PHOTOPOLYMERIZATION-INDUCED CRYSTALLIZATION IN RELATION TO SOLID-LIQUID PHASE DIAGRAMS OF BLENDS OF POLY(ETHYLENE OXIDE)/MULTI-FUNCTIONAL ACRYLATE MONOMERS

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ABSTRACT

The goal of the present dissertation is to elucidate the phenomenon of photopolymerization-induced phase transition (PIPT) in order to provide guidance to the fabrication of polymer photonic crystals via photolithography. The phenomenon of photopolymerization-induced phase separation and crystallization is a phase transformation process driven by photochemical reaction, in which the phase ordering occurs during the photo patterning. Although the reaction-induced phase separation is well investigated, the photopolymerization-induced crystallization is new in this field. First, the solid-liquid phase diagrams of the starting blends of polyethylene oxide (PEO)/multi-functional acrylate monomers have been established by means of differential scanning calorimetry and optical microscope. It was found that the PEO/acrylate systems reveal various coexistence regions including isotropic (I), the coexistence of crystal + liquid (Cr$_1$+L$_2$) and the crystal + crystal (Cr$_1$+Cr$_2$) gaps. A phase field theory pertaining to the solid-liquid phase transition in conjunction with the Flory Huggins theory for liquid-liquid phase separation has been developed to test with these experimental phase diagrams. The aforementioned coexistence regions have been further verified experimentally by probing the spatio-temporal emergence of crystalline structure and phase morphology using time-resolved optical microscopy following several
temperature-quenches into these individual coexistence regions. The effects of molecular weight of PEO and acrylate arm topology of acrylate monomers on their blend phase diagrams have been explored.

Guided by these established phase diagrams of the PEO/multi-functional acrylate blends, photopolymerization-induced crystallization experiments have been carried out at the isotropic temperatures slightly above the depressed melting points of PEO crystals corresponding to the liquidus line. The depressed melting curve shifts upward to the elevated temperatures and eventually surpasses the reaction temperature which in turn drives the system into the unstable gap triggering the photopolymerization-induced crystallization. Various crystalline phase morphologies including development of spherulites in the continuum of the isotropic region were observed in the crystal + liquid coexistence region. At higher reaction temperatures, above the melting temperature, viscous fingering (or fractal growth) takes place during photopolymerization, showing phase separated domains within these advancing viscous fingering structures. Finally, the study was extended to holographic photopolymerization that allows the reaction to occur predominantly in high intensity regions to create periodic patterns. Of particular interest is the growth of the hierarchical structures of PEO crystals and two-phase morphology within the stripes or interconnected channels and/or arrays of spheres.
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Photopolymerization-induced phase transitions (PIPT) are a non-equilibrium phase transformation phenomenon involving mesophase ordering in liquid crystals, or crystallization, or phase separation driven by photochemical reaction.\textsuperscript{1,2} Polymerization-induced phase separation (PIPS) is commonly used in the manufacture of polymer dispersed liquid crystal (PDLC) for displays.\textsuperscript{3} It consists of liquid crystal droplets dispersed in a polymer matrix. One way to fabricate PDLC is to prepare a homogeneous mixture of polymer and liquid crystal (LC), and then quench the system to a temperature inside the miscibility gap in order for the constituents to phase separate. This method is known as temperature-induced phase separation (TIPS).\textsuperscript{4,5} An alternative approach widely practiced is PIPS\textsuperscript{1,6-10}, in which the initial mixture consisting of monomers and LC phase separate due to the increase in molecular weight during polymerization. In the case of TIPS, when the system has the upper critical solution temperature (UCST), the system temperature is reduced from the one-phase region to the two-phase region. However, in the PIPS, the reaction temperature remains unchanged while the binodal and spinodal lines are progressively pushed upwards as the polymerization proceeds, and the phase separation begins when the coexistence line surpasses the temperature of the system.
While this provides a convenient approach and physical insight, the kinetics is not always the same as in TIPS. The shape of the binodal and spinodal curves can change as the miscibility gap is pushed up, and as a result the nucleation-initiated spinodal decomposition takes place. In contrast, this phenomenon is not likely to occur in any thermal quenching of TIPS. During polymerization or crosslinking reaction of the reactive constituents, the molecular weight of the reactive species increases, which in turn, causes the system to become unstable and drives phase segregation of the blends.\textsuperscript{9,11-13} In crystalline or liquid crystalline polymer mixtures, not only liquid-liquid phase separation occurs but also crystal solidification or mesophase ordering takes place during photopolymerization.\textsuperscript{13-17}

Whereas polymer-liquid crystal blends have been of interest and widely studied, miscible blends containing a crystallizable component and thermosetting polymer have attracted less interest.\textsuperscript{18-20} In a partially miscible blend of a crystalline polymer and a monomer, the melting temperature of the polymer is depressed. As the other component starts to polymerize, the melting point curve of the crystalline component moves upward and straightens out. From a thermodynamic point of view, an increase in the molecular weight of either component of a miscible blend should reduce the entropy of mixing. Phase separation induced by cross-linking is expected for systems with a positive (endothermic) enthalpy of mixing.\textsuperscript{21}

Crystallization in thermosetting polymer blends containing a crystallizable component is greatly affected by both the miscibility and phase behavior of the crosslinked blends and topological effect of the network. The crystallization kinetics and semicrystalline morphology in miscible or immiscible polymer blends containing one
crystallizable component have hitherto received relatively little attention. In these systems, curing results in chain extension, branching, crosslinking and significant changes in chemical and physical properties of the non-crystallizable component. This may influence the chain mobility and the free energy of nucleation, and hence has a dramatic influence on crystallization of the crystallizable component. Since it is difficult to envision the segregation process of a crosslinked, thermosetting polymer in the blend during the crystallization process of the network of crosslinked components, the competition between the crystallization and phase segregation should be considered. It is therefore important to investigate the semi-crystalline spherulite and lamellar structures of this type of thermosetting polymer blends.

The concept of polymerization-induced crystallization is similar to that of phase separation in binary polymer blends undergoing thermally initiated polymerization or photo-initiated polymerization. While the polymerization-induced phase separation has been well investigated experimentally and theoretically, the phenomenon of polymerization-induced crystallization is completely new.

Establishing this concept of the photopolymerization-induced crystallization is the preliminary objective of the present study. By using a crystalline polymer with a photo reactive monomer (instead of liquid crystals) followed by photopolymerization increases the molecular weight of the blends. This increase in molecular weight drives the crystallization process. Also, in this research, directional phase transitions such as oriented crystallization induced by photo-intensity gradient during photopolymerization of a binary mixture of crystalline polymer/photo-curable monomer will be elucidated. Furthermore, the idea of photopatterning process has emerged from the recent theoretical
simulation for developing arrays of electrically tunable liquid crystal micro lenses with well-controlled size and uniform spacing.\textsuperscript{14,23,24} This technique can be used to fabricate polymeric composite films for applications such as contact lenses with high oxygen permeability, chemical filtrations, bio-mimetic membranes, and polymer photonic devices.\textsuperscript{25} The technique is based on spatially anisotropic photopatterning via optical interference subjected to photopolymerization reaction called pattern photopolymerization.

A typical methodology is to use interfering light to irradiate the photo reactive monomer/liquid crystal mixtures in the homogeneous state, triggering phase separation by pattern photopolymerization. The photopatterning technique operates on the principle of constructive and destructive interference between the two vertical waves and/or two horizontal waves, which generate regulated microchannels and/or microdroplet arrays.

When light is irradiated on the sample by patterning via constructive and destructive interference of multi-waves, monomers are selectively polymerized in the high intensity region of irradiation, whereas little or no reaction takes place in the low intensity region. This results in a spatial concentration variation in the monomer field. Polymer chains, once formed, cannot diffuse away because of the chemical cross-links, although these molecules may undergo Brownian motion between the chemical junctions. However, monomers can be transported through the polymer network. Strictly speaking, there may be some solubilizing agents and/or surfactants, though diminutive in amount, diffusing from high intensity regions to low intensity regions to fill the vacancy left by the monomers, and vice versa. In principle, the diffusion of monomers causes contrast between the high intensity region and the low intensity region. The three objectives of the
The research presented here are: (a) to investigate the growth of crystallization which is induced by photopolymerization and the influence of different reactive monomers and crystallizable polymers, (b) to establish the in depth understanding of the relationships among photopolymerization, crystallization, and phase morphology by in-situ monitoring, and (c) to demonstrate the fabrication of photo patterning using multi- wave interference and investigate how the crystals grow in those patterned templates.

The dissertation is organized as follows. Chapter I gives a brief introduction and the objectives of the completed research. Chapter II contains the fundamental knowledge and background to conduct the research and presents the existing work in the literature. Chapter III describes experimental materials and methods used in this work. Chapter IV demonstrates the phase diagram and the morphology evolution of poly disperse PEO/triacrylate monomer before curing. Chapter V reveals the phase diagram and morphology for binary crystalline blends in polydisperse PEO and diacrylate. Chapter VI shows the effect of molecular weight of PEO in multi-acrylate monomers on phase diagrams and morphology development. Chapter VII investigates the photopolymerization kinetics to get the guidance to photopolymerization-induced crystallization. Chapter VIII shows the experimental observation of the PEO/diacrylate monomer after photopolymerization to investigate the crystal behavior while photopolymerization takes place. Chapter IX shows the PEO/triacrylate monomer after photopolymerization to investigate the crystal behavior and phase separation while photopolymerization takes place. Chapter X illustrates the effect of molecular weight and acrylate arms on the photopatterned polymerization-induced crystallization. Chapter XI serves as the summary of this dissertation and recommendation for future research.
2.1. Phase Behavior of Polymer Blends

Commercially, polymer blending has been a common practice to reduce the production cost while maintaining price with desired properties. The miscibility of two polymer components is the main role of polymer blends because polymer blends do not form a single phase system under most conditions. To measure, interpret, and predict the miscibility properties of polymer blends, the thermodynamic approach is required. The determination of thermodynamic parameters for polymer blends, as the phase diagram or the Flory-Huggins binary interaction parameter, $\chi_{FH}$, has been investigated by many researchers.

2.1.1. Phase Equilibria of Polymer Systems

The polymer blends are ultimately determined by thermodynamic variables (temperature, pressure, number, type and distribution of the phase) of blend.

The stability of a polymer blend under constant temperature $T$ and pressure $P$ can be expressed by the Gibbs free energy of mixing, $\Delta G_m$, as follows:
\[ \Delta G_m = \Delta H_m - T \Delta S_m \] (2.1)

where T is the absolute temperature, \( \Delta H_m \) and \( \Delta S_m \) are the enthalpy and entropy of mixing, respectively, which can be predicted by the famous Flory-Huggins expression,\(^{18,26,27}\) \( \Delta S_m \) of a polymer and a solvent is given

\[ \Delta S_m = -k_B (N_1 \ln \phi_1 + N_2 \ln \phi_2) \] (2.2)

where \( k_B \) is the Boltzmann constant, \( N_i \) is the number of molecules of component ‘i’, \( \phi_i \) is the volume fraction of ‘i’ component which is defined as the number of each polymer-occupied lattice sites, respectively, the chain length, \( r_i \)

\[ \phi_i = \frac{N_i r_i}{N_i r_i + N_j r_j}, \quad i \neq j \] (2.3)

The Flory approach has assumed the system to be incompressible, i.e., the volume remains unchanged upon mixing. The entropy of mixing is expressed in terms of volume fraction as

\[ \Delta S_m = -N k_B \left( \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right) \] (2.4)

According to Flory’s approach, the enthalpy of mixing for a polymer solution or blend, \( \Delta H_m \), can be expressed in terms of the interaction parameter \( \chi_{FH} \) between a polymer and a solvent,

\[ \Delta H_m = N k_B T \chi_{FH} \phi_1 \phi_2 \] (2.5)

From Eqns. (2.1), (2.2), and (2.4), the Gibbs free energy of mixing can be written as follows,

\[ \frac{\Delta G_m}{N k_B T} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi_{FH} \phi_1 \phi_2 \] (2.6)
where $\phi_1$ and $\phi_2$, representing the volume fractions of component 1 and 2, respectively, also volume fractions can be given by $\phi_1 = n_1r_1/n$, $\phi_2 = n_2r_2/n$, and $n = n_1r_1 + n_2r_2$. $n_1$ and $n_2$ are the number of solvent and polymer molecules, respectively. $\chi_{FH}$ represents the Flory-Huggins interaction parameter, which is generally calculated in terms of the athermal and thermal contributions with a reciprocal dependence on absolute temperature.

$$\chi_{FH} = A + \frac{B}{T} \tag{2.7}$$

where A and B are constants. If A is negative, the LCST coexistence curve is established. If it is positive, then UCST is observed. The constant B is generally positive in polymer solutions so that $\chi$ decreases with increasing temperature. The original Flory-Huggins theory was considered to depend only on temperature, but several empirical modifications to the Flory-Huggins interaction parameter have been reported in the literature. According to Koningsveld,$^{28}$ a modified $\chi$ is expressed as a product of a temperature contribution multiplied by a concentration contribution.

$$\chi(T, \phi) = \left( A + \frac{B}{T} + C \ln T \right)(1 + D\phi + E\phi^2) \tag{2.8}$$

The thermodynamic criterion for phase stability under the fixed temperature $T$ and the constant pressure $P$ conditions is given by $^{29,32}$

$$\Delta G_m < 0 \tag{2.9}$$

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi^2} \right) > 0 \tag{2.10}$$
The sign of $\Delta G_m$ depends on the sign of $\chi$. If the sign of $\chi$ is negative, the polymer system is miscible at all temperature and composition values. For the positive $\chi$, the miscibility is not favored at all temperatures.

For a binary system in equilibrium, the chemical potentials of each component in two phases must be same,

$$\mu_1^\alpha = \mu_1^\beta \tag{2.11}$$

$$\mu_2^\alpha = \mu_2^\beta \tag{2.12}$$

where the superscripts denote the two equilibrium phases.

Binodal points are obtained by simultaneously solving Eqns. (2.11) and (2.12).

The chemical potentials are expressed as follows

$$\frac{\Delta \mu_1}{RT} = \ln(1-\phi) + \left(1 - \frac{r_1}{r_2}\right)\phi + \chi r_1 \phi^2 \tag{2.13}$$

$$\frac{\Delta \mu_2}{RT} = \ln \phi + \left(1 - \frac{r_2}{r_1}\right)(1-\phi) + \chi r_2 (1-\phi)^2 \tag{2.14}$$

Figure 2.1 shows several types of phase diagram that may be calculated based on this principle. The most popular types are the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST). The UCST system shows a convex curvature with the critical temperature being the maximum peak. On the other hand, the LCST exhibits a concave curvature, the critical temperature being the minimum point.
Figure 2.1 Typical phase diagrams encountered in polymer solutions and blends:
(A)-completely miscible system, (B)-UCST, (C)-LCST, (D)-closed loop, (E)-UCST
and LCST, (F)-hourglass\textsuperscript{29}
Similarly the phase diagram can be calculated using the double tangent method. In the double tangent method, drawing the tangent line to the free energy curve through the two points having the same slope corresponds to the binodal points at a specific temperature. The spinodal point, which separates the metastable from the unstable region, can be calculated by taking the second partial derivatives of the free energy of mixing.

\[
\frac{\partial^2 \Delta G_m}{\partial \phi_i^2} = \frac{\partial^2 \Delta G_m}{\partial N_i^2} = 0
\]  

(2.15)

The critical point is determined by applying taking third order partial derivative of the free energy of mixing

\[
\frac{\partial^3 \Delta G_m}{\partial \phi_i^3} = \frac{\partial^3 \Delta G_m}{\partial N_i^3} = 0
\]  

(2.16)

The critical volume fraction \(\phi_c\) and critical interaction parameter \(\chi_c\) can be defined by solving the conditions of critical point.

\[
\phi_c = \frac{\sqrt{r_2}}{\sqrt{r_1} + \sqrt{r_2}}
\]  

(2.17)

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

(2.18)

Figure 2.2 is a schematic phase diagram showing the phase diagram corresponding to the free energy of isotropic mixing and its derivative at a given temperature.
2.1.2. Dynamics of Phase Separation

Phase separation occurs when a binary system is brought instantaneously from a single phase to a two-phase by thermal quenching. The dynamics of phase separation can be classified into two categories.\textsuperscript{29} One is the nucleation and growth (NG),\textsuperscript{34} and the other is the spinodal decomposition (SD).\textsuperscript{35} A metastable region of the phase usually triggers the nucleation and growth if there is a large enough concentration fluctuation while any small fluctuation in the unstable region will be amplified to initiate phase separation through
spinodal decomposition. A schematic representation of these two mechanisms is shown in Figure 2.3. From a morphological point of view, NG shows the irregular droplet structure. However, the SD shows periodic network (modulated) structure.

Figure 2.3 Schematic evolution of concentration profiles to illustrate the difference between the spinodal decomposition (SD) mechanism and nucleation and growth (NG) \(^{33}\)

2.1.2.1. Nucleation and Growth (NG)

The nucleation and growth mechanism \(^{34}\) mostly occurs in the phase transition processes such as liquid-solid transition, liquid-vapor transition, and crystallization. In the metastable regions, the excess free energy continuously gives the initial intermediate unstable embryos. In these regions, initially the system needs to overcome a certain energy barrier. Thus a finite fluctuation is necessary for the phase transition to occur. So the nucleation and growth require activation energy to originate the process and a critical
size has to be formed before it is energetically favorable for it to grow. These embryos later serve as nuclei and possess the equilibrium composition and subsequently grow on individual nuclei, and the liquid-liquid phase separation finally leads to the droplet in matrix morphology.

A nucleus possesses excess surface energy that induces an aggregation process and forms a new stable phase. This activation energy, $\Delta G^*$, required to initiate the NG process can be expressed as

$$\Delta G^* = -\frac{4}{3} \pi r^3 \Delta G_i + 4\pi r^2 \sigma$$ \hspace{1cm} (2.19)

where the first term is the free energy contribution of the volume created by the nucleus and the second term is the free energy contribution of the interface between the nuclei and the mother phase. $\Delta G_i$ represents the free energy difference between the mother phase and nucleus. $\sigma$ is the interfacial energy per unit area and $r$ is the radius of the nucleus that can be obtained by minimizing the free energy with respect to $r$,

$$r = \frac{2\sigma}{\Delta G_i}$$ \hspace{1cm} (2.20)

When the nuclei are formed, the system decomposes with a decrease in the free energy causing nucleus growth and eventually forming in irregular droplet domains.

2.1.2.2. Spinodal Decomposition (SD)

The spinodal decomposition mechanism occurs usually in the second-order phase transitions involving the phase separation of polymer blends. The fundamental difference from the nucleation and growth mechanism is that the concentrations do not have a step
change to form an embryo. Instead, the concentration fluctuations are typical causes of spinodal decomposition associated with phase separation. The SD is unstable at infinitesimal concentration fluctuations and thus occurs spontaneously without requiring any activation energy.

The formulation of the spinodal decomposition process was first discussed by Cahn and Hilliard for metallic alloys.\textsuperscript{36} They adopted the concentration gradient terms in the expression of free energy for the non-uniform system.\textsuperscript{37-39} The process of SD goes through three stages according to time dependence on concentration fluctuations: “early”, “intermediate”, and “late”. The growth rate of concentration fluctuations of the early stage of SD can be characterized by a linearized diffusion equation which has been solved analytically by Cahn and Hilliard.\textsuperscript{36,37} The phase boundaries are diffused and gradually become shaper. Finally, it involves to interconnected morphology. In SD both composition and size depend on time, while in NG the composition of the separated domains are constant and only the size and size distribution of the nuclei change with time.\textsuperscript{40}

2.1.3. Modification of the Flory Diluent Theory for Crystalline Polymer Blends

The addition of low molecular weight soluble components to crystalline polymers results in a melting point depression. This phenomenon is due to interaction between the two miscible components. Thus, the extent of melting point depression can provide a measure of the interaction parameter between the two components and is given by Flory
for polymer solutions and was later extended to crystalline polymer blends by Nishi and Wang\textsuperscript{19} in their study of PVDF-PMMA.

We shall consider a crystalline polymer blend in which only one component can crystallize and the other is a non-crystallizable amorphous polymer. The total free-energy density of mixing of a crystal-amorphous polymer blend may be expressed as the weighted sum of the free-energy density pertaining to crystal order parameter of the crystalline constituent with its volume fraction ($\phi$) and the free energy of liquid-liquid mixing as described by the Flory-Huggins theory of mixing. The free-energy density of solidification was weighted by its volume fraction to ensure that the solidification potential vanishes in the limit of zero concentration of the crystalline constituent. As pointed out earlier, we relax the last assumption retained in the Flory diluent theory by taking into consideration all possible interaction terms such as amorphous-amorphous and crystal-amorphous interactions.

Polymer crystallization has been described in the framework of a phase field free energy pertaining to a crystal order parameter $\psi$ in which $\psi = 0$ defines the melt and assumes finite values close to unity in the metastable crystal phase, but $\psi = 1$ at the equilibrium limit. The crystal phase order parameter may be defined as the ratio of the lamellar thickness ($l$) to the lamellar thickness of a perfect polymer crystal ($l^0$), i.e., $\psi = l/l^0$, and thus it represents the linear crystallinity, i.e. the crystallinity in one dimension. The free energy density of a polymer blend containing one crystalline component may be expressed as

$$f(\psi, \phi) = \phi f(\psi) + \frac{\phi}{r_1} \ln(\phi) + \frac{(1-\phi)}{r_2} \ln(1-\phi) + \left(\chi_{aa} + \chi_{ca} \psi^2\right) \phi (1-\phi)$$

(2.21)
where $f(\psi)$ is the free energy of crystallization of the crystalline component expressed as a Landau expansion in $\psi$ that is weighted by its concentration or volume fraction in the mixture. This weighting assures the free energy of the mixture to approach its pure crystal limit, i.e., $f(\psi, \phi) \rightarrow f(\psi)$ when $\phi \rightarrow 1$. The natural log terms represent the entropic contribution whereas $\chi_{aa}(1-\phi)$ is the enthalpic contribution to the Flory-Huggins free energy of liquid-liquid demixing. The quantity $\chi_{ca} \psi^2 (1-\phi)$ representing the solid-liquid interaction is complimentary to the amorphous-amorphous interaction term $\chi_{aa}(1-\phi)$. The $\chi_{ca}$ parameter is called the crystal-amorphous interaction parameter, which is repulsive and may be evaluated from the heat of fusion of the crystalline constituent.

When the linear crystallinity $\psi$ is multiplied by its volume fraction, their product $\phi \psi$ signifies the bulk crystallinity. Moreover, $(1-\phi)\psi$ represents the amount of the non-crystalline component interacting with the crystal phase. The physical interpretation of $\chi_{ca} \psi^2 (1-\phi)$ would therefore be the crystal-amorphous interaction term. It should be noted that the present modified theory reverts to the original Flory diluent theory in the extreme limit of complete rejection of the polymeric solvent from the crystal phase, i.e., when the repulsive interaction between the crystal solute and amorphous solvent, $\chi_{ca}$ becomes very strong or a neat crystal phase is formed in the blend.

The free energy density of the crystal solidification may be expressed in the context of the asymmetric Landau expansion, $f(\psi)$ as

$$
f(\psi) = \frac{F(\psi)}{k_B T} = \left[ \frac{\zeta(T) \zeta_0(T_u)}{2} \psi^2 - \frac{\zeta(T) + \zeta_0(T_u)}{3} \psi^3 + \frac{1}{4} \psi^4 \right]
$$

(2.22)
where $W$ is a coefficient representing the energy cost for the system to overcome the nucleation barrier while $\zeta(T)$, and $\zeta_0(T_m)$ represent the location of the nucleation hump on the $\psi$ axis and the solidification potential both of which are melting temperature dependent. This kind of asymmetric Landau potential has been utilized in the phase field crystallization. It should be cautioned that the coefficient of the cubic order must be non-zero in order to apply the Landau potential to the first-order phase transition; otherwise, the potential is applicable only to a second-order phase transition or at equilibrium where the two minima are equivalent. The uniqueness of the present theory of polymer solidification is that these model parameters $W$, $\zeta$ and $\zeta_0$ can be related to the material properties of the individual components and the experimental conditions. This Landau-type free energy of solidification has been successfully applied to describing the spatial temporal emergence of polymer single crystals, dendrite growth patterns, and dense lamellar branching in spherulites.

The establishment of phase diagrams using the phase field model of crystallization is accomplished by minimizing the free energy of the mixture with respect to the non-conserved order parameters and finding the minimum free energy of the mixture at each composition. We then minimize $f(\psi, \phi)$ with respect to $\psi$ in order to find the roots, leading to

$$\frac{\partial f(\psi, \phi)}{\partial \psi} = W(\psi - \zeta)(\psi - \zeta_0) + 2\chi_{ca}(1 - \phi) = 0$$

or

$$W(\psi_c - \zeta)(\zeta_0 - \psi_c) = 2\chi_{ca}(1 - \phi)$$

(2.23)
in which only one solution is real, i.e., $\psi_c = \psi_{\text{min}}$ at the minimum solidification potential well of the crystal order parameter. At a given temperature of crystallization and concentration, $W$ representing the penalty for overcoming the unstable potential hump, $\zeta$ and the solidification potential well, $\zeta_0$ are known and thus $\chi_{ca}$ can be estimated analytically from the heat of fusion, $\Delta H_u$ of PP crystals in the blends through

$$\chi_{ca} \propto W = 6(\Delta H_u / k_B T)(1 - T / T_m^0)(1/2 - \zeta)^{-1}.$$

Figure 2.4 shows the comparison with the melting point depression date of the crystalline-amorphous blend of PVDF and PMMA reported by Nishi and Wang. In the calculation, the statistical segment values of $r_1=3371$ and $r_2=866$, as estimated from the respective molecular weights of PVDF and PMMA, were utilized. From the theoretical fit with the experimental melting points, the value of $\chi_{ca} = -0.141$ at $165^\circ$C was obtained (based on the $\chi_{ca}$ value of 0.58 for the above-mentioned $r_1=3371$ and $r_2=866$). It should be cautioned that the present $\chi_{ca}$ parameter is molecular weight dependent. As in the case of the FH interaction parameter, the estimated value of $\chi_{ca} = -0.141$ is smaller in magnitude (smaller attractive interaction) than the reported result by Nishi and Wang; that is, $\chi_{ap} = -0.31$ obtained from the melting point depression results in the vicinity of the melting temperature of pure PVDF, but it is much closer to that of the small-angle of pure PVDF, but it is even closer to that of the small angle neutron scattering data of the same PVDF/PMMA blends, i.e., $\chi_{aa} = -0.226$ and -0.077 for two different concentrations of PVDF/PMMA by Stein and Hadziioannou and -0.14 by Canalda et al., and -0.03/-0.16 from SAXS by Wendorff.
In the Flory diluent theory, the repulsive crystal-amorphous interaction $\chi_{ca}$ was completely ignored, and thus the $\chi_{aa}$ had been overestimated as compared to those values from other experiments. If the $\chi_{aa}$ value is determined directly from an independent experiment such as SANS or SAXS in the isotropic state, the actual value of $\chi_{ca}$ may be obtained from the melting point depression data. This kind of uncertainty may be eliminated completely in a partially miscible system where the solid-liquid-phase transition is competing with the UCST type liquid-liquid-phase separation.

Figure 2.4 Theoretically calculated phase diagram of PVDF/PMMA blend (●). Experimental data and material parameters were determined by Nishi and Wang(19)
2.2. Crystallization of Polymer Blends

Polymers are a unique class of materials that rarely reach equilibrium during crystallization due to the long chain nature of the molecules. It is necessary to understand the theory of crystallization for homopolymer and the subsequent modification for polymer blends.

2.2.1. Crystallization of Homopolymers

Crystallization is the process whereby an ordered structure is produced from a disordered phase, usually a melt or dilute solution. Crystallization is a non-equilibrium phase transition process. When the temperature of a polymer melt is reduced to the melting temperature, the random, entangled molecules in the melt become aligned and form small ordered regions. This process is known as nucleation and the ordered regions are called nuclei. These nuclei are only stable below the melting temperature of the polymer since they are disrupted by thermal motion above this temperature. The second step in the crystallization process is growth whereby the crystal nuclei grow by the addition of further chains. Crystallization is therefore a process, which takes place in two distinct steps, nucleation and growth, which may be considered separately.

Primary crystallization is followed by secondary crystallization, which is usually associated with two processes (1) additional crystallization within the boundary of spherulites (formation of new lamellae of lamellar thickening), and (2) the crystallization
in inter-spherulitic region. During secondary crystallization process, crystallinity increases much more slowly compared to that during primary crystallization.

