsuperscript{116-118}

4.3.2. Nucleation and Growth Dynamics of Azobenzene Single Crystal

In polymer crystallization, the single crystal grown from the polymeric melt is considered to originate on the substrate, where the crystalline chains are oriented perpendicular to the substrate while folding back-and-forth.\textsuperscript{108-110} The same nucleation mechanism is perceived to be operative for solution crystallization despite the differences between those from the melt and from the solution. An important question is how the pyramidal (or 3D) single crystal grows in the present case, i.e., whether the nucleation occurs at the solution-air interface or solution-substrate interface.

To elucidate the mechanism of nucleation, the spatio-temporal emergence of the azobenzene single crystal was video-taped at the 35 wt % azobenzene concentration. Figure 4.4a shows the time-lapsed video images of azobenzene single crystal, growing at two locations (please see the picture at 52 s). These two diamond shape single crystals approach toward each other while their crystal dimensions keep increasing (see 69 s). When the two crystals are in close proximity, the smaller one submerges downward (76 s) presumably influenced by the neighboring larger crystal. After some elapsed time, it floats back (87 s), which may be due to the shallow depth of the bottom substrate, where
the downward thrust of the rejected solvent might have pushed the crystal back to the surface. The observed sink and float behavior implies that the crystal nucleation occurs at the solution-air interface.

When the submerged crystal on the right approaches the cell wall, multiple small diamond-shaped single crystals suddenly form and rapidly swim away from the larger crystal. The same but more pronounced behavior is observed for the crystal on the left at 93 s. Two possible mechanisms of this phenomenon may be hypothesized. First, the tip of a large crystal can break off in the collision with the wall and the broken fragments can serve as new nucleation sites for the baby single crystals. Second is the surface tension driven growth instability. As the crystal approaches the container wall, the convective flow of the rejected fluid may be expedited thereby creating spatial variability of concentration. When the spatially varying local concentration exceeds a critical value, crystal nucleation can be triggered. When the fluid flow bounced back (or directed away) from the container wall, the new-born crystals move toward the free zone in the middle as shown in Figure 4.4.

To the best of the author’s knowledge, the sink or swim behavior of the azobenzene single crystal in TA solution is the first observation of such phenomenon reported in open literature. The azobenzene chromophore is known to undergo elastic deformation due to the mechanical torque generated by the \textit{trans-cis} isomerization upon irradiation with UV light.\textsuperscript{119, 120} Although such isomerization can contribute to the crystal swimming, it is inconsequential here because only a weak diffuse white light was used in probing the growth dynamics of azobenzene single crystal. It should be emphasized that liquid-liquid phase separation occurred in azobenzene/TA solution in competition with crystallization
Figure 4.4 (a) Temporal evolution of azobenzene crystal in 35 wt % solution, showing swim, sink, float, and birth & growth of baby single crystals and (b) the proposed mechanisms: (drawing at left) unbalanced forces of the solvent rejection from the lateral crystal growth fronts of azobenzene (35 wt % solution) propelling the single crystal to swim in the plane of the surface, (drawing at middle) occurrence of the stationary crystal growth when the propelled forces by the rejected solvent from the faceted crystal growth fronts (30 wt % azobenzene in TA solution) are more or less balanced, and (drawing at right) the solvent rejection in the vertical direction causing the pyramid crystal to float.
of azobenzene during thermal quenching from the single phase isotropic temperature into the crystal + liquid coexistence region. It is this competing liquid-liquid and liquid-solid phase separation which has led to the rejection of TA solvent from the growing faceted azobenzene single crystal fronts in the lateral directions (i.e., in the plane of the surface) as well as in the downward direction. It can be visualized that the TA solvent will be enriched near the crystal-solution interface, and thus creating a concentration gradient leading to the spatial gradient of surface tension, which is known as the Marangoni effect.

When the growth front of the diamond crystal shape is truncated at one end or growing preferentially in another crystal plane (or facet), the flows due to the surface tension gradients and/or the forces driven by the solvent rejection would become unbalanced. This unbalanced solvent rejection probably propels the faceted single crystal to swim in a given resultant direction; otherwise the crystal remains stationary (Figure 4.4b). On the other hand, the solvent rejection in the vertical direction can exert downward thrust, making the pyramidal crystal buoyant. When the solution crystallization is near its completion, the solvent action diminishes and thus the single crystal may no longer stay afloat. Consequently, the diamond-shape single crystal sinks to the bottom due to gravity.

In order to remove the uncertain effect of container cell geometry, we further perform the crystallization in a flat rectangular cell having 1 mm depth. The crystal growth by ‘seeding’ method can provide another avenue for investigating of crystal swimming. Since the seed crystal is solid, no solvent is expected to involve. To our astonishment, we observed the rhombus baby crystals to swim and sink, and then float back, similarly to those observed in the case of the concave container cell (Figure 4.5). It may be hypothesized that when the seed crystal is in contact with the azobenzene/TA
solution, the solute will be pulled into the solid crystal during growth; therefore the spatial variation of solvent concentration is created near the solid-liquid interface. In principle, any concentration fluctuation at the interface can lead to the spatial variation of the surface tension. Solvent rejection may not be the only criterion contributing to the crystal swimming, but it certainly affect the concentration gradient, which in turn can influence the surface tension driven phenomena. So long as there is a concentration gradient at the solid-liquid interface; the surface tension can propel the floating crystals to move.

Figure 4.5 Temporal crystal growth of azobenzene crystal after ‘seeding’ in a flat bottom cells, showing nucleation, swim, sink, and float of baby crystals with time.
In a regular thermal-quench experiment with the 38 wt % azobenzene in TA solution without adding a seed crystal, we are able to observe the same crystal nucleation and the same swimming, floating or sinking behavior in a flat-bottom container (Figure 4.6). The crystal grows slowly from the top of the cell (top line). At 1135 s, the first baby crystals come out from the stationary mother crystal (indicated by arrow) and then swim away. The fronts of mother crystal have needle-like structure. It is inferred that the rejected solvent from the needle-like crystal in turn induces the oscillatory concentration gradient. When the local concentration exceeds the critical concentration at some distances from the solid-liquid interface, crystal nucleation takes place, giving birth to newer crystals. These baby crystals are shooting out very rapidly like a jet stream and later move away at a constant velocity while growing. Hence, it is reasonable to conclude that the container geometry plays little or no role in the observed swim or sink phenomena.

Figure 4.7 demonstrates the effect of UV intensity gradient on crystal growth in the 26 wt % azobenzene solution. Since the T-quench is shallow for this concentration, the emerged rhombus crystal grows with little or no movement and after some elapsed time, the crystal virtually remains stationary. Then UV light is irradiated on this stationary crystal from one end of the cell (top right of Figure 4.7). It can be seen clearly that the rhombus crystal moves away from the light source upon irradiation. According to Fujishima et al., azobenzene crystal itself is capable of changing not only their molecular shape in solution, but also the crystal surface topology under UV light, i.e., narrowing the layered spacing of terrace surface. In the present case, the emerged single crystal is a solvated form and thus the molecules would have greater mobility and more free space. Since the trans-cis conversion of the crystal front close to the light is higher than that of
Figure 4.6 Temporal evolution of azobenzene crystal at 38 wt % solution in a rectangular flat cell. The baby crystals shoted out from the mother crystals and moved away.
the opposite side, the mechanical force generated by the *trans-cis* isomerization can propel the crystal to move. Another possibility is that the *trans*- to *cis*-isomerization increases the polarity of azobenzene and thus the solubility of azobenzene crystal in triacrylate solvent might have been altered. This change in solubility makes the system to become unstable, which in turn drives phase segregation, and thus the solvent rejection rates from the growing crystal front close to the UV illumination may be different that of the opposite end. This differential flow rates can further propel the crystal to swim away from the light. It should be emphasized that the present swimming behavior of the azobenzene single crystal driven by the UV irradiation is similar to the liquid crystalline elastomers grafted with azobenzene that swim away from the light.
4.4. Conclusions

We have demonstrated the spatio-temporal emergence of a gigantic single crystal of azobenzene in triacrylate solution at various concentrations following temperature quenches into the solid-liquid coexistence regions of the phase diagram. We are intrigued by the fact that the emerged single crystal may swim propelled by the surface tension gradient due to unbalance solvent rejection. Moreover, the gigantic azobenzene single crystal can sink or float due to the downward thrust pumped by the solvent rejection. Further, the present work unambiguously confirmed that the azobenzene crystal nucleation occurs at the solution-air interface, unlike the nucleation of the solution-grown polymer single crystals, which is perceived to take place on the substrate. Trans-cis photoisomerization induced mechanical deformation is an additional source of swimming of the azobenzene crystal, which is otherwise stationary.
5.1. Introduction

By virtue of reversible photo-switching capability, azobenzene chromophores have gained considerable attention in various applications such as optical switching, optical grating, waveguide, and erasable holographic memory storage\textsuperscript{121-126}. It is well documented that azobenzene chromophores change their molecular conformations from trans- to cis-state by selective irradiation with ultraviolet light (UV) 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 rod-like assembly to a bent-shaped organization. This reversible phase transformation of rod-to-bent assemblies driven by photoisomerization results in reversible photomechanical deformation (i.e., contraction/expansion); the bending moment thus generated during this photomechanical deformation has led to actuator applications. Since then various modifications have been made to the azobenzene chromophores by either attaching with flexible groups or doping in flexible polymer matrix to impart liquid crystalline (LC)
properties; typical examples include liquid crystalline elastomers and photoresponsive gels. Of particular importance is that liquid crystalline azobenzene chromophore can be driven by either photo-optical or electro-optical means through change of director orientation of the LC mesogens and/or trans–cis isomerization of the chromophore.\textsuperscript{127-130}

According to a recent paper by Nakayama et al., the occurrence of trans–cis photoisomerization of the azobenzene crystal has led to the surface undulation upon irradiation in the solid crystalline state, in which the interlayer spacing of the trans-state was found to be increase as compared to that of the cis-state. These authors concluded that the photo-induced structural transformation occurs only at the azobenzene crystal surface, but not in the bulk.\textsuperscript{131}

In the present chapter, 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. Like 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). In an effort to contain LCAC in matrix resins such as reactive mesogenic diacrylate (i.e., RMDA), it is of paramount importance to understand the individual roles of photopolymerization-induced phase separation and trans–cis photoisomerization of LCAC on morphology development that ultimately governs 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/RMDA without adding any photo-initiators to prevent photopolymerization.

5.2. Experimental Section

4-4’Dipentylazobenzene, i.e., liquid crystalline azobenzene chromophore (LCAC), was synthesized according to a well-established synthesis protocol reported by Barrado et al. Reactive mesogenic diacrylate monomer (RMDA, $M_w = 588.6$ 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/RMDA blends were prepared by dissolving in carbon tetrachloride (CCl₄) 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 by under a fume hood and further dried in a vacuum oven at room temperature over night and again at 40°C for 24 h. No particular surface treatment was done on the glass slides.

Phase transition temperature of the mixtures obtained before and after photoisomerization was determined using regular DSC and photo-DSC, respectively. The morphology change during phase transition was investigated by means of polarized optical microscopy (POM, BX60, Olympus) 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). 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.

5.3. Results and Discussion

We presented the experimental and theoretical phase diagram of RMDA/LCAC blends. As *trans-cis* isomerization of LCAC may induce isothermal nematic-isotropic phase transition and crystal melting point is slightly depressed, we investigate the change of phase diagram after photoisomerization.

5.3.1. Phase Diagram of RMDA/LCAC Mixtures

Figure 5.1 shows the UV/Vis spectra of liquid crystalline azobenzene chromophore (LCAC) before and after UV irradiation. In the trans-state, the dilute LCAC solution shows two absorption peaks, i.e., a strong peak at around 330 nm attributable to $\pi-\pi^*$ electronic transition and a weak peak at around 440 nm due to forbidden $n-\pi^*$ excitation of the LCAC caused by the interaction with solvent.\[^{133,134}\] However, upon UV irradiation, the peak intensity of $\pi-\pi^*$ transition decreases, whereas the 440 nm peak intensifies slightly, suggesting that the trans-to-cis isomerization may not have reached full conversion in the methanol solution. An alternative account is that the azobenzene units may have relaxed back to its stable trans-state because of the greater mobility of LCAC in the very dilute methanol solution.

Phase transition temperatures of *as-synthesized* LCAC are shown in Figure 5.2. The heating and cooling DSC runs exhibit three distinct endo-/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. The optical micrographs, taken at 10 and 27 °C, show some resemble to each other, but one can notice different crystal modifications in close examination. However, the pictures clearly show the nematic disclinations at 35 °C and the isotropic phase at 45 °C, respectively. These observations

![Figure 5.1 UV/Vis absorption spectra of liquid crystalline azobenzene chromophore (LCAC) in methanol solution before and after UV irradiation.](image)

Figure 5.1 UV/Vis absorption spectra of liquid crystalline azobenzene chromophore (LCAC) in methanol solution before and after UV irradiation.
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 5.3 depicts the DSC thermograms of RMDA/LCAC mixtures obtained at a heating rate of 5 °C/min. The neat RMDA 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 nonequilibrium crystals that formed during cold crystallization or a different type of crystal modification. Since this minor peak of neat RMDA is no longer discernable in the RMDA/LCAC blends, we shall focus only on the major $T_{Cr-N}$ peaks.
The endothermic peak corresponding to $T_{Cr-N}$ of both RMDA 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 RMDA decreases drastically with the addition of LCAC; such movement of $T_{NI}$ is more apparent in the enlarged scale of some RMDA compositions, especially in 70~30 wt % RMDA. 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 (OM).

In Figure 5.4 is shown 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 $r_1 = r_2 = 2$ with $\chi_{crit} = 0.5(1/n_1^{1/2} + 1/n_2^{1/2})^2$, $A = 0.6$ ($\chi_{aa} = A + B/T$), $T_{crit} = -50^\circ C$, $\Delta H_1^u = 33.3$ kJ / mol at $T_{Cr-N,1} = 66^\circ C$, $\Delta H_2^u = 16.9$ kJ / mol at $T_{Cr-N,2} = 33^\circ C$, $\chi_{ca} = 0.7$ at $T_{Cr-N,1}$, $\chi_{ac} = 0.4$ at $T_{Cr-N,2}$, $c_v = 0.9$, and $c_w = 0.01$. 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 the descending order of temperature, various coexistence regions can be identified including nematic + isotropic ($N_1 + I_2$), crystal + isotropic ($Cr_1 + I_2$), 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 wt % or < 5 wt % RMDA, respectively. The predicted solidus lines of Cr$_1$ + Cr$_2$ region are close to the axis of the pure constituent and thus the emerged RMDA and LCAC crystals are mostly pure.
Figure 5.3 DSC thermograms of RMDA/LCAC mixtures obtained at a heating rate of 5 °C/min, showing a systematic shift of crystal-melting and nematic-isotropic transitions as a function of blend composition. The inset shows the enlarged N-I transition endotherms of the intermediate compositions.
The morphologies at various coexistence regions are further investigated by polarized optical microscopy. Pictures a–e in Figures 5.4 exhibit the polarized optical micrographs of the 60/40 and 90/10 RMDA/LCAC blends. The coexistence regions are labeled on the phase diagram. Upon heating the 60/40 RMDA/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 (Figure 5.4, picture b). But RMDA remains in the crystalline phase and thus their coexistence phases correspond to the Cr₁ + N₂ coexistence region. When the temperature reaches 50 °C, the nematic LCAC further transforms completely to the isotropic phase and therefore their RMDA/LCAC mixture belongs to the Cr₁ + I₂ coexistence phase (Figure 5.4, picture c). Upon further heating to 64 °C, the RMDA crystals melt to a nematic phase, showing Schlieren textures in the magnified view (Figure 5.4, picture d). At high concentrations of RMDA (e.g., 90 wt % at 90 °C), the Schlieren texture covers the entire view of the enlarged inset, indicative of a single nematic phase (N₁) (picture e). These emerged morphologies at each composition and each temperature gap are in good agreement with the coexistence regions predicted by our theory. At ambient temperature below the Cr₁ + Cr₂ coexistence line, the formation of separate RMDA and LCAC crystals can be clearly confirmed clearly in the intermediate composition of 40/60 RMDA/LCAC (picture ii). However, at a high concentration, the crystalline morphology is dominated by the majority component (i.e., LCAC crystal) with the minority crystal (RMDA being entrapped in the interlamellar regions (Figure 5.4, picture i)) and vice versa the RMDA crystals dominate the crystalline morphology as depicted in picture iii of Figure 5.4. More importantly, these POM investigations confirm the formation of separate crystals in this Cr₁ + Cr₂ coexistence gap.
Figure 5.4 Comparison between theoretical and experimental phase diagrams of RMDA/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 indicated by (a)-(d) and the 90/10 RMDA/LCAC mixtures indicated by (e). The phase diagram consists of crystal + crystal (Cr$_1$ + Cr$_2$), crystal + nematic (Cr$_1$ + N$_2$), crystal + isotropic (Cr$_1$ + I$_2$), and nematic + isotropic (N$_1$ + I$_2$) phase, and the single phase nematic (N$_1$). The cocrystal structures are also clearly seen at (ii) 40 wt % RMDA, but single component dominates at (i) 20 and (iii) 90 wt % RMDA.
5.3.2. Photoisomerization of Neat LCAC

Figure 5.5 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. As demonstrated in Figure 5.5a, the nematic phase of neat LCAC remains unchanged under the illumination by green light for a prolonged period of 600 s. However, upon illumination with the white light in the same area, the nematic disclinations transform to isotropic state within 120 s (Figure 5.5b). With UV light (40 mW/cm$^2$), the isotropization time is shortened to 30 s (Figure 5.5c) as the nematic phase is destabilized by the trans–cis photoisomerization of LCAC as well as 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 that 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 show any morphological change in the crystalline state (see the picture at 0 sec Figure 5.6a). This crystalline texture remains the same even after 24 hrs.
Figure 5.5 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. 0 s means before UV exposure.

However, when the same crystallization was conducted under the continuous irradiation using the UV light at 28 °C and hold isothermally, the LCAC crystals grow in size with time. When a specific area of optical micrograph at 1,500 s, indicated by a white dashed box, is magnified for 5 times, one can clearly notice multiple striations on the crystal surface (Figure 5.6b; i upper right picture). Upon increasing temperature to 30 °C under the UV irradiation, the striations persist for sometime (see Figure 5.6b, picture (ii) at 60 s) while the isotropic dark region gets expanded, and finally the crystals melt away. Upon recrystallization from the melt of 30 °C to 28 °C by natural cooling,
numerous rhomboidal single crystals developed (Figure 5.6c). Under the continuous UV irradiation, these crystals grow while the stratified stripes developed on the crystal surface as illustrated in Figure 6b, picture iii.

The POM and AFM images at 1,500 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 (Figures 5.7a and 5.7b). A similar occurrence of periodic undulations on rectangular single crystals of syndiotactic polypropylene was found to occur during thermal quenching from the melt. This ripple formation has been attributed to the volumetric shrinkage driven by a sudden change of density at the solid–melt interface during crystallization. In the present case the mechanical deformation driven by trans-to-cis isomerization of LCAC may have caused the volume shrinkage during crystallization under the UV illumination. As a matter of fact the distance between 4- and 4'-positions of the azobenzene rings, where the flexible pentyl groups (C$_5$H$_{11}$) were appended, is 9.0 Å in the trans-configuration, whereas it is 5.5 Å in the cis-state. Hence, the volume of the cis-form would be appreciably smaller than that of the trans-form, therefore the volume shrinks upon UV irradiation. It is this volume shrinkage that drives the surface undulation of the azobenzene single crystals as manifested in the AFM topology (Figure 5.7b).

5.3.3. Effect of Photoisomerization on Phase Diagram of RMDA/LCAC Mixtures

Photoisomerization-induced phase transition has been extended to RMDA/LCAC mixtures. The samples containing different concentration of LCAC were heated up to isotropic phase and then cooled down below $T_{NI}$ of RMDA. After confirming the stable nematic phase under the green light, the white light was exposed isothermally. Figure 5.8
Figure 5.6. 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 zero second means before exposing to UV light.
Figure 5.7 (a) POM and (b) AFM morphology of LCAC crystal after UV exposure for 1500s, showing the corrugated structures.

shows the optical micrographs of 40, 60, and 70 wt % RMDA mixtures. At 40 wt % RMDA, a variety of dark area appears in 4 min and subsequently expands with exposure time. In contrast to neat LCAC there is still residual birefringence even after 30 min. The isotropization proceeds slowly and more nematic area is identified when RMDA concentration is increased up to 60 wt % (Figure 5.8b). According to phase diagram, the RMDA constituent at N$_1$ + I$_2$ coexistence region is not pure as evidenced by solidus line which is apart from the axis. Consequently, isotropization at 40 and 60 wt % RMDA may be attributable to the residual LCAC, i.e., the bent-shaped cis-LCAC reduces the long range orientaional order of nematic RMDA. When RMDA concentration is higher than 70 wt %, the LCAC concentration is not sufficient to induce phase transition, maintaining Schlieren texture even after 2 hrs (Figure 5.8c).

Figure 5.9 displays the photo-DSC thermograms measured under the continuous irradiation of UV light at an intensity of 40 mW/cm$^2$. The neat LCAC exhibits a single
Figure 5.8 Optical micrographs of (a) 40/60, (b) 60/40, and (c) 70/30 RMDA/LCAC mixtures under the white light. The former two compositions show isotropization with exposing time, whereas the latter remains Schlieren textures even after 120 min.