For polymer crystallization to start the primary nucleation first needs to take place. The nucleation itself can be defined as formation of a small amount of crystalline material due to fluctuations in density or order in the supercooled melt. The formation of these initial or primary nuclei is the first step starting crystallization and the phenomenon is called primary nucleation. The continuation of crystallization on the growth surface by induction of more and more polymer molecules is referred to as secondary nucleation. Another way of classifying nucleation is by invoking the prerequisite for the original site where the nucleation occurs. If no second surface or existing nuclei (i.e. any type of second phase) is present and the nuclei formation takes place spontaneously only due to supercooling, then the phenomenon is referred to as homogenous nucleation. However, if any second phase is required (it may be a foreign particle or surface from the same polymer nuclei/crystal), then the nucleation is termed heterogeneous nucleation.

Wunderlich et al \cite{46} based on an earlier work \cite{47} have further advocated the subdivision of this classification by incorporating a third category called self-nucleation. This nucleation is due to pre-existing/residual nuclei that survived the initial melt conditions (or the dissolution conditions if it is solution crystallization). Another way of categorizing primary nucleation is on the basis of time dependent effects at approximately the same time then the nucleation is referred to as thermal nucleation. One aspect of such nucleation is that it leads to spherulites of roughly the same size during isothermal crystallization. On the other hand, if the nucleation is such that new nuclei form throughout the crystallization at a particular temperature and thus different
spherulitic (crystal) sizes are obtained than the nucleation is referred to as athermal nucleation. It thus may not be difficult to visualize that homogeneous nucleation is often of the thermal type (the converse is not true) whereas the heterogeneous nucleation maybe thermal or athermal.

For the formation of stable nuclei to take place (primary or secondary), the free energy barrier to crystallization needs to be overcome. The size of the critical nucleus required obviously depends upon this free energy barrier, larger critical nuclei requiring times to form.

In any nucleation process, the free energy of the nucleation process (crystallization) is given by

$$\Delta G = \Delta G_c + \sum A \sigma$$

(2.24)

where the specific surface free energy is given by $\sigma$. For the general case of a spherical crystal nucleus of radius $'r'$, the free energy change can be expressed as

$$\Delta G = \frac{4\pi r^3}{3} \Delta G_c + 4\pi r^2 \sigma$$

(2.25)

These two opposing contributions to the free energy lead to an initial rise in $\Delta G$ till a certain critical maximum in surface free energy surface is reached at $\sigma$, beyond which there is a precipitous drop in the free energy leading to formation of a stable nucleus. The critical point is found out by differentiating the above equation w.r.t. $'r'$ and equating it to zero. The values for such critical points thus obtained are

$$r = r^* = \frac{2\sigma}{\Delta G_c} = \frac{2\sigma T_m^o}{\Delta H / \Delta T_c}$$

(2.26)
\[ \Delta G = \Delta G^* = \frac{16\pi \sigma^3}{3\Delta G_c^2} = \frac{16\pi \sigma^3 (T_m^*)^2}{3(\Delta H_f)^2 \Delta T_c^2} \]  

(2.27)

Figure 2.5 A schematic diagram illustrating the variation of free energy with nucleus size.\textsuperscript{46}

The initial free energy barrier needs to be crossed for the nucleus to become stable. Primary nucleation involves the largest specific area while the area is somewhat reduced for secondary nucleation on the surface. Tertiary nucleation which can be defined as nucleation at an edge, involves even less specific area. Thus, in terms of difficulty of the nucleation process, it goes \textsuperscript{46}

Primary nucleation > Secondary nucleation > Tertiary nucleation.

The large specific area to volume ratio of such entities offsets the decrease in free energy that can be obtained by crystallizing the small volume element of the nucleus.
Crystal growth occurs by secondary and tertiary nucleation. The initial step is the formation of a secondary nucleus, which is followed by a series of tertiary nucleation events. The growth rate kinetics of bulk semicrystalline homopolymers have been determined by Mandelkern et al.\textsuperscript{50} and Hoffman and Lauritzen\textsuperscript{51} using a modified version of the theory of nucleation of Turnbull and Fisher\textsuperscript{52,53}

\[ I = N_0 \exp(-E_d / RT - \Delta G^* / RT) \]  

(2.28)

\(N_0\) is the number of molecules in a unit volume of the liquid. \(\Delta G^*\) is the free energy of formation of the critical size nucleus derived above, and \(E_d\) is akin to the free energy of activation for diffusion of chain segments to the phase boundary. The temperature dependence of the transport term \(E_d\) is similar to that of viscosity, which remains nearly constant at high temperature and increases rapidly at temperatures close to the glass
transition. Whatever the form of the nucleus, $\Delta G^*$ is the dominant term at small degree of supercooling because it is inversely proportional to $\Delta T^2$. Thus the nucleation rate is zero at $\Delta T_m^0$ due to $\exp(-\Delta G^*/RT)$. At still larger supercooling the influence of $E_d$ term begins to increase and the nucleation rate reaches a maximum. At temperatures below this maximum, the nucleation rate is dominated by the transport term and has a large positive temperature coefficient with the rate falling to zero at temperatures below the glass transition $\Delta T_g$. The relative variations of these two terms explain the bell shape, and particularly the existence of a maximum of nucleation rate in the temperature range. At low supercooling, the growth rate is nucleation controlled, while at high supercooling it is diffusion controlled. The number of nuclei is very sensitive to the degree of supercooling such that more nuclei are formed at lower crystallization temperature.

2.2.2. Crystallization of Miscible Polymer Blends

In a crystallizable miscible blend, the presence of an amorphous component can either increase or decrease the tendency to crystallize depending on the effect of the composition of the blend on its glass-transition and on the equilibrium melting point of the crystallizable component. The spherulite growth of the crystallizable component in miscible blends is influenced by the type and molecular weight of the amorphous component, the former affecting the intermolecular interactions between both components and the latter the amorphous component diffusion. The blend composition, the crystallization condition, the degree of miscibility, the mobility of both blends components, and the nucleation activity of amorphous component are important factors.
with respect to the crystallization kinetics. The melting of crystallizable miscible blends often reveals multiple DSC endotherms, which can be ascribed to recrystallization, secondary crystallization, or liquid-liquid phase separation. In general, the major impact of blending is a change in the spherulite size and semicrystalline morphology of the matrix.

Most polymers show a spherulitic texture when crystallization takes place from the melt (Figure 2.7). The spherulites consist of lamellar stacks of alternating crystalline and amorphous layers, radiating from the center (the primary nucleus). When the crystallizable polymer blends with an amorphous one, the morphology is largely determined by the type of segregation of the amorphous component. Crystallization in a miscible blend involves two types of polymer transport: diffusion of the crystallizable component towards the crystallization front and simultaneous rejection of the amorphous component. This latter phenomenon is called segregation; it can take place at three different levels: interspherulitic, interfibrillar and interlamellar (Figure 2.8).

![Figure 2.7 Schematic representation of the spherulitic texture of a semicrystalline polymer](image)

Figure 2.7 Schematic representation of the spherulitic texture of a semicrystalline polymer
Interspherulitic segregation, in which the spherulite is imbedded in an amorphous matrix, can be distinguished from the other two types using optical microscopy. In the case of interspherulitic segregation, a volume-filling texture is observed; the amorphous components can be located either between the lamellae (interlamellar) or between stacks of lamellae (interfibrillar). To find out whether or not interlamellar segregation occurs, small angle X-ray scattering (SAXS) can be used. The increase of the long spacing, which is the sum of the average thickness of the crystalline and amorphous layers, as well as the increase of the thickness of the amorphous layers between the crystalline lamellae are parameters often used as indications for interlamellar segregation.

Most studies concerning the segregation behavior of amorphous components in a miscible crystallizable blend deal with PCL as the crystallizable component. Stein et al.\(^{56}\) and Khambatta et al.\(^{57}\) have shown the segregate interlamellar. The interfibrillar or interspherulitic also was well determined by many researchers like Cruz et al., Defieuw\(^{58,59}\) and Vanneste et al.\(^{60}\)
The influence of the tacticity of PMMA on segregation in PEG/PMMA blends was investigated by Silvestre et al. Attactic and syndiotatic PMMA were found located in between the lamellae of PEG, whereas isotatic PMMA was reported to segregate into interfibrillar or interspherulitic systems. It should, however, be noted that a low molecular weight iPMMA was used in this study. In other PEG blends, the amorphous component resided in the interlamellar regions. All three segregation types were detected by Stein et al and Morra et al. They reported the existence of a compositional interphase (a region of varying polymer composition) between lamellae and the amorphous interlayer. The order-disorder interphase seemed to contain pure PMMA, while in the remaining interlamellar region a homogeneous mixture of PMMA and amorphous PVDF was identified. Also Runt et al experimentally studied blends of crystallizable PEG with three different amorphous components (PMMA, PVAc and Polyhydroxystyrene(PHS)).

2.2.3. Crystallization Kinetics

The crystallization kinetics of blends can be described by the Avrami equation:

\[
\alpha = 1 - \exp[-kt^n]
\]  

(2.29)

where \( \alpha \) is the normalized degree of crystallinity at time \( t \), \( n \) is the Avrami index depending on the type of nucleation and growth process, and \( k \) is the crystallization rate constant.

\[
k = \ln(2/t_{1/2}^n)
\]  

(2.30)
where $t_{1/2}^n$ is the half time of crystallization (the time for half the crystallinity to develop), which is often used as a measure for the overall rate of crystallization. The Avrami index is a measure of the type of nucleation. An increase in the Avrami index is usually attributed to a change from instantaneous to sporadic nucleation. Nucleation prefers homogeneous to heterogeneous with the decreasing of the Avrami exponent. However, the experimental data can deviate from these values due to the unrealistic assumption of Avrami theory. Therefore, Avrami indexes have been reported to be affected by molecular weight, nucleation type and secondary crystallization. In Figure 2.9 typical crystallization isotherms were obtained by plotting $\alpha$ versus the crystallization time for the PEG/PEMA 80/20 blend at different crystallization temperatures. From such curves, the half time of crystallization, $t_{1/2}^n$, can be deduced.

$$\log[\ln(1 - \alpha)] = \log k + n \log t$$

(2.31)

Plotting the left part of this equation against log$t$ should result in a straight line, from which both Avrami parameters, $n$ (slope) and $k$ (intercept), can be easily obtained. Cimmino et al calculated the half time of crystallization ($t_{1/2}^n$) for some PEG blends. Blends of PEG with PVAc had the smallest $t_{1/2}^n$, while the PEG/PEMA blends showed the highest values for the half time of crystallization. The type of amorphous component added to PEG also seems to affect the half time of crystallization. The differences observed in $t_{1/2}^n$ (and also in the values of G) depend on the degree of miscibility and mobility of the crystallizable and amorphous components, the amorphous component depends on the nucleation of PEG and the noncrystallizable component depends on the
secondary nucleation or the crystallization regime (neat PEG and PEG/PEMA crystallize in regime I, whereas PEG/PAc and PEG/PMMA crystallize in regime II).

Adding PMMA to PEG results in a decrease of $k = \ln(2/t_{1/2}^n)$, an effect that is clearly seen in Figure 2.10 where $1/t_{1/2}$ is plotted against crystallization temperature.\textsuperscript{20}

Figure 2.9 Crystallization isotherms for the PEG/PEMA 80/20 blend crystallized at different $T_c$.\textsuperscript{71}
2.2.4. The Behavior of Crystallization and Phase Separation in Polymer Blends

Semi-crystalline polymer blends may undergo two kinds of phase separations (1) liquid-liquid phase separation due to immiscibility of amorphous phases, and (2) solid-liquid phase separation due to crystallization of crystallizable components. When one or both components of polymer blends are crystalline, there can be mutual interference of phase separation and crystallization. The competition between these two non-equilibrium processes may produce a great variety of liquid-liquid phase separation coupled with crystallization. Tanaka and Nishi \textsuperscript{73} demonstrated for the first time that competition between crystallization and liquid-liquid phase separation in blends with upper critical solution temperature (UCST) and one crystallizable component can cause a large variety
of new morphologies. When two or more non-equilibrium phenomena take place simultaneously, the final phases strongly depend on their dynamics and cannot be determined by an equilibrium phase diagram. In the competition between crystallization and phase separation, which occur when quenching the material from the one phase melt region to a crystallization temperature, the melting curve and binodal and spinodal lines were described in Figure 2.11

![Figure 2.11 Schematic phase diagram of a polymer blend of PCL and PS](image)

$\phi$ is the concentration of PS in the blend and $T$ is the temperature. $T_m(\phi)$ represents the melting curve. The melting curve is below the binodal line represented by the dot-dashed line, which is obtained by considering only crystallization. Strictly speaking, the binodal line below the melting curve cannot be defined in an equilibrium phase diagram and it is represented by the dashed line. Arrows A, B, C and D indicate the quenching conditions.

A: Simultaneous spinodal decomposition and crystallization
B: The crystallization and the NG-type phase separation take place and a droplet-like structure will appear.
C: The crystallization can induce phase separation because the amorphous polymer is
removed by crystallization and regions whose composition is within the binoidal line are formed. D: The phase separation can induce crystallization due to quenching of the melt into the two-phase region of the phase diagram and below the melting curve. They also stated the final structures with phase separation (A and B regions) are grouped into several types by the relationship between the degree of undercooling for the crystallization ($\Delta T_m = T_m - T_c$) and the depth of quench into the ordered two-phase region $\Delta T_p = T_p - T_c$; ($T_p$ is the phase separation temperature). When the crystallization process is faster than the phase-separation, the scale of the crystals formed as a spherulite is larger than the wavelength of the concentration modulation, which is equal to the Cahn wavelength for SD. In the opposite case, the length scale of the macroscopic phase separation is larger than the radius of the spherulite.

Case A and C of Figure 2.11 were discussed by Tanaka and Nishi for a system of PCL and PS. In case A, the coarse spherulite result includes PS droplets, while in case C the spherulites are separated and show large droplets on their surface. Li et al.\textsuperscript{74,75} investigated case B and C for PCL/low molecular weight PS. Shibanow and Godovsky\textsuperscript{76} determined the PPE/PEG and PEG/PPG systems to discuss case A and B with this and other systems.\textsuperscript{77-79} The dependence of the resulting structure and the phase morphology on these routes and the relative rates of crystallization and phase separation, particularly in relation to the growth rate of the crystalline entities $V_c$ and the rate of diffusion of the non-crystallizable component. In case (1) where $V_c >> V_d$, the released non-crystallizable component (NC) is trapped within the growing spherulite and will be inserted between the crystallization lamellae; in case (2) where $V_c << V_d$, the NC is completely segregated into the bulk melt, thus slowly increasing its concentration. After
reaching the miscibility gap, the melt phase separates homogeneously and binodally. But in the intermediate case (3) where $V_c \sim V_d$, a part of the amorphous component is trapped and another part is segregated from the growing crystals. The composition of this component increases with crystallization and finally phase separation occurs, resulting in the formation of droplets at the spherulite surface.

Morphology control of binary polymer mixtures through spinodal decomposition and crystallization was observed by Inaba et al.\textsuperscript{80,81} using polypropylene (PP) and ethylene propylene random copolymer (EPR) as a model system. The morphology studies showed the texture consisted of dual morphological units, (i) the modulated network structure resulting from spinodal decomposition and its coarsening processes in the isothermal demixing of the mixture in the molten liquid state and (ii) the spherulite structure resulting from crystallization by subsequent cooling of the demixing liquid. Rapid crystallization after quenching from de-mixed state (in ice-water) or isothermal crystallization below $145^\circ C$ resulted in morphology with space-filling spherulites containing “structure memory” of liquid-liquid phase separation by spinodal decomposition, and subsequent coarsening before crystallization. However, isothermal crystallization at higher temperatures ($145^\circ C$) resulted in long-range rearrangement of modulated spinodal structures inside PP spherulites and accumulation of segregated EPR at the spherulitic boundaries. A non-linear spherulitic growth was observed in this case.

There have also been theoretically explained phase diagrams for polymer blends, which exhibit both crystallization and liquid-liquid phase separation. Flory and co-workers\textsuperscript{26} were the first to show the existence of a UCST liquid-liquid phase separation above the melting transition of polymer/ solvent systems. This UCST curve depends
strongly on the type of solvent used and the solubility parameters involved. Burghardt\textsuperscript{82} extended the Flory-Huggins solution thermodynamic theory to compute the phase diagrams for polymer mixtures with inter-mixed crystallization and phase-separation processes. The author showed that interaction of crystallization and liquid-liquid demixing results in a monotectic phase structure. Below the monotectic point, the binodal curve has no equilibrium significance since at that stage crystallization is the more preferred thermodynamic transformation. However, due to kinetic factors liquid-liquid phase separation may play an important role in governing crystalline morphology. Matkar and Kyu\textsuperscript{41,42} have modified the Flory-Huggins free energy for amorphous-amorphous isotropic mixing by combining it with the Landau free energy of polymer solidification. (e.g., crystallization) They relaxed the complete immiscibility assumption of the polymeric solvent in the neat solid crystal by taking into consideration the crystal-amorphous interaction in addition to the amorphous-amorphous interaction of the pair.

2.2.5. Crystallization of Immiscible Polymer Blends

The crystallization behavior of neat polymers will be applied to the immiscible polymer blends, where the crystallization of the crystallizable component takes place within domains of a nearly pure component. Although the immiscible components are physically separated like droplets in melt, the presence of these domains can disturb the overall crystallization kinetics, spherulite growth rate, and morphology of semicrystalline etc. These changes are strongly dependant on crystallization condition, blend composition, size of dispersed particles and the nature of component.
There is much evidence showing that the presence of immiscible non-crystalline polymers can strongly affect the nucleation density. For example, it was found that the addition of elastomers, such as EPDM or EPR, increased nucleation density in iPP crystallization.\textsuperscript{70} In the case of iPP/EPDM blends, the number of spherulites per unit area increased monotonically with the percentage of rubber. In contrast, for blends such as: iPP/ PVME\textsuperscript{71} and sPS/ PVME,\textsuperscript{83} iPP/ LDPM\textsuperscript{83} or iPP/HDPE,\textsuperscript{84} nucleation density decreased with increasing contents of the non-crystallizable component (observations were made above melting points of LDPE and HDPE). The decrease in nucleation density for the iPP/ LDPE systems was explained by assuming heterogeneous nucleation, wherein the nuclei developed during the crystallization of iPP are possibly washed out by the presence of LDPE during the process of mixing. More likely, slow homogeneous nucleation took place instead causing a strong depression of the overall crystallization rate for the iPP/ LDPE system.

The effect of composition on nucleation mechanism was described in immiscible blends of iPP/aPS by Santana and Miller.\textsuperscript{85} They found that when PP was the major component in the blend, its crystallization behavior was not affected by the presence of PS. For lower contents of PP, however, it was dispersed in the immiscible PS matrix and the nucleation mechanism changed from predominantly heterogeneous to homogeneous as long as the size of PP droplets was below a critical value (1-2 $\mu$m).

In several other systems with components immiscible in the melt, no influence of the non-crystallizable polymer on crystallization behavior has been found by Greco et al.\textsuperscript{86} In the mixture of Poly (3-hydroxybuturate) (PHB)/ethylene-propylene copolymer rubber (EPR) system, the PHB spherulites grow in the presence PHB melt containing EPR
domains as the dispersed phase. During growth, the phase-separated ethylene-propylene rubber (EPR) particles are first rejected and then occluded in inter-spherulitic regions. O’Malley et al. described the thermal behavior of PEG/PS blends in which PEG was dispersed into fine droplets. A clear indication of fractionated crystallization combined with a simultaneous decrease in the total degree of crystallinity with increasing weight fraction of PS has been observed. Again, a slight decrease of the melting temperature, $T_m$, with about 2°C was detected, although $\Delta H_m$ remained unaffected. This was attributed by the authors to the formation of less perfect crystalline lamellae during the crystallization at higher undercooling. Chang et al. reported on the melting behavior in PC/POM blends. The blends were found to behave in a similar way as the above-described PEG/PS blend.

2.3. Photopolymerization

Recently, photoinduced polymerization has gained immense interest since it is mostly solvent-free and polymerization can be carried out under a wide range of conditions, allowing variations in the monomer structures, the number and type of reactive functional groups, temperature, radiation intensity, and photoinitiator type and concentration. A typical UV curable formulation generally involves the absorption of light by a distinct photoinitiator and a reactive monomer or oligomer. The photoinitiator is of a paramount importance as it is responsible for absorbing photons from the light source and generating active radicals. In addition, it governs both the rate of initiation and the penetration of the incident light into the sample. In order to have successful radicals,
the absorption bands of the photoinitiator have to overlap with the emission bands of the light source used. Therefore, the choice of an efficient photoinitiator is critical despite the fact that it is generally present in very small amounts as an additive to monomer systems in photopolymerization formulations. Highly crosslinked polymer formed as a result of the photopolymerization has excellent properties including high strength, thermal stability, high abrasion resistance, and good adhesion to a number of substrates. Due to the high volatility of monomers, unsaturated polyesters were substituted entirely or partially with multi-functional acrylates widely used light curable systems owing to the high reactivity of the acrylate monomers. Over the last three decades, a considerable number of comprehensive reviews have been devoted to photopolymerization. These reviews focused mainly on the design of high performance formulations and the relationship between kinetics of photopolymerization and system variables (e.g. monomer, initiator, temperature, atmosphere and oxygen).

2.3.1. Free Radical Polymerization

Photopolymerization is an example of radical chain polymerizations, which occur when radicals are produced by ultraviolet and visible light irradiation of a reaction system. Generally, radicals are produced in two ways from light absorption. One is the excitation of the radical by energy absorption and subsequent decomposition. The other one is the excitation of the radical by the interaction with second compound by either energy transfer or redox reaction to form radicals derived from the latter and/or former compounds.
In free radical polymerizations, multi-functional monomers such as acrylates and methacrylates frequently lead to the formation of crosslinked 3D network structures. When a multi-functional monomer is incorporated into the network through the reaction of one double bond, the remaining unreacted double bond hangs off the network structure and is referred to as a pendant double bond. When this pendent double bond reacts with the propagating radical on another kinetic chain (intermolecular crosslinking), a three dimensional network structure is formed.  

2.3.2. Photopolymerization Kinetics

Photopolymerization utilizes electromagnetic radiation (or light) as the energy source for polymerization of functional monomers. Photoinitiators absorb light in the UV-visible spectral range (250-450nm) and convert this light energy into chemical energy in the form of reactive intermediates, such as free radical and reactive cations, which subsequently initiate polymerization of functional monomers to form linear polymers, whereas the multi-functional monomers give three dimensions, or crosslinked networks.

Free radical polymerization basically consists of three reactions: initiation, propagation and termination.  
\[
\frac{d[R^\ast]}{dt} = \Phi I_a - k_i[R^\ast][M] \tag{2.32}
\]
\[
\frac{d[P^\ast]}{dt} = k_i[R^\ast][M] - k_r[P^\ast]^2 \tag{2.33}
\]
\[
\frac{d[M]}{dt} = -k_i[R^*][M] - k_p[M][P^*]
\] (2.34)

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

The rate of photochemical initiation is given by

\[
R_i = \Phi I_a
\] (2.35)

in which \(R_i\) is the rate of initiator. \(\Phi\) is the number of propagating chains initiated per light photo absorbed. \(\Phi\) is often referred to as the quantum yield for initiation. \(I_a\) is the intensity of absorbed light in moles, which is called Einsteins in photochemistry.

There is an argument that there should be a factor of two associated with the right-hand side of the equation on the ground that two radicals are produced per molecule undergoing photo initiation.

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 conveniently expressed as

\[
I_a = \varepsilon I_0 [A] b
\] (2.36)

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, \([A]\) is the initial concentration of photoinitiator and \(b\) is a sample thickness.

For thick films where \(I_a\) varies with 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.
\[ I = I_0 e^{-\kappa t} \]  

(2.37)

For a close 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:

\[ R_p = -\frac{d[M]}{dt} = k_p[M][P^\ast] \]  

(2.38)

The monomer fractional conversion is defined as

\[ \alpha = \frac{[M]_0 - [M]}{[M]_0} \]  

(2.39)

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

\[ R_p = k_p (1 - \alpha)[M]_0[P^\ast] \]  

(2.40)

Customarily photopolymerization can be analyzed by pseudo-steady state kinetics\(^93\), which assumes that all radical concentrations reach the steady state very quickly so that

\[ \frac{d[R^\ast]}{dt} = 0 \]  

(2.41)

and

\[ \frac{d[P^\ast]}{dt} = 0 \]  

(2.42)

Again the polymerization rate can be written as

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

(2.43)

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

(2.44)
After reorganization of the equation above, the kinetic equation can be further simplified as

\[
\frac{d\alpha}{dt} = \frac{k_p}{k_i^{1/2}} (\Phi I_0) (1 - \alpha)
\]  (2.45)

Equation (2.45) serves as a linkage between the time-dependent monomer concentrations to reaction kinetics. It captures the kinetics of photopolymerization in the simplest and most precise form possible. The demonstration of its most fundamental impact on phase separation can be found in its use in dynamic theories.

2.3.3. Photopolymerization-Induced Phase Separation

Photopolymerization-induced phase transition (PIPT) is a non-equilibrium phenomenon of phase transformation involving liquid-liquid phase separation, crystallization and/or mesophase ordering from isotropic liquid (or melt) driven by photochemical reaction.\(^1,^2\) During the course of photopolymerization of the reactive monomer, the average molecular weight of the reactive constituent in the polymer blends increases, which in turn enables the system to become unstable and eventually drives phase segregation.\(^1,^2,^9,^11,^12\) In crystalline or liquid crystalline polymer mixtures, liquid-liquid phase separation occurs in competition with crystal solidification or mesophase ordering during photopolymerization.\(^13,^14,^17,^22,^97\)

Photopolymerization-induced phase separation has been well investigated experimentally and theoretically. Experimental studies of photopolymerization can be employed by real-time Fourier transform infrared spectroscopy (FTIR). Recently, photocolorimetry and real
time IR are the most versatile techniques to archive quantitative measurement of the conversion of ultra-fast curing reactions of multifunctional monomers. \(^{98,99}\)

In photocalorimetry, the real-time photoinduced polymerization is followed via the heat flow, which is proportional to the number of monomer units reacted, which are measured directly as a function of time. \(^{100}\) The first calorimetric analysis of the photopolymerization process was developed by Bengough and Melville \(^{101}\) using a very simple thermocouple calorimeter to calculate the kinetic rate constants (propagation and termination) of neat vinyl acetate, methyl methacrylate, butyl acrylate and acrylonitrile monomers. Later, Tryson and Shultz \(^{102}\) extended Moore \(^{103}\) et al’s work to measure the kinetics of the photopolymerization of lauryl acrylate, 1,6-hexanedianaladiacrylate and pentaerythritol tetraacrylate. In addition to the direct calculation of propagation and termination rate coefficients, the critical factors such as light intensity, initiator concentration, and temperature were investigated. In real-time IR, the sample is placed in an IR spectrophotometer chamber and exposed simultaneously to a UV beam and an IR analyzing beam to monitor the decrease of the IR absorbance of the monomer reactive group. \(^{91}\) The use of infrared spectroscopy for probing kinetics of multifunctional photopolymerization was pioneered by Decker \(^{91,104-106}\) Real-time IR technique supplies the complete vibrational spectra of the monomer-to-polymer transition during polymerization and correspondingly, real-time information about baseline shifts, peak convolution, and evolution and decay of other absorbance due to vibrational transitions relevant to the reaction in question.

Real-time IR was chosen over Photo-DSC for the acrylate polymerizations by many scientists \(^{90,104,107,108}\) owing to the volatility of the sample and the rapid rate of
polymerization. A unique advantage of real-time IR photospectroscopy lies in its high sensitivity, since changes as small as 1% in the monomer concentration can be detected instantly in a 2 mm thick coating. In addition, other techniques monitor the physical effects, like the heat evolved (P-DSC) or changes in volume (dilatometry) upon irradiation of light. Real-time IR spectroscopy also permits one to follow chemical processes by monitoring in-situ the disappearance of the monomer reactive group upon UV exposure. Additionally, the sample preparation for real-time IR minimizes sample loss during polymerization.

Doane et al. demonstrated that the polymerization-induced phase separation method (PIPS) can be utilized to fabricate binary composite materials called polymer dispersed liquid crystals.  

Polymer-dispersed liquid crystals (PDLCs) are thin films composed of microdroplets of liquid crystalline material in a polymer matrix. These materials possess great utility as light shutters used in many electro-optical devices and control applications. The way to prepare these films is polymerization-induced phase separation, which occurs when a homogeneous mixture of monomers and liquid crystals (LC) is polymerized. The switching properties of these materials depend strongly on a variety of parameters such as UV intensity, LC concentration, curing temperature, cross-link density, etc. The switching voltage increases in value as the droplet is distorted from a perfect sphere but decreases as the droplet size increases. Smaller droplets dispersed randomly in the matrix give the material the highest contrast, which is the ratio of on-state to off-state light transmission. Experimental investigation of the PIPS process in the formation of PDLC materials has shown that the phase separation process occurs by spinodal decomposition. High-speed operations of liquid crystal(LC) optical devices
with lower switching voltages and better reflection or diffraction efficiencies are highly desired. The curing temperature also does not have to be below the nematic-isotropic transition temperature of the liquid crystal.

Kyu et al. determined experimental and theoretical phase diagrams for a system composed of nematic LC (K21) and a photo-cross-linkable optical adhesive (NOA65) with excellent agreement. They found that the segment length between crosslink points exerted the greatest effect on the phase diagram; a decrease in length resulted in tighter network formation less able to accommodate the LC species. The phase diagram is greatly influenced by the network elasticity exhibiting no critical point when the monomer is cross-linked. Kyu and coworkers also theoretically studied the dynamics of the process by incorporating the photopolymerization kinetics into the coupled TDGL-Model C equations. They found that patterns for the orientational order parameter lagged those of the concentration order parameter. LC domain size grew with increasing LC concentration and lower reaction rate due to the thermal relaxation of the system. The simulated patterns were in excellent agreement with experimental findings.

Serbutovietz and Kloosterboer et al investigated the morphology of polymerization-induced phase separation which is important for achieving better optical properties in PDLCs. They used the simultaneous photo-DSC/turbidity measurement to provide the conversion at the appearance of a nematic phase and optical microscopy for showing the developing morphology. The dependence of the initial morphology on the LC content, temperature of the reaction, and cross-linker content were explained using conversion-phase diagrams obtained from 4-\textit{n}-pentyl-4’-cyanobiphenyl (K15) and tetraethylene glycol diacrylate (TEGDA).
Smith\textsuperscript{7} was among the first to apply calorimetric studies to investigate the phase separation process in the PDLC system. In the system of E7 (5CB) and NOA65 (Norland UV-curable optical adhesive 65 with photo initiator), he found that the specific heat of mixing of a binary system vs. liquid crystal concentration plot showed a minimum consistency with the Flory-Huggins theory.

Mucha and coworkers studied phase separation in the system of W-52(nematic mixture) with UV curable oligoester resin and W-52 with thermal cured acrylic acid.\textsuperscript{117, 118} By cloud point measurements they were able to draw the phase diagrams for the systems. They found the phase diagram curves moving to higher temperature in the case of initially cured systems.

Brochar and coworkers employed the Flory-Huggins and Maier-Saupe theory for binary nematic mixtures of two nematogens which can have different order parameters in the mixture.\textsuperscript{119} The phase diagram established numerically was for the cases of chemical similarity. There were many models of the dynamics of phase separation in the polymer/LC systems. Dorgan introduced a time-dependent Landau-Ginzburg model to solve the problem of simultaneous phase separation and ordering kinetics in mixtures containing a nematic component.\textsuperscript{120} The solutions to these equations were explicit expressions for the structure factors for concentration and orientation.

Lin and Taylor employed a Monte Carlo simulation on triangular lattice to study the formation of PDLC systems.\textsuperscript{121} They found that the resulting structures were dependent not only on temperature and concentration but also on the relative rates of diffusion and polymerization. The effective phase diagram obtained by Monte Carlo simulation could also be approximated by the Flory-Huggins Mean Field theory.
Kim and coworkers utilized light scattering to study the dynamics of polymerization induced phase separation in the system of nematic liquid crystals (E7) and Epoxy (Epon 828) and curing agent Capcure 3-800. The comparison with the thermal quench system turned out to show a similar scaling relation. A second phase separation inside the already phase-separated domains was observed.

Wen and McCormick studied the radical trapping in photopolymerization of multifunctional monomers with an improved kinetic model, they were able to predict that the active radical concentration passed through a maximum while trapped radical concentration increased monotonically. The higher the light intensity was, the higher the final conversion would be.

Elliott and Bowman developed a kinetic model for crosslinked polymers formed by free-radical polymerization. Their model accounted for the effect of monomer functionality on the polymer network formation. Both their experimental and simulation result pointed to the conclusion that the trivinyl monomers were more effective than divinyl monomers because they reacted faster and produced more crosslinks.

Goodnear and Bowman addressed the heat transfer due to the generation of heat by reaction and light absorption. In a comprehensive free radical photopolymerization model, they coupled the energy with the reaction kinetic equation incorporating the primary radical termination and inhibition in addition to initiation, propagation and termination mechanisms.

Champbell et al. first introduced the four-wave interference to fabricate 3D polymeric photonics. They developed diffraction gratings by combining photopolymer holography and PDLC, which resulted in a new type of material known as the
holographic PDLC, H-PDLC. Holograms are usually made by making two beams of light interfere with each other and then storing the resultant intensity pattern via a light induced chemical change in a photosensitive precursor. For three-dimensional porous solids, two additional waves may be employed in the thickness direction in addition to four beams. The size of the holes is controlled by simply changing the angle of interference. A 3D laser interference pattern exposes a photosensitive polymer precursor rendering exposed areas insoluble; unexposed polymeric areas are dissolved away forming periodic structures. Polymeric photonic crystal that is formed in this way consists of only an interpenetrating network with air-filled voids.

Turberfield\textsuperscript{126} used the holographic pattern to create a photonic crystal structure in an epoxy-type photoresist consisting of a highly functional (eight epoxy groups per monomer) epoxy resin and a photoacid generator(triarylsulphonium salt). Sutherland et al \textsuperscript{97} employed a six or four beam interference technique to fabricate liquid crystal-polymer 3D structures. They exposed a homogeneous mixture of monomer, liquid crystal, and photo-initiator dye to a specific configuration of multiple laser beams. This technique relies on the anisotropic diffusion and phase separation of a liquid crystal in a polymerizable monomer when the solution is subjected to an inhomogeneous pattern of light.

Bowley et al\textsuperscript{127} used a three-beam interference pattern in their experimental and theoretical study and they observed that in the three-beam system the significant mismatch in beam intensities results in decreased fringe visibility, thus resulting in undesired polymerization in the dark fringes, reducing the efficiency of the gratings.
Due to the unique features of the LC materials, such as a liquidity, large birefringence and low driving voltage, one can easily change the molecular orientation state in the whole patterned area by application of an axially symmetrical electric field. Recently, composite systems consisting of liquid crystals and polymer materials have been widely investigated\textsuperscript{128} and polymer-dispersed LC and polymer-stabilized LC have attracted interest for various display applications.

Changes that may be locally induced by varying the composition of the material are the refractive index, the phase (e.g., isotropic or liquid crystalline), or the chirality. PDLC films consisting of submicrometer-sized nematic liquid crystal (LC) droplets distributed in well-defined planes in a rigid polymer binder\textsuperscript{129} exhibit high diffraction efficiencies due to the alternation of lines of optically oriented and isotropic materials. Several attempts to place LC domains spatially within a polymeric host have been reported\textsuperscript{130}. Examples have included the use of a mask to introduce an intensity profile in the curing radiation, which results in spatially periodic LC domain sizes throughout a film. Spatially controlling the placement of LC in a polymer matrix, using surface relief gratings, which are then back-filled with LC, has also been demonstrated by Murai et al\textsuperscript{131}. This technique produces films with periodic striations alternating LC-rich and polymer-rich layers as a result of interference of constructive and destructive UV waves. Another approach to overcome the limited performance of surface gratings is to back-fill periodic microscopic voids formed in a photochemically cured polymer system to form volume gratings. More recently, Sutherland and Bunning\textsuperscript{128,130,132-134} described the use of PDLC formulations for holographic recordings (H-PDLC) by using the interference of two coherent laser beams in a photosensitive monomer, liquid crystal (LC) mixture. This
technique combines the ease of photochemical curing with a spatially varying intensity profile to form films with alternating channels of polymer and LC.\textsuperscript{135}

Caputo et al\textsuperscript{136} modeled spatial mass transfer of components that takes place during spatially inhomogeneous polymerization process when the LC/monomer mixture is exposed to two-wave interference. Figure 2.12 shows their model predictions during H-PDLC polymerization. Some of the theoretical modeling of hologram recording in photopolymers have been published.\textsuperscript{15,127,137,138} When the polymerization reaction is very fast, the diffusion process does not have enough time to redistribute the material between the bright and dark regions. For optimal recording, the rate of photo curing, the material will be under-or over-exposed, and the holographic pattern will be weak or highly non-uniform. A high diffusion rate relative to the reaction rate is the most desirable condition for hologram formation.

Van Nostrum et al\textsuperscript{114} also investigated the effect of phase behavior of starting mixture on holographic gratings for a liquid crystalline diacrylate and an isotropic monoacrylate mixtures. Holographic polymer dispersed liquid crystals (HPDLCs) have a number of applications which include reflecting flat panel displays, optical interconnects, diffraction lenses with switchable focus, optical data storage, application-specific lenses, and image capture applications. Tunable filters, dynamically variable focal length lenses, fiber optic switches and 3D television are among many of the potential devices that can apply this type of technology.\textsuperscript{132}
Figure 2.12 Distribution of liquid crystal, monomer and polymer molecules. (a) at the beginning and (b) at the end of H-PDLC film formation
CHAPTER III

MATERIAL SPECIFICATIONS AND EXPERIMENTAL TECHNIQUES

3.1. Materials

The experimental materials are classified to reactive monomers and crystalline polymer.

3.1.1. Reactive Monomers

1,6-hexanediol diacrylate (DA) having a weight average molecular weight ($M_w$) of 226 g/mol was supplied by Aldrich Chemical Co. in a clear liquid form. The density is 1.01 g/mL at 25 °C. The molecular formula is [H$_2$C=CHCO$_2$(CH$_2$)$_3$-]$_2$. The boiling point is 107 °C and the melting point is 5 °C-12 °C. The structural formula is also shown in Figure 3.1.
Figure 3.1 Chemical structure of 1,6-hexanediol diacrylate

Trimethyolpropane triacrylate (TA) having a weight average molecular weight (M\textsubscript{w}) of 296.32 g/mole was supplied by Aldrich Chemical Co. in a clear viscous liquid form. The density is 1.1 g/mL at 25 °C. The molecular formula is \((\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_2\text{CH}_2\text{H}_5\text{)}_3\text{CC}_2\text{H}_5\). The flash point is more than 130 °C. The structural formula is also shown in Figure 3.2.

Figure 3.2 Chemical structure of trimethyolpropane triacrylate

Pentaerythritol tetraacrylate (Tetra) having a weight average molecular weight (M\textsubscript{w}) of 352.34 g/mole was supplied by Aldrich Chemical Co. in a clear viscous liquid form. The density is 1.19 g/mL at 25 °C. The molecular formula is \((\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_2\text{H}_5\text{)}_4\text{C}\). The flash point is more than 130 °C. The structural formula is also shown in Figure 3.3.
Figure 3.3 Chemical structure of pentaerythritol tetraacrylate

Dipentaerythritol penta-/hexa-acrylate(Penta) having a weight average molecular weight ($M_w$) of 524.51g/mole was supplied by Aldrich Chemical Co. in a clear viscous liquid form. The density is 1.155 g/mL at 25 °C. The molecular formula is $O[CH_2C(CH_2OR)]_2$, $R$=COOCH=CH$_2$ or H. The flash point is more than 130 °C. The structural formula is also shown in Figure 3.4.

Figure 3.4 Chemical structure of dipentaerythritol penta-/hexa-acrylate

The material properties of multi-functional acrylate monomers are summarized in Table 3.1.
Table 3.1. Summary of physical properties of multi-functional acrylate monomers.

<table>
<thead>
<tr>
<th>Reactive Monomer (Identification)</th>
<th>Molecular Weight (g/mol)</th>
<th>Density (g/ml) at 25°C</th>
<th>Structural Formula</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,6-hexanediol diacrylate (DA)</td>
<td>226</td>
<td>1.01</td>
<td>[H₂C=CHCO₂(CH₂)₂]₂</td>
<td>5-12°C</td>
<td>107</td>
</tr>
<tr>
<td>Trimethylopropyne triacrylate (TA)</td>
<td>296.32</td>
<td>1.1</td>
<td>(H₂C=CHCO₂CH₂)₃CC₂H₅</td>
<td>-</td>
<td>&lt;130°C (flash point)</td>
</tr>
<tr>
<td>Pentaerythritol tetraacrylate (Tetra)</td>
<td>352.34</td>
<td>1.19</td>
<td>(H₂C=CHCO₂CH₂)₄C</td>
<td>-</td>
<td>&lt;130°C (flash point)</td>
</tr>
<tr>
<td>Dipentaerythritol penta-/hexa-acrylate (Penta)</td>
<td>524.51</td>
<td>1.155</td>
<td>O[CH₂C(CH₂OR)₃]₂, R=COOCH=CH₂ or H</td>
<td>-</td>
<td>&lt;130°C (flash point)</td>
</tr>
</tbody>
</table>

3.1.2. Poly(ethylene oxide) (PEO)

The polymeric derivatives of ethylene oxide are divided into two classes defined by molecular weight. Low molecular weight polymers with an average $M_n$ of 200-20,000 are called poly(ethylene glycol)s. Polymeric derivatives with $M_n$ of $1 \times 10^5$-5$ \times 10^6$ are called poly(ethylene oxide).

Poly(ethylene oxide) is a crystalline, thermo-plastic and water-soluble polymer with the general formula $(\text{CH}_2\text{CH}_2\text{O})_n$. (Figure 3.5) PEO has a glass transition temperature ($T_g$) of about -67 °C and a melting temperature in the range of 63-72 °C. In the crystalline state, the poly(ethylene oxide) polymer chain contains two helical turns per fiber identity period, 19.34 Å. The crystallographic unit cell contains four molecular chains and is
monoclinic with $a=7.96\ \text{Å}$, $b=13.11\ \text{Å}$, $c=19.39\ \text{Å}$ and $\beta=124.48^\circ$. The chains have dihedral symmetry, two-fold axes, one passing through the oxygen atoms and the other bisecting the carbon-carbon bond.\textsuperscript{139}-\textsuperscript{142} The conformational assignments to internal rotation about the O-CH$_2$,CH$_2$,CH$_2$, and CH$_2$-O bonds are trans, gauche, trans, respectively.\textsuperscript{143}

Single crystals of poly(ethylene oxide) are flat platelets\textsuperscript{144} with the c-axis normal to the basal plane. Single crystal lamellae have been grown from dilute solution,\textsuperscript{145} and investigation of bulk crystallized polymer by electron microscopy has shown the existence of lamellar structures. Spiral growths are typical crystals in solution and hedrites and spherulites have been observed.\textsuperscript{146} Detailed x-ray crystallographic analysis of poly(ethylene oxide) single crystal\textsuperscript{144} has been archived. Melt-crystallization of such fractions results in multilevel crystal lamellae whose growth velocities relate to molecular weight as well as to supercooling. Main works are the observation and explanation of integral and non-integral chain-folding; that is, the ability of the chains to utilize their entire length in traversing the crystal $(m+1)$ times, where $m$ denotes the number of folds per chain. That integral folding should be observed indicates the regularity of the crystallization. During the 1970’s, Kovac et al\textsuperscript{147}-\textsuperscript{149} reported a series of systematic investigations of the melt crystallization, melting and annealing of PEO single crystals of low molecular weight. They found that low molecular weight PEO fractions(molecular weights studied were 2000 and 10000g/mol) crystallized from the melt in the low supercooling range(supercooling $T<11^\circ \text{C}$) in the form of integral-folding(IF) lamellar single crystals. In the IF crystals, the chains are either folded in an integral number $(n>1)$ of times or are fully extended $(n=0)$. In both cases, the chain ends (-OH) are located on
the lamellar surface. It has also been observed that the folded chain crystals in these fractions are metastable with respect to the extended chain crystal of the corresponding fractions. They concluded that for a crystallization temperature region near the melting temperature, low molecular weight PEO fractions are integrally folded.

Cheng et al.\textsuperscript{150-156} also observed the existence of NIF crystals over wide crystallization temperature regions and for various molecular weight. The kinetics and morphology of melt-crystallization of higher molecular weight fractions of PEO, the material of the present work, has been reported by Mandelkern and coworkers.\textsuperscript{50,157}

Recently, Polyethylene oxide isothermal crystallization in crystals, spherulites and other crystalline morphologies can be followed by in situ AFM technique.\textsuperscript{158,159-161}

In general, very regular spherulites are found. The growth kinetics of the spherulites exhibits all regimes of chain attachment behavior. Again, PEO shows all signs of regular crystallization. The regularity of the spherulitic growth behavior of PEO, the relative sluggishness of the growth rate, and the low temperatures at which crystallization occurs (the melting point of PEO is 65 °C) make PEO an optimal subject for in situ AFM investigation of melt-crystallization.

PEO has been blended with a number of polymers. In the case of poly(methyl methacrylate)(PMMA), a number of studies have demonstrated miscibility of the polymer in the amorphous phase when the PMMA is atactic.\textsuperscript{162,163} PEO/poly(vinyl acetate) blends\textsuperscript{164} are miscible in the melt over the entire composition range. Melt-quenched, solid state blends are miscible up to 40% weight fraction of poly(vinyl acetate). Blends of PEO and poly(vinyl chloride) are also compatible in the melt.\textsuperscript{165}
For investigating the influences of PEO molecular weight on PEO and multifunctional acrylate monomers, various PEO has been used. The summarized PEO material properties due to molecular weight are given in Table 3.2.

**Table 3.2. Summary of physical properties of Poly(ethylene oxide).**

<table>
<thead>
<tr>
<th>Molecular Weight (M&lt;sub&gt;n&lt;/sub&gt;)</th>
<th>Number Average Molecular Weight (M&lt;sub&gt;n&lt;/sub&gt;)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>Structural Formula</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5400</td>
<td>5000</td>
<td>1.08</td>
<td>HO-[CH&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-O]&lt;sub&gt;n&lt;/sub&gt;-H</td>
<td>58.2, 62.5</td>
</tr>
<tr>
<td>11300</td>
<td>10500</td>
<td>1.08</td>
<td>HO-[CH&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-O]&lt;sub&gt;n&lt;/sub&gt;-H</td>
<td>63.1</td>
</tr>
<tr>
<td>57000</td>
<td>52000</td>
<td>1.10</td>
<td>HO-[CH&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-O]&lt;sub&gt;n&lt;/sub&gt;-H</td>
<td>63.6</td>
</tr>
<tr>
<td>66000</td>
<td>34111</td>
<td>1.94</td>
<td>(-CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>65</td>
</tr>
</tbody>
</table>
3.2. Experimental Procedures

Detailed experimental procedures, techniques and instruments are given in following sections.

3.2.1. Blend Preparation

Poly (ethylene oxide) (PEO) in powder form was purchased from Scientific Polymer Products, Inc. having various reported average molecular weight ($M_w$) from 5400 to 66000. Various multifunctional acrylate monomers like 1,6-hexanediol diacrylate(DA), Trimethylolpropane triacrylate(TA), Pentaerythritol tetraacrylate(Tetra) and Dipentaerythritol penta-/hexa- acrylate(Penta) having weight average molecular weight ($M_w$) from 226 to 524 were supplied by Aldrich Chemical Co. and used as received. Various concentrations of PEO were dissolved in multifunctional acrylate monomer by stirring for 15h at 70 °C on a hot-plate using a magnetic stirrer bar. Samples for DSC and OM were obtained by taking melted various compositions of PEO and multifunctional acrylate monomer. Regarding photopolymerization, Rose Bengal photo initiator (1wt% of reactive monomer)\textsuperscript{166} was used with the aid of N-phenyl glycine (co-initiator), N-vinyl pyrrolidone (solubilizing agent), and octanoic acid (surfactant).\textsuperscript{17,97} in PEO and multifunctional acrylate monomers(Figure 3.6). Before taking the sample for DSC and OM, the blended samples with RBAX were mixed in a water bath by a magnetic stirring bar at 70 °C on hot-plate.
3.2.2. Instrumental Techniques

All instrumental techniques used for experiment have been described in following sections.

3.2.2.1. Differential Scanning Calorimetry (DSC)

Melting point depression, crystallization temperatures and glass transition ($T_g$) of the PEO/DA blends were determined using DSC (Model Q-1000, Thermal Analysis instruments, TA®). Samples weighing 7-10mg were sealed in aluminum hermetic DSC
pans using an encapsulating press. An empty aluminum pan was used as a reference. Nitrogen gas was purged to the unit to maintain an inert atmosphere. Various heating rates were carried out for whole PEO/DA mixtures (e.g. 2°C/min, 5°C/min and 10°C/min). The second runs of DSC curves were used to avoid the thermal history.

3.2.2.2. Photo-DSC (PDSC)

The photo curing reaction was carried out using a photo-DSC (Model Q-1000 series) equipped with a photocalorimeter accessory((PCA, TA® Instruments)) under UV irradiation at 365 nm. Both the reference compartment containing the empty pan and the sample holder containing PEO/multifunctional acrylate mixtures (weighing 7mg) were irradiated at intensities of 40 and 150 mW/cm² for 10min at 70 °C to ensure that all PEO crystals were melted before curing by UV light. To avoid the possible influence of residual solvent and thermal history, only the second runs were reported for establishment of the relationship between melting temperatures versus concentration of PEO. Samples were allowed to equilibrate isothermally for 2 minutes prior to irradiation wavelengths and isothermal photopolymerization temperature and intensity are given for various experimental conditions. The diagram of PDSC is shown in Figure 3.7.
3.2.2.3. Real-Time (RT) Fourier Transform Infrared (FTIR) Spectroscopy

Real-time (RT) Fourier transform infrared (FTIR) spectroscopy, developed by Decker and Moussa, is a powerful technique for investigating photopolymerization. It makes it possible to follow in situ and in RT a reaction with excellent temporal definition. RT- FTIR has several advantages over other methods, such as photo-DSC, which has a lower time resolution (instrument response function=5-10 s). An analytical function was proposed for smoothing the experimental kinetic curves. The excellent time resolution of RT-FTIR, combined with an appropriate choice of a smoothing function for the kinetic data, makes the calculation of the derivative of the conversion ratio (e.g., the polymerization rate ($R_p$)) more precise in some aspects than the calculations of other methods.

The effects of various parameters on both the photopolymerization kinetics and $R_p$ were investigated. The schematic diagram of RT-FTIR is given in Figure 3.8.
3.2.2.4. Optical Microscope (OM)

The blend samples were heated in the hot stage (Linkam, TMS 93) under the optical microscope (Olympus, BX 60) at the desired experimental temperatures (i.e., above the melting point of each blend composition) for 10 minutes. The light source was a halogen of 12 V and 100 W. The sandwiched samples were exposed to green light illuminated at 17 µW/cm² in order to trigger photopolymerization of DA in the mixtures. The emerged microstructures were photographed using a digital camera (Canon, EOS 300D) for various blends and isothermal reaction temperatures under suitable magnifications ranging from 50 to 1000x.

Figure 3.8 Experimental setup for the investigation of photopolymerization reactions by real-time FT-IR/ATR spectroscopy.\textsuperscript{168}
3.2.2.5. Scanning Electron Microscope (SEM)

The Scanning Electron Microscopy (SEM) is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. Due to the way these images are created, SEM micrographs have a very large depth of focus yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This great depth of field and the wide range of magnifications (commonly from about 25 times to 250,000 times) are available in the most common imaging mode for specimens in the SEM. Compositional analysis of a material may also be obtained by monitoring secondary X-rays produced by the electro-specimen interaction. Characterization of fine particulate matter in terms of size, shape, and distribution as well as statistical analyses of these parameters may be performed. The SEM generates a beam of electrons in a vacuum. That beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils (Figure 3.9).
3.2.2.6. Atomic Force Microscope (AFM)

Atomic force microscope (AFM) was chosen to investigate the surface morphology in range of micrometer down to few nanometers. Like all other scanning probe microscopes, the AFM utilizes a sharp probe moving over the surface of a sample in a faster scan. In the case of the AFM, the probe is a tip on the end of a cantilever which bends in response to the force between the tip and the sample. The contact between the probe and sample is used to generate an image of the surface topology. The probe can be vibrated at its resonant frequency (WaveMode) to make intermittent contact with the sample. Figure 3.10 demonstrates the working principle of AFM; as the cantilever flexes, the light from the laser is reflected onto the split photo-diode. The movement of the tip or sample is performed by an extremely precise positioning device made from piezo-electric ceramics, most often in the form of a tube scanner. The scanner is capable of performing
a sub-angstrom resolution in x-, y- and z-directions. The z-axis is conventionally perpendicular to the sample.

Figure 3.10 A schematic diagram of the AFM system.

3.2.2.7. Photopatterning Techniques

Mixtures of multi-functional and PEO were used for the photopatterning experiment. The photo reactive syrup was prepared as depicted in section 3.2.1.

A schematic diagram of the experimental holographic optical apparatus for the two-wave interference is depicted in Chapter X. The apparatus consists of a UV laser (wavelength of 365nm), beam splitters, spatial filters, plano-convex lens, mirrors, etc in the optical trains. Similarly the holographic optical apparatus was constructed for the four-wave interference with one two-wave interference unit on the top and the other two-wave interference unit on the bottom as shown in Figures 10.2 (a) and (b). The two units were crossed at 90 degrees to each other to generate the micro array droplet pattern. However, the PEO crystal formed a larger structure than the patterned grid which is
produced by two- and four-wave interference setup. The Axicon used for getting a bigger grid, contains the PEO crystal.

The pattern photopolymerization was realized through interference of the split coherent laser beams, giving a fringe width of 1 to 3 µm. The laser intensity at the sample was approximately 100mW/cm$^2$ and the exposure time was 10 minutes unless indicated otherwise. Once the pattern photopolymerization was accomplished, morphological characterization was performed using the Optical Microscope (OM), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) for surface topology investigations. The detailed experimental setup and results are propagated in Chapter X.
CHAPTER IV

MISCIBILITY CHARACTERIZATION, PHASE DIAGRAM AND MORPHOLOGY DEVELOPMENT IN PEO/PHOTO REACTIVE TRIACRYLATE MONOMER BLENDS

4.1. Introduction

Blending polymers is one of the most common practices to produce new materials economically with a variety of properties. Miscibility of polymer blends has been studied extensively, with most of the investigated systems representing mixtures of two amorphous polymers. However, blends in which one or both components are crystalline polymers have received very little attention compared to fully amorphous systems. Investigating the blends of two crystalline polymers is more complicated and interesting since both components are able to crystallize and provide diverse conditions to study the crystallization behavior and morphology in polymer blends. Until now, only a small number of works have been reported on miscible polymer blends of one or two crystalline constituents with different chemical structures.¹⁶⁹⁻¹⁷⁴ Flory-Huggins (FH) free energy has been widely used for describing phase diagrams of amorphous-amorphous polymer blends. The FH theory further affords the determination of polymer-polymer
miscibility through the amorphous-amorphous interaction parameter, known as Flory-Huggins (FH) interaction parameter.\textsuperscript{18} When one of the components in the blend is a crystalline polymer, the liquid–solid phase transition occurs in addition to the liquid-liquid phase segregation.\textsuperscript{175,176} Depending on the quality of polymeric solvent, melting temperatures of crystalline polymer solutions can be altered significantly upon mixing.

Miscibility and crystallization behavior of crystalline polymer blends have been extensively studied both experimentally and theoretically.\textsuperscript{177-181} Thermodynamic phase diagrams have been employed as a tool to interpret the emerging crystal morphology in a manner dependent on the pathways of phase separation dynamics. In addition, phase diagrams offer practical guidance to explain crystallization phenomena in relation to the phase separation process.

In this chapter, triacrylate monomer (TA) has been employed as polymeric solvent to polyethylene oxide (PEO) crystals. First, the phase behavior of several blends consisting of PEO ($M_w = 66,000$, PDI=1.94) and triacrylate monomer was investigated by means of DSC and OM without the involvement of crosslinking. The lowering of the melting point of PEO crystals was observed which may be a consequence of the molecular interaction between PEO crystals and triacrylate monomer. Morphology evolution and crystal growth behavior of this crystalline PEO–amorphous triacrylate system were examined under non-isothermal and isothermal conditions.

4.2. Experimental Section

The experimental phase diagram of the PEO/triacrylate monomer was established by means of polarized optical microscopy and differential scanning calorimetry. Blends for
the establishment of the phase diagram of PEO/triacrylate were prepared by weighing the appropriate amounts of multifunctional triacrylate and PEO mixing without any solvent in small vials. Various concentrations of PEO were dissolved in triacrylate monomer by weighing and mixing at room temperature then heated in a water bath controlled at approximately 70 °C on a hot-plate using a magnetic stirrer bar. These PEO/TA blend specimens were solvent cast at ambient temperature for thermal and optical investigations.

Non-isothermal crystallization experiments were carried out by differential scanning calorimetry (DSC). Various heating rates were carried out for whole PEO/TA mixtures (e.g 2, 5, and 10 °C/min). Melting point depression, crystallization temperatures and glass transition (T_g) of the PEO/TA blends were determined from the second heating scan. T_g was taken from the midpoint of the heat capacity peak with temperature of the second heating scan.