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–nematic transition ($T_{Cr-N}$). Therefore, the isotropization of LCAC crystal at 30 °C in Figure 5.6(b) may result from the depressed melting point in which the transition starts from near 28 °C. In blends, the $T_{Cr-N,2}$ of each constituent declines from 66 to 60 °C in mixtures of < 70 wt % RMDA, but a lesser extent from 31 to 30 °C at < 80 wt % LCAC, respectively (indicated by the arrows). We further analyze the DSC trends of phase transition by numerical calculation and optical microscopy.
In order to establish the theoretical phase diagram of photoisomerized mixtures, the free energy of nematic ordering from the second component was removed because LCAC did not show nematic–isotropic transition. The crystal–isotropic point ($T_{m2}$) and the corresponding heat of fusion ($\Delta H^a_2$) of the photoisomerized LCAC were determined from the photo-DSC experiments. The parameters used in the self-consistent calculation

![Figure 5.9 Photo-DSC thermograms of RMDA/LCAC mixtures under the continuous UV irradiation at 40 mW/cm$^2$. The thermograms were obtained at a heating rate of 5 °C/min.](image)

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are \( r_1 = r_2 = 2 \), \( A = 0.6 \), \( T_c = -50 \, ^\circ\text{C} \), \( \Delta H_1^u = 33.3 \, \text{kJ/mol} \) at \( T_{\text{Cr-N},1} = 66 \, ^\circ\text{C} \),
\( \Delta H_2^u = 12.7 \, \text{kJ/mol} \) at \( T_{\text{Cr-N},2} = 31 \, ^\circ\text{C} \), \( \chi_{ca} = 0.7 \) at \( T_{\text{Cr-N},1}, \chi_{ac} = 0.3 \) at \( T_{\text{Cr-N},2} \), and \( c_w = 0.01 \). As plotted in Figure 5.10, the phase diagram consists of nematic + isotropic (\( N_1 + I_2 \)), crystal + isotropic (\( \text{Cr}_1 + I_2 \)), and crystal + crystal (\( \text{Cr}_1 + \text{Cr}_2 \)) coexistence regions, and the single phase nematic (\( N_1 \)) and the crystalline phase (\( \text{Cr}_1, \text{Cr}_2 \)) in a manner depending on composition and temperature. Upon photoisomerization, the nematic phase (\( N_2 \)) of neat LCAC completely disappears (enlarge view) and consequently the \( \text{Cr}_1 + \text{Cr}_2 \) coexistence region directly transforms to \( \text{Cr}_1 + I_2 \) without passing through the \( \text{Cr}_1 + N_2 \) coexistence region. It should be noted that the liquidus and solidus line of nematic + isotropic (\( N_1 + I_2 \)) coexistence region shifts to higher RMDA compositions, implying that the photoisomerization of LCAC also reduces the nematic ordering of RMDA. However, the \( \text{Cr}_1 + I_2 \) gap is not significantly affected by trans–cis isomerization.

The pictures a–e in Figure 5.10 show the morphological evolution of 60/40, 90/10, and 95/5 RMDA/LCAC mixtures taken at a heating rate of 1 \( ^\circ\text{C/min} \) under the continuous UV irradiation. At 60 wt \% RMDA, the LCAC crystals become isotropic phase at 33 \( ^\circ\text{C} \) at which the RMDA crystals are interspersed in dark background (Figure 5.10, picture b). Upon further heating to 64 \( ^\circ\text{C} \), the crystalline RMDA directly transforms to the isotropic state. At 90 \( ^\circ\text{C} \), the 90 wt \% RMDA shows the nematic disclinations dispersed in the isotropic liquid (dark) suggesting the nematic + isotropic (\( N_1 + I_2 \)) region (Figure 5.10, picture d). At 95 wt \% RMDA, the Schlieren texture develops suggestive of the single phase nematic (\( N_1 \)) (picture e). Pictures i–iii in Figure 5.10 show the crystalline morphologies of the 20, 40 and 90 wt \% RMDA at 25 \( ^\circ\text{C} \), respectively. The crystalline structures in pictures i and iii are seemingly dominated by the majority component, where
Figure 5.10 Comparison between theoretical and experimental phase diagrams of RMDA/LCAC mixtures. To confirm the coexistence regions, the polarized optical micrographs were taken under 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 (N2) of LCAC disappeared due to trans-cis photoisomerization. The images (i)-(iii) show the single component crystal and cocrystals morphology depending on composition at ambient temperature.
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, suggestive of the Cr\(_1\) + Cr\(_2\) coexistence region.

To clarify the isomerization effect, theoretical phase diagram with or without UV has been summarized in Figure 5.11. The arrow represents the phase transformation after UV illumination. It is apparent that the single phase nematic (N\(_2\)) and isotropic + nematic coexistence regions (I\(_1\) + N\(_2\)) are replaced by isotropic region due to photoisomerization. Moreover, the liquius and solidus line of nematic + isotropic (N\(_1\) + I\(_2\)) coexistence region is found to shift to the higher RMDA composition and thus N\(_1\) + I\(_2\) and N\(_1\) regions become narrower. The extent of N-I transition is significantly influenced by the LCAC
composition. Photoisomerization did not affect the melting point of RMDA constituent in blends as evidenced by the close resemblance of Cr$_1$ + Cr$_2$ and Cr$_1$ + I$_2$ coexistence regions.

5.4. Conclusions

The effect of photoisomerization on phase behavior of RMDA/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 + isotropic (N$_1$ + I$_2$), crystal + isotropic (Cr$_1$ + I$_2$), 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$_1$ + I$_2$ coexistence regions. Moreover, the photoisomerization of LCAC induced the suppression of nematic-isotropic transition of its counterpart (RMDA). 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 of common occurrence 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.
6.1. Introduction

Recent advances in optoelectronic devices require creation of new materials for fast information processing. Among many potential materials, organic chromophores have received considerable attention because of light-driven reversible and spontaneous change of physical and chemical properties for rendering precision controls.\textsuperscript{136, 137} Taking advantage of different optical properties in the bistable isomeric states, these chromophores may be incorporated in a variety of matrices in order to produce various multifunctions such as photomechanical response, photoalignment of anisotropic materials, molecular assembly, and so forth.\textsuperscript{46, 138-146} Especially, liquid crystalline chromophores and liquid crystals (LC)/chromophore mixtures have been investigated extensively by virtue of their potential applications including image recording, in which the molecular ordering/disordering of liquid crystalline system can be manipulated by light-induced preferential alignment.\textsuperscript{147-150} The light-manipulation of molecular architecture of these LC/chromophore systems has a practical significance, e.g., thin LC films containing photochromic molecules can be easily inscribed by means of an interference wave pattern. Moreover, the coherent light induces surface relief of the
structure by mass migration at the surface and/or in the bulk for a variety of volume holographic gratings.\textsuperscript{151-155}

Photochromic spiropyran (SP) and its derivatives are one of the frequently used chromophores because of their geometrical isomerization and bi-stability. Upon exposure to UV light (320 - 400 nm), the C-O bond of the SP molecules undergo heterolytic cleavage by transforming from the colorless closed spiropyran structure (SP) to the colored open merocyanine (MC). Merocyanine is capable of returning to the initial SP form by irradiation with visible light or thermal agitation. Various applications using SP chromophores have been reported in the fields of optical switch, image storage, and surface modification using their reversible property changes.\textsuperscript{156-159}

On the other hand, reactive mesogenic diacrylate (RMDA) monomers have been used to fabricate the macroscopically aligned polymer films. Upon polymerization, the reactive mesogens containing more than two polymerizable end groups yield the macroscopically ordered polymeric networks while maintaining their orientations as well as their mesophase structures permanently up to their degradation temperatures.\textsuperscript{14, 160-162} 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 non-mesogenic networks. The blends of spiropyran and mesogenic diacrylate are therefore of immense interest because the alignment of polymeric LC network can be controlled by the SP-MC transition. 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/RMDA mixtures is of paramount
importance from the fundamental as well as practical viewpoints.

In this chapter, phase behavior of spiropyran and mesogenic acrylate (RMDA) mixture has been investigated by determining phase transition temperatures using differential scanning calorimetry (DSC). A theoretical phase diagram was calculated by self-consistently solving the combined free energies of Flory-Huggins (FH), Maier-Saupe (MS), and phase field (PF) model. From the orientational order parameter of nematics and crystal phase order parameters of each constituent, the phase transition temperatures were determined and the coexistence points were determined by means of a double tangent method via balancing the chemical potentials of each phase. Wide-angle x-ray diffraction (WAXD) and optical microscopy (OM) techniques were employed to verify the coexistence regions obtained theoretically by seeking self-consistent solution. Furthermore, the photoisomerization-induced phase transition of the mixtures has been investigated.

6.2. Experimental Section

Spiropyran chromophores undergo photoisomerization to merocyanine upon exposure to UV light and revert back to its ground state by thermal treatment or irradiation with a blue light. It exhibits a single melting transition around 178 °C. The reactive mesogen has acrylate double bonds at the ends of the backbone that are capable of photo-initiated radical reaction (or photo-crosslinking). It reveals crystal-nematic \((T_{CN})\) and nematic-isotropic \((T_{NI})\) transitions at 71 °C and 128 °C at the first heating run. The samples containing different SP contents were prepared by dissolving in a common solvent, i.e., nonpolar carbon tetrachloride (CCl\(_4\), B.P. = 76 °C). The solution was
mechanically stirred until they became homogeneous and then cast onto the slide glasses. The solvent was completely removed by drying in a vacuum oven at 40 °C for 24 h.

The photoisomerization of SP molecules has been recorded using UV/Vis spectrophotometer (Model 8453, Hewlett-Packard). The dilute spiropyran solution in carbon tetrachloride (CCl₄) has been filled into the quartz couvett and scanned from 200 to 800 nm. Differential scanning calorimetry (DSC) analysis was carried out using a DSC apparatus (Model Q-1000, TA Instruments), which is equipped with a refrigerated cooler. The sample (3~5 mg) sealed in the aluminum hermetic cell has been scanned at a heating rate of 5 °C/min. The cell was continuously purged with nitrogen gas at a flow rate of 40 ml/min. In optical microscopy (BX60, Olympus) analysis, the morphological development following several thermal quenches onto the hot stage (TMS93, Linkam) was taken using a digital camera (EOS 300D, Cannon). Moreover, isothermal mesophase transition under UV light has been undertaken. The intensity of UV light is about 40 mW/cm². The detailed procedures were described in experimental section.

6.3. Results and Discussion

Following the same procedures described in previous chapter, we established the experimental and theoretical phase diagram of SP/RMDA mixtures and then investigated isothermal nematic-isotropic and isotropic-nematic phase transition under the UV light.

6.3.1. Phase Diagram of SP/RMDA Mixtures

The initial SP/n-Hexane solution is transparent without any color and shows no discernible UV/Vis absorption peak (Figure 6.1). Upon UV irradiation, the transparent
SP/n-Hexane solution turned to a dark blue color, suggestive of the structural transformation of SP to merocyanine (MC) due to the cleavage of C-O bond in the spiro position. When 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 at 410 nm upon UV irradiation, which are characteristics of the blue-colored merocyanine. The intensity of both peaks progressively increases with irradiation time, indicative of the forward SP-to-MC conversion. After 3 min, the peak intensities show a tendency of leveling off as the molecular transformation between SP and MC approaches asymptotic equilibrium.