The morphology of the blends was examined using an optical microscope (OM) and microscope Linkam hot stage. The isotropic melt sample taken from the heated vial in the water chamber was sandwiched between two optical glass slides then was put on the microscope hot stage. The sample was first heated to 80°C to get an equilibrium melt and then cooled down to room temperature. The development of morphology at different temperatures and compositions was observed. The experiment was repeated to check at least twice for reproducibility. Isothermal experiments were carried out by quenching the samples from 80 °C to various temperatures below the melting points of PEO in the phase diagram of PEO/triacrylate monomer mixtures to investigate the morphology that emerged in relation to various coexistence regions of the phase diagram such as crystal +
isotropic liquid and crystal solid. Detailed information about materials and procedure of experimental equipment was given in Chapter III.

4.3. Results and Discussions

DSC was utilized to study the thermal behavior. Melting point depression has been suggested widely in literature as a useful tool to determine whether systems show blend miscibility. However, during the DSC scan, the scanning rate affects the melting transitions, which can be explained by various mechanisms of crystal reorganization,\textsuperscript{182,183} e.g., through lamellar thickening or crystal perfection.

The equilibrium melting point of a polymer is seldom measured directly because chain folding limits the crystal thickness and the experimental melting points are much lower than that of the equilibrium crystal. The equilibrium melting point can however be determined, although often with considerable uncertainty, by suitable extrapolation of experimental data. The Hoffman-Weeks method\textsuperscript{184} determines the equilibrium melting point by linear extrapolation of $T_m = f(T_c)$ data to the $T_m = T_c$ line. This method is strictly applicable only to a series of samples with crystals of a certain constant crystal-thickening factor. However, the crystallization temperature conditions vary, as the crystal morphology could be the cause of multiple peaks. Furthermore, blending could depress the crystalline order then it is hard to reach the finite crystal lamellar thickness. In view of thermal lag of DSC and uncertainty of $T_m$ dependence on $T_c$, zero-extrapolated melting temperature is used as a pseudo-equilibrium melting temperature in this research.
Figure 4.1(a) exhibits the DSC thermograms of PEO/TA blends obtained at a heating rate of 2°C/min, showing the melting transition of neat PEO in the vicinity of 65°C. This melting transition shows a lowering of melting temperature with increasing TA content. The observed depression trend of melting point of PEO with TA content is consistent with those reported for other miscible or partially miscible blends, except that there appear dual melting peaks of PEO in the thermograms at low PEO concentrations. Such dual peaks are reproducible at 5 and 10°C/min in the enlarged scale shown in the inset, further confirming that these dual peaks at low PEO concentrations are reproducible.

As the PEO composition increases, the melting point of PEO in the triacrylate system shifts to higher temperatures and the dual peak disappears.

One of the most commonly used criteria for establishing the phase behavior in amorphous binary polymer blends is the presence of one or more $T_g$’s. In a single phase blend, a single $T_g$ lying between the values for each component may be detected and characterizes the mixture. If the blend is two-phase, then two $T_g$’s are observable in the vicinity of those of the neat components. Thus, for an immiscible blend, two $T_g$’s generally appear on the DSC scan, whereas for miscible blends, only one $T_g$ is observed.

Figure 4.1(b) depicts a single $T_g$ in all blend compositions. The $T_g$ values of pure PEO and TA were -60.7 and -65.8 °C, respectively. The observed single $T_g$ suggests miscible character of PEO/TA blends at the temperatures investigated. Moreover, the $T_g$ values of the blends shift to higher temperatures with the increase of PEO content. This fact indicates the miscibility of the PEO/TA blends in the amorphous state.

However, the two $T_g$’s in close proximity could bring the overlapping of the glass transition temperatures. Bikiaris and Pronos suggested using the first derivative of $T_g$
to confirm the single or multiple $T_g$'s. This still leaves the problem of picking the right heat transition. Since the high crystallinity of PEO gives a broadened glass transition, the on-set and off-set length were lengthened as PEO composition increased. The dependence of $T_g$ on blend composition can be evaluated by the classic Fox eq. (1)\textsuperscript{188} or the Gordon-Taylor eq.(2)\textsuperscript{189} as follows:

$$\frac{1}{T_{g, \text{blend}}} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}}$$

(1)

$$T_{g, \text{blend}} = \frac{W_1 T_{g,1} + k(1-W_1)T_{g,2}}{W_1 + k(1-W_1)}$$

(2)

where subscripts 1 and 2 represent PEO and TA, respectively; $W_i$ is the weight fraction of component i; k is the Gordon-Taylor parameter that equals $\Delta \alpha \frac{1}{\Delta \alpha_1}$; and $\Delta \alpha$ is the difference in the volume expansion coefficients between glassy and liquid rubbery states.

Figure 4.2(b) shows the measured $T_g$ as a function of PEO content in comparison with the fitting curves of the Fox equation and Gordon-Taylor equation. It was found that the measured $T_g$ fit well with the predicted $T_g$ value by the Fox equation and Gordon-Taylor equation with k=1.295. It may be inferred that a single $T_g$ along with the melting point depression suggests the blends miscibility of PEO/TA at the temperature range investigated.

Figure 4.2(a) shows the experimental melting points($T_m$) as obtained from the DSC melting peak for PEO/TA at various heating rates and subsequently extrapolating to a zero heating rate. Although this peak temperature at zero rate does not represent true equilibrium, it may be sufficient for describing the relative trends of the $T_m$ values as a function of the blend concentrations. These blends reveal a depression of the melting
transition of PEO as TA content increases. The phase diagram exhibits three distinct regions: isotropic melt (I), crystal-isotropic melt (Cr+I) and crystal (Cr). The phase diagram of PEO/TA is solved self-consistently in accordance with the theory of Matkar and Kyu\textsuperscript{42} for describing binary crystalline polymer phase diagrams. In their model, the original assumption of the Flory diluent theory of crystalline polymer solutions-namely the complete rejection of polymeric solvent from the crystalline phase\textsuperscript{41,42} was removed and by taking into consideration the coupling between the solid-liquid phase transition and the liquid-liquid phase separation. In order to describe the crystallization in blends, the free energy of a crystalline polymer blend was expressed in terms of a combination of free energy of liquid-liquid mixing given by FH theory, free energy of crystallization given by Landau-type double well potential and the coupling free energy representing interaction between amorphous and crystalline phases\textsuperscript{190,191}

$$f_{\text{overall}}(\psi, \phi) = f_{\text{mixing}} + f_{\text{crystal}} + f_{\text{interaction}}$$

(3)

The Flory-Huggins free energy of mixing of a crystalline polymer blend in the melt state can be written as,\textsuperscript{12}

$$f_{\text{mixing}} = \frac{\phi \ln \phi}{r_1} + \frac{(1-\phi) \ln(1-\phi)}{r_2} + \chi_{FH} \phi(1-\phi)$$

(4)

where $\phi_1 = \phi$ and $\phi_2 = (1-\phi)$ are the volume fraction of the crystalline component and amorphous polymer(or solvent), respectively. $r_1$ and $r_2$ represent the statistical chain lengths of the crystalline and amorphous polymeric solvent components, respectively, and $\chi_{\text{am}} = \chi_{FH} = A + B / T$ where A and B are constants, representing amorphous-amorphous interaction. The phase field free energy of crystallization is described in terms of the Landau-type free-energy expansion in the crystal order parameter, $\psi$\textsuperscript{190,192}.
\[ f_{\text{crystal}} = W \left[ \frac{\psi^4}{4} - (\zeta + \zeta_0) \frac{\psi^3}{3} + \zeta \zeta_0 \frac{\psi^2}{2} \right] \]  

where \( W \) is the coefficient that represents the penalty for the nucleation process. \( \zeta \) and \( \zeta_0 \) represent the positions of the free energy maximum and the solidification potential of crystallization well (minima) on the crystal order parameter axis, respectively. \(^{191,193}\)

Physically, the crystal order parameter (\( \psi \)) can be considered the ratio of the lamellar thickness (\( l \)) to the lamellar thickness of a perfect crystal (\( l^0 \)), that is, \( \psi = l / l^0 \), and thus \( \psi = 0 \) refers to the reference liquid (melt) state, whereas \( \psi = \zeta_0 \) indicates the crystalline solid state. \(^{190,191}\)

The free energy of interaction between the crystalline constituent and the amorphous component is given via the coupling term, viz.,

\[ f_{\text{interaction}} = \chi_{ca} \phi (1 - \phi) \psi^2 \]  

where \( \chi_{ca} \) is the interaction parameter, which is directly proportional to the heat of fusion, \( \Delta H_u \), but inversely proportional to absolute temperature \( T \), \( \chi_{ca} \propto \Delta H_u / RT \).\(^{42}\)

The overall free energy of a blend containing a crystalline constituent becomes\(^{18,42}\)

\[ f = \frac{\phi \ln \phi}{r_1} + \frac{(1 - \phi) \ln(1 - \phi)}{r_2} + \chi_{ca} \phi (1 - \phi) + W \left[ \frac{\psi^4}{4} - (\zeta + \zeta_0) \frac{\psi^3}{3} + \zeta \zeta_0 \frac{\psi^2}{2} \right] + \chi_{ca} \psi^2 \phi (1 - \phi) \]  

However, the analytical solution for the melting point depression was not attempted in these previous studies.\(^{41,42}\) Recently, an analytical expression was derived by Pankaj et al.\(^{194}\) for the determination of the crystalline-amorphous interaction parameter from the experimental melting point depression data. Using the experimentally obtained \( \chi_{ca} \).
value, the validity of the present methodology is compared with the experimental phase diagrams of the crystalline-amorphous polymer blends.

The phase diagrams of crystalline polymer blends are governed by the competition between the crystalline solid-amorphous melt phase transition and the liquid-liquid phase separation. Although the FH interaction parameter controls the UCST, it plays no significant role in the determination of the melting point depression behavior. Contrary to the general perception, it is the crystal-amorphous interaction that has led to the lowering of the melting point. Hence, it is important to distinguish the types of interactions, viz., liquid-liquid versus solid crystal-liquid interactions.

As depicted in Figure 4.3, the self-consistent solution reveals a solid-liquid coexistence gap bound by the solidus and liquidus lines. To demonstrate the role of the crystal-amorphous interaction in the phase diagram, the critical temperature was taken as \( T_{\text{crit}} = -260^\circ C \) along with the crystal-amorphous interaction parameter, \( \chi_{ca} = 0.203 \), \( \chi_{aa} = 0.0134 \) at 40 \( ^\circ C \), \( r_1 = 110 \), \( r_2 = 2 \), \( A = 0 \).

The close resemblance of the predicted trends of the solidus and liquidus lines to the experimental melting transition points indicates that the observed dual DSC peaks are real, which can be attributed to the solidus and liquidus phases.
Figure 4.1 (a) DSC thermograms of PEO/triacrylate (TA) blends showing a lowering movement of the melting peak of PEO with the addition of TA. (The heating rate was 2 °C/min). Note that high TA content blends show dual melting endotherms. The inset represents the enlarged dual melting peaks of PEO/TA 30/70 in various heating rates. b) DSC thermograms of PEO/TA blends showing a systematic shift of \( T_g \)s with PEO contents.
Figure 4.2 Plots of (a) melting point depression of PEO in its blends with TA (b) glass transition temperature signifying amorphous-amorphous miscibility. (The heating rate was 2 °C/min)
Figure 4.3 Comparison between self-consistent solutions (solid lines) and experimental melting temperatures of PEO/TA blends showing the crystal solid-liquid coexistence region bound by the liquidus and solidus lines. The parameters used were $\chi_{na} = 0.0134$, $\chi_{ca} = 0.203$, at 40 °C, $r_1=110$, $r_2=2$, $A=0$ at $T_{crit} = -260$ °C.
Blends of PEO and triacrylate offer interesting possibilities for studying the relationship between phase behavior and structural evolution. The purpose of this portion of the study is to elucidate the effect of supercooling on the crystalline morphology in this system at various blend compositions. Moreover, it is of interest to determine the morphological phase diagram of the system. Various morphological structures at various coexistence regions of the phase diagram were determined under isothermal conditions.

In general, spherulites have been characterized as rounded aggregates of radiating lamellar crystals with a fibrous appearance, which originates from a nucleus such as particle of contaminant, catalyst residue, or fluctuation in density created by chance. These structures often grow through various stages-first, formation of lamellar plates or needles; second, lamellar bundles via stacking; third, lamellar aggregation leading to sheaf-like structure; and finally, the spherulites with lamellar branching, the diameter of which can range from submicrons to several hundred microns. In the case of polymers, spherulites may be conveniently viewed under a polarized optical microscope, which consists of a large number of lamellae growing radially outward from a primary nucleus at the core. Often some lamellae may be twisted about their long axes, which results in the concentric bands or spiral structures. The spherical shape arises usually due to side branching and splaying of microstructures, while such a structure in the initial to intermediate stages may not be spherical, but rather resembles a sheaf-like morphology.

Figure 4.4(a) displays the time evolution of crystalline morphologies in the blend of 5/95 PEO/TA following temperature quench from an isotropic melt (80 °C) to 35 °C. In the early stage of growth at 35 °C, a single lamella breeds more lamellae. As the primary
lamellae grow at the two ends, they splay apart from each other. As a result of this continuous growing and splaying, the initial lamellae gradually evolve into a needle-like lamella which is also shown in observation during non-isothermal crystallization. When the 5/95 PEO/TA is quenched to 25 °C, the PEO crystal shows the more opened lamellar structures (sheaf) because of the insufficient amount of PEO to form the well developed spherulite.

As PEO composition increases in triacrylate blend systems, PEO initially forms needle-like lamellae changing to sheaf-like then to fully developed spherulites. 10/90 PEO/TA shows sheaf-like structures (Figure 4.4(b)). When the blends are heated to isotropic melt then quenched to 40 °C, a single lamellae starts to grow the more lamellae. Grown lamellar tips splay apart from each other. Subsequently, splaying parts are gradually transformed into a sheaf-like structure. Due to the less PEO contents in TA blends, when the isotropic melt was quenched to 25 °C the more the PEO lamellae splayed crystal relative to the needle-like crystal of 5/95 PEO/TA. Like the 10/90 composition, 20/80 PEO/TA mixtures also follows a similar progression to sheaf-like crystal. As PEO composition increases, the crystal structures evolve from the sheaf-like lamellae to spherulite. In Figure 4.4(c), the PEO/TA 40/60 mixture shows the fully developed spherulite crystal when the isotropic melt is quenched to 45 °C. However, all the compositions were quenched to a temperature which is between liquidus and solidus line hereafter designated as the Cr+I region in which the PEO crystals regardless of the crystal shapes develop in the continuum of TA-rich liquid. Figure 4.5 represents the optical micrographs displaying the emerged crystalline morphologies of the 5/95, 20/80 and 50/50 PEO/TA blend after quenching from 80 °C to 25 °C (deep supercooling) which
is confirmed as the existence of single-phase crystal region (Cr). The phase diagram provides a reference map to indicate the positions of temperature to which the samples were quenched from the isotropic melt at 80 °C. It was found that at 25 °C, the spherulites developed quickly and impinged with others except for the lower concentration of 5/95 because of insufficient amount of PEO forming a more opened lamellar structure.

In these temperature quenches, the system transverses through the isotropic state (I), crystal+ isotropic liquid (Cr+I) to the single phase crystal (Cr) state. The coexistence gap bound by the liquidus and solidus lines was the coexistence region which consisted of TA-rich and crystal of PEO. Similar experiments have been undertaken to investigate the effect of super cooling depths on PEO crystal size and growth rates in 50/50 PEO/TA composition. From these experimentally confirmed morphologies along with DSC melting points, we are able to confirm all coexistence regions of the phase diagram predicted by the observation of the Matkar-Kyu.

The present author was intrigued by Y. Okabe et al.\textsuperscript{201,202} regarding the rhythmic growth of spherulites of crystalline polymer blends which are observed in the blend of PEO/TA following various isothermal thermal quenches. In the case of PEO/TA 5/95, of the lower PEO fraction prefers the lamellar crystals to fully developed spherulites. A less dense spherulite of PEO mainly consists of long edge on lamellae with a sheaf like morphology. The PEO spherulite consists of fibrillar bundles that are made up of long and continuous edge-on lamellae. Then it branches out from the main strum to the horizontal direction after the vertically grown long lamellar developed.\textsuperscript{(Figure 4.6(a))}

The PEO lamellae formed the long stream first in the longitudinal direction then it branched out all directions. This indicates that the growth of PEO lamellae shows a
rhythmic change. Similar experiments have been done for the PEO/TA 50/50 composition to compare with 5/95(Figure 4.6(b)) Due to the high fraction of PEO, crystals form the fully developed spherulite. However, the spherulite consists of bundles of lamellae. As in the case of PEO/TA 5/95, the crystal forms the main stem originally then starts to branch out. It should be emphasized that these rhythms in each direction are not necessarily synchronized. Hence, there is a good possibility that the overall growth of their open spherulites would be averaged out and lose the rhythmic character in which they are perfectly synchronized. Consequently, the average growth will follow the linear or power-law growth.

4.4. Conclusions

The PEO/TA blends show a lowering of melting transition of PEO crystals as triacylate concentration increases. It should be noted that PEO is miscible with triacylate monomer as revealed by a single T_g measurement. The dual melting peaks in lower composition can be attributed to the Cr+I coexistence region bound by the liquidus and solidus coexistence lines. It further provides the experimental means of determining crystal-amorphous interaction directly from the melting point depression of the crystalline polymer blends. The Matkar-Kyu theory suggests that the melting point depression of the crystalline polymer blends should be analyzed in the context of solid-liquid phase transition that yields the crystalline-amorphous interaction parameter. This approach should be contrasted with the Flory-Huggins interaction parameter representing the liquid-liquid demixing, which may only be valid under the assumption of the complete rejection of the amorphous solvent from the crystalline phase. The combined

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phase field model combined and the FH demixing theory is capable of describing the experimental phase diagrams of the present PEO/TA system.

Since the triacrylate acts like the polymeric solvent in PEO, the solubility of PEO is the main reason to bring the melting point depression. The morphology evolution also confirmed the DSC results for melting behavior of mixtures in the non-isothermal crystallization condition. The isothermal crystallization of PEO/TA mixtures shows the interesting growth behavior of PEO crystal. The PEO crystal shows spherulites at deeper quenching instead of showing the needle or sheaf-like structures. The low composition of PEO shows the needle like crystal due to the lower amount of PEO in triacrylate. At the shallower quenching depth, the area in between the liquidus line and solidus line, there was a coexistence of the PEO crystals and the TA rich isotropic liquid. When it was quenched to 25 °C, the sample formed the spherulitic crystals of PEO, which is presumably solvated.
Figure 4.4 Time evolution of the crystalline structure of PEO in the blend of the PEO/TA at an isothermal crystallization temperature of: (a) the evolution of needle-like structure in PEO/TA 5/95 at 35 °C;
Figure 4.4 Time evolution of the crystalline structure of PEO in the blend of the PEO/TA at an isothermal crystallization temperature of: (b) the evolution of sheaf structure in PEO/TA 10/90 at 40 °C; (continued)
Figure 4.4 Time evolution of the crystalline structure of PEO in the blend of the PEO/TA at an isothermal crystallization temperature of:

(c) the evolution of spherulite structure in PEO/TA 40/60 at 45 °C. (continued)
Figure 4.5 Emerged PEO crystal structures following the isothermal crystallization by quenching to 25 °C: (a) 5/95, (b) 20/80 and (c) 50/50, showing the solvated spherulites in conformity with the single phase crystalline region of the phase diagram.
Figure 4.6(a) Plots of lamellar crystal size versus time of PEO/TA (5/95) at 35 °C;
Figure 4.6(b) Plot of PEO spherulite crystal size versus time of PEO/TA (50/50) in different directions and at 49 °C (continued)
CHAPTER V

MISCIBILITY CHARACTERIZATION, PHASE DIAGRAM AND MORPHOLOGY DEVELOPMENT IN PEO/PHOTO REACTIVE DIACRYLATE MONOMER BLENDS

5.1. Introduction

In the previous Chapter, we demonstrated the development of crystalline morphology in relation to the solid-liquid phase transition. In this Chapter, it is of our continued interest to investigate the effect of the melting transitions on the crystalline structures and phase morphology of crystalline-crystalline polymer blends.

Since the miscibility depends on the natural property of blending materials, polymer blends including semi-crystalline/amorphous and semi-crystalline/semi-crystalline blends can exhibit a complicated phase behavior and variety of morphology and structure.\textsuperscript{178,203-206} It can be anticipated that blend miscibility could be complicated by the second crystalline constituent. It is well known that, depending on the crystallization temperature and composition, the second constituent (low temperature crystallizing component) may be included in or rejected from the propagating crystal front of the first
crystallizing component.\textsuperscript{207,208} It was reported that isotropic amorphous phase may exist in interlamellar or interfibrillar regions.\textsuperscript{209,210} Therefore the crystallization of the second component should be controlled not only by the crystallization conditions, but also by the hierachical structure of the first component in to-crystalline-amorphous system as a continuation study of PEO/TA existence with the melt. Since diacrylate is a crystalline material, its blends with PEO could be treated as in crystalline-crystalline systems unlike triacrylate system (crystalline-amorphous system).

Recently, a thermodynamically self-consistent theory has been established by Martkar and Kyu\textsuperscript{41} to describe binary phase diagrams for two-crystalline polymer blends by taking into consideration all possible interactions such as amorphous-amorphous, crystal-amorphous, amorphous-crystal, and liquid-liquid and crystal-crystal interactions. Their theory combined Flory-Huggins free energy for amorphous-amorphous isotropic mixing and the Landau free energy of polymer crystallization of the crystalline components. Subsequently, they determined a phase diagram involving various coexistence regions like liquid-liquid, liquid-solid, and solid-solid coexistence regions bound by the liquidus and solidus lines.

In this chapter, the phase behaviors of several blends consisting of PEO and diacrylate have been investigated for binary crystalline-crystalline polymer blends. The miscibility determination, phase diagram and morphology development were observed depending upon melting point and crystallization temperatures by means of DSC and OM. To determine the co-existence regions, isothermal crystallization experiments were performed to confirm the regions predicted by calculated theory.
5.2. Experimental Section

The experimental phase diagram of the PEO/diacrylate monomer was established by means of polarized optical microscope (OM) and differential scanning calorimetry (DSC). Blends for the establishment of the phase diagram of PEO/diacrylate were prepared by mixing the various compositions of PEO/diacrylate in small vials.

The materials, characteristics, and experimental procedures are the same as those described in the Chapter (Chapter. IV).

5.3. Results and Discussions

Figure 5.1 depicts the DSC thermograms of the diacrylate monomer crystal obtained at various heating rates. The melting peak shifts slightly with increasing heating rate. It appears that the fast heating rate might miss the equilibrium melting, showing a shift to a higher temperature. On the other hand, a very slow heating might suffer the annealing effect.

Figure 5.2(a) shows the DSC thermograms of the PEO/DA blends covering the whole range of compositions with a heating rate of 2 °C/min. The melting peak widens and systematically shifts to lower temperatures when the DA concentration increases. For pure PEO, the melting transition \( T_m \) was evident near 65 °C. It is noticed that the \( T_m \) of PEO in the blends decreases with increasing DA content. This observed depression trend of the melting point of PEO with DA content is consistent with those reported for other miscible or partially miscible blends, \(^{19,185,186}\) except that there appear dual melting peaks of PEO in the thermograms at low PEO concentrations. Such dual peaks can be seen
more clearly in the enlarged scale shown in the inset. Concurrently, the neat DA shows the melting peak at approximately 10°C, showing little or no movement in its blends with PEO. In view of the non-equilibrium nature of these melting peaks, additional DSC runs were performed at 5 and 10 °C/min, which further confirms that these dual peaks at low PEO concentrations are reproducible.

Similar melting point depression phenomena have also been reported in other binary crystalline polymer blends, such as PET/PBT, PBT/PAR and PBSU/PEO.\(^{211,186,212}\) For miscible blends, the melting point of the crystalline component is usually lowered with respect to the pure polymer as a result of thermodynamically favorable interactions between the crystal and the surrounding amorphous constituent.\(^ {213}\) Thus, the melting point depression has been used extensively to evaluate the miscibility of polymer blends. In addition to the thermodynamic effect on the melting point depression, morphological variables such as lamellar thickness and crystal perfection can profoundly affect the melting point.\(^ {214}\)

Figure 5.2(b) shows the composition dependence of \(T_m\) of PEO/DA blend. The pseudo-equilibrium melting points (\(T_m^0\)) were obtained by extrapolating the \(T_m\) at various heating rates to zero heating rate. A similar attempt has been made to estimate the pseudo-equilibrium crystallization temperature, \(T_c^0\). However, the determination of the equilibrium-phase transition temperature is usually ambiguous due to the non-equilibrium nature of polymer crystallization (i.e. the strong dependence of crystallization on the cooling rate). Hence, only the pseudo-equilibrium crystal-melting temperatures of PEO and DA as obtained from the DSC studies are included in the phase diagram. The dual melting peaks of a neat crystalline polymer have been customarily interpreted as due to
the melting point depression or the phase transformation of different crystal modifications. In small molecule crystal mixture such dual melting peaks have been attributed to the liquidus and solidus phases. This concept has been shown to be valid for eutectic crystals of various crystalline polymer blends.

Figure 5.1 DSC thermograms showing the dependence of melt transition on various scanning rates for diacrylate monomer. (2, 5, and 10 °C/min heating rate)
Figure 5.2(a) DSC thermograms of PEO/DA blends obtained at a heating rate of 2 °C/min, showing a systematic movement of the melting peaks of PEO and of DA as a function of concentration. The inset represents the enlarged dual melting peaks of PEO in the blends. (b) Plotted melting points of PEO/DA blends obtained at a heating rate of 2 °C/min.
Morphology development during crystallization has been determined as a function of composition and supercooling based on optical microscopy (OM). Figure 5.3 shows the crystal morphologies of neat PEO and DA. Neat PEO and neat DA crystalline morphologies give guidance to crystal appearance in the PEO/DA blends. To better understand the emerged crystalline morphology in PEO/DA blends, several experiments were performed by cooling from a single phase melt (80 °C) to the segregated crystalline phases at a predetermined cooling rate of 1 °C/min. The progression of crystalline texture from a needle-like PEO texture can be discerned in the PEO/DA 10/90 during the course of cooling. The needle-like PEO crystal appears around a comparable temperature as obtained by DSC. When the temperature of sample falls below the melting point of DA, e.g. around -10 °C, it suddenly shows birefringent appearance characteristic of DA crystal. (Figure 5.4(a)).

Similar experiments have been undertaken for various compositions. As the PEO concentration increases, the crystal structures transform from the needle-like structure to fully developed spherulites through the intermediate structure, called sheaf-like crystal (Figure 5.4(b) 30/70 and (c) 40/60)). As expected the crystalline morphology is strongly influenced by both composition and temperature of crystallization.

To substantiate the solid crystal-liquid melt coexistence regions, the melting temperatures were plotted against composition in Figure 5.5 by comparing with the self-consistently solved solidus and liquidus lines. The present theory is an extension of the Flory-Huggins (FH) theory\textsuperscript{18} of liquid-liquid demixing to the crystal solid-amorphous liquid phase separation by taking into consideration the crystal-amorphous interaction\textsuperscript{12} in addition to the conventional amorphous-amorphous interaction. The total free energy
density of mixing of such crystal-amorphous polymer blends consists of the free energy density pertaining to the crystal order parameter of the crystalline constituent weighted by its volume fraction \( \phi \) and the FH free energy of liquid-liquid demixing, viz.,

\[
f(\psi_1, \phi) = \phi f(\psi_1) + (1 - \phi) f(\psi_2) + \frac{\phi}{r_1} \ln(\phi) + \frac{(1 - \phi)}{r_2} \ln(1 - \phi) + (5.1)\]

\[
\{\chi_{aa} + \chi_{ca} \psi_1^2 - \chi_{ca} \psi_1 \psi_2 + \chi_{cc} \psi_2^2\} \phi (1 - \phi)
\]

where \( \chi_{aa} \) is the FH interaction parameter representing the amorphous-amorphous interaction of the constituent chains in the isotropic melt, whereas \( \chi_{ca} \) represents the repulsive crystal-amorphous interaction parameter. Note that the order of the subscripts denotes the constituent 1 (crystal) and constituent 2 (monomer). \( r_1 \) and \( r_2 \) correspond to the statistical segmental lengths of the respective components.

To clarify the physical essence of the enthalpic contribution, Eqn. (5.1) may be rewritten as

\[
f(\psi_1, \phi) = \phi f(\psi_1) + \frac{\phi}{r_1} \ln(\phi) + \frac{(1 - \phi)}{r_2} \ln(1 - \phi) + \chi_{aa} \psi_1 (1 - \phi) + (5.2)\]

\[
\chi_{aa} [\phi \psi_1 (1 - \phi) \psi_1] - \chi_{ca} [\phi \psi_1 (1 - \phi) \psi_2] + \chi_{cc} [(1 - \phi) \psi_2] [\phi \psi_2]
\]

where the crystal phase order parameter \( \psi_1 \) can be defined as the ratio of the lamellar thickness \( (l_1) \) of the first constituent to the lamellar thickness of a perfect crystal \( (l_1^0) \), i.e., \( \psi_1 = l_1 / l_1^0 \), and thus it represents the linear crystallinity (i.e., one-dimensional crystallinity) of the crystallizing component. \(^{42,191,218}\) Then the product of \( \phi \) and \( \psi_1 \) in the last term of Eqn. (5.2) corresponds to the bulk crystallinity of the constituent 1 in the blend, whereas the product of \( (1 - \phi) \) and \( \psi_1 \) implies the amount of amorphous materials interacting with the crystalline phase, and hence the last term, \( \chi_{aa} \phi \psi_1 (1 - \phi) \psi_1 \), signifies
the repulsive crystal-amorphous interaction. The same argument applies to the second crystalline constituent. In the case of co-crystals, the terms $[\phi \psi]$ and $[(1-\phi)\psi_2]$ represent the crystallinity of each crystalline constituent, and $\chi_{cc}$ representing the strength of crystal-crystal interaction within the co-crystals may be expressed according to the geometric means, i.e., $\chi_{cc} = c_\omega \sqrt{\chi_{ca} \cdot \chi_{ac}}$, where $c_\omega = 1$ signifies the ideal case and $c_\omega = 0$ indicates the complete immiscibility between the individual crystalline phases, forming separate crystals, viz., $\chi_{ca}$ and $\chi_{ac}$ may be treated as independent. Since the co-crystals are rare for most crystalline polymer blends, the crystal-crystal interaction term may simply be dropped from Eqn. (5.1) like in the present case.

The aforementioned crystal order parameter ($\psi$) may be described in the context of phase field based on the Landau-type free energy expansion, viz.,

$$f(\psi_i) = \frac{F(\psi_i)}{k_B T} = W_i \left[ \frac{\zeta_i(T)\zeta_i(0)(T_{m,i})}{2} \psi_i^2 - \frac{\zeta_i(0) + \zeta_i(0)(T_{m,i})}{3} \psi_i^3 + \frac{1}{4} \psi_i^4 \right] \tag{5.3}$$

where subscript $i$ represents each constituent. The coefficients of the Landau free energy expansion are treated as temperature dependent so that the free energy has the form of an asymmetric double well at a given crystallization temperature or supercooling; but it reverts to the symmetric double well at equilibrium. It should be cautioned that the coefficient of the cubic power term must be non-zero in order to apply the Landau potential to the first-order phase transition, otherwise, Eqn. (5.3) is applicable only to a second-order phase transition. The parameter $\zeta$ represents the unstable hump for the crystal nucleation and $W$ is the coefficient that represents the penalty to overcome the...
energy barrier for the nucleation process. $\zeta_0$ represents the crystal order parameter at the solidification potential of crystallization that is treated to be crystal melting temperature dependent.

As depicted in Figure 5.5, the self-consistent solution reveals a solid-liquid coexistence gap bound by the solidus and liquidus lines. To demonstrate the role of the crystal-amorphous interaction in the phase diagram, the critical interaction parameter was taken as: $\chi_{ca}=0.27$ at $T=40^\circ$C along amorphous-crystal interaction parameter $\chi_{ac}=0.01$, and amorphous-amorphous interaction parameter $\chi_{aa}=0.61$, $A=-0.9$, $r_1=110$, $r_2=1$ at $T_{crit}=42^\circ$C. The close resemblance of the predicted trends of the solidus and liquidus lines to the experimental melting transition points implies that the observed dual DSC peaks are attributable to the solidus and liquidus phases. The present predicted trends are consistent with other binary systems such as metal alloys or liquid crystalline mixtures, and thus it can remedy the deficiency of the original Flory diluent theory $^{18,19}$ that predicts only a single liquidus line.

![Figure 5.3 Crystal morphologies of neat components (a) neat PEO at 25 °C and (b) neat DA at -10 °C.](image)

Figure 5.3 Crystal morphologies of neat components (a) neat PEO at 25 °C and (b) neat DA at -10 °C.
Figure 5.4 Optical micrographs of PEO/DA (a) 10/90 after cooling from isotropic melt (100 °C) to various temperatures at rate of 1 °C/min. (b) 30/70 and (c) 40/60.
Figure 5.5 Comparison between self-consistent solution (solid lines) and experimental melting temperatures of PEO/DA blends showing the crystal solid-liquid coexistence region bound by the liquidus and solidus lines. The parameters used were $\chi_{ac} = 0.01$, $\chi_{ca} = 0.27$, and $\chi_{aa} = 0.61$ at 40 $^\circ$C along with $r_1=110$, $r_2=1$, and $A=-0.9$ at $T_{crit} = 42$ $^\circ$C.
The blend shows little or no depression of melting transition of DA. The phase boundary displays four distinct regions: isotropic (I), co-existence of crystal-isotropic liquid (Cr₁+I), crystal-liquid (Cr₁+L₂) and crystal-crystal (Cr₁+Cr₂) (Figure 5.5). At high PEO compositions, a single phase crystal (Cr₁) can be discerned. When the temperature of the sample falls well below the melting point of DA, around -10°C, more birefringent entities develop which is indicative of DA crystal formation.

To elucidate the effect of supercooling on the crystalline morphology at various blend compositions, further experiments have been taken for 20/80, 50/50 and 70/30 at 38, 40, and 50°C, respectively. Moreover, this permits us to determine the morphological phase diagram of the system. Various morphological structures at different points of the phase diagram were examined under isothermal conditions (Figure 5.6).

Figure 5.6(a) displays the time evolution of crystalline morphologies in the blend of PEO/DA 20/80 following temperature quench from an isotropic melt (80°C) to 38°C. In the early stage of growth at 38°C, lamellar branching occurs from a single lamella. The lamellae grow predominantly in the directions of the two ends, and these lamellae splay apart from each other. As a result of this continuous growing and splaying, the initial lamellae gradually evolve to a sheaf-like structure, and finally to an open spherulitic structure. More importantly these hierarchical crystals are shown to coexist with the isotropic melt, which is consistent with the motion of the Cr₁+I region.

As PEO composition increases in diacrylate blend systems, the needle-like lamellae of PEO transform following a T quench to fully developed spherulites. In Figure 5.6(b), PEO/DA 50/50 shows the dense spherulite structures to 40°C from the melt. The 50/50 composition and the 70/30 PEO/DA mixture reveal a similar progression of dense
spherulitic morphology. As PEO composition increases, the spherulitic structures form predominantly. Figure 5.6(c) shows the time sequence of the fully developed spherulites in the 70/30 PEO/TA blend upon quenching to 50 °C. However, all the compositions were quenched to the temperatures which are in the gap between the liquidus and solidus lines, i.e. the Cr₁+I region.

Figure 5.7 represents the optical micrographs displaying the crystalline morphologies of the 20/80, 50/50 and 70/30 PEO/DA blends after quenching from 80°C to various temperatures within the gap of Cr₁+I bound by the liquidus and solidus lines and the Cr₁ region corresponding to the solvated PEO crystal. The upper figure indicates the positions of temperature to which the samples were quenched from the isotropic melt of 80°C with reference to the phase diagram. It was found that at 38 °C, the open spherulitic morphology developed in the case of the low concentration of 20/80. A similar open spherulitic morphology can be discerned in the T quenching to 35 °C. In both cases these open lamellar structures co-existed in the matrix of the DA-rich isotropic melt, confirming the Cr₁+I region. Once composition of PEO increased to 70/30, fully developed spherulite PEO crystal formed and filled the entire microscope view, suggesting the correspondence of the Cr₁ region and the solvated PEO crystal. It seems that DA may be intimately mixed with these PEO spherulites. In the case of 50/50 composition, it also coincided with the coexistence line and thus the emerged structure can be assigned unambiguously to the Cr₁+I or Cr₁+L₂ region because the phase in Cr1+1 and Cr₁+L₂ is similar to each others.

It should be noted that in the T quench of 70/30 to 38 °C, the system passes from isotropic state (I) to crystal state (Cr₁+Cr₂) state through the crystal+isotropic liquid gap
(Cr\textsubscript{1}+I). These morphology studies along with DSC melting points confirmed the theoretically predicted various coexistence regions.

The dashed line in Figure 5.8 represents the peritectic line demarcating temperatures between Cr\textsubscript{1}+I and Cr\textsubscript{1}+Cr\textsubscript{2}. Upon quenching to 25 °C depending on PEO composition and the lower line distinguished the phase of Cr\textsubscript{1} from PEO and Cr\textsubscript{2} from DA crystals accordance with DA crystal when system quenched to -10 °C from the isotropic melt state. As expected for the Cr\textsubscript{1}+I region, the 10/90 and 20/80 blends show the aggregates of needle structures in the continuum of isotropic melt at 25°C (Figure 5.8 upper row). When the PEO composition is higher than 40/60, every composition shows the fully developed spherulite PEO crystal in a short time (Cr\textsubscript{1}) and when every blend quenched to around -10°C, the second crystal structure from DA is established (Cr\textsubscript{1}+Cr\textsubscript{2}).

From this temperature quenching, the system passed through from the isotropic state (I), crystal+ isotropic liquid (Cr\textsubscript{1}+I) to the crystal (Cr\textsubscript{1}+Cr\textsubscript{2}) state. The dual peak gap was the intermediate state where the melted PEO, DA and crystal of PEO coexist. From these experiments confirmed morphology along with DSC melting points, we can obtain a phase diagram which is comparable to the one calculated by theory.

5.4. Conclusions

The blends show a lowering of melting transition of PEO/DA with increasing DA concentrations. It should be emphasized that PEO is partially miscible the solid-liquid phase diagram exhibiting the liquidus and solidus lines pertaining to the crystal-melt transition in conjunction with the coexistence curves of the UCST phase diagram. The
phase diagram of the PEO/DA system consists of isotropic (I), the coexistence of crystal + liquid (Cr$_1$+L$_2$) and the crystal + crystal (Cr$_1$+Cr$_2$) regions. The Cr$_1$ gap corresponding to the PEO crystal is clearly discernible in the phase diagram, but the Cr$_2$ gap is extremely narrow as it appears coincided virtually with the neat DA crystal axis. These self-consistently calculated coexistence regions have been further confirmed by means of time-resolved optical microscopy through inspection of the temporal evolution of the crystalline phase morphology following several temperature quenches into these individual regions.

The isothermal crystallization of PEO/DA mixtures shows the interesting growth behavior of PEO crystal. The PEO crystal is showing the spherulites at deeper quenching instead of showing the needle which has opened lamellar structures instead of fully developed spherulite. The low composition of PEO shows the needle-like crystal due to less amount of PEO in diacrylate. At the shallow quenching depth, at the area in between the liquidus line and solidus line, the morphology prefers to form the crystal in diacrylate-rich blend. (Cr$_1$+I). When it is quenched to 25 °C, the sample forms the spherulite PEO crystal in really fast rate, confirming that the crystal phase under the solidus line is at higher composition than 40/60(Cr$_1$). When the system is quenched to -10 °C, the DA crystal appears followed by PEO spherulites which are evidence that two crystalline phases existed (Cr$_1$+Cr$_2$).
Figure 5.6 Time evolution of the crystalline structure of PEO in the blend of the PEO/DA at an isothermal crystallization temperature of:

(a) 38 °C showing the evolution of needle like structure in PEO/DA 20/80.
(b) 40 °C showing the evolution of spherulite structure in PEO/DA 50/50
Figure 5.6 Time evolution of the crystalline structure of PEO in the blend of the PEO/DA at an isothermal crystallization temperature of:
(c) 50 °C showing the evolution of spherulite structure in PEO/DA 70/30 confirming the region of PEO crystal and DA-rich PEO(immiscibility gap between liquidus and solidus line).(continued)
Figure 5.7 The phase diagram confirmed the region of Cr$_1$+I by quenching the system from isotropic melt to the immiscibility gap which is between the liquidus and solidus lines. The various PEO compositions in DA for the condition of isothermal crystallization by quenching to various temperatures: 20/80, 50/50 and 70/30.
Figure 5.8 The phase diagram which shows that the phase boundary displays four distinct regions: isotropic (I), co-existence of crystal-liquid (Cr₁+I), single crystal phase (Cr₁) and crystal-crystal (Cr₁+Cr₂) (C₁ and C₂ correspond to crystals of PEO and DA, respectively). The isothermal crystallization performed by quenching the system from isotropic melt (80 °C) to 25 °C or -10 °C. The upper line shows the Cr₁+I region and Cr₁ region, while the lower line shows the Cr₁+Cr₂.
6.1. Introduction

The phase diagrams and morphology development in blends of polydisperse PEO and triacrylate as well as diacrylate have been investigated in Chapters IV and V, respectively. It has been well documented that molecular weight and polydispersity can affect the liquid-liquid phase equilibria. Recently, Meng\textsuperscript{221} and coworkers reported the profound influence of functional acrylate arms on the phase diagrams of eutectic liquid crystals and multiarm acrylate systems. It is our continued interest to investigate the effect of the molecular weight of PEO and acrylate arms of monomer on the melting transition and morphology development in their blends. It is important to investigate the factors controlling polymer-polymer phase behavior such as choice of monomers, molecular architecture, composition, and molecular size.
In this chapter, the influence of the polymer molecular weight on the phase diagram and morphology in multi-functional acrylate monomers will be demonstrated. We will utilize the current theories and experiments that deal with the equilibrium thermodynamics and non-equilibrium dynamics of polymer mixtures, which are described in terms of these experimentally accessible parameters as determined in the previous chapters.

When one of the components in the blend is a crystalline polymer, the liquid–solid phase transition occurs in addition to the liquid-liquid phase segregation.\textsuperscript{175} Flory-Huggins (FH) free energy has been used for describing phase diagrams of amorphous-amorphous polymer blend, specifically upper critical solution temperature (UCST). The FH theory is attractive as it affords the determination of polymer-polymer miscibility through the amorphous-amorphous interaction parameter, known as Flory-Huggins (FH) interaction parameter or $\chi$ parameter.\textsuperscript{18} This $\chi$ parameter has been modified by adding athermal entropic contribution to the interaction term to account for the behavior lower critical solution temperature (LCST) which is found to be prevalent in polymer blends.

Although the FH theory is valid for describing the phase diagrams of amorphous-amorphous polymer blends, its extension to crystalline polymer blends, especially in the determination of $\chi$ parameter from the melting point depression has been questioned. A thermodynamically self-consistent theory has been proposed to establish binary phase diagrams for two-crystalline polymer blends by taking into consideration all possible interactions such as amorphous-amorphous, crystal-amorphous, amorphous-crystal, and crystal-crystal interactions in Chapter V. Recently, Kyu and Matkar\textsuperscript{42} introduced a mean-field theory for crystalline-amorphous blends, which basically combines the Flory-
Huggins free energy for amorphous-amorphous mixing with the Landau free energy of crystal solidification of the crystalline components. It was demonstrated that their theory is capable of determining the phase diagram involving various coexistence regions like liquid-liquid, liquid-solid, and solid-solid coexistence regions bound by liquidus and solidus lines. Since diacrylate exhibits a melting peak, its blends with PEO could be treated as a crystalline-crystalline system, unlike the tri-, tetra- and penta-acrylate systems, which are of the crystalline-amorphous nature.

In this chapter, the effects of acrylate arms of multifunctional acrylates and of molecular weights of PEO on phase behavior and concomitant emergence of the crystalline blend morphologies will be investigated following thermal quenching. The amorphous-amorphous blend miscibility has been determined on the basis of the variation of the glass transition temperature with composition. The phase diagram involving solid-liquid phase transition has been examined via determination of the melting point depression behavior using DSC. Various coexistence regions have been confirmed by thermal quenching experiments using optical microscopy (OM). The acrylate arms are varied from di-, tri-, tetra- and penta-acrylate. To determine the effect of the molecular weight of PEO on the melting transition and coexistence regions, the number average molecular weight of PEO has been varied from 5000 to 52000.

6.2. Experimental Section

The experimental phase diagram of the PEO/multifunctional monomer was established by means of polarized optical microscopy and differential scanning calorimetry. Blends of PEO/multifunctional acrylate(s) were prepared by mixing the
desired amounts of multifunctional acrylates and PEO in small vials. Various concentrations of PEO were dissolved in multi-functional monomers by stirring on a hot-plate using a magnetic stirrer bar, and then the water bath temperature was raised gradually to about 70 °C until all PEO crystals were completely melted and the solution became isotropic.

In order to explore the effect of molecular weight of PEO and acrylate arms, various multifunctional acrylate monomers such as 1,6-hexanediol diacrylate(DA), trimethylolpropane triacrylate(TA), pentaerythritol tetraacrylate(Tetra) and dipentaerythritol penta-/hexa- acrylate(Penta) were melt mixed with PEO having various molecular weights ranging from 5000 to 52000 in the mono-disperse form. In addition, a polydisperse PEO was used to determine the influence of polydispersity, if any. Detailed material information may be found in Chapter III.

In this chapter, we have investigated the effect of functional acrylate arms as well as the effect of the molecular weight of PEO on phase diagrams of the mixtures PEO/multifunctional acrylates. The development of crystalline structure and phase morphology was examined using OM. Isothermal experiments were carried out by quenching the samples from 80 °C to various coexistence regions. The blend samples, covered with glass slides, were heated until they were optically transparent (i.e., isotropic), and then cooled down slowly. Thereafter, the samples were reheated to their isotropic states prior to performing thermal quench experiments.

Melting point depression, crystallization temperatures and glass transition ($T_g$) of the PEO/acrylate monomer blends were determined using DSC (Model Q-1000, TA instruments). Samples for calorimetric measurements were prepared by introducing
approximately 7-10 mg of the initial mixture into aluminum hermetic DSC pans, which were sealed to avoid evaporation during the heat treatment. Nitrogen gas was purged into the unit to maintain an inert atmosphere. Various heating rates were carried out for whole PEO/acrylate mixtures (e.g. 2, 5 and 10 °C/min). Melting and crystallization temperatures of these PEO/acrylate monomer blends were determined based on the second heating cycle. The development of crystalline structure and blend morphology was studied using OM (Olympus-BX) with the aid of Linkam hot stage.

The blend samples were first heated to 80 °C to equilibrate in the melt and then cooled down to the room temperature to identify the coexistence regions of the phase diagram. The development of morphology at different temperatures and compositions was examined. Subsequently, isothermal experiments were carried out by quenching the samples from 80 °C to various temperatures below the melting points of PEO in the phase diagram of various molecular weights of PEO and multi-functional acrylate monomer mixtures to investigate the morphology development in relation to various coexistence regions such as isotropic, crystal+liquid, crystal solid and crystal+crystal for each blend.

6.3. Results and Discussions

The molecular weight of PEO and acrylate functionality of monomers effect on melting behavior will be discussed in following sections.
6.3.1. Molecular Weight Effect on Melting Behavior of PEO(LM) and Multi-functional Acrylate Systems

Figure 6.1 shows the melting transition curves as a function of molecular weights of PEO. Two notable features can be discerned: (1) the melting temperature increases with increasing PEO molecular weight and (2) the dual melting transitions were observed in the lowest molecular weight PEO having $M_n$ of 5,000. The increase in melting transition with increasing molecular weight is in line with the general perception of polymer crystallization. It is possible that this increasing trend will level off asymptotically with continued increase in the molecular weight of PEO. The dual peaks in very low molecular weight PEO have been reported by others. In conventional crystalline materials, such dual melting transition peaks have been attributed to either melting-recrystallization or the crystal-crystal transformation of different modifications.

Buckley and Kovacs\textsuperscript{222,223} investigated that the PEO chains may be extended or folded within the lamellae in the low molecular weight fractions of PEO crystallized from the melt to form lamellae. Cheng et al\textsuperscript{151,153,224} introduced an intriguing conception from the studies of crystallization of low molecular weight PEO fractions that brings the integral (IF) and nonintegral folding (NIF) structure to explain the nature of step-wise reduction of lamellar thickness during crystallization. Since the low MW PEO crystals thicken in a step-wise manner, in the DSC, two (or more) melting peaks are found corresponding to sufficiently separated endotherm along the temperature scale. The folded chain crystals are metastable relative to the extended chains; hence the melting points of the different crystal structures decrease as the number of folds increases. As the molecular weight of the PEO is raised, the kinetic stability of the folded chain forms
increases. They demonstrated that the large molecular weight of PEO exhibits only folded-chain crystals\textsuperscript{225}, whereas PEG 3000 may only exist in the extended or once-folded chain forms\textsuperscript{148,149}. In the samples in once-melted materials, a mixture of the crystalline lamellae with different folding periods was formed after cooling down, in a manner dependent on the temperature and annealing time. The DSC analysis of the melting endotherm makes it possible to separate the melting points for these lamellae with different thicknesses but with the same molecular weight\textsuperscript{222}.

According to Beech\textsuperscript{226}, PEO 6000 is the highest limit for which extended chain morphology predominates in mature crystals of PEO. The DSC thermogram shows a shoulder or a poorly resolved second endotherm next to the main melting endotherm of PEG 6000, suggesting the existence of two crystal forms of PEG 6000, assigning the low melting endotherm to the once-folded modification and the higher melting to the extended modification.

These authors also showed that chain unfolding (crystal thickening) either gradually or stepwise during the heating runs in DSC. It is attributed to multi melting peaks in low molecular weight of PEO. Like the double endotherm peaks reported by many researchers for low molecular weight of PEO, PEO with 5000 molecular weight of PEO also could have the double melting peak due to the annealing condition. During the annealing, the PEO crystal chains are thickened by unfolding, which may be attributed to the multiple melting peaks.

To elucidate the effect of PEO molecular weight on the phase behavior of the PEO/acrylate monomer blend, low molecular weight monodisperse PEO (M\textsubscript{n}=5000) was utilized. Figure 6.2 depicts the DSC diagrams of the PEO (LM)/diacrylate mixtures
showing the depression of the primary melting peak (i.e., attributable to the folded chain crystals) with increasing diacrylate monomer amounts. This higher temperature minor peak, attributable to the extended chain crystal, appears inconsequential as it diminishes with the addition of DA. Hence only the primary peak that is involved in the melting point depression will be considered here by relating to the solid-liquid phase transition. The dual melting peaks in binary mixtures of tristearin/tripalmitin have been attributed to the solidus and liqudus phases by Kerridge.\textsuperscript{215} Similar assignment has been given to polymer blends, notably by Manley et al.\textsuperscript{185} and Guenet et al.\textsuperscript{216,217,227}

A complementary experiment has been conducted by means of optical microscope. Figure 6.3 displays the melting of the PEO crystals: (a) 10/90, (b) 30/70, (c) 50/50 and (d) 70/30 PEO/DA blends during the course of heating at the rate of 1\degree C/min. It was found that the PEO crystals melt away completely at about 1~2 \degree C higher as compared to that of the DSC melting peaks of the corresponding PEO/DA blends. Subsequently, the phase diagram was established experimentally based on the DSC and OM studies of PEO(LM)/DA blends (Figure 6.4). The physical significance of this phase diagram will be analyzed later.
Figure 6.1 Differential scanning calorimetry of various molecular weights of PEO, DSC scans were taken for 5°C/min (a) 1st run and (b) 2nd run. (PD represents to polydisperse PEO) (PD represents polydisperse PEO). LM, IM, HM represents low, intermediate and high molecular weight PEO respectively.

Figure 6.2 The differential scanning calorimetry thermograms of PEO(LM)/diacrylate blends before photopolymerization. The heating rate was 2 °C/min.
Figure 6.3 Morphology development of PEO(LM)/diacrylate; (a) 10/90, (b) 30/70 systems during heating (heating rate is 1 °C/min).
Figure 6.3 Morphology development of PEO(LM)/diacrylate; (c) 50/50 and (d) 70/30 systems during heating (heating rate is 1 °C/min). (Continued)
Figure 6.4 Variation of melting temperatures of PEO(LM)/DA as a function of blend composition as obtained by DSC and OM techniques. The heating rate was 2 °C/min for the DSC studies and the heating rate was 1 °C/min for the OM studies.
Similar DSC experiments have been carried out for other multi-functional acrylate systems such as PEO(LM)/TA, PEO(LM)/Tetra and PEO(LM)/Penta blends. Figure 6.5 exhibits the DSC thermograms of (a) PEO/TA, (b) PEO/Tetra and (c) PEO/Penta, showing the two endotherms in the neat PEO(LM) and also at high concentrations, which may be associated with the extended and folded chain crystals, respectively. Again, the primary melting peak, appearing at a lower temperature, shows significant depression with increasing acrylate monomer content whereas the higher temperature minor peak simply disappears. The same behavior can be confirmed in other PEO systems of different molecular weights as shown in Figure 6.6 (a) the DSC thermogram for intermediate molecular weight PEO (IM) and (b) high molecular weight of PEO (HM) blends with DA.

To emphasize the effect of molecular weight and acrylate arms topology, the segmental length has been addressed respect to acrylate arm numbers. Each functional arm has two respect parts. The schematic drawings of reactive parts respect to multi-functional acrylate monomer arms in relation to segmental length have given in Figure 6.7. As demonstrated in the previous Chapters IV and V, the calculated phase diagram of various molecular weights of PEO and diacrylate monomers has been compared in Figure 6.8. All phase diagrams show a similar trend, consisting of isotropic, isotropic + crystal and crystal + crystal coexistence regions bound by the neat crystal regions.

However, the phase diagrams of different molecular weight PEO and different functional arms of acrylate systems are different from those of PEO/DA systems. As shown in Figure 6.9, the phase diagrams of PEO(LM), (b) PEO(IM) and (c) PEO(HM)/di-, tri-, tetra- and penta acrylates consist of isotropic, followed by coexistence of crystal
+ isotropic and single phase crystalline regions in the descending order of temperature. The upper critical solution temperature (UCST) is located below the glass transition temperatures of the systems.

A few notable features with increasing acrylate arm functionality include (1) the increase in the acrylate arm topology as the solid-liquid phase transitions moves upward slightly and concurrently (2) the UCST rises more noticeably (upper row of Figure 6.9). At a given acrylate arm topology, the increase in molecular weight affects profoundly on the UCST phase diagrams, but the liquidus and solidus lines pertaining to the solid-liquid phase transition show only a minor influence, i.e., the UCST peak clearly moves to higher temperatures while shifting to the lower PEO content side with increasing molecular weight of PEO. Hence it is reasonable to conclude that the solid-liquid phase diagrams of the mixtures of PEO and multi-functional acrylate are more sensitive to the arm functionality than the effect of PEO molecular weight. However, the UCST is affected both by the acrylate arm topology as well as by the molecular weight of PEO.
Figure 6.5 DSC thermograms of PEO(LM) and multiacrylate:
(a) PEO(LM)/triacrylate blends before photopolymerization, respectively. The heating rate was 2 °C/min. (TA represents triacrylate, Tetra represents tetraacrylate, and Penta represents pentaacrylate).
Figure 6.5 (b) PEO(LM)/tetraacrylate and (c) PEO(LM)/pentaacrylate blends before photopolymerization, respectively. The heating rate was 2 °C/min. (TA represents triacrylate, Tetra represents tetraacrylate, and Penta represents pentaacrylate) (continued).
Figure 6.6 (a) Differential scanning calorimetry thermograms of PEO (IM)/diacrylate, (b) PEO (HM)/diacrylate blends before photopolymerization. The heating rate was 2 °C/min.
Figure 6.7 Schematic drawings of reactive parts respect to multi-functional acrylate monomer arms in relation to segmental length.
Figure 6.8 Comparison between calculate phase diagrams and experimented data of PEO 5000, 10500 and 52000 /diacylate. (PEO(LM), r1=17, PEO(IM) r1=35, PEO(HM) r1=175, r2=1 (for DA)) (a) $T_{\text{crit}}= 48$ °C, $A=-6$, $\chi_{dd} = 0.82$, $\chi_{ac} = 0.01$, $\chi_{ss} = 0.26$, $\chi_{cc} = 0.0001$, at 40 °C (b) $T_{\text{crit}}= 45$ °C, $A=-6$, $\chi_{dd} = 0.79$, $\chi_{sc} = 0.21$, $\chi_{as} = 0.013$, $\chi_{cc} = 0.0001$, at 40 °C (c) $T_{\text{crit}}=45^\circ C$, $A=-6$, $\chi_{dd} = 0.68$, $\chi_{ac} = 0.01$, $\chi_{ss} = 0.20$, $\chi_{cc} = 0.0001$ at 40 °C.
Figure 6.9 Comparison between calculated phase diagrams and experimented data of PEO 5000, 10500 and 52000 /triacrylate, tetraacrylate and pentaacrylate. (a) molecular weight (b) multi-arms (PEO(LM), r₁=17 PEO(IM) r₁=35, PEO(HM) r₁=175, r₂ for DA=1, for TA=2, Tetra=3, Penta=4) In case LM/TA, $\chi_{da}=0.02$, $\chi_{ca}=0.18$ at 25 °C, T_{c1}=260 °C. In case IM/TA, $\chi_{da}=0.095$, $\chi_{ca}=0.242$ at 25 °C, T_{c1}=-200 °C, and in case for HM/TA, $\chi_{da}=0.0134$, $\chi_{ca}=0.02175$ at 25 °C, A=0. T_{c1}=-260 °C
6.3.2. Development of Crystalline Morphology in Relation to Phase Diagrams of Blends of PEO(IM)/Multi-Functional Acrylates

Although the theoretical calculation based on the self-consistent solution closely matches with the experimental phase diagram obtained by DSC and OM studies, it is imperative to confirm the coexistence regions. Isothermal temperature quench experiments were conducted by time-resolved optical microscopy. Figure 6.10(a) exhibits the spatio-temporal evolution the PEO crystals following a thermal quench of the 30/70 PEO(IM)/TA blend from an isotropic melt temperature of 80 °C to a temperature (43 °C) within the crystal + isotropic region bound by the liquidus and solidus lines. Two lamellar aggregates can be noticed in close proximity. These lamellar aggregates grow in size with elapsed time through branching and tip splitting and eventually emerge to open spherulite with lamellar branching morphology in the continuum of isotropic TA-rich melt. A similar observation can be confirmed in the case of thermal quenching of the 50/50 blend into the Cr₁ + I coexistence gap of 47 °C. As shown in Figure 6.10(b) the spherulite appears denser relative to that of the 30/70 composition. It should be emphasized that the coexistence gap of the Cr₁ + I phase can be confirmed for both systems.