Figure 6.1 UV/Vis absorption spectra of SP solution as a function of UV irradiation time, showing the increase of absorption band of merocyanine at 590 nm.
Figure 6.2 DSC thermogram and optical micrographs of neat RMDA. The RMDA exhibiting crystal-nematic (71 °C) and nematic-isotropic (128 °C) phase transformation maintains its crystal and nematic morphology up to 250 °C after photopolymerization.

The DSC thermogram of neat RMDA 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 taken at 26, 100, and 130 °C in (Figure 6.2a), the low temperature peak at 71 °C corresponds to the crystal-nematic ($T_{Cr-N}$) transition, whereas the highest peak at 128 °C may be attributed to nematic-isotropic ($T_{NI}$) transition. When photopolymerization was carried out at temperatures corresponding to the isotropic, nematic, and crystalline states of neat RMDA, these hierarchical morphologies got permanently fixed due to the curing of the diacrylate...
networks. More importantly, these structures persisted up to the highest experimental temperature of 250 °C without undergoing any melting or mesophase transformation (Figure 6.2b).

Figure 6.3 depicts the DSC thermograms of the SP/RMDA blends obtained at a heating rate of 5 °C/min. The crystal melting point \( T_m = 178 \) °C of neat spiropyran and crystal-nematic \( T_{CN} = 71 \) °C and nematic-isotropic \( T_{NI} = 128 \) °C phase transition of neat RMDA decrease by adding counterpart, as indicated by arrows. The enlarged view

![Figure 6.3 (a) DSC thermograms of SP/RMDA mixtures, showing a variation of endothermic peaks in a manner dependent on composition. DSC scans were conducted at a heating rate of 5 °C/min.](image-url)
of melting point at 40 – 20 wt % SP is shown as an inset. Compared to $T_m$ of SP, the depression of $T_{Cr-N}$ of RMDA is not significant because of less plasticizing effect by SP crystal. On the other hand, the $T_{NI}$ of RMDA decreases drastically from 128 to 88 °C with addition of 10 wt % of SP. In order to identify these transition peaks in mixtures, it is imperative to conduct theoretical calculation and thermal quenching experiments.

Figure 6.4 describes the variation of crystal and nematic order parameters of each constituent as a function of temperature in their neat and blend compositions. The order parameter of pure SP crystal ($\psi_1$) drops off discretely at 178 °C. Upon adding RMDA, the discontinuity takes places at reduced temperature and at the same time its value deviates from the unity (please see the inset). The lower value of crystal order parameter in mixtures suggests that the emerged SP crystal is solvated and less perfect. Similar trend is discerned for RMDA crystal ($\psi_2$). As illustrated in Figure 6.4b, the crystal-nematic phase transition shifts from 71 to 61 °C at 85 wt % RMDA with its value around 0.99. In contrast to SP, one more discontinuity is found at higher temperature due to nematic-isotropic phase transition. According to Maier-Saupe (MS) theory, there exists universal critical order parameter, $s_c = 0.429$, below which nematic order parameter ($s_2$) drops discontinuously to zero (isotropic). It is apparent that the reduction of nematic-isotropic transition point is more significant than that of the crystal-nematic transition at a given composition. By inserting these values into respective free energy density and combining them together, total free energy curve can be drawn. Subsequently, theoretical phase diagram is constructed by connecting the coexistence points at a given temperature.

Figure 6.5 illustrates total free energy curve obtained at different temperature. The single well curve at 190 °C changes to double well with decreasing temperature because
Figure 6.4 Crystal and nematic order parameters of SP and RMDA as a function of temperature at different compositions: (a) crystal order parameter of SP ($\psi_1$); (b) crystal and nematic order parameter ($\psi_2$, $s_2$) of RMDA.
Figure 6.5 Variation of total free energy curve from a combined FH/MS/PF model and a double tangent line, exhibiting phase equilibria involving crystal + isotropic (Cr$_1$ + I$_2$), isotropic + nematic (I$_1$ + N$_2$), crystal + nematic (Cr$_1$ + N$_2$), and crystal + crystal (Cr$_1$ + Cr$_2$) with decreasing temperature.

of the anisotropic ordering of crystalline or nematic phase. At 150 °C, spiropyran having high melting point ($T_m = 178$ °C) crystallizes first and thus free energy from phase-field model contributes to the total free energy. The cusp at $\phi_{sp} = 0.9$ indicates that the free energy from PF model takes into effect. When temperature reduces to lower than the $T_{NI}$ of RMDA ($T_{NI} = 128$ °C), the nematic ordering takes place at RMDA rich concentration.
Therefore, the two double tangent lines at 100 °C correspond to isotropic + nematic (I₁ + N₂) and crystal + isotropic (Cr₁ + N₂). At 80 °C, the free energy of crystal solidification from SP and nematic ordering of RMDA dominates over the whole composition and thus crystal + nematic (Cr₁ + N₂) coexistence line is observed. Upon further cooling to 30 °C, RMDA is also crystallized from nematic phase, forming crystal + crystal (Cr₁ + Cr₂) double tangent line. By connecting those equilibrium compositions, theoretical phase diagram is constructed.

Figure 6.6 plots the predicted phase diagram at different critical temperature (Tₖ). Critical temperature is related to amorphous-amorphous interaction parameter (χₐₐ) through χₐₐ = A + (χₖ−A)Tₖ/T, where χₖ represents the critical interaction parameter. At Tₖ = 190 °C (Figure 6.6a), corresponding to χₐₐ > χₖ, the liquid + liquid coexistence region (L₁ + L₂) develops above the Cr₁ + I₂ at the intermediate composition due to poor interaction. Upon lowering critical temperature below Tₘ of SP (Figure 6.6b,c), i.e., χₐₐ < χₖ, the L₁ + L₂ phase disappears and the liquidus line of Cr₁ + I₂ coexistence region is suppressed. Moreover, at low SP concentration, neat N₂ and I₁ + N₂ region are more pronounced. Regardless of critical temperature, the broad coexistence regions are observed at intermediate compositions.

The predictive capability of self-consistently calculated phase diagram has been tested by comparing with the experimental transition points. In Figure 6.7, the solid line and circular symbol represent the theoretical curve and DSC data, respectively. The material and model parameters used for numerical calculation were r₁ = r₂ = 1, A = 0, B (∆H₁) = 306 K at Tₖ = -120 °C, ∆H₁ = 20 kJ/mol at Tₘ₁ = 178 °C, ∆H₂ = 30.7
Figure 6.6 The effect of $T_c$ ($\chi_{ca}$) on theoretical phase diagram of SP/RMDA system: (a) $T_c$ = 190 °C; (b) $T_c$ = 0 °C.
Figure 6.7 The experimental and theoretical phase diagram of SP/RMDA system and polarized optical micrographs of 5/95 and 60/40 mixtures taken after 3 hrs of thermal quenches, exhibiting (a) pure nematic (N2), (b) crystal + isotropic (Cr1 + I2), and (c) crystal + nematic (Cr1 + N2) phases. The symbol represents the phase transition points measured by DSC and the solid line denotes the theoretical curve calculated based on a FH/MS/PF model.
kJ/mol at $T_{C1-N,2} = 71 \degree C$, $T_{NI,2} = 128 \degree C$, $c_w = 0.6$. The predicted liquidus and peritectic lines describe well the experimental phase diagram. In a descending order of temperature, the various coexistence regions including crystal + isotropic (Cr$_1$ + I$_2$), crystal + nematic (Cr$_1$ + N$_2$), and crystal + crystal (Cr$_1$ + Cr$_2$) are discernible. At extreme RMDA composition (< 10 wt % SP), the single phase nematic (N$_2$) appears below the $T_{NI}$ of RMDA. It should be emphasized that the isotropic phase transforms to single phase nematic (N$_2$) by passing through the narrow isotropic + nematic (I$_2$ + N$_2$) coexistence region. The single phase crystal region (Cr$_1$, Cr$_2$) is hard to identify in the phase diagram because the solidus lines of Cr$_1$ + Cr$_2$ region are virtually overlapped with each axis, implying that the SP and RMDA molecules prefer to form the separate individual crystal.

The thermal quenching experiments were undertaken to verify the observed single and coexistence regions. Figure 6.7(a)-(c) show the polarized optical micrographs of 5/95 and 60/40 SP/RMDA mixtures taken after 5 hrs following temperature quench from isotropic to a given temperature. The corresponding regions are marked on the phase diagram. At 5 wt % SP, the Schlieren textures with two and four brushes representing the strength of line disclination of $\pm 1/2$ and $\pm 1$ emerges at 90 $\degree$C (Figure 6.7a). As it covers the whole area, it can be denoted as single phase nematic (N$_2$). The morphological evolution of Cr$_1$ + I$_2$, Cr$_1$ + N$_2$, and Cr$_1$ + Cr$_2$ coexistence regions was investigated by changing quench depths at 60/40 SP/RMDA. When quenched from 170 to 110 $\degree$C, the numerous isolated crystals are dispersed in the continuum of surrounding isotropic liquid (Figure 6.7b), which corresponds to Cr$_1$ + I$_2$ coexistence region. Upon increasing quench depth to 75 $\degree$C, the isotropic RMDA transforms to nematic phase and thus bright area with dark brushes can be seen at the edge of the existing crystals (please see the enlarge
view). The still existing dark area may be attributable to either homeotropic alignment of RMDA molecules or the coexistence of crystal, isotropic, and nematic phase after passing through the eutectic point.

Figure 6.8 shows the temporal evolution of crystalline morphology following temperature quench from 170 to 28 °C (indicated by ‘d’ in phase diagram). The crystal + isotropic (Cr₁ + I₂) and crystal + nematic (Cr₁ + N₂) coexistence regions were observed at early stage due to the memory effect before reaching stable equilibrium state. With elapsed time, the isotropic and nematic regions are slowly replaced by RMDA crystals and finally the whole microscopic area is covered with the SP and RMDA crystals (340 min). Compared to previous morphologies (b and c), the number of crystal increases, but with smaller size. These thermal quenching experiments clearly demonstrate the validity of the established phase diagram.

X-ray diffraction technique is employed to verify the phase sequence of the coexistence regions. Upon increasing temperature from 28 °C to 75 °C, the peaks located at a low 2θ angle at 3.66 (corresponding to a d spacing of 2.412 nm) and wide angle at 15.36 (0.576), 17.06 (0.519), and 17.86 (0.496) simply disappear, indicative of absence of ordered structure from RMDA crystals (Figure 6.9). In general, the diffraction pattern of an unaligned nematic phase is hard to distinguish from that of isotropic phase, and thus no discernible change is observed between 75 and 110 °C, which corresponds to crystal + nematic (Cr₁ + N₂) and crystal + isotropic (Cr₁ + I₂) coexistence region, respectively. Upon further heating to 170 °C, the crystalline SP completely melts into isotropic phase. At this temperature, diffraction patterns show only an amorphous halo without any distinct peaks.
Figure 6.8 Temporal evolution of phase morphology following temperature quenches from isotropic phase (170 °C) to 28 °C for the 60/40 SP/RMDA blends. The nematic phase appears at the edge of crystal and then crystals cover the whole microscopic view.
Figure 6.9 1D WAXD patterns of 60/40 SP/RMDA blends measured at 28, 75, 110, and 170 °C, exhibiting the phase transition of \((\text{Cr}_1 + \text{Cr}_2) - (\text{Cr}_1 + \text{N}_2) - (\text{Cr}_1 + \text{I}_2) - (\text{I})\) during heating. The scan rate was 1 °/min over a 2θ angle range from 2.5 to 35°.