Upon quenching of the aforementioned 30/70 (Figure 6.10(c)) and 50/50(Figure 6.10(d)) PEO (PD)/TA blends to the single phase crystal region 25 °C, well-developed spherulitic structures can be discerned over the entire microscopic view. If any solvent were to exist, it would be mixed with the crystals via swelling, which lends support to the predicted idea of the single phase crystals. The existence of similar solvated crystals has been reported by Guenet et al.\textsuperscript{216,217} for various crystalline polymer blends.
The same observations can be made for other systems including PEO/Tetra and PEO/Penta acrylate systems. Figure 6.11 shows the development of spherulitic morphology of the 30/70 and 50/50 PEO(IM)/Tetra blend upon quenching into the Cr$_1$ + I coexistence gap from the isotropic melt of 80 °C. Similarly, the T quenches into the single phase crystal region of 25 °C reveal the well grown spherulitic morphology covering the whole microscopic view. This finding is the same for the PEO (IM)/pentaacrylate system as shown in Figure 6.12 showing consistency with other PEO/multifunctional acrylate systems.

To demonstrate the effect of polydispersity of PEO on the solid-liquid phase diagram in its triacrylate blends, the melting temperatures as obtained by the DSC studies were plotted versus composition of PEO for the blends of polydisperse PEO(HMPD)/DA and monodisperse PEO(HMMD)/DA (Figure 6.13(a)) and also for the blends of polydisperse PEO(HMPD)/TA and monodisperse PEO(HMMD)/TA (Figure 6.13(b)). The melting points for both systems virtually overlapped, indicating that the polydispersity may not affect significantly on the solid-liquid transitions although such an effect is pronounced in the case of liquid-liquid phase separation such as UCST.

6.4. Conclusions

The effects of acrylate functional arms as well as the PEO molecular weight on the melting transitions of their blends were investigated. It was found that the solid-liquid phase transition bound by the solidus and liquidus lines shows greater sensitivity to the acrylate arm topology relative to that of the molecular weight of PEO. The UCST pertaining to the liquid-liquid phase separation is seemingly affected by both
contributions. Furthermore, the polydispersity also does not take the major role in the solid-liquid phase transition, viz., the melting behavior of the PEO/TA blends, although its influence is known to be profound on the liquid-liquid phase diagrams.
Figure 6.10 Emerged PEO crystal structure in following the isothermal crystallization by quenching to (a) 43 °C 30/70 and (b) 47 °C 50/50 PEO(IM)/TA showing the spherulite crystal structure which is floating in the triacrylate liquid. (c) and (d) show the fully developed spherulite crystal when the system is quenched from Isotropic to Crystal region.
Figure 6.11 PEO(IM)/Tetra blends show the spherutic crystal structure in following the isothermal crystallization by quenching from Isotropic to Crystal + Isotropic region (a) 45°C 30/70 and (b) 47°C 50/50, and Crystal region (c) 25°C 30/70, (d) 25°C 50/50.
Figure 6.12 PEO(IM)/Penta blends show the spherulitic crystal structure in following the isothermal crystallization by quenching from Isotropic to Crystal + Isotropic region (a) 47°C 30/70 and (b) 50°C 50/50, and Crystal region (c) 25°C 30/70, (d) 25°C 50/50.
Figure 6.13 Comparison between experimental phase diagrams for PEO(HMPD) and PEO(HMMD) in (a) diacrylate, and (b) triacrylate system. Polydisperse PEO with similar molecular weight of PEO does not show significant effect on melting point depression of the blends.
7.1. Introduction

In past decades, photopolymerization has been mainly utilized in the fabrication of polymer/liquid crystal composite films with desired structures and physical properties. Photopolymerization entails the use of radiation such as ultraviolet (UV) or tunable laser light sources to polymerize and crosslink multifunctional photoreactive monomers. The technique is of immense interest scientifically and technologically because of its several advantages over thermal curing. The major advantages of photopolymerization are fast curing speed, uniformity, and ease of controlling the reaction. Polymerization temperature can be low; therefore, the loss of volatile ingredients (e.g., monomer, curing agent, etc.) and degradation of the polymer can be suppressed considerably. In addition, the photopolymerization process is solvent-free and clean, and thus it has diverse applications in the areas of polymer thin films, coatings, adhesives, composites, and advanced optical devices such as flat panel displays, optical switches, and photoimaging plates among others. Depending on the
functionality of the starting monomer, linear, branched, or cross-linked network structures may emerge. The multifunctional (i.e., three or more functional sites) monomers are customarily sought for photopolymerization to achieve polymer networks with good mechanical strength and chemical and thermal stability. Several factors such as temperature, composition, and photoinitiator concentration can influence photopolymerization steps involving initiation, propagation, termination, chain transfer, and inhibition/retardation reactions. Other factors such as incident radiation intensity, sample thickness, and sample to radiation source distance may be kept constant to avoid further complications.

In most formulations, two or more ingredients are involved in the polymerizing system. When one or both components are photopolymerized, the molecular weight of the polymerizing species increases, which in turn causes the system to be unstable, thereby inducing phase separation. It is well-known that the resulting phase-separated structures of such a polymerizing system can exert a profound influence on its physical properties. It is therefore of crucial importance to understand the emergence of two phase structures during photopolymerization-induced phase separation (PIPS).\textsuperscript{1,2} This emergence is ultimately determined by the competition between photopolymerization kinetics and the dynamics of reaction-induced phase separation. This phase separation phenomenon is similar that of crystallization when the photopolymerization takes place in PEO/multi-acrylate monomer systems.

As the phase separation phenomenon in a polymerization-induced phase separation system is a kinetic process in which the transport parameters have an important role in determining the domain size and the amount of the LC separated from the polymer matrix,
the crystallization induced by photopolymerization also needs to be studied for photopolymerization kinetics to investigate the influence of crystal during photopolymerization. Therefore, a full understanding of cure kinetics is necessary in order to establish a relationship between morphology of the films and the system variables (temperature, intensity, and concentration). In addition, it is possible to regulate the microdroplet size, and hence the electro-optical properties by controlling the cure kinetics of photopolymerization.

In this chapter, the phase diagram of mixtures of multifunctional photoreactive acrylate based monomers and various molecular weights of PEO is established by means of optical microscopy and differential scanning calorimetry (DSC). The effects of temperature and monomer concentration on the photopolymerization behavior involving reaction rate constants, photopolymerization rates, and conversions are examined by using a photo-DSC method. As a supplemental method, the real-time FTIR (Fourier transform infrared spectroscopy) was used for conducting the photo kinetics. The real-time infrared (RTIR) can be applied to monitor the depletion of specific monomer (acrylic group) as a function of time. The reaction kinetic constant may be deduced from the variation of specific IR bands associated with C=C double bonds of the acrylic group.

7.2. Photopolymerization Rate, Conversion and Kinetic Constant Determination

Free radical photopolymerization comprising initiation, propagation, and termination reactions may be described customary by the kinetic equations that are well explained in the Chapter 2.1.3.3.
The polymerization rate $R_p$ in a light induced reaction depends (i) on the number of absorbed photons, (ii) the efficiency to use the deposited energy for the generation of radicals, and (iii) the reactivity of those radicals with the monomer and the growing chain. It can be calculated according to

$$R_p = \frac{k_p}{k_t^{1/2}} (\Phi I_a)^{1/2} [M]$$  \hspace{1cm} (7.1)

where $k_p$ and $k_t$ are the rate constants of propagation and termination, respectively, $[M]$ is the monomer concentration, $\Phi$ is the quantum yield or photochemical efficiency, and $I_a$ is the absorbed radiation intensity in the sample. The absorbed intensity is related to the intensity of the incident radiation ($I_0$) by

$$I_a = I_0 (1 - \exp(-2.303A))$$  \hspace{1cm} (7.2)

$A$ is the absorbance of the sample which is given by Lambert-Beer’s law as

$$A = \varepsilon[PI]d$$  \hspace{1cm} (7.3)

where $\varepsilon$ is the molar extinction coefficient at the wavelength of the light, $[PI]$ is the photoinitiator concentration, and $d$ is the thickness of the sample.

Using Eqns. (7.2) and (7.3), the polymerization rate can be expressed as

$$R_p = \frac{k_p}{k_t^{1/2}} [M](\Phi I_0(1 - \exp(-2.303\varepsilon[PI]d)))$$  \hspace{1cm} (7.4)

Eqn. (7.4) describes a relationship between the polymerization rate and the photoinitiator concentration. However, this relationship naturally depends on $[M]$ even when $[PI]$ is the only experimental parameter which is varied.

The heat flow versus time data from the isothermal photo-DSC were used to calculate the experimental conversion rate ($s^{-1}$) and the photopolymerization rate ($mol \ L^{-1}s^{-1}$).
1) based on the equations. If the heat flow $dH/dt$ is known, the rate of polymerization $R_p$ can be calculated from Eq. 7.5.

$$\frac{d \alpha}{dt} = \frac{1}{\Delta H_0 n} \frac{dH}{dt}$$

(7.5)

$$R_p = \frac{d \alpha}{dt}[M]$$

(7.6)

where $dH/dt$ is the heat flow in J.s$^{-1}$ from Photo-DSC. $[M]$ is the monomer concentration in mol.L$^{-1}$, $\Delta H_0$ is the standard heat of polymerization in J.mol$^{-1}$, and $n$ is the number of double bonds per monomer molecule. A literature value of $\Delta H_0 = 86.25$kJ/mol was used as the heat generated during the photo reaction of acrylic double bonds. The C=C double bond conversion $\alpha$ may be obtained by integrating the area under the heat flow vs. time curve normalized by a reference literature value of the 100% conversion.

$\Delta H_{ideal}$ can be calculated from Eqn. (7.7)

$$\Delta H_{ideal} = \frac{n \Delta H_0}{MW} = \frac{n(86250)}{MW} (J / g)$$

(7.7)

Once the value for the heat of polymerization is determined in J/g, it is then straightforward to calculate the percent conversion by direct comparison of the theoretical heat generated to the measured heat of polymerization for full conversion of the monomer.

$$\alpha = \frac{\Delta H_p}{\Delta H_{ideal}}$$

(7.8)

where $\Delta H_p (J)$ is the apparent heat of polymerization for incomplete acrylate monomer conversion obtained from the numerical integration of the area under the digitized heat
flow curve up to time \( t \); i.e., \( \Delta H_p = \int_0^t (dH/ dt) dt \). The conversions for the photopolymerized mixtures are then calculated. Since \( \alpha \) is known experimentally, the concentration of the unconverted acrylate monomer may be calculated by the following equation;

\[
[M] = (1 - \alpha)[M]_0
\]

(7.9)

\[
\frac{k_p}{k_r^{1/2}} \left( \Phi I_a \right)^{1/2} = \frac{d\alpha}{dt} \frac{1}{(1 - \alpha)}
\]

(7.10)

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

(7.11)

7.3. Experimental Section

Photopolymerization experiments were carried out on various mixtures of multifunctional acrylate(s)/Poly(ethylene oxide) mixtures by using Rose Bengal derivatives (RBAX) as the main photoinitiator. Photo-Differential scanning calorimetry (Photo-DSC) results were obtained using a differential scanning calorimeter (DSC Q-1000, Thermal Analysis) instrument equipped with a dual beam photo-calorimetric accessory and a lid specially designed for the photochemical measurements. Each blend, weighting (7 mg) was placed in a hermetic aluminum DSC pan. An empty DSC pan was used as reference. Low sample weights and initiator concentrations were chosen to ensure the applicability for uniform light intensity across the sample.

Detailed information about the photocurable precursors, PEO as well as the preparation of multifunctional monomer(s)/PEO blends, may be found in Chapter III.
Further information about the photoinitiator system and experimental procedure for preparing a photopolymerization recipe was given in Chapter III.

The mixtures were mixed homogeneously for 15 hrs and then heated in the water bath at an isotropic state (70 °C). The isotropic liquid mixture of PEO/multifunctional acrylate/RBAX was weighed (7 mg) in a hermetic aluminum DSC pan. Prior to application of the UV radiation, the DSC cell was flushed with nitrogen for about 5 minutes in order to prevent the oxidation of the sample. The sample temperature was then adjusted to the required temperature for exposure by the medium pressure mercury lamp equipped with a 365 nm band-pass filter.

Two different intensities (40 and 150 mW/cm²) were used in order to investigate the effect of the intensity on the photopolymerization kinetics. Similarly, in order to monitor the temperature effect on the photopolymerization kinetics three different temperatures (25, 50 and 70 °C) were used. During polymerization, the sample and the reference pans were left uncovered in the photo-DSC instrument.

FTIR is a powerful tool in examining the reaction kinetics by monitoring the absorbance of specific functional groups at a certain frequency of the spectra. In order to monitor the polymerization kinetics, a FT-IR spectrophotometer (Thermo Nicolet model Nexus 870) equipped with a DTGS-TEC detector was used. Omnic series software was used to collect data and used for data analysis. Real time-IR was modified in order to avoid the strong inhibition effect of atmospheric oxygen on the photopolymerization and to create a controlled temperature environment. Samples were exposed to a UV or laser light via an optical fiber cable in a sealed glass reactor cell equipped with quartz windows that was evacuated and saturated with pure nitrogen prior to irradiation. Two different
sources were used: a UV source (Linos Photonics, LQ UV1000) with 40 mW/cm² intensity at 365 nm and a green laser beam (19 mW/Cm²) for photopolymerization at 532 nm wavelength. We were interested in monitoring the absorption of acrylate groups at the 1635 cm⁻¹ band of the spectra. The conversion of the acrylate group can be calculated according to the following equation. 99

\[
\text{Conversion} = \frac{A_0 - A_t}{A_0}
\]  

(7.12)

where \(A_0\) and \(A_t\) represent the absorbance at time zero and time \(t\), respectively.

Figure 7.13 illustrates the spectrum of the diacrylate at time zero. The wavenumber of 1635 cm⁻¹ was assigned to the C=C double bond stretching of diacrylate, whereas 811 cm⁻¹ was attributed to the C=C twisting. The rate of polymerization (\(R_p\)) can be determined at any moment of the reaction since the change in the absorbance is directly proportional to the number of acrylate functional groups that have polymerized.

\[
R_p = [M]_0 \frac{(A)_{0} - (A)_{t}}{(A)_{0} (\Delta t)}
\]  

(7.13)

Here \([M]_0\) is the initial monomer concentration and \(\Delta t\) is the time increment from the beginning of photopolymerization. The individual reaction diffusion constants (\(k_t\) and \(k_p\)) were measured as a function of conversion by stopping the initiation at various conversions and monitoring the dark reaction.

The spectrophotometer was operated in the absorbance mode, and the detection wavelength set either at 811 cm⁻¹, where acrylate monomers show a distinct and sharp peak (C=C twisting), or at 1635 cm⁻¹ for the acrylate monomer (C=C stretching). The decrease of the sample absorbance upon irradiation was monitored in real time on a
transient memory recorder or on a personal computer. Because the IR absorbance is proportional to the monomer concentration, conversion versus time profiles were then directly obtained from the curves recorded.

7.4. Results and Discussions

The PDSC and real time FTIR experiments determined the photopolymerization kinetics under various conditions.

7.4.1. Effect of Photoinitiator Concentration

The effect of the photoinitiator concentration on the conversion of diacrylate with UV light irradiation is shown in Figure 7.1. Usually, an increase of the initiator content strongly accelerates the photopolymerization of the diacrylate, and the maximum polymerization rate is achieved earlier\textsuperscript{90}. In contrast, 1% of the Rose Bengal initiator shows the optimum conversion and maximum polymerization rate. The effect of the photoinitiator concentration on the polymerization rate of diacrylate with UV light irradiation is shown in Figure 7.2. As described in Eq.(7.4), the relationship between the polymerization rate and the photoinitiator concentration naturally depends on [M] even when [PI] is the only experimental parameter which is varied. Indeed, it can be assumed that increasing photoinitiator content will provoke a decrease of the average polymer chain length\textsuperscript{18}. As a consequence the PEO/multi-acrylate blend miscibility increases, thus explaining the shift of the observed phase diagrams from Figure 7.3. The increase
photoinitiator amount drives the lowering melting point before polymerization due to the effect of plasticizing on the blend. When the PEO/multi-acrylate 30/70 composition was irradiated at 70 °C for 10 min with 40 mW/cm², the increasing melting points could be observed as molecular weight of acrylate monomer increased.

One can see that for PEO/TA 30/70 the conversion decreased with increasing Rose Bengal content which clearly indicates a lower extent of the degree of polymerization and therefore lower average polymer chain lengths. The increase of the melting point of PEO/multi-functional acrylate monomer 30/70 which was irradiated at 70 °C for 10 min with 40 mW/cm² was getting the highest melting point with 1% RBAX amount in the blend (Figure 7.4). This trend, showing similar behavior, is valid regardless of acrylate arms. From this observation, the 1% RBAX was concluded to be the optimum amount on the neat or PEO/multi-functional acrylate blend. Figure 7.5 shows the incensement of PEO/TA 30/70 melting points after curing at 70 °C with 150 mW/cm² power for various times. Beyond 10 min, there is no significant increment on the melting point of PEO/TA blend. The addition of photoinitiator tends to plasticize the mixture as manifested by the decrease of the polymer melting points and the improved miscibility between PEO and acrylate monomer.
Figure 7.1 Effect of the photoinitiator concentration on the conversion of DA (diacrylate) upon irradiation with 40 mW/cm².

Figure 7.2. Effect of the photoinitiator concentration on the photopolymerization rate of DA on irradiation with 40 mW/cm² at 70 °C for 10 min by PDSC. The inset shows the polymerization rate ($R_p$) vs conversion.
Figure 7.3 Effect of the photoinitiator concentration on the melting point of PEO/multifunctional acrylate 30/70 blends before curing. The plasticizing effect of RBAX causes melting point depression of blends.

Figure 7.4 Effect of the photoinitiator concentration on the melting point of PEO/multifunctional acrylate 30/70 blends with 40 mW/cm² irradiation at 70 °C for 10min by PDSC.
Figure 7.5 Effect of the photoinitiator concentration on the melting point of PEO/TA 30/70 blends with 150 mW/cm² irradiation at 70 °C for various exposure times by PDSC.

7.4.2. Effect of Intensity

Figure 7.6 shows the effect of light intensity on the final conversion (e.g., 58% at 40 mW/cm², 77% in 150 mW/cm²). The maximum rate is reached for the shortest time period with the highest UV light intensity (150 mW/cm²). The enhanced final conversion with light intensity has been observed experimentally in the photopolymerization of many multifunctional acrylates.236-238

The use of a higher intensity leads to rapid consumption of initiator molecules. This creates shorter chains and a faster polymerization rate. Thus, higher polymerization rates create excess free volume in the crosslinking system, and therefore the propagation rate constant \( k_p \) should increase more rapidly giving rise to higher overall double bond conversion.
The relative contributions of monomolecular and bimolecular terminations can be estimated based on the light intensity exponent. The classical kinetic model given by Tryson and Schultz\textsuperscript{102} has been widely used for the kinetic analysis of free radical photopolymerization. With the incorporation of additional kinetic features, the model has made considerable advances over the last three decades, and it appears adequate for describing general linear photopolymerization under steady state. Recent experimental observations indicate that the classical kinetic model fails to predict reaction kinetics accurately over a range of multifunctional monomers undergoing monomolecular termination or radical trapping and cyclization reactions.\textsuperscript{122,237,239-241} According to the classical kinetic model, the polymerization rate is treated to be proportional to the square root of $I_a$ at equal monomer conversions as shown in Eqn.\textsuperscript{(7.14)}

$$-\frac{d[M]}{dt} = k[M][\Phi I_a]^m$$

where $m$ is the reaction exponent and $k$ is lumped rate constant given as $k=k_p/k_t^m$ in the classical kinetic model\textsuperscript{102} $m$ is taken as 0.5 because of the inherent assumption of bimolecular termination reaction between macroradicals. The dependence of the polymerization rate on the light intensity was examined by plotting the maximum rate value $R_p^{\text{max}}$ as a function of $(I_{av})^m$ for various simple hypothetical values of $m$.\textsuperscript{20} According to a bimolecular termination for the kinetic chain. It is approximately obeyed that $I_a^{0.5}$ was valid only in the initial stage of the reaction, but as in the steady state, where termination by trapping is competing with termination by combination, $k$ changes according to $I_a$, i.e., $m=1$.\textsuperscript{242}
The exponent values between 0.5 and 1 for the multifunctional acrylate polymerizations have been proposed by other groups.\textsuperscript{105,243} If the monomolecular termination was occurring exclusively, a value of unity would be expected. Decker and Moussa\textsuperscript{106} confirmed the linear first-order relationship dependence between $R_p$ and the intensity of a multifunctional polyurethane-diacrylate monomer and photoinitiator (i.e., lc-651). However, in practice most of the multifunctional monomer systems do not show linear or square root dependence due to the simultaneous occurrence of monomolecular and bimolecular terminations as well as cyclization reactions. Duran et al.\textsuperscript{244} determined and found experimental rate coefficients ($k_p$ and $k_t$) and its ratio $k=k_p/k_t$ as well as the exponent value ($m$) being in the range 0.82-0.94.\textsuperscript{244} It was concluded that the combined monomolecular and bimolecular termination mechanisms seem to dominate the termination process of the present multifunctional monomers.

![Figure 7.6](image)

Figure 7.6 Polymerization rate versus conversion of double bonds during the photopolymerization of neat diacylate with various UV intensities (40 mW/cm\textsuperscript{2} and 150 mW/cm\textsuperscript{2}) at 25 °C for 10min irradiation.
7.4.3. Effect of Temperature

An increase of temperature leads to an increase of the reaction rate in most thermally induced polymerization reactions. Consequently, a similar behavior is also expected for photopolymerization reactions. Photopolymerization induced by purely monochromatic UV light is predestined for such investigations since no additional heating from the radiation source occurs. The effect of temperature on the polymerization rate of diacrylate with UV light irradiation is shown in Figure 7.7. The degree of cure is considerably improved by an increase in temperature. A rise of the conversion of double bond from 58% at 25 °C to 73% at 70 °C is achieved. An explanation for this remarkable effect could be that a temperature rise expedites segmental motion of the polymer chains and causes more residual unsaturation sites to take part in the polymerization. It is important to point out that the viscosity greatly affects the temperature dependence of the polymerization rate and conversion.

A rapid drop in viscosity due to an increase in the polymerization temperature causes a rapid increase in the polymerization temperature, the polymerization rate, and the conversion. In addition to applied external temperature, during the UV or laser curing process the sample temperature rises dramatically due to heat generated by the exothermal polymerization reaction (e.g. formation of carbon-carbon single bond).

The rise of temperature makes more residual double bonds accessible for polymerization due to the enhancement of the segmental mobility in the network. Similar results were presented by Scherzer and Decker\textsuperscript{245} using Darocure 1173 as photoinitiator in tripropylene glycol diacrylate (TPGDA). In this system, the polymerization rate does
not significantly depend on the temperature during irradiation, whereas the final degree of cure increases with rising temperature.

As depicted in Figure 7.8, the ratio $k = k_p/k_t$ increases at low concentrations and then reaches a plateau regardless of temperatures. According to Andrzejewska,$^{100}$ the observed trend of $k = k_p/k_t$ with conversion may be explicable in terms of the mixed monomolecular and bimolecular terminations. Previously obtained $m=0.82$~$0.94$ is well matched in lumped $k$ ratio for the real experimental cases.
Figure 7.7 Polymerization rate versus conversion of double bonds during the photopolymerization of neat diacrylate with various temperatures at 365nm with power of 40 mW/cm² for 10min irradiation.

Figure 7.8 Lumped $k$ constant ($m=0.82\text{--}0.94$) versus conversion for diacrylate monomers cured by UV 40 mW/cm² for 10min at various temperatures by PDSC.
7.4.4. Effect of Acrylate Monomer Functionality

Dramatic changes of the properties for the media take place in photopolymerization of multifunctional acrylate systems. Figure 7.9(a) and (b) illustrate the conversion versus time for multi-functional acrylates at 25 °C and 70 °C, respectively. The effect of monomer structure on the polymerization rate and double bond conversion has been described in many reviews.\textsuperscript{16,236,240} It was well established that higher degrees of functionality (greater numbers of double bonds per monomer molecule) led to higher reaction rates (due to higher concentrations of functional group), more rapid onset of gelation and vitrification, and higher density of crosslinks.

Figure 7.10(a) and (b) show the dependence of the polymerization rate versus the degree of conversion for neat diacrylate, triacrylate, tetraacrylate and pentaacrylate precursors at 25 °C and 70 °C, respectively. Figure 7.10 presents the influence of the acrylate functionality ($f$) on the kinetics of photopolymerization as obtained by PDSC. When the functionality rose from 2 to 4, the maximum polymerization rate increased as expected. However, the maximum polymerization rate for pentaacrylate ($f=5$) was located in those of DA ($f=2$). It turns out that the pure pentaacrylate is a very viscous liquid and the mobility restriction and more dense networks during polymerization reduce the extent of double bond conversion, leaving a large portion of them unreacted (even 50\%\textsuperscript{89}).

The conversions of DA, TA, tetraacrylate and pentaacrylate are 58\%, 63\%, 48\% and 32\% at 25 °C (Figure 7.9(a)) and 73\%, 71\%, 54\% and 51\% at 70 °C (Figure 7.9(b)). As the temperature increases, the viscosity of acrylate monomers rapidly drops, which brings faster polymerization rate and higher conversion.
In general, as the functionality of the monomer is increased, the average crosslinking density of the system is increased. This increased crosslinking led to an earlier dominance of the reaction diffusion in these systems causing a lower value for the termination rate coefficient for monomers with higher functionality.

The polymerization rate coefficient showed a sudden increase at the beginning of the irradiation. This sudden increase may also be attributed to the onset of auto-acceleration. Indeed, a large concentration of radicals is created within a very short time in samples exposed to UV irradiation. This greatly increases the chain propagation, leading to a larger propagation rate constant. Finally, the propagation also becomes diffusion-controlled (auto-deceleration) and the coefficient decreases.

Higher degrees of functionality lead to higher reaction rates. The network will form more rapidly and the mobility restrictions leading to a diffusion-controlled termination will occur at a lower conversion. Thus, it is expected that auto-acceleration and auto-deceleration, incomplete functional group conversion, and radical trapping will occur at a lower conversion in the polymerization that undergoes more crosslinking. All of this behavior occurs due to the extremely low mobility of reacting species in the crosslinked network. Therefore, more dense networks limit the extent of double bond conversion, leaving a large portion of them unreacted.

Figure 7.11(a) and (b) illustrates further the effect of temperature on the kinetic rate constants. At 25 °C, the lumped rate coefficient, \( k = k_p / k_t \), increased to 5% conversion and after this point it remained almost constant forming a plateau as conversion increased in the case of multi-functional acrylates. The ratio \( k = k_p / k_t \) first increased abruptly at lower
conversion and then reached a plateau regardless of monomer functionality. This observation is consistent at 70 °C.