6.3.2. Phase Behavior of SP/RMDA Mixtures under UV Light

Guided by the phase diagram, photoisomerization-induced mesophase transition has been explored. UV light was irradiated at single phase nematic (N\(_2\)) and isotropic phase (I) in order to induce isothermal nematic-isotropic (N → I) or isotropic-nematic (I → N) phase transition. Figure 6.10 displays the optical micrographs obtained before and after UV irradiation at 100 °C (corresponding to single phase nematic) for 60 s. It does not reveal any morphological change during UV irradiation. When the sample is heated up, it is noticed that the Schlieren texture persists up to 200 °C without phase transition.
Figure 6.10 Optical micrographs of 2/98 SP/RMDA mixture subjected to UV irradiation at 100 °C (single phase nematic region), showing the infusible Schlieren texture.

We further investigate the effect of photoisomerization on isotropic phase at the same composition. The sample was heated up to 125 °C, i.e., 4 °C higher than isotropization temperature. As seen in Figure 6.11a, the numerous birefringence droplets appear from isotropic phase after UV exposure for 60 s. Like previous case, this induced phase is infusible up to 200 °C. The fixation of anisotropic property is one of the characteristics of reactive mesogen.21 Polymer network prepared from neat RMDA maintained the crystalline and nematic structure of monomer up to 250 °C (Figure 6.2). Even though zwitterion is a major product of photoisomerized SP, the stable biradicals or ionic radicals are also detected at intermediate state.33,34 Therefore, the freezing phenomena in SP/RMDA mixture may be attributable to the polymerization initiated by those radicals. The UV-generated isotropic-nematic phase transformation may take place either by expanded nematic region of RMDA networks or stabilization of nematic phase with merocyanine (MC) isomer. Figure 6.11b depicts the DSC thermograms before and
Figure 6.11 (a) Optical micrographs of 2/98 SP/RMDA mixture under UV light at 125 °C, showing the evolution of infusible nematic droplets from isotropic phase. (b) Comparison of DSC thermograms before and after UV irradiation. The crystal-nematic and nematic-isotropic transition peak from RMDA completely disappears after UV irradiation. The zero second denotes right after exposing to UV light.
after UV exposure at isotropic phase (125 °C). Two distinct endothermic peaks from crystal-nematic (69 °C) and nematic-isotropic (121 °C) phase transition of RMDA completely disappear. It is supportive of the fixation phenomena in optical microscopy. The solidification of 3/97 SP/triacrylate solution is another clue of the occurrence of photopolymerization under UV light.

6.4. Conclusions

Equilibrium phase diagram of spiropyran and RMDA blends has been presented on the basis of DSC results and theoretical calculation. The predicted phase diagram based Flory-Huggins (FH), Maier-Saupe (MS), and phase field (PF) model described well the change of crystal melting point of SP and crystal-nematic and nematic-isotropic transition of RMDA in mixtures. It consists of single component mesophases (N₁₂) and Cr₁ + I₂, Cr₁ + N₂, Cr₁ + Cr₂ coexistence phases. The observed single and coexistence regions have been further confirmed by examining the morphological development subjected to thermal quenching. The crystal and nematic order parameters of each constituent demonstrated that phase transition took place at lower temperature by adding counterpart and the emerged crystals were solvated. The UV light irradiation at single phase nematic and isotropic phase triggered the photopolymerization of RMDA because of the radicals formed during the course of photoisomerization of SP.
CHAPTER VII
EQUILIBRIUM PHASE DIAGRAM AND PHOTOPOLYMERIZATION INDUCED PHASE SEPARATION OF MESOGENIC DIACRYLATE MONOMERS AND LOW MOLECULAR MASS LIQUID CRYSTAL BLEND

7.1. Introduction

Anisotropic mechanical, optical, and electrical properties of macroscopically oriented polymeric film have many potential uses in optical storage, electro-optical displays, and electric sensors. Generally, the orientations of polymer are accomplished by viscous flow in a melt or solution and mechanical stretching such as melt extrusion, gel drawing, and spinning techniques.\textsuperscript{165,166} However, the alignment of polymer is confined within small area and processing time is relatively long because of its high viscosity. To overcome such deficiencies, the anisotropic network prepared from reactive mesogen (RM) has gained great attention\textsuperscript{149-151}.\textsuperscript{5} It contains polymerizable end group (e.g., acrylate, epoxy, vinylether) and forms densely cross-linked network after polymerization. The anisotropic properties of network are maintained up to high temperatures. As the polymer chains are aligned in monomeric state, the external magnetic/electric force or surface treatments can be utilized to stimulate network.

The anisotropic polymer networks are often incorporated into low molecular weight liquid crystals (LMWLC) in order to help alignment and motion.\textsuperscript{167,168} The conventional
surface treatment has limitation in that it is difficult to align the LC molecules in thicker cells, resulting in the irreversible switching. With RM, the switching capability can be significantly improved even at low threshold voltage and the light loss can be minimal. Many studies of polymer dispersed liquid crystals (PDLC, < 50 wt % LC) and polymer stabilized liquid crystals (PSLC, > 95 wt % LC) have focused on developing liquid crystal displays (LCD) and light shutters based on RM system.

The PDLC and PSLC films are commonly fabricated by thermally-induced phase separation (TIPS), solvent-induced phase separation (SIPS), and photopolymerization-induced phase separation (PIPS) process. Among them, the PIPS method is advantageous because the curing parameters are chosen freely and the orientation of networks is easily controlled within short time. Depending on polymerization conditions, i.e., temperature and monomer concentration, the final morphology and performances of the composites are significantly influenced.\textsuperscript{169-172} Therefore, in-depth understanding of phase behavior is crucial.

The main objective of present study is to establish the phase diagram in mixtures of reactive mesogenic diacylate monomer (RMDA) and low molecular weight liquid crystal. Phase transition temperature was determined by means of differential scanning calorimetry (DSC) and optical microscopy (OM). The numerical calculation was performed by self-consistently solving a combined free energy density of Flory-Huggins (FH), Maier-Saupe (MS), and phase-field (PF) model in order to predict the phase transition of nematic and crystalline phase. The validity of theoretical phase diagram has been tested with OM by thermal quenching experiment. The photopolymerization behavior of neat MDA and its mixtures with LMWLC was monitored by DSC and OM techniques.
7.2. Experimental Section

The mixtures of various RMDA/E7 compositions were heated above their clearing point (isotropic state) and stirred thoroughly until they became homogeneous. Subsequently, the samples were directly placed in aluminum DSC pans and glass slides for OM analysis. Phase transition temperature of neat RMDA and E7 and their mixtures was determined using DSC apparatus (Q-1000, TA Instruments) equipped with refrigerated cooler. The sample sealed in the hermetic pans was analyzed in the temperature range from 0 to 130 °C at the same heating and cooling rate of 1 °C/min. The cell was purged with nitrogen gas at a rate of 40 ml/min. In the case of optical microscopy analysis, the morphology evolution during heating/cooling or thermal quenches has been captured using a digital camera at a magnification of 200×. The sample temperature of various concentrations was controlled on Linkam Scientific Instruments hot stage.

Photopolymerization of neat RMDA has been initiated by adding 3 wt % of photoinitiator, 2,2-dimethoxy-1,2-diphenylethane-1-one (Irgacure 651, Ciba Additives). Both RMDA and Irgacure 651 were melted into isotropic state and then cooled down to crystalline and nematic phase. The UV light having an intensity of 40 mW/cm² was irradiated to the sample for 300 s. Optical microscopy and photo-DSC were used to monitor photopolymerization behavior, i.e., morphological change of polymerized RMDA during heating/cooling process and the heat liberated at isothermal condition. In blends, polymerization was conducted at single phase isotropic (I) and nematic (N) phase, which is about 5 °C higher and lower than isotropization temperature. The mixtures were handled in dimmed red light and stored in a refrigerator to avoid undesired reaction.
7.3. Results and Discussion

Phase diagram of binary mesogenic mixtures has been constructed experimentally and theoretically. By performing photopolymerization, the anisotropic RMDA networks were prepared and subsequently phase separation took place in mixtures.

7.3.1. Phase Behavior of RMDA/E7 Mixtures

Figure 7.1 illustrates the DSC thermograms of RMDA/E7 mixtures obtained at a heating rate of 1 °C/min. Pure RMDA exhibits two endothermic peaks at around 66 and 128 °C from crystal-nematic ($T_{Cr-N,1}$) and nematic-isotropic ($T_{NI,1}$) phase transition, while pure E7 shows a single nematic-isotropic transition ($T_{NI,2}$) at around 59 °C. When these two materials are blended, the isotropization temperature shifts between $T_{NI}$s of pure constituent, showing almost linearly relationship. The $T_{Cr-N,1}$ of RMDA is found at reduced temperature with increasing E7 content up to 60 wt % and then disappears. The single and coexistence regions bound by liquidus and solidus lines are further proved using optical microscopy (OM), wide angle x-ray diffraction (WAXD), and numerical calculation.

Figure 7.2 shows the optical micrographs of 10/90 and 60/40 RMDA/E7 mixtures taken during cooling at 1 °C/min. At 10 wt % RMDA, numerous birefringence LC droplets evolve from the dark area (isotropic melt) at around 64 °C and get expanded through coalescence upon continued cooling. When temperature reaches at 63 °C, typical Schlieren texture with the strengths of line disclination of ±1/2 and ±1 is fully developed, indicative of a single phase nematic (N). Similar morphological evolutions are observed
at 60 wt % RMDA, but the droplets appear at around 94.4 °C because of the $T_{NI}$ of RMDA being high. It should be emphasized that the phase transition from isotropic to nematic phase takes place by passing through a narrow isotropic + nematic (I + N) coexistence region.

Figure 7.1 DSC thermograms of RMDA/E7 mixtures at various compositions. The transition temperatures of RMDA including $T_{NI}$ and $T_{KN}$ shift to a lower temperature by adding E7. Below 30 wt % RMDA, the RMDA was not crystallized, showing single endothermic peak. These DSC scans were obtained at a heating rate of 1 °C/min.
Figure 7.2 Optical micrographs of 10/90 and 60/40 RMDA/E7 mixtures, showing phase transformation from isotropic phase to the nematic phase. The images were taken at a cooling rate of 1 °C/min.
The numerical calculation of RMDA/E7 system was performed based on the combined free energy of Flory-Huggins, Maier-Saupe, and phase-field theory (FH/MS/PF). The mesophase transition has been determined by minimizing the total free energy with respect to the nematic ($s_1$, $s_2$) or crystal ($\psi_1$) order parameter. The temperature and composition dependence of order parameters are found in our previous papers. Figure 7.3 reveals the experimental and theoretical phase diagram of RMDA/E7 system. The circular and square symbols represent DSC and OM results and the solid line is the calculated curve. The liquidus lines of isotropic + nematic (I + N) and crystal + nematic (Cr$_1$ + N$_2$) coexistence regions are in good accord with experimental results. The theoretical phase diagram has been established using $r_1 = r_2 = 1$, $A = -0.8$, $T_c = -200$ °C, $\chi_{aa} = -0.25$ at 100 °C, $\Delta H_i^u = 33.3$ kJ/mol at $T_{CrN,1} = 66$ °C, $T_{NI,1} = 128$ °C, $T_{NL,2} = 59$ °C, $c_v = 0.98$. The value of cross interaction ($c_v$) is inferred from the change of composition-dependent isotropization temperature. In a descending order of temperature, isotropic (I), isotropic + nematic (I + N), and crystal + nematic (Cr$_1$ + N$_2$) are discernible. The I + N coexistence region gets narrower at RMDA and E7 rich region and the solidus line of Cr$_1$ + N$_2$ coexistence region at high RMDA concentrations overlaps with the axis. When RMDA concentration is reduced less than 20 wt %, the crystal phase from RMDA disappears and therefore broad homogeneous nematic phase is observed.

The optical micrographs shown below phase diagram illustrate the temporal morphological evolution of 70/30 RMDA/E7 mixture after thermal quenching from 110 °C to 45 °C. The corresponding region is denoted by “×” in phase diagram. It takes more than 200 min to crystallize. Initially, the crystals grow in the continuum of nematic phase (bright background) and impinge together after 250 min. Even though the nematic phase...
Figure 7.3 The experimental and theoretical phase diagram of the RMDA/E7 system and optical micrographs obtained after thermal quench from 110 °C (isotropic) to 45 °C (crystal + nematic). The symbol represents the phase transition points measured by DSC and POM, and the solid line denotes the theoretical curve calculated based on a FH/MS/PF model.
is hard to identify due to crystalline morphology, the dark area observed between the crystal boundaries may be attributable to the nematic phase being trapped.

As shown in Figure 7.4, the several distinct peaks of 70/30 RMDA/E7 mixture at 45 °C involving $2\theta = 3.76^\circ$ (corresponding to d spacing 2.35 nm), 15.5 (0.572 nm), 17.2 (0.515 nm), 18.0 (0.493 nm), 22.2 (0.40 nm), 24.0 (0.37 nm), and 24.8 (0.359 nm) disappear upon heating to 65 °C because the crystalline RMDA melts into form nematic phase (N). Since the diffraction pattern of an unaligned nematic phase is not much different from that of the isotropic phase, no significant change is observed between 65 and 110 °C.

7.3.2. Curing Effect on Phase Morphology of Neat RMDA

The curing effect on anisotropic property of pure RMDA has been investigated by performing photopolymerization at crystal and nematic phase. During heating/cooling scans, the green-filtered light is utilized in order to prevent the unexpected reaction. As seen in Figure 7.5, the anisotropic morphologies of RMDA showing crystal-nematic-isotropic phase transformation are virtually frozen after photopolymerization for all temperature range. That is to say, the original crystal (Figure 7.5b) and nematic (Figure 7.5c) structures are infusible up to the highest temperature investigated (250 °C). It may be hypothesized that the acrylate functionalities are probably located at the crystal surface, and thus crystal phase is photo-curable. Due to the ordering in the monomeric state, the volumetric shrinkage of the polymer matrix may be relatively low.

The photo-DSC and FT-IR techniques are employed to elucidate the photopolymerization capability of crystalline and nematic phase of RMDA. As shown in
Figure 7.4 WAXD diffraction patterns of 70/30 RMDA/E7 mixtures obtained during heating. It showed phase sequence of crystal + nematic – nematic – isotropic. The scan rate was 1°/min over a 2θ angle range from 2.5 to 35°.
Figure 7.5 Photopolymerization effect on the morphology development of pure RMDA. The monomeric RMDA shows phase transformation (a) from crystal to nematic (73 °C) and isotropic (130 °C), whereas (b) the crystal and (c) the nematic phase persist its textures up to 250 °C after photopolymerization. The heating/cooling rate was 1 °C/min.
Figure 7.6, in the presence of photoinitiator the exothermic peak evolved during continuous UV exposure at isothermal condition and the intensity decrease of acrylate group at 1630 cm\(^{-1}\) (C=C stretching) and 812 cm\(^{-1}\) (=CH\(_2\) stretching) ensure that the photopolymerization takes place at crystalline and nematic phase. However, it should be noted that the polymerization rate is much faster in nematic phase.

The structure fixation anchoring effect is further manifested by conducting \textit{in-situ} photopolymerization during the course of the crystal growth. Figure 7.7a depicts the crystallization and its growth from nematic phase at room temperature. When UV source was exposed, the mesogenic acrylate was cured to terminate the growth and the morphology no longer showed any phase transformation with time (Figure 7.7b) and temperature (Figure 7.7c). These structural fixation effects may facilitate the early stage of nucleation and the time dependent studies as the cure-time is significantly faster than the crystal growth process.

7.3.3. Effect of Photopolymerization on Phase Behavior

The effect of photopolymerization on phase behavior of RMDA/E7 system has been investigated. Photopolymerization was undertaken at single phase isotropic (I) and nematic (N) phase, i.e., 5 °C above and below nematic-isotropic transition point at each composition. Figure 7.8 depicts the DSC thermograms obtained after photopolymerization. Regardless of curing temperature, it shows a similar trend, exhibiting a single weak endothermic peak in the vicinity of 50–60 °C. The peak position implies that the transition may originate from the phase separated E7. The increase of molecular weight of RMDA by photopolymerization causes the homogeneous mixtures
Figure 7.6 Comparison of photo-DSC thermograms and FT-IR spectra of photopolymerized RMDA at (a) crystal (30 °C) and (b) nematic phase (75 °C), showing the photopolymerization capability at anisotropic phase. The intensity of UV light was approximately 40 mW/cm².
Figure 7.7 Optical micrographs of UV-exposed pure RMDA. Before polymerization it shows (a) the crystal growth from nematic phase during cooling, but this morphology got fixed right after illuminating UV light and did not show any phase transition as a function of (b) time and (c) temperature.
to be unstable, which eventually leads to phase separation. The slight depression of transition point and correspondingly the decrease of enthalpy ($\Delta H_{NI}$) suggest that the E7 still contains the dissolved monomer or prepolymer. As described earlier, the cross interaction between RMDA and E7 is similar to that of individual mesogen, and thus it may be difficult to get a complete phase separation. The absence of an endothermic peak above 60 wt % RMDA probably results from the suppression of N-I transition of E7 molecules or the diffusion effect.

Figure 7.9 shows the morphological change of 10/90 and 90/10 RMDA/E7 mixtures obtained after photopolymerization at single phase isotropic (I) and nematic (N), and crystal + nematic (Cr$_1$ + N$_2$) coexistence regions. In the case of photo-curing at isotropic phase (Figure 7.9a), the small birefringent LC domains completely disappear at around 60 °C. In contrast to the uncured system (Figure 7.2a), liquid crystalline molecules do not form the Schlieren textures during slow cooling because the solidified RMDA networks may prevent the flow and coalescence of E7 molecules. When photopolymerization was performed at nematic phase (Figure 7.9b), the macroscopic nematic textures are observable even at 150 °C as a consequence of fixation of nematic networks. The birefringence change can be seen clearly above and below 60 °C. We have not heated up above 150 °C because of the thermal instability of E7. Infusible crystal phase in mixture are further investigated by performing photopolymerization at crystal + nematic (Cr$_1$ + N$_2$) coexistence region. As illustrated in Figure 7.8c, the initial crystal phase at 90/10 RMDA/E7 mixture maintains its ordering up to 150 °C. The appearance of small dark spot on crystal surface at 60 °C may occur due to isotropization of E7.
Figure 7.8 DSC thermograms of RMDA/E7 mixture after photopolymerization at (a) a single phase isotropic and (b) nematic region. At < 50 wt % E7, it shows single transition peak in the vicinity of 50–60 °C. Heating rate was 1 °C/min.
(a) Isotropic phase curing of 10/90 RMDA/E7

(b) Nematic phase curing

(c) Crystal phase curing of 90/10 RMDA/E7

Figure 7.9 The optical micrographs taken after photopolymerization in mixture of 10 wt % RMDA at (a) isotropic and (b) nematic phase, and 90 wt % RMDA (c) at crystal phase.
Figure 7.10 Experimental and theoretical phase diagrams for mixtures of RMDA networks and E7 obtained after polymerization at isotropic phase, consisting of nematic + isotropic (N₁ + I₂) to isotropic + isotropic (I₁ + I₂).

Figure 7.10 display the experimental and theoretical phase diagram of RMDA/E7 mixtures after photopolymerization at isotropic phase. The elastic free energy has been added to total free energy, while nematic ordering for E7 has been retained for calculation. Theoretical phase diagram (solid line) obtained using elasticity parameters of \( f = 3 \) and \( r_c = 100 \) describes well the DSC (as denoted by ‘○’) and polarized optical microscopy (□) results. It is apparent that the immiscible nematic + isotropic phase at > 30 wt % E7 transformed to isotropic + isotropic (I₁ + I₂) upon increasing temperature above \( T_{NI} \) of E7, which is different from the phase behavior of uncured mixtures. It indicates that once the RMDA is polymerized to form networks, the mixtures can no longer dissolve each other.
7.4. Conclusions

The theoretical phase diagram constructed by solving self-consistently the combined FH/MS/PF accorded reasonably well with the observed DSC and POM transition points. It exhibited isotropic + nematic (I + N) and crystal + nematic (Cr\textsubscript{1} + N\textsubscript{2}) coexistence regions and single phase nematic (N) depending on composition and temperature. Upon photopolymerization, the crystal and nematic phase of neat RMDA were frozen and maintained its anisotropy up to 250 °C. In blend, the photopolymerization performed at single phase isotropic (I) and nematic (N) region induced phase separation between RMDA networks and E7 and therefore the DSC curve exhibited the single transition peak close to the $T_{NI}$ of E7. Morphology changes taken after photopolymerization indicated that the phase separation took place even in crystal + nematic (Cr\textsubscript{1} + N\textsubscript{2}) coexistence region. The theoretical phase diagram of polymerized mixtures established by taking into account the elasticity of polymer networks accorded well with experimental results.
CHAPTER VIII

INDUCED SMECTIC PHASE IN MIXTURES OF HYPERBRANCHED POLYESTER AND LIQUID CRYSTAL MESOGENS

8.1. Introduction

By virtue of the recent emergence of optical devices and display technology along with a large data storage capacity, liquid crystal displays (LCD) have received immense interest in the information technology.\textsuperscript{173-175} A major challenge is the development of field-active flexible photonics with fast LCD switching capability and high resolution. To meet the aforementioned challenges, various functional polymers and liquid crystals (LC) have been designed and developed. Subsequently, the dispersed LC domains are contained in polymer binders through phase separation either by thermal quenching or crosslinking reaction, which is widely known as polymer dispersed liquid crystals (PDLC). Some of the most desired features of the PDLC films are the fast switching capability and the high contrast between the dispersed LC phase and the matrix polymer. The former goal may be achieved by selecting higher order LC mesophase such as smectic liquid crystals or ferroelectric liquid crystals. The latter goal of the high refractive contrast between the dispersed mesogenic phase and the isotropic matrix can be achieved via controlled phase separation. However, the choice of the matrix polymer network is of paramount importance, because the polymer networks from the
conventional linear chains generally show severe shrinkage during the crosslinking reaction, which makes their products to be non-uniformly birefringent. Birefringence is a phenomenon caused by molecular chain orientations, especially in molded optical components where the residual stress drives the birefringence to rise, thereby degrading the performance of optical devices that require maintaining the polarization state of the incident light.