The temperature increase provides more mobility to the acrylate network and better conversions. The change of behavior as a function of temperature might be explained by the enhanced mobility of system causing a delay in the onset of gelation. It can be speculated that faster rates of polymerization due to the temperature rise create excess free volume in the system causing a delay for the plateau to appear.
Figure 7.9 Conversion versus time of multi-functional acrylates during photopolymerization with 40 mW/cm$^2$ light intensity for 10 min at (a) 25 °C, (b) 70 °C.
Figure 7.10 Polymerization rate versus time of multi-functional acrylates during photopolymerization with 40 mW/cm² light intensity for 10 min at (a) 25 °C and (b) 70 °C.
Figure 7.11 Lumpd $k$ ($m=0.82-0.94$) versus conversion for multi-functional acrylate monomers cured by UV 40 mW/cm² for 10 min at (a) 25 °C and (b) 70 °C by PDSC.
7.4.5. Effect of PEO Composition on Photopolymerization Kinetics

During the course of polymerization of multifunctional monomer/PEO mixtures, the polymerization kinetics may be influenced by a series of changes in the medium such as PEO crystallization and phase separation due to an increase in the molecular weight. As the polymerization proceeds, the polymer may not be miscible in the PEO, resulting in a phase separation as well as crystallization into a polymer-rich phase and a PEO-rich phase. In addition to the phase separation, the crystallization present in PEO may alter the PEO phase behavior. Changes in diffusion, solubility, and PEO crystallization which occur as a result of the anisotropic environment may significantly affect the mechanism and the kinetics of certain photopolymerization reactions. Morphology development and the dynamics of crystallization of multifunctional acrylate/PEO blends will be investigated in detail in Chapter VII.

The effect of PEO composition on the polymerization rate as a function of time is shown in Figure 7.12(a)). The maximum polymerization rate \( (R_p)_{\text{max}} \) was found to decrease with increasing PEO content. This observation agrees well with the results of other similar previous studies for LC and acrylate mixtures. \(^{246,247}\) The observed reduction in the rate of polymerization may be attributed to the reduced molecular mobility within the PEO-rich phase.

The polymerization rate has decreased by the rising PEO composition. After a fast start, the polymerization progressively slows down due to severe mobility restrictions of the reactive sites caused by diacrylate networks. Conversion decreases with an increase of composition of PEO from 10 to 90. Figure 7.12(b) shows the lumped kinetic
coefficient as a function of increasing PEO content. The rate constants decrease as PEO content increases. This might be explained by the weaker probability of interaction of reactive polymers with monomers in the PEO-rich phase. In addition to the crystallization effect of the PEO component, the diluent effect by PEO and variations in the amount of light absorbed by the photoinitiator due to the light scattering by different medium texture PEO should also be taken into account. This is particularly important since the variation in the amount of absorbed light intensity by the photoinitiator due to scattering may hinder the rate and/or quantum yield for photoinitiated free radical polymerization processes in mesomorphic media. Another important effect of the PEO component is that the final conversion also decreases with increasing PEO concentration.

Once crystallization occurs, some unreacted monomers could be trapped within the PEO-rich region and thus the probability of collision between the growing polymers and the residual monomers is diminished. Moreover, the acrylate monomer concentrations in the PEO-rich phase would be low leading to incomplete conversion.
Figure 7.12 (a) Polymerization rate versus conversion, (b) Lumped $k$ constant versus conversion for various composition of PEO/DA blends during 40 mW/cm$^2$ UV curing at 70 °C for 10 min by PDSC.
7.4.6. FTIR Measurement of Photopolymerization Kinetics

An FTIR spectrophotometer with diamond ATR (Thermo Nicolet Nexux 870) was used to measure IR absorption. A spot was created on the samples by dropping to ensure good contact with the ATR crystal.

Figure 7.13 illustrates the spectrum of the diacrylate at time zero. Acrylate conversion was determined by measuring the absorbance at 1635 cm\(^{-1}\) which is assigned to the C=\(\text{C}\) double bond stretching.\(^{105}\) To standardize the measurements, a baseline from 1554 to 1658 cm\(^{-1}\) was used. We monitored the depletion of absorption peak at 1635 cm\(^{-1}\) as a function of time.

The Rose Bengal photoinitiator possesses two absorption peaks near 365 and 532 nm; their ratio is about approximately 2:1, which was already accounted for in calibration.\(^{31}\) Moreover, the different wavelengths used in P-DSC and FTIR experiments may be calibrated in accordance with the absorption spectrum of Rose Bengal to validate the comparison of the apparent reaction kinetics vs time curves obtained by the above two methods.

The conversion versus time for multi-functional acrylate monomers irradiated for 10 min with 19 mW/cm\(^2\) green laser at 25\(^{\circ}\)C was given in Figure 7.14(a), showing the conversions of DA, TA, tetraacrylate and pentaacrylate to be 66%, 62%, 57% and 48% at 25 \(^{\circ}\)C which are less than that of PDSC. As like in the case of PDSC, multi-functional monomers decrease the conversion as acrylate arms increases due to the mobility restriction. As shown in Figure 7.14(b), the ratio \(k_p/k_i\) initially increases with conversion and then it levels off. The kinetic constant showed a similar trend to that was observed in the experiment of P-DSC. It may be inferred that the lumped rate coefficient \(k\) remains
constant with conversion, except for the very early stage of the reaction. On the other hand, only 66% of overall conversion was achieved by green laser which has less power than UV. From the UV irradiation, FTIR experiment reliable to investigated photopolymerization kinetics. The conversion of diacrylate is 79% by FTIR beside the acrylate conversion was reached to 73% by PDSC due to sensitivity of FTIR. (Figure 7.15(a))

The difference between the P-DSC and FTIR results is not surprising if we take a look at the two experiments. For the P-DSC experiment a 365 nm, UV was used with 40 mW/cm² intensity while in the FTIR a 532 nm green laser with 19 mW/cm² intensity was used. The absorption of the initiator at 360 nm and 532 nm was quite different, which meant that the results in Figure 7.15(b) needed calibration. The values of the kinetic constant of the FTIR were about half of those in the case of PDSC. Figure 7.15(b) presented a calibrated reaction kinetic constant curve vs. conversion. The reaction constants from the P-DSC and FTIR were still showing a large difference of reaction kinetic constant from P-DSC and FTIR after calibration of absorbed intensity $I_a$. To properly evaluate the results above, we need to bear in mind that although the intensity difference in power source was minor, the actual intensity difference on the sample might be quite significant, depending largely on the distance light traveled to the sample. Moreover, the absorbed intensity variation has influence on the value of the kinetic constant of propagation and termination. With those uncertainties, it is common practice to see the difference between PDSC and FTIR results. It is very difficult, if not impossible, to compare the two experiments quantitatively. Nevertheless, the comparison
of the PDSC and FTIR results offers a qualitative trend that may occur in the presence of high- and low-intensity of radiation.

These differences arise from the fundamentals of two techniques. i.e. PDSC measures the total heat evolved during photopolymerization. Although it is assumed that the released heat is directly proportional to the number of monomer units reacted via carbon-carbon single bond formation, there is another contribution of heat due to initiation reactions (light absorption). Therefore, the reaction enthalpy liberated to the PDSC thermograms involves the complex contributions to heat release by various photopolymerization steps. In the case of FTIR techniques, it affords the direct measurement of the reaction through the depletion of C=C bonds.

7.5. Conclusions

The primary aim of this chapter has been to determine the conversion and lumped reaction rate constants as a function of monomer type (functionality), intensity differences from UV and green laser and presence of PEO. The results of the cure kinetics are represented mainly as a function of conversion with changing temperature, intensity, and light source. Although the trends of lumped $k$ ratio appear slightly different between the FTIR and PDSC techniques utilized, the lumped rate constant ($k=k_p/k_t$) shows a consistent trend in neat multifunctional monomers. Moreover, the observed exponent value ($m=0.82-0.94$) of $I_a$ Implies that the combined monomolecular and bimolecular termination mechanisms may be most reasonable for describing the termination steps of multifunctional monomers. However, upon addition of PEOs, the decaying trends of $k$ values with conversion show some deviations from those of the pure
monomer case, attributing to sample turbidity caused by possible phase separation and/or crystallization of the blends.

It was established that 1% RBAX is optimal for photo curing of all multiarm-acrylate systems. The PEO molecules act as an obstacle for photo polymerization and changing the amount of light absorption by the photoinitiator due to the scattering of the light.

The photopolymerization kinetic studies in this chapter give the guide line for the photopolymerization induced crystallization in next chapter (Chapter VIII).
Figure 7.13 FTIR spectra of diacrylate exhibiting characteristic absorbance bands at 1635 cm\(^{-1}\) corresponding to C=C of stretching and 811 cm\(^{-1}\) assigned to the C=C bond of twisting.
Figure 7.14 (a) Conversion versus time (b) Lumped k constant versus conversion for multi-functional acrylate monomers cured by 19 mW/cm² for 10 min at 25 °C.
Figure 7.15 (a) Comparison of conversion versus time between diacrylate by PDSC and FTIR with 40 mW/cm² for 10 min at 25 °C. (b) Calibrated Lumped k values for diacrylate monomer by UV(40 mW/cm²) and Green laser(19 mW/cm²) for 10 min at 25 °C.
CHAPTER VIII

MORPHOLOGY DEVELOPMENT IN BLENDS OF PEO/DIACRYLATE VIA PHOTOPOLYMERIZATION-INDUCED CRYSTALLIZATION

8.1. Introduction

Photopolymerization-induced phase transition (PIPT) is a phase transformation process such as mesophase ordering in liquid crystals or crystallization or phase separation driven by photochemical reaction.\textsuperscript{1-2} During the polymerization or crosslinking reaction of reactive constituent, the molecular weight increases which in turn makes the system unstable and drives phase segregation in polymer blends.\textsuperscript{1,2,9,11,248} In crystalline blends of liquid crystalline polymer mixtures not only liquid-liquid phase separation occurs, but also crystal solidification or mesophase ordering can take place during photopolymerization.\textsuperscript{13,17,22,97} The phenomenon of photopolymerization-induced crystallization bears some resemblance to crystallization in thermally quenched blends that occurs in competition with liquid-liquid phase separation.\textsuperscript{73,175,249,250} However, it should be noted that, even though the reaction is usually carried out at a constant temperature, supercooling increases with progression of the reaction, and thus the
crystallization process during photopolymerization is analogous to nonisothermal gradual cooling.

The primary goal of the present study is directed to elucidation of the phenomenon of directional phase transitions (e.g., crystallization) induced by photopolymerization of a binary mixture of liquid crystal (or crystallizable polymer)/photo-curable monomer. The concept of polymerization-induced crystallization is similar to that of phase separation in binary polymer blends undergoing thermally initiated polymerization or photo-initiated polymerization.\textsuperscript{13,22} While polymerization-induced phase separation has been well investigated experimentally and theoretically, the phenomenon of polymerization-induced crystallization is relatively new.

In this chapter, the melting point depression of polyethylene oxide (PEO) in its mixture with diacrylate monomer has been determined by means of differential scanning calorimetry (DSC). Photopolymerization has been carried out in the isotropic melt above the melting point depression curve. By virtue of partial miscibility in the PEO/DA blends, melting point depression occurs. With the progression of the reaction, the melting transition curve moves upward and eventually surpasses the reaction temperature. The emergence of PEO crystals has been investigated by means of polarized optical microscopy as a function of reaction time and composition. When the spatially non-uniform incident beam is utilized, directional solidification occurs by virtue of light intensity gradient (i.e., intensity distribution profiles of the incident beam) during photocuring. The development of diverse spherulitic morphologies or seaweed microstructures has been discussed in relation to the geometry of the non-uniform illumination of the incident beam.
8.2. Experimental Section

Poly (ethylene oxide) (PEO) in powder form was purchased from Scientific Polymer Products, Inc. having a reported weight averaged molecular weight of $M_w = 66,000$, $M_w/M_n = 1.94$. 1, 6-Hexanediol diacrylate (DA) having a weight averaged molecular weight of 226 was supplied by Aldrich Chemical Co. Detailed information is given in Chapter III.

Various concentrations of PEO were dissolved in diacrylate monomer by stirring for 15h at a low speed using a magnetic stirrer hot-plate. The mixtures were then heated in a water bath to above the melting temperature of PEO at 65 °C. Samples for DSC and optical microscope studies were taken by dropping on the hermetic pan (7 mg) or on slide glasses from the clear isotropic solution. Regarding photopolymerization, the samples preparation was followed from Chapter VII. Since photopolymerization experiments were carried out at two different wavelengths (365nm and 532nm) using two different radiation sources, Rose Bengal acetate ester (RBAX) was found to be the preferred choice as a main photoinitiator. On a more general note, RBAX is a xanthone, analogous to the thioxanthones which are common commercial UV photoinitiators. The first step in the mechanism of their initiating polymerization is the electron transfer from a donor, a tertiary amine, to one or another thioxanthone excited state. The Rose Bengal ester two broad absorptions in the regions of 350-440 and 450-560nm (Figure 8.1) and has a high triplet quantum yield (0.76)$^{128,166}$

Differential scanning calorimetry (DSC, Q-1000, TA *) was used for heat treating the samples and for the calorimetric study under several temperature conditions like 2, 5
and 10 °C/min heating rates. In each test, the sample weighed approximately 7 mg. The photocuring reaction was carried out on the photo-DSC under the UV irradiation (365 nm). Both the reference compartment containing empty sample pan and the sample holder containing PEO/DA mixtures (weighing 7 mg) were irradiated at an intensity of 40 mW/cm² for 10 min at 70 °C to ensure that all PEO crystals were melted before curing by UV. The melting points of the irradiated samples were determined by means of the conventional DSC. To avoid the possible influence of residual solvent and thermal history, only the second runs were used for establishing the relation between melting temperatures versus concentration of PEO.

In the optical microscopic studies, all samples sandwiched between the glass and cover slides were melted at 70 °C for 10 min and then quenched to 25 °C. These crystallized samples are heated in the hot stage (Linkam, TMS 93) of the optical microscope (Olympus, BX 60) at the desired experimental temperatures (i.e., above the melting point of each blend composition) for 10 min. The sandwiched samples were exposed to filtered green light thereby triggering photopolymerization of DA in the mixtures. The emerged microstructures were photographed by digital camera (Canon, EOS 300D) as a function of exposure time, blend compositions and temperature under suitable magnifications ranging from 50 X to 500 X.
8.3. Result and Discussions

Figure 8.2 shows the DSC thermogram of PEO/DA after photopolymerization. When these mixtures were exposed to the UV light under the photomDSC cell at a power of 40 mW/cm² at 70 °C for 10 min, photopolymerization of DA took place in its PEO blends. The cured blend samples were quenched to room temperature for the subsequent DSC experiments. As expected, the melting transition temperatures of PEO in the cured blends appreciably shifted upward beyond the melting temperatures of the uncured blends (Figure 8.3) suggesting that photopolymerization induced crystallization has taken place. That is to say, the increase in molecular weight of polyacrylate drives the melting point curve to surpass the reaction temperature, thereby thrusting the system into the unstable region which in turn induces the crystallization to occur. Another interesting
observation is the lack of the DA melting peak which may be attributed to the curing in
the isotropic state, which prevented the crystallization of DA.

Figure 8.3 exhibits the plotted DSC thermograms of PEO/DA blends which
contained 1% Rose Bengal initiator with another coininitiator against acrylate monomer
obtained at a heating rate of 2 °C/min, showing the melting transition of neat PEO in the
vicinity of 65 °C tends to shift to lower temperatures with increasing DA content. The
Rose Bengal is acting as a plasticizer in PEO/DA blends. Therefore, the melting
depression of PEO/DA is more pronounced. As mentioned in Chapter V, VI the acrylate
arms effect on PEO/multiacrylate blends does not show the significant depression in the
system with plasticizers. Still, at low PEO concentrations, dual melting peaks of PEO
appear in the thermograms like without Rose Bengal initiator. Concurrently, the melting
peak of the neat DA is evident around 5 °C, which shows a plasticizer effect by adding
Rose Bengal. However, a very minor movement with increasing PEO content is obtained
like the system without Rose Bengal. We could assume that the curing agents are
miscible to acrylate monomer.

The photopolymerization phase diagram calculation was followed by the current
theory which was used for demonstrating the binary blend before curing combined with
crystal order parameters in Chapters IV and V. Regarding determination of the crystal-
liquid (melt) phase transition of the constituents, the free energy was first minimized with
respect to the individual crystal order parameters for each temperature. Subsequently, a
common tangent algorithm was employed to determine the coexistence curves by
equating the chemical potentials of each phase. The detailed description of the
aforementioned approach may be found elsewhere.
During the course of polymerization, the value of $r_2$ changes from unity (i.e., for monomer) to $r_p$ representing the statistical segment length of the emerged polymer, under the constraint that $\phi_2 = \phi_m + \phi_p$. Assuming that the monomer and the polymer thus formed are completely miscible and the Flory-Huggins free energy of mixing of a crystalline polymer blend in the melt state (Chapter V) can be written as,

$$f_{\text{mixing}} = f(\phi) = \frac{\phi_1 \ln(\phi_1)}{r_1} + \frac{\phi_m \ln(\phi_m)}{r_p} + \frac{\phi_p \ln(\phi_p)}{r_p} + \chi_{\text{mix}} \phi_1 (1 - \phi)$$

(8.1) assuming that the equilibrium is reached at each conversion. The total free energy of the polymerizing system may be expressed for each conversion step as

$$f(\psi, \phi) = \frac{\phi_1 \ln(\phi_1)}{r_1} + \frac{\phi_m \ln(\phi_m)}{r_p} + \frac{\phi_p \ln(\phi_p)}{r_p} + \chi_{\text{mix}} \phi_1 (1 - \phi)$$

$$+ W \phi_1 \left( \frac{\phi_2 - \phi_m}{2} \psi^2 - \frac{\phi_2}{3} \psi^3 + \frac{1}{4} \psi^4 \right) + \chi_{\text{mix}} \phi_1 \phi_m \psi^2$$

(8.2)

The snapshot equilibrium of the phase diagram during the course of polymerization reaction was calculated using the instantaneous volume fractions of the monomer and the polymer formed from it.

$$\alpha = \frac{\phi_2 - \phi_m}{\phi_2}, \quad \phi_p = \alpha \phi_2 \quad \text{or} \quad \phi_m = (1 - \alpha) \phi_2$$

(8.3)

where $\alpha$ is conversion of the monomer into polymer. The rate of conversion of the monomer into polymer is described by the first order reaction and it is given as,

$$\frac{d\alpha}{dt} = k(1 - \alpha)$$

(8.4)

In actual photopolymerization, the lumped rate constant $k$ includes the propagation and termination rate constants, i.e., $k = k_p / k_t^m$, where $m$ is the reaction
exponent and is $0.5$ because of the assumption of the bimolecular termination reaction between macroradicals. The conversion rate is proportional to the one-half power of the intensity of irradiation, i.e., $I_a^{0.5}$ which is valid in the initial stage of the reaction, but at the steady state, where termination via trapping is competing with termination by combination, $k$ changes with intensity with a power of unity, i.e., $I_a^{m=1}$. However, in practice, the combined monomolecular and bimolecular termination mechanisms may be a likely scenario for the termination process with the $m$ value varying between $\frac{1}{2}$ and $1$.

The phenomenon of photopolymerization-induced crystallization is explicable in terms of crystallization induced by slow cooling from the melt. A substance favors a state of the lowest free energy; when quenched below its melting temperature the free energy of solid crystalline state becomes lower and thus favorable compared to the liquid state and emergence of solid crystalline phase can be seen. The melting point, the transition point from melt state to the solid state, can be understood from Figure 8.4 showing a self-consistently solved phase diagram of a partially miscible blend containing a crystalline PEO and a photoreactive monomer before and after polymerization. After establishing the polymerization-induced phase transitions the dynamics of liquid-liquid and liquid-crystal transitions induced by photopolymerization were investigated as a function of polymerization conversion. As the monomer was transformed to the polymer through the progression of polymerization reaction, its interaction with the PEO decreased. Decrease in the miscibility with the reactive component resulted in the rise of the melting temperature of the crystalline component. The reaction condition was chosen such that the starting blend was in the isotropic melt state at the beginning. As the reaction
proceeded, the melting temperature of the PEO in the blend rose above the reaction temperature triggering crystallization which was induced by photopolymerization.

In the blends of crystalline polymer, phase separation and crystallization compete with each other. Even during polymerization, the increasing molecular weight of the reactive component can make the blend unstable and drive liquid-liquid phase separation along with crystal-liquid phase segregation and crystallization.\textsuperscript{42} As the polymerization reaction converted monomer into polymer, the phase diagram moved above the reaction point to trigger phase separation along with crystallization.
Figure 8.2 Blends of PEO (PD)/DA curing at 70 °C for 10min by PDSC power with 40mW/cm². As photopolymerization takes place, the DA melting points disappear due to network formation.

Figure 8.3 Plotted DSC thermogram of PEO/DA before and after curing at 70 °C for 10min UV intensity 40 mW/cm² by PDSC. By the plasticizing effect of RBAX, the melting point depressed little more.
Figure 8.4 Calculated phase diagrams of PEO/DA before and during photopolymerization. As conversion increases, the UCST moves upward and finally passes the reaction temperature which drives the crystallization.
To mimic the solidification of the PEO crystals, the 10/90 PEO/DA blends were illuminated with green-filtered light intensity gradient in the optical microscope that has a truncated Gaussian beam profile in which the outer peripheral has a lower intensity distribution relative to the truncated core region that appeared uniform (Figure 8.5 (a)). During photopolymerization, it can be anticipated that phase separation takes place where the reactive DA monomers diffuse into the high-intensity region, whereas the non-reactive PEO molecules diffuse to the low-intensity circumference region where crystallization of PEO is expected to occur. As can be witnessed in the time sequence of the PEO spherulites in Figure 8.5(b-f), the crystallization seems to take place in the core region where the illuminated intensity is higher than that of the circumferential region. At a glance, this observation is counter-intuitive. However, after careful perusal, it seems plausible that phase separation takes place first in the mixture that drives the DA monomer and PEO chains to diffuse to the high and low intensity regions, respectively. The reaction occurring in the high intensity region can locally drive the crystallization of PEO because this PEO lean region is already below the melting point curve of the cured system and thus PEO crystallization is possible. On the other hand, the reaction at the high PEO region may not be strong enough to raise the originally depressed melting transition points. Consequently, it takes more time for the PEO-rich concentration to move from the isotropic melt state and then cross the melting transition line before the crystallization can take place. As a consequence, the predominance of the spherulitic growth at the high intensity core region was discerned experimentally.

The above conjecture can be verified in the isothermal photopolymerization-induced crystallization studies of the 30/70 PEO/DA blend subjected to the aforementioned
truncated intensity profile of the light intensity gradient. When such spatially non-uniform incident beams are utilized, directional solidification can occur by virtue of light intensity gradient at the circumference of the beam during photoreaction. It is not surprising for the nucleation to occur early in the core region as compared to the circumference (Figure 8.6) where the seaweed growth occurs at the circumference propagating toward the core direction. After some elapsed reaction time, the spherulitic and seaweed structure impinge without running upon each other thereby forming the grain boundary. The growth of the seaweed from the outer circumference presents the first experimental evidence of the directional growth driven by the photointensity gradient. The observed phenomenon is conceptually analogous to the directional growth caused by the thermal gradient in small molecule systems as well as some polymer spherulites.

Figure 8.7 exhibits the emerged spherulites at the core and the seaweed-type microstructures at the circumference for various blends of PEO/DA. The illumination was performed under green light at 17 \( \mu \text{W/cm}^2 \) at various temperatures, i.e., 5 °C above their respective melting temperatures for various exposures. Lo and behold, one can confirm the development of the dual microstructures such as spherulites at the core region and the directional seaweed growth at the outer circumference toward the core for all concentrations investigated ranging from the 10/90 to 50/50 PEO/DA blends. The signature of the photopolymerization-induced directional crystallization in this PEO/DA blends is the prevalent reaction that drives the PEO molecules to diffuse along the radial directions while diacrylate networks predominantly form at the center. The extent of
reaction reduces in accordance with the intensity profile. Hence, solidification of seaweed occurs from the outer peripheral to the inward.

Another intriguing phenomenon is concerned with the viscous fingering when photopolymerization was undertaken at elevated temperature of 55 °C. This temperature is sufficiently higher than that of the melting temperatures of the original as well as the photo-cured 30/70 PEO/DA blends, and thus crystallization can no longer take place. Hence the observed viscous fingering may be attributed to photopolymerization-induced liquid-liquid phase separation, which can take place in the melt at 55 °C. As shown in Figure 8.8(a) the viscous fingering starts at the peripheral circumference and it propagates with elapsed reaction time toward the center by branching and tip splitting. At 200 min, the fingers were broken down into smaller domains due to the instability of the viscous fluids. In the enlarged pictures, one can clearly identify the PEO rich domains that show birefringent character upon quenching to room temperature.(Figure 8.8(b))

The viscous fingering and concomitant liquid-liquid phase separation observed in the 30/70 PEO/DA blend can also be confirmed in the 40/60 (Figure 8.9(a)) and 50/50 PEO/DA (Figure 8.10(a)) compositions. This observation lends support to the idea that liquid-liquid phase separation competes with crystallization kinetics during the course of photopolymerization. In this particular system, the PEO crystallization outgrows the phase-separated domains, especially when the reaction temperature is 53 °C or lower. At 54 or 55 °C, the temperature is too high for crystallization to occur, and thus only viscous fingering of PEO melt occurs within the DA continuum networks.

Figure 8.910 shows that the temperature depends on the crystal and viscous fingering in 50/50 PEO/DA. When the reaction temperature increases, the phase diagram
moves to elevated temperature such that the reaction temperature is located in Cr+I or L+L phases during photopolymerization.

The higher compositions like 40/60 (Figure 8.9) and 50/50 (Figure 8.10) also show the temperature dependency on the crystal growth induced by photopolymerization. The truncated light intensity profile, which is given by the nature of optical light source, could be generated by adjustment of the focusing lens on the sample. Alternatively, the sample stage may be moved up and down to change the beam profile incident on the sample. Adjusting the focusing distance gives the desired focal length to various intensity profiles which have an intensity gradient from the core to the peripheral. This trend gives us the idea when the directional crystal growth comes out from the peripheral side into center.

Furthermore, the influence of PEO molecular weight on the photopolymerization-induced crystallization in diacrylate has been investigated by PEO(LM)/DA, PEO(IM)/DA and PEO(HM)/DA. These increased molecular weights have led to the increased melting temperature of the cured PEO/DA system due to the increase of molecular weight of acrylate monomer. The same behavior was observed for the mixture of PEO(IM)/DA and PEO(HM)/DA blend.(Figure 8.11)

Figure 8.12 exhibits spherulite crystal from photopolymerization produced by filtered green light with power of 17 µW/cm² for various times at various temperatures. Similar spherulitic crystal growth occurred in the high intensity core and propagated toward the peripheral and covered the whole area. An interesting phenomenon was observed in the case of PEO(HM)/DA at 55 °C isothermal photopolymerization. At 55 °C, the crystal, which is induced by the supercooling effect from the increased molecular weight of DA in PEO blends, is starting to grow from the high intensity core then a
fractal like structure, which may be attributed to viscous fingering of immiscible fluids. The viscous fingering advances with elapsed time and entire microscopic view. Subsequently, the structure breaks down into tiny droplets reminiscent of liquid-liquid phase separated domains. Upon cooling to room temperature, PEO crystals develop within these phase separated domains, confirming the phase separation between PEO-rich and DA-rich regions.

8.4. Conclusions

In this Chapter, the novel phenomenon of photopolymerization-induced crystallization in the blends was introduced. The phase field model of crystallization coupled with FH theory of mixing of polymer blends was used to model the phenomenon. Phase diagrams, showing the effect of polymerization on melting temperature, were established to guide the trajectory of the concentration path traversed by the polymerizing system. It was later illustrated using showing crystal growth as a function of time and polymerization. We have demonstrated experimentally that photopolymerization-induced crystallization was carried out at the isotropic temperatures slightly above the depressed melting temperature of PEO crystals corresponding to the liquidus line.

The depressed melting curve shifts upward to the elevated temperatures close to the $T_m$ of PEO crystals and surpasses the reaction temperature which in turn drives the system into the unstable gap resulting in crystallization called photopolymerization-induced crystallization. Various crystalline phase morphologies including development of spherulites in the continuum of isotropic were observed. At higher reaction temperatures above the $T_m$, viscous fingering (or fractal) growth takes place during
photopolymerization, showing phase-separated domains within these emerging viscous fingering structures. However these phase separated domains tend to disappear if the reaction temperature is too high relative to the UCST at low conversions.