To overcome the problem of matrix shrinkage, dendrimers and hyperbranched supramolecules have been synthesized for applications as optical distortion-free matrices. Dendrimers are one of the first nano-scaled synthetic materials that can be tailored with consistent structural characteristics producing controlled length, uniform size distribution, and surface functionality. The dendrimers are basically fractal-like branched molecules spanning out from a common center, pointing to every directions. Thus, these dendrimers are optically isotropic as their branches are randomly oriented, and therefore no birefringence will develop in the matrix of their optical products. Moreover, these dendrimers can be tailored to create a precise composition and with alteration of the terminal functionality, surface control can be facilitated. On the same token, hyperbranched polymers and discotic liquid crystals receive great attention because of the random orientation rendered by their molecular arms (i.e., fractal branches), and therefore the matrix would be birefringence-free which can give a greater contrast with the dispersed anisotropic LC domains. Furthermore, the hyperbranched polyester under study is photopolymerizable and capable of forming a uniform film with little or no shrinkage, and thus it gives additional flexibility in designing and fabricating holographic polymer dispersed liquid crystals (H-PDLC) or 2-D/3-D photonic crystals.
More importantly, the resulting products of H-PDLC are virtually defect free, thereby receiving immense interest in academia and industries.

The present chapter describes unique observations in the photocurable hyperbranched polyester/eutectic nematic liquid crystal (E7) system; (i) induced higher order mesophase at some specific compositions, which is absent in their neat constituents and (ii) possible escape of some ingredients during prolonged annealing. It is essential to identify the extracted material first, and then investigate the phenomenon of induced phase transition guided by the complex phase diagram in conjunction with the emerged mesophase structures.

8.2. Experimental Section

The as-synthesized HB polyester was mixed with E7 by dissolving in a common solvent, THF at room temperature to form a 15~20 wt % solute concentration. An aliquot of the E7/HBPEAc-COOH solution was spread on a glass slide to form a thin film (~10 \( \mu \)m thickness). The dry film was put in a vacuum oven at room temperature for 3 days to remove any residual solvent. Subsequently, the sample was further annealed at 80 °C for 24 hours for use in polarized optical microscopy (POM), differential scanning calorimetry (DSC), and wide angle x-ray diffraction (WAXD) experiments.

An optical microscope (BX60, Olympus) equipped with a 35 mm camera (EOS 300D, Canon) and a hot stage (TMS 93, Linkam) were used for POM experiments. Each mixture was heated or cooled at 1 °C/min. Thermal analysis was conducted using DSC 7 apparatus (Perkin-Elmer) equipped with refrigerated cooler (Intracooler, 1P). After the recommended amount (3~5 mg) of the sample was sealed in the hermetic pans, DSC measurements were performed in the temperature range between 25 and 140 °C at a
heating and cooling rate of 10 °C/min unless indicated otherwise. The program consists of first heating and followed by cooling and heating cycle. The cell was purged with nitrogen gas at a rate of 20 ml/min. FT-IR spectra were obtained by using a Nicolet 380 (Thermo Scientific) spectrometer with a resolution of 4 cm\(^{-1}\). The spectra of the pure or mixed samples were the average of 32 scans acquired at room temperature. Wide-angle x-ray (AXS D8, Bruker) generator was operated at 40 kV and 40 mA using Cu-K\(\alpha\) radiation with a wavelength of 0.154 nm. A 2-D detector (HI-STAR, Bruker) was used to identify the existence of mesophase structure at room temperature. Samples were scanned over a \(2\theta\)-angle range from 2.5 to 35 ° at a scanning rate of 2 °/min.

8.3. Results and Discussion

During the course of preparing the hyperbranched polymer/E7 composite film, we observed the induced smectic phase at intermediate composition. We systematically examined the phase behavior of the mixtures and demonstrated this unique phenomena.

8.3.1. Elucidation of Extraction Phenomena

As evidenced in the present thermogravimetric analysis (TGA) investigation, the pure E7 reveals comparable thermal stability before and after prolonged annealing (Figure 8.1a). This thermal stability of E7 can further be confirmed in the FT-IR scans, showing virtually the same IR transmittance spectra (Figure 8.1b). It is reasonable to infer that E7 is thermally stable in the neat form. However, when small amount of HBPEAc-COOH is added, the peak intensities of some chemical bonds, i.e., the peaks at 1604 and 1494 cm\(^{-1}\) corresponding to the C=C phenyl ring stretching as well as those at
Figure 8.1 Thermal stability of the neat E7 before and after annealing; (a) TGA analysis at a heating rate of 10 °C/min under nitrogen atmosphere and (b) FT-IR spectra recorded at room temperature.
1180 and 1004 cm\(^{-1}\) associated with the C-H aromatic bending, decline in the peak height (or the area under the peak) with annealing without involving any peak movement. In addition, the peak intensity at 2230 cm\(^{-1}\) corresponding to the C≡N stretching decreases upon prolonged annealing. On the other hand, the C-O-C stretching at 1250 cm\(^{-1}\) that belongs to 8OCB remains virtually invariant. These peaks associated with the phenyl rings are nonreactive; any loss in these peaks must be attributed to the loss of the LC constituents of E7. That is to say, some constituents of eutectic mixture E7 such as 5CB and 7CB having relatively low \(T_{NI}\) may be vulnerable to extraction relative to the 8OCB and 5CT with high \(T_{NI}\). In literature, the fractionation of multicomponent LC mixtures is known to occur due to the preferential solubility of the constituents to some polymer matrices\(^{184-186}\). In the present case, the low \(T_{NI}\) LC constituents of E7 such as 5CB and 7CB may be segregated out due to their relatively weaker affinities to HBPEAc-COOH, and thus are susceptible to extraction during the prolonged annealing, especially under vacuum.

Figure 8.2 presents the normalized IR transmission of 90 wt % E7 based on C-O-C stretching (1250 cm\(^{-1}\)) from 8OCB, which is known to be thermally stable at the annealing temperature range investigated. The IR spectrum clearly shows the decrease of peak height at 2230 (corresponding to C≡N stretching), 1604, 1494 (C=C phenyl ring stretching), and 1180, 1004 (C-H aromatic in-plane bending). The calculation based on the relative peak intensity ratio, i.e., the area under the C≡N stretching peak relative to that of C-O-C stretching, shows a reduction for approximately 30 %, suggesting that some LC constituents containing the C≡N groups might have been extracted during annealing especially under vacuum.
Figure 8.2 FT-IR spectra of 90/10 E7/HBPEAc-COOH showing the decrease of peak intensity of the annealed sample at 2230 (corresponding to the C≡N stretching), 1604, 1494 (the C=C phenyl ring stretching), and 1180, 1004 (the C-H aromatic bending) compared to the C-O-C stretching at 1250 cm⁻¹ that belongs to 8OCB.

In order to identify the origin of the extracted components, we trapped the evaporated LCs by condensing them on the cover glass during prolonged annealing at 110 °C on a microscope sample hot stage for 10 hrs. Subsequently, the phase transition of these condensed LC was analyzed using POM in conjunction with the chemical structural analysis by FT-IR spectroscopy. Figure 8.3 shows the comparison IR spectra of the neat 5CB and the condensed LC; the striking similarity between these two spectra indicates that the LC component that is extracted is 5CB. This inference can be further confirmed in the optical microscopic study (Figure 8.4) showing a similar phase transition for the
neat 5CB and the condensed LC, except for a slight increase of $T_{NI}$ for about two degrees. This enhanced $T_{NI}$ can be further confirmed by the DSC study showing only a single $T_{NI}$ at 63 °C. However, one cannot rule out a possibility that some traces of 7CB might have escaped along with the 5CB.

Figure 8.3 FT-IR spectrum of the condensed LC on the slide glass during annealing of the 90/10 E7/HBPEAc-COOH mixture in comparison with those of neat HBPEAc-COOH, 7CB, and 5CB, confirming that the condensed LC on the cover glass is predominantly 5CB.
8.3.2. Establishment of Phase Diagram

Upon addition of anisotropic solvent such as $a$-E7, the $T_g$ of hyperbranched polyester decreases noticeably below 60 °C and it continues to decline with increasing LC concentration. The ratio of $a$-E7/HBPEAc-COOH mixtures was calibrated based on the weight loss of 5CB. Concurrently, several thermal transitions can be noticed in the DSC traces (Figure 8.5). At the LC rich compositions, new thermal transitions were detected at elevated temperatures significantly above those of both neat constituents. As indicated by the arrows in Figure 8.5, these transition temperatures were suppressed with increasing hyperbranched polyester.

The origins of these transition peaks are difficult to identify on the basis of the DSC results alone, and thus POM study was undertaken on the 17/83 $a$-E7/HBPEAc-COOH mixtures.
Figure 8.5 DSC thermograms of various $a$-E7/HBPEAc-COOH mixtures, exhibiting various phase transition endotherms. The samples containing 87~55 wt % of $a$-E7 show enhanced phase transitions at elevated temperatures significantly above the TNI of neat $a$-E7. Note that the mixtures containing < 9 wt % of $a$-E7 reveal only a single glass transition temperature corresponding to that of HBPEAc-COOH. These DSC scans were obtained from the second heating cycle at a heating rate of 10 °C/min.
composition which shows a dark appearance at 80 °C suggestive of the isotropic melt (Figure 8.6a). Upon cooling at a rate of 1 °C/min, some tiny birefringent droplets start to appear at in the vicinity of 69 °C, indicative of the emergence of the nematic LC domains in the continuum of isotropic hyperbranched polymer rich phase (Figure 8.6b). At ambient, the whole microscopic view is filled with those LC domains (Figure 8.6c). In the case of 74/26 a-E7/HBPEAc-COOH blend, the system is completely isotropic at 112 °C, but upon cooling to 108 °C, the dispersion of numerous large birefringent LC droplets can be discerned in the polarized microscopic view of Figure 8.6d. These nematic domains grow through coalescence with continued cooling. This temperature range may be identified as the nematic + isotropic (N + I) coexistence region. When the temperature approaches 65 °C, the Schlieren textures, characteristics of the nematic phase, develop with two- and four- dark brushes indicating that the strengths of these line disclination are ±1/2 and ±1 (Figure 8.6e). Upon further cooling the nematic disclination structure transforms into the more ordered phase showing a corrugated fan texture, suggestive of a focal conic smectic-A phase (Figure 8.6f). Moreover, the smectic focal conic structure seemingly emerges from the existing nematic line disclinations.

Similar temperature scanning experiments have been conducted for other a-E7/HBPEAc-COOH compositions at a rate of 1 °C/min. The low E7 concentrations (< 45 wt %) show the glassy nematic domain appearance at ambient temperature similar to that of the 17/83 a-E7/HBPEAc-COOH. However, upon increasing a-E7 to 55 wt %, a nematic disclination structure was found to coexist with numerous tiny nematic domains (Figure 8.7). With further increase of E7 content to 63-93 wt %, the focal conic smectic texture can be discerned, which is consistent with those of the 74 wt % a-E7 composition.
This focal conic smectic-A phase persists up to 93 wt % \( a\)-E7, but the texture becomes somewhat fuzzy. At 97 wt % LC, the Schlieren textures with the strength of ±1 and ±1/2 develop, indicative of the nematic disclinations. It should be emphasized that the neat \( a\)-E7 and the LC concentrations > 93 wt % exhibit only the nematic phase in the vicinity of room temperature.

Figure 8.6 Optical micrographs of 17/83 \( a\)-E7/HBPEAc-COOH mixture showing (a) the isotropic state transforming to (b) the nematic droplets and (c) the glassy nematic phase, whereas the 74/26 \( a\)-E7/HBPEAc-COOH shows the mesophase transformation from (d) nematic domains in the continuum of isotropic matrix to (e) nematic disclinations and (f) induced smectic phase. The heating/cooling rate was 1 °C/min.
Figure 8.7 Optical micrographs of \( a\)-E7/HBPEAc-COOH mixtures taken at room temperature. When E7 concentration is lower than 93 wt %, the focal conic fan-shaped texture develops but the texture changes to glassy phase at < 55 wt % of \( a\)-E7. The 2D WAXD pattern of 87 wt % \( a\)-E7 shows the multiple diffraction peaks in the vicinity of \( 2\theta = 20\text{–}30^\circ \), suggestive of the emergence of the induced smectic-A phase.

The 1-D and 2-D WAXD-\( 2\theta \) scans were acquired for the high \( a\)-E7 content specimens. The last figure in Figure 8.7 exhibits a typical \( 2\theta \)-scan of the 87/13 \( a\)-E7/HBPEAc-COOH composition, showing several diffraction peaks at \( 2\theta = 7.15^\circ \) (corresponding to \( d \)-spacing of 1.235 nm), \( 20.0^\circ \) (0.443 nm), \( 23.1^\circ \) (0.384 nm), \( 23.5^\circ \) (0.378 nm), and \( 26.0^\circ \) (0.342 nm). It should be emphasized that those diffraction peaks are completely absent in the neat amorphous hyperbranched polyester or in the neat nematic (\( a\)-E7). The combination of the POM and WAXD experiments suggests that a higher order mesophase thus developed in the \( a\)-E7/HBPEAc-COOH blends is the induced smectic-A phase.
Figure 8.8 exhibits the temperature versus volume fraction phase diagram of the \(a\)-E7/HBPEAc-COOH mixtures based on the aforementioned DSC and POM studies. The \(T_g\) of HBPEAc-COOH supramolecules is about 89 °C, but it shows appreciable depression upon adding \(a\)-E7. It should be pointed out that the annealing temperature of 80 °C is appreciably higher than the \(T_g\) of the blends. Both DSC and optical microscopic investigations revealed the higher temperature mesophase transitions above the \(T_{NI}\) of \(a\)-E7. These enhanced phase transitions is characterized by an upper azeotrope phase diagram in which the nematic phase in the mixed state is more stable than that of the neat \(a\)-E7. As evidenced in the POM study, the phase diagram is of an upper azeotrope type, representing nematic + liquid (N + I) coexistence phase, pure nematics (N), followed by the induced smectic-A (S\(_{mA}\)) phase in the descending order of temperature. The phase transition of nematic to smectic-A being a first order phase transition, it usually passes through a coexistence gap of nematic + smectic-A (N + S\(_{mA}\)) between the pure nematic and the induced smectic phase, as demonstrated both experimentally and theoretically for other binary nematics, nematic-smectic, and binary smectic mixtures.\(^{72,187-189}\)

8.4. Conclusion

In this chapter, we have established the phase diagram of \(a\)-E7/HBPEAc-COOH blend with emphasis on the induced smectic phase. The observed smectic-A phase in the blend is unique, since the neat HBPEAc-COOH and the annealed E7 did not possess any higher order mesophase. The eutectic mixture E7 showed the compositional fractionations upon adding hyperbranched polymer, leading to the extraction of 5CB due to its relatively weak affinity to the hyperbranched polyester. It appears that the induced
Figure 8.8 Phase diagram of the $\alpha$-E7/HBPEAc-COOH system, exhibiting isotropic + nematic (I + N) coexistence phase and a single nematic (N) and induced smectic (SmA) regions in a manner dependent on composition and temperature. The symbol represents the phase transition points obtained from POM and DSC experiments. The coexistence lines were drawn to guide the eyes in accordance with the theoretical phase diagram of induced smectic-A in nematic mixtures.
smectic phase at 63–93 wt % E7 in the $\alpha$-E7/HBPEAc-COOH blend may be influenced by the shift of eutectic nematic point in $\alpha$-E7. As evidenced by DSC and POM studies, the phase diagram of the $\alpha$-E7/HBPEAc-COOH blend is of an azeotrope type, exhibiting the isotropic (I), isotropic + nematic (I + N), pure nematic (N), nematic + smectic-A (N + $\text{Sm}_\text{A}$), and induced smectic-A ($\text{Sm}_\text{A}$) phase in a manner dependent on composition and temperature. A theoretical account for establishing such an induced phase diagram including the lower temperature crystalline phases is reserved for a future publication.
CHAPTER IX
OVERALL SUMMARY AND RECOMMENDATIONS

9.1. Overall Summary

The equilibrium phase diagrams of photochromophores and reactive mesogenic diacrylate monomer mixtures have been demonstrated. The theoretical liquidus and solidus lines obtained by self-consistently solving a combined Flory-Huggins (FH)/Maier-Saupe (MS)/phase-field (PF) model described well the DSC transition points and provided the phase boundary of various single and coexistence regions. The simple phase diagram of crystalline azobenzene and triacrylate liquid blends which consisted of isotropic (I) and crystal + isotropic (Cr$_1$ + I$_2$) coexistence region got complicated with increasing crystalline and nematic phases of the constituent. For instance, the binary crystalline and nematic mixtures of reactive mesogenic diacrylate monomers (RMDA)/liquid crystalline azobenzene chromophores (LCAC) system exhibited the single phase crystalline (Cr$_1$, Cr$_2$) and nematic (N$_1$, N$_2$), and nematic + isotropic (N$_1$ + I$_2$), crystal + isotropic (Cr$_1$ + I$_2$), crystal + nematic (Cr$_1$ + N$_2$), and crystal + crystal (Cr$_1$ + Cr$_2$) coexistence phases. In chapter 6 to 7, the phase diagram of binary crystals + single nematic (spiropyran/RMDA), and single crystal + binary nematic (RMDA/E7) system were also established.

During the course of thermal quenching experiments, we found that azobenzene single crystal in triacrylate solution can shoot, swim, and sink/float while growing.
Azobenzene crystals that develop early in the crystallization process have unstable interface morphologies with needle-like branches. Unexpectedly, numerous rhomboidal “baby” single crystals were found to nucleate near these branches and rapidly swim away from the “mother” crystal. These baby crystals then suddenly slow down and either sink or float on the surface of solution. We conjecture that the observed motion of azobenzene crystals is primarily due to solvent rejection and associated convective flows, and spatial variability of surface tension responsible for Marangoni effect. The mechanical deformation driven by trans-cis photoisomerization is an additional source of swimming crystal.

The effect of photoisomerization on mesophase transition has been discussed using liquid crystalline azobenzene and spiropyran chromophores which were blended with RMDA. With *trans-cis* conformational change, the nematic phase of LCAC completely disappeared and concurrently the nematic ordering of RMDA was significantly reduced. The theoretically established phase diagram clearly revealed the composition-dependent suppression of isopropization temperature. The striation formation on LCAC crystal surface while exposing UV light indicated that photoisomerization took place even in a condensed solid state. The spiropyran molecules were vulnerable to the UV light and easily degraded. The radicals formed during photodegradation reacted with acrylate group of RMDA. As a result, the nematic droplets appeared from the isotropic phase, and the single phase nematic phase frozen its ordering.

As pure RMDA was able to polymerize in nematic and crystalline phase, anisotropic ordering persisted up to highest temperature investigated. Photopolymerization of homogeneous RMDA/E7 mixtures induced the phase separation and therefore phase
diagram exhibited immisible nematic + isotropic \((N_1 + I_2)\) and isotropic + isotropic \((I_1 + I_2)\) coexistence regions.

Finally, we examined the phase behavior of hyperbranched polymer/annealed E7 mixtures. During the annealing process, the fractionation of the eutectic mixtures took places, extracting the 5CB constituent which has low crystal-nematic and nematic-isotropic transition point. The E7 deviated from eutectic composition showed smectic-A \((S_mA)\) phase at ambient temperature. The observed phase diagram was an azeotrope, exhibiting nematic-isotropic transition higher than pure E7.

9.2. Recommendations

The nucleation and growth dynamics of a gigantic azobenzene single crystal has been demonstrated in relation to undercooling and UV effect. The baby single crystals nucleated at needle-like jagged branches or fragmentation of mother crystals can shoot, swim, sink/float during the crystal growth. It is associated with unbalanced solvent rejection and thereby surface tension gradient. Mechanical deformation triggered by \textit{trans-to-cis} contraction can also induce crystal swimming that moved away from light source. Our observation may help elucidating polymer crystallization mechanism from solution. By performing theoretical simulation on growth dynamic in the context of phase-field theory of solidification involving surface tension, gravity field, convective flow, and \textit{trans-cis} isomerization rates, the mechanism of shooting, swimming, sinking/floating behavior can be clarified.

The comparison phase diagram of photoisomerized mixtures described the suppression of isotropization temperature as a function of the amount of chromophores
added. If temperature is set between nematic-isotropic transition \( T_{\text{NI}} \) of \textit{trans}- and \textit{cis}-form, the nematic phase changes to isotropic under UV light. The validity of our results should be tested with the actual devices such as light shutter, erasable holography, and display. For instance, the control of transmittance by phase transition is the basis of photon-mode ferroelectric LC, and formation of phase-type holographic gratings can form fast and repeatable recording with high resolution.

As described earlier, liquid crystalline networks are useful for compensating the positive birefringence of LC molecules and controlling the alignment of liquid crystalline molecules. In addition to phase diagram, dynamics of spatio-temporal morphology development of photopolymerization-induced phase separation may help controlling the final morphology. With chiral agent, RMDA/E7 mixtures can exhibit cholesteric and blue phase. Especially, the blue phase that typically appears within a very narrow temperature range (1~2 °C) can be stabilized by photopolymerization of RMDA, which subsequently broadens the range of blue phase more than 60 °C. Blue phase is promising for LCD because it does not require any alignment layers such as polyimide and SiO\(_2\) along with low power consumption and broader viewing angle. We can determine the suitable operational condition by constructing experimental and theoretical phase diagram.
REFERENCES


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