The effect of molecular weight shows little or no influence on the morphology development subjected to polymerization of the PEO/diacrylate systems. It was demonstrated that the intensity gradient profile of light resulted in the directional crystal growth of the photopolymerizing system.
Figure 8.5 Truncated intensity profile of the incident beam after passing through the Iris diaphragm and temporal emergence of PEO microstructures during photopolymerization-induced crystallization of 10/90 PEO/DA blend at 48 °C, showing the spherulitic growth. The photoinitiator utilized was Rose Bengal at 1% of DA under filtered green light illuminated at an intensity of 17µW/cm².
Figure 8.6 Directional crystal growth of PEO during photopolymerization-induced crystallization of 30/70 PEO/DA blend at 52 °C, showing the spherulitic growth at near the core as well as seaweed growth from the outer peripheral edge. The photo-initiator utilized was Rose Bengal at 1% of DA under filtered green light illuminated at an intensity of 17μW/cm².
Figure 8.7 The emerged spherulites at the core and the seaweed-type microstructures at the circumference for various blends of PEO/DA. The illumination was performed under green light with the power of 17µW/cm² at various temperatures (5 °C above their respective melting temp) for various exposure times using 1% of Rose Bengal initiator with respect to the DA contents in the blends.
Figure 8.8 Viscous fingering during photopolymerization-induced crystallization of 30/70 PEO/DA blend at (a) 55 °C followed by the break-up of degenerate patterns into liquid-liquid phase separated domains. When the sample quenched to room temperature, the PEO crystal confined the phase separated domains in (b).
Figure 8.9 The PEO/DA 40/60 are showing the crystallization induced by photopolymerization at (b) 50 °C; and at higher temperatures such (a) 55 °C, which is too high to develop crystals, the liquid-liquid phase separation prefers to be obtained.
Figure 8.10 The PEO/DA 50/50 are showing the crystallization induced by photopolymerization which shows the dependency on the reaction temperature. At higher temperature like (a) 54 °C which is too high to develop crystals, the liquid-liquid phase separation prefers to be obtained instead of crystallization at (b) 53 °C.
Figure 8.11(a) the emerged spherulites for PEO(IM)/DA 30/70 (b) the photopolymerization-induced crystals from the various PEO molecular weight and DA mixture 30/70. The illumination was performed under green light with 17 μW/cm² at various temperatures for various exposure times using 1% of Rose Bengal initiator with respect to the DA contents in the blends.
Figure 8.12 The emerged spherulites coexist with phase separated structures for PEO (HM)/DA 50/50 by the photopolymerization-induced crystals. The illumination was done using green light with 17 µW/cm² at 55 °C.
CHAPTER IX

PHOTOPOLYMERIZATION-INDUCED CRYSTALLIZATION AND PHASE SEPARATION IN BLENDS OF PEO/TRIACRYLATE

9.1. Introduction

In Chapter V, we have established the phase diagram of blends of polyethylene oxide (PEO)/diacrylate (DA) by means of differential scanning calorimetry (DSC) and optical microscopy. The phase diagram was characterized by an upper-critical solution temperature intersecting with the solid-liquid phase transition line forming a solid-liquid coexistence region bound by the liquidus and solidus lines. The liquidus line seemingly coincided with the melting point depression of PEO in its mixture with diacrylate monomer. Subsequently in Chapter VIII, photopolymerization was carried out in the isotropic melt above the melting point depression curve. With the progression of the reaction, the melting transition curve moves upward to a higher temperature and eventually surpasses the reaction temperature, which results in crystallization of the constituent polymer driven by the changing supercooling, i.e., the thermodynamic driving force. The spatio-temporal emergence of PEO crystals has been investigated by means of polarized optical microscopy as a function of reaction time at various compositions. It
was demonstrated that when the spatially non-uniform incident beam is utilized, directional solidification occurs by virtue of light intensity gradient (i.e., intensity distribution profiles of the incident beam) during photo-patterning. The development of diverse spherulitic morphologies as well as seaweed microstructures has been discussed in relation to the geometry of the non-uniform illumination of the incident beam.

In this chapter, we further explore the phenomenon of polymerization-induced crystallization in a complementary system, viz., PEO /triacrylate (TA) mixture for the purpose of completeness. Of particular interest is the interplay between phase separation and photopolymerization-induced phase separation in the PEO/TA blend which eventually determines the kinds of crystalline blend morphology that develops in relation to the coexistence gaps of the phase diagram.

9.2. Experimental Section

Poly(ethylene oxide) (PEO) was purchased from Scientific Polymer Products, Inc. having a reported average molecular weight of $M_w = 66,000$ with a polydispersity of 1.94. Trimethylolpropane triacrylate (TA) was purchased from Aldrich Chemical Co; the detailed molecular information is given in Chapter III.

Various concentrations of PEO were dissolved in triacrylate monomer by stirring for 15h using a magnetic stirrer hot-plate. The mixtures were then heated in a water bath to above the melting temperature of PEO at 70 °C. For DSC and optical microscope studies, film samples were prepared by spreading a few drops of the PEO/TA isotropic solution on slide glasses and subsequently sandwiched via cover glass.
Differential scanning calorimetry (DSC, Q-1000, TA®) was used to determine the melting temperatures of the blends at the heating rates of 2, 5 and 10 °C/min. In each scan, the weight of the sample was approximately 7 mg. The photocuring reaction was carried out on the photo-DSC under the UV irradiation (365 nm). Both the reference compartment containing the empty sample pan and the sample holder containing PEO/DA mixtures (weighing 7 mg) were irradiated under the uniform illumination (40 mW/cm²) for 10 min at 70 °C. The melting points of the irradiated samples were subsequently determined by means of the conventional DSC at several heating rates. To avoid the possible influence of residual solvent and thermal history, only the second runs were utilized in the establishment of the solid-liquid phase transition temperature versus concentration phase diagram of the PEO/TA blend.

In the optical microscopic studies, all samples were sandwiched between the glass and cover slides and melted at 70 °C for 10 min. These sandwiched samples were exposed to green filtered light to trigger photopolymerization of triacrylate in the mixtures. The emerged microstructures were photographed using a digital camera (Canon, EOS 300D) as a function of exposure time, blend composition, and reaction temperature under suitable magnifications raging from 50X to 500X.

9.3. Results and Discussions

Figure 9.1 shows the DSC thermograms of PEO/TA after photopolymerization, showing slight movement of the melting transition peaks with composition. By virtue of the crosslinking reaction of the TA, the melting transition temperatures of PEO in the cured blends appreciably shifted upward beyond those of the uncured blends. This effect
of photocuring can be witnessed more clearly in the $T_m$ versus concentration plot in Figure 9.2. In addition, the melting temperatures of the PEO/TA blends with or without containing Rose Bengal initiator syrup (including coinitiator, solubilizing agent, surfactant, etc.) were provided for comparison. The amount of photoinitiator syrup was 1% with respect to the acrylate monomer amount. The addition of the low molar mass photoinitiator syrup shows a minor plasticization depression of the melting point including the dual melting peaks of PEO at lower PEO concentrations. As pointed out in Chapter IV, these dual peaks may be attributed to solid-liquid phase separation into the liquidus and solidus phases. Moreover, a single glass transition is discerned in all blends investigated, which suggests that PEO and TA are miscible at least in their amorphous state. The $T_g$ of the blend was found to be slightly lower than that without the photoinitiator syrup, which may be attributed to the plasticization effect caused by the residual monomeric ingredients.

To elucidate the solid-liquid phase separation occurs between the PEO crystals and TA-rich melt as manifested by the dual melting peaks, the self-consistent solution has been sought in accordance with the model of Matkar and Kyu \(^{42}\) by combining the Flory-Huggins free energy of liquid-liquid demixing and the phase field free energy for the crystal solidification. Figure 9.3(a) exhibits the immiscibility gap of solid-liquid phase separation bound by the liquidus and solidus lines in comparison with the DSC melting temperatures. The upper critical solution temperature (UCST) of the PEO/TA mixture is virtually located below the glass transition temperatures of the blends. Such solid-liquid phase diagram is important to the subsequent studies of photopolymerization-induced phase transitions. When free radical polymerization is triggered by photoinitiation of the
Rose Bengal in the isotropic state slightly above the depressed melting temperature, the molecular weight of TA increases and subsequently undergoes crosslinking. Figure 9.3 (b) shows the snapshots of the UCST curves moving progressively with the extent of the reaction, protruding beyond the melting transition curve. Concurrently, the depressed melting curve moves upward while restoring back to the original melting temperature. At some conversion, say 20%, the UCST as well as the solid-liquid transition line surpasses the reaction temperature, thereby triggering the liquid-liquid phase separation as well as crystallization of the constituent polymer.
Figure 9.1 DSC thermograms of blends of PEO (PD)/TA as a function of blend ratio after curing at 70°C in PDSC operated at 40 mW/cm² under uniform illumination for 10min.

Figure 9.2 Variation of melting temperatures of PEO/TA with and without the curing agent and before and after curing at 70 °C for 10min subjected to the UV intensity of 40 mW/cm² in PDSC.
Figure 9.3 Self-consistent solutions in comparison with the experimental phase diagram of PEO/TA before and during photopolymerization. With the progression of reaction, the UCST moves upward and finally surpassed the reaction temperature, thereby inducing crystallization.
To investigate the development of crystalline structure and phase morphology during photopolymerization of TA, the 20/80 PEO/TA blends were illuminated using green-filtered light intensity in the optical microscope having a truncated Gaussian beam profile in which the outer peripheral has a lower intensity distribution relative to the truncated core region that is uniform (Please see the beam profile in Chapter VIII). Upon irradiation, the photo-crosslinking reaction of TA raises not only its molecular weight, but also thrusts the system into the unstable region. As pointed out above, the melting point curve, in concert with the UCST, moves upward to a higher temperature and eventually surpasses the reaction temperature, which in turn drives crystallization of the constituent polymer as well as phase separation. The reactive TA monomers diffuse to the high-intensity region and form a dense network whereas the non-reactive PEO molecules diffuse to the low intensity circumference region where the crystallization of PEO occurs.

Figure 9.4 shows the temporal evolution of (a) phase separated domains and (b) crystalline structure of the 20/80 PEO/TA blend. Note that the polymerization induced phase transition was triggered at two different temperatures corresponding to the point (a), i.e., at or slightly above the monotectic line and to the point (b), which is slightly below it. In the former, the emergence of the interconnected domains can be discerned under the optical microscope view, which is a signature of liquid-liquid phase separation occurring via spinodal decomposition. However, no orientation fluctuation develops under the polarized condition, suggesting the lack of crystalline structures. In the latter case, multiple tiny spherulites develop which grow in size with elapsed time. These spherulites seem to coexist with the isotropic TA rich melt. The same phenomenon of polymerization-induced liquid-liquid phase separation and crystallization can be made in
another composition, viz., 30/70 blend at (a) 55 °C in the L\(_1\) + L\(_2\) region, i.e., above the monotectic line and (b) 50 °C within the Cr\(_1\) + L\(_2\) coexistence region that is slightly below the monotectic line (Figure 9.5(a) and (b)). These emerged morphologies following the isothermal quenches are of crucial importance to confirm the L\(_1\) + L\(_2\) and Cr\(_1\) + L\(_2\) coexistence regions. These observations lend support to the idea that liquid-liquid phase separation competes with the crystallization kinetics during the course of photopolymerization.

The polymerization-induced crystallization can also be confirmed in the 40/60 PEO/TA blends at the reaction temperature of 50 °C which is slightly below the monotectic line of the snapshot phase diagram of the 20% conversion (Figure 9.6). When the polymerization reaction temperature is further elevated above the monotectic line to 55 °C, the viscous fingering takes place in the PEO/TA 40/60 (Figure 9.7). As shown in Figure 9.7(b), the viscous fingering starts at the peripheral circumference and it propagates with elapsed reaction time toward the middle by branching and tip splitting. Of particular interest is the occurrence of liquid-liquid phase separation within these viscous fingering patterns. These phase-separated domains tend to diminish with further progression of reaction time. However, such phase-separated domains are found to be absent in the case of polymerization at a higher temperature of 62 °C (Figure 9.7(a)). This temperature accidentally corresponds to the isotropic region, i.e., the above the liquid-liquid coexistence curve of the 20% conversion and thus the phase-separated structures if any would have homogenized. This conjecture may be only valid if and only if the reaction is very slow. With continued reaction, liquid-liquid phase separation is anticipated to occur.
9.4. Conclusions

In summary, we have demonstrated experimentally that photopolymerization-induced crystallization takes place in competition with liquid-liquid phase separation in various blends of PEO/TA. Photopolymerization at temperatures slightly above the depressed melting temperatures can trigger crystallization. However, when the temperature is slightly the monotectic line of the snapshot phase diagram of the 20% conversion, liquid-liquid phase separation dominates. Caution should be exercised that the present polymerization induced phase transitions are non-equilibrium, which only gives the pathway for the emerged morphologies as the system traverses across the phase boundaries.
Figure 9.4 Time evolution of the crystallization during photopolymerization of TA in the blends of 20/80 PEO/TA at (a) 42 and (b) 50 °C, respectively. The dark appearance indicates the lack of orientation fluctuation (i.e., no crystalline order). The dashed line is the monotectic line representing the coexistence of liquid + liquid + solid phases.
Figure 9.5 (a) The PEO crystal growth during photopolymerization of 30/70 PEO/TA and (b) phase separation domains formed elevated temperature at 50 °C, due to the highly dense networks formed by triacrylate photopolymerization.
Figure 9.6 The PEO crystal growth during photopolymerization of 40/60 PEO/TA at 50 °C, in which the reaction temperature is lower than the monotectic line. The crystal growth restricted due to the highly dense networks formed by triacrylate photopolymerization.
Figure 9.7 Spatio-temporal evolution of the phase separated domains showing the finger-like growth during photopolymerization of TA in the blends of 40/60 PEO/TA upon exposure at 17 µW/cm² of filtered green light: (a) at 57 °C phase separation within the viscous fingering pattern and (b) at 62 °C showing no phase separation in the viscous fingering.
10.1. Introduction

In recent years, research on photopolymerization-induced phase separation in liquid crystal/polymer mixtures has attracted immense attention, especially in the fabrication of holographic polymer-dispersed liquid crystal (H-PDLC) with potential electrophotonic applications such as optical switches, information storage media, and microlenses, among others. A typical methodology is to irradiate interfering laser beams over the photoreactive monomer/liquid crystal mixtures in the homogeneous state, triggering phase separation by pattern photopolymerization. The photopatterning technique operates on the principle of optical wave interference created by the constructive and destructive interference of two vertical waves and/or two horizontal waves, which produces regulated microchannel layers and/or microdroplet arrays. The mechanism governing photopolymerization-induced phase separation in a binary system has been vigorously
investigated by several research groups.\textsuperscript{11,15,136} Recently, pattern photopolymerization has been extended to preparing microporous films.\textsuperscript{23,256}

All of the aforementioned holographic methods generally involve a binary mixture as a starting material for the photopatterning.\textsuperscript{257,258} In this chapter, the microchannel layer patterns in PEO/multi-acrylate monomer systems similar to those formed by photopatterning photopolymerization in the liquid crystal binary blends. When light is irradiated on the sample by patterning via constructive and destructive interference of multi-waves, monomers are predominantly polymerized in the high-intensity region of irradiation, whereas in the low-intensity region little or no reaction takes place. This creates a spatial concentration variation in the monomer field. Polymer chains, once formed, cannot diffuse away because of the chemical crosslinks, although these molecules may undergo Brownian motion between the chemical junctions. Monomers are the ones that can transport through the polymer network. Strictly speaking, there may be some solubilizing agents and/or surfactant, though diminutive in amount, diffusing from high-intensity regions to low-intensity regions to fill the vacancy left by the monomers, and vice versa. In principle, the transport of monomers creates the polymer concentration contrast between the high-intensity region and the low-intensity region.

In this chapter, dynamics of photopolymerization-induced patterning in a PEO/multi-acrylate system, which is governed primarily by transport rather than thermodynamics, is investigated. The effect of molecular weight of PEO is also investigated in the photopatterned network. Other effects such as swelling of the network and dimensional shrinkage are not covered in this work, but it is by no means saying that
those effects are not important to the dynamics studies and certainly deserves critical evaluation in the future.

10.2. Experimental Section

The materials (multi-functional acrylate(s), various molecular weights of PEO and initiators), their sources and sample preparation procedures were described in Chapter III and Chapter VII. A prepared sample was a drop on a glass slide and covered with a cover slip to obtain a uniform film. The samples thus removed the cover slip to investigate the surface after photopatterning. The opened samples were exposed to the interfering light beams for the duration of experiment. Two and four wave interference patterns were formed on the pure monomer and monomer and PEO mixture with photoinitiator. After photopolymerization, the patterns formed were observed using an optical microscope. For the surface study and behavior of PEO crystal in confined patterns, the profile of the grid and grating formed was characterized using SEM and AFM.

10.3. Development of H-PDLC

The interference pattern consists of fringes of “bright” and “dark” regions created by constructive and destructive interference. In the “bright” fringes sensitizing dyes absorb light and interact with initiators, and photopolymerization of monomers occurs. As monomers are consumed during photopolymerization, concentration and density gradients form prompting net migration of monomers from the “dark” regions into the “bright” regions. One can discern the sinusoidal variation of the polymer concentration
for some initial periods. However, with the progression of the reaction, the peaks, corresponding to the polymer network region, tend to broaden, which is consistent with what was observed experimentally.\textsuperscript{16} Of particular interest is the transformation of polymer concentration profile from initially sinusoidal to various truncated wave forms (Figure 10.1). That is to say, with the progression of reaction time, the sinusoidal peaks level off, and then gradually gets truncated by flattening the top. A concave profile subsequently develops on the top of the truncated profile.\textsuperscript{16} A similar profile transition has been revealed by other groups.\textsuperscript{127,137} It may be speculated that the transition of such a sinusoidal to a truncated wave behavior is influenced by the competition between reaction kinetics and diffusion. At the onset of photopolymerization, the reaction kinetics tend to make the polymer concentration field sinusoidal, arising from the spatially modulated light intensity while the monomer diffusion tries to keep the monomer concentration field uniform. In the early time steps, the rate of conversion is large, and the reaction kinetics dominates such that the profiles of emerging polymer appear sinusoidal.

In the intermediate to late time steps, the reaction kinetics slow, and thus diffusion becomes dominant. It can be noticed in the polymer concentration field that the reaction occurs predominantly at the interface. As monomers are pulled into the high-intensity region, those monomers are reacted at the interface close to the high-intensity region before these monomers can reach the interior region. Thus, the polymer concentration at the high-intensity region increases preferentially at the edges of the interface, while the low-intensity region shrinks due to the monomer depletion. As a consequence, the interface gradient becomes steeper. Since monomer molecules can hardly reach the bulk
polymer region due to the fast reaction at the interface, the concentration profile of the polymer-rich region increasingly becomes truncated with time.\textsuperscript{16} Such an observation is believed to occur, especially when the intensity of the laser irradiation is sufficiently high. As is well-known, holographic polymer dispersed liquid crystal (H-PDLC) refers to a unique composite material bearing periodic alignment of polymer and liquid crystal in stratified layers.\textsuperscript{129} It is noticed that these H-PDLC films structure-wise match the definition of one-dimensional photonic crystals except that one-dimensional photonic crystal should have a much broader classification of periodic structure material which is not limited to liquid crystal and polymer.\textsuperscript{259} A key feature in photonic crystals is that these materials possess photonic band-gap (PBG) structure in which a designated frequency range light cannot pass through.\textsuperscript{130,131} The photonic crystal structure opens the door of a variety of potential applications ranging from beam steering, optical gauge, and electro-optical communication devices to information storage media.\textsuperscript{132,260}

The general approach to fabricate H-PDLC is via photopolymerization-induced phase separation, which involves two beams reflected to the sample surface at a certain incident angle. By virtue of the constructive and destructive interference of the incoming waves, high intensity regions and low intensity regions are created in the sample.

Alternatively, four waves interference may be employed to generate multi-dimensional photonic structures. The pattern photopolymerization approach is advantageous in its ultra-fast processing, chemical versatility and reproducible results, making it a possible candidate for holographic applications.
10.3.1. Two-wave Interference Setup

The setup is shown schematically in Figure 10.2(a). It consists of a UV laser source of 365 nm wavelength with an output power of 100 mW/cm$^2$. The beam was first reflected by a mirror before entering a non-polarizing beam splitter. The use of the mirror helps in fine-tuning the beam position. The beam splitter splits the beam into two nearly equal intensity beams, which travel through different optical paths before impinging on the sample. Each optical path consists of a spatial filter arrangement to clean the beam and to generate a collinear wave front. The spatial filter consists of a microscope objective lens, to focus the beam to a spot, which then passes through a pinhole of 25 µm. The stray high frequency noise is reflected and the low frequency beam with most of the energy emerges out of the pinhole as a diverging beam, which is made parallel by using a plano-covex lens. The two beams were made to interfere on the sample by using mirrors, which controlled the angle of incidence thereby determining the spatial profile or periodicity. All the mirrors used in this experiment led to less than $\lambda/10$ path difference and the overall path difference between the beams was kept below the coherence length of the laser. The entire setup was built on a breadboard, which was placed on an optical bench with air suspension.

10.3.2. Four-wave Interference Setup

The four wave setup was used for developing three-dimensional photonic crystals. The setup consisted of four beams impinging on the sample from the top (Figure 10.2(b)). The beam pairs were normal to each other and to the sample plane with their polarizations in the same direction leading to a face centered cubic lattice. Since the
patterned grids are in nano size from the four-wave interference set up, alternative optics setup performed using an axicon which is a specialized type of lens having four sectioned triangles forming pyramid shape from the top view. An axicon images a point source into a line along the optic axis, or transforms a laser beam into grid in center and grafting at edges. The schematic diagram is given in the Figure 10.2(c).

Figure 10.1 Profiles of emerging polymer volume fraction vs distance at various time steps from a vertical slice of the microchannel layer patterns, $k = 0.0001$.\(^{16}\)
Figure 10.2 (a) Schematic diagram for UV set-up, (b) four-wave and two-wave set-up and (c) four-wave interference set up using an axicon.
10.4. Results and Discussions

Figure 10.3(a) shows the optical micrograph of a two-wave interference pattern formed in neat acrylate monomers (Tetra- and Pentaacrylate) after exposure to the UV laser 100 mW/cm\(^2\) power using an axicon for a period of 10 minutes at 55 °C. Figure 10.3(b) shows the optical micrograph of a four-wave interference pattern formed by in the same condition as Figure 10.3(a). The axicon produces the pattern which is given in the grid in the center and grafting at the edges by the optics alignment. In the case of diacrylate monomer, diacrylate syrup was less viscous than other monomers. After photo patterning, diacrylate patterns could melt away by uncured liquid. Since the tetra-and pentaacrylate have high viscosity, unreacted monomers were hard to diffuse. The 2D patterns by UV laser using axicon can be clearly observed in the higher number of acrylate arms. In Figure 10.3(c), the AFM image of tetraacrylate shows a near perfect grid patterns clearly visible as peaks and valleys being formed out of selective photo reaction by the laser beam passing through the axicon. The average size of these individual droplets (or peak-to-peak distance) is approximately 2-3 µm. As mentioned before, this pattern is formed by a single step process without any post processing done on the sample.

Figure 10.4 shows the optical microscopy images to investigate the effect of molecular weight on PEO/DA 10/90 blends (a) LM(M\(_n\)=5000), (b) IM(M\(_n\)=10500),(c) HM(M\(_n\)=52000) and (d) HMPD(M\(_w\)=66000,PDI=1.94) by four-wave photo patterning using an axicon under UV laser (100 mW/cm\(^2\)) irradiation at 55 °C for 10 min then quenching to the room temperature to observe the PEO crystal in the confined regions. As
the molecular weight of PEO increases in diacrylate monomers, the PEO crystal prefers to grow over the patterned grids. Since the patterns formed by laser beam passing through the axicon provide about 2 µm size grids, the high molecular weight PEO crystal is hard to distinguish because PEO crystal is approximately 20 µm thereby outgrowing the small sized patterns.

Figure 10.5 shows the optical microscopy images to investigate the effect of compositions on PEO/DA blend which has a PEO $M_n$ as 5000. In Figure 10.5 (a) 5/95, (b) 10/90, (c) 20/80 and (d) 30/70 are shown the patterned morphologies of various blends exhibiting confined growth of the PEO crystals. In the case of low molecular weight PEO in diacrylate, the PEO crystal is contained in the grid patterns. However, increasing the composition of PEO exhibits the domination of PEO crystals. Birnkrant and Li et al.\textsuperscript{261} researched the various molecular weights in crosslinkable Norland adhesives to photopatterning. This group used the glass prism to get the gratings of Norland 65 and PEG 2000. They observed the PEG layers which form a continuous layered structure with a lamellar spacing of ~200nm. This is unlike holographic polymer-dispersed liquid crystal systems which form droplets of 100-200nm in diameter confined within the polymer matrix. This unique morphology may be attributed to a slower phase separation process of PEG and Norland during polymerization as opposed to LC/Norland system. They did not observe the outgrowth of spherulites PEO crystal over the confined patterns. Instead PEG lamellae are formed within these regions. The range of molecular weight of PEO covered from 2000 to 8000. These phenomena support that the low molecular weight PEO is not eligible to produce the spherulite crystal in four-wave confined patterns.
Figure 10.6 and Figure 10.7 show the PEO(LM)/DA 10/90 and PEO(LM)/DA 30/70 which is photo-patterned by four-wave interference using an axicon under UV-100 mW/cm$^2$ power for 10 min at 55 °C for isotropic state then quenching to room temperature. From optical microscopy and SEM images confirm that the low molecular weight PEO crystal is contained within the grid patterns.

Figure 10.8 shows (a) optical microscopy image and (b) AFM images showing the PEO crystal overgrows the patterns of PEO(HM)/DA 10/90 by four-wave photo patterning. As molecular weight increases, the PEO crystal tends to outgrow the confined patterns due to fast crystallization process of PEO.

Figure 10.9 clearly shows that the optical and SEM pictures of PEO(HM)/DA 20/80 by four-wave photo patterning using an axicon under UV laser (100 mW/cm$^2$) irradiation at 55 °C for 10 min then quenching to room temperature tends to show that the PEO crystal dominated in the confined grid pattern. As evidenced by (a) optical microscopy image and (b) enlarged SEM image, the PEO crystal outgrows the patterns.

As depicted in Figure 10.10, the PEO(HM)/DA 20/80 reveals PEO crystal in the form of spherulite outgrowing the grid patterns. When the sample was heated then cooled to distinguish the PEO crystal from the patterns, the PEO spherulite once melted away then came back when the sample cooled to 25 °C. As pointed out, the high molecular weight of PEO in diacrylate has a tendency of outgrowing the patterns by formed four-wave interference.

The driving force of phase separation in the blends containing a higher weight molecular of PEO leads to larger PEO crystals. To overcome this problem, the PEO was mixed with a tetraacrylate, which can undergo network formation to contain the PEO
molecules. Figure 10.11 shows the optical microscopy images of PEO(HM)/Tetraacrylate 10/90 formed by four-wave photo patterning. The overgrowing PEO crystals observed in (a) parallel mode coexisted with the grid pattern (b) cross polarized image showing the PEO crystals.

The confined areas formed by photopatterning technique restricted the growth of PEO crystal in the case of low molecular weight. However, high molecular weight PEO crystals can outgrow the patterned area after quenching to room temperature.

10.5. Conclusions

Gratings and grids were formed in neat acrylate monomers by four-wave interference holography using axicon. The patterns formed were characterized by optical microscope (OM) and Scanning electron microscope (SEM) and atomic force microscope (AFM). The grids formed showed ideal periodicity and surface contrast. The holography setup allows the micron size channels by using axicon and nano size periodicity by wave interference without major modifications. Grid patterns showing PEO crystal formation were realized in monomer PEO by four-wave interference holography. The confined areas created by photopatterning techniques restricted the growth of PEO crystal in the case of low molecular weight PEO. However, the high molecular weight PEO crystals tended to outgrow the patterned area after quenching to room temperature. In the case of low molecular weight of PEO in diacrylate, the PEO crystal is trapped in the confined region due to the slow crystal growth unlike the case of high molecular weight of PEO. These 3D-patterns which contain the PEO crystals can be used for many interesting, novel applications. For example, functional modification of acrylate monomer in the
patterned template can lead to thermally switchable or membranes. Overall, the technique of holographic interference provides a fast, easy, and economical route to produce micro-sub micron scale patterns with potential diverse applications.
Figure 10.3 Optical microscopy images of neat acrylate monomers which were photo patterned using an axicon under UV laser (100 mW/cm²) irradiation at 55 °C for 10 min. (a) two-wave (1-D pattern) at edges, (b) four-wave (2-D) in the center. (c) AFM image followed by the enlarged the patterns of neat tetraacrylate.
Figure 10.4 The optical microscopy images to investigate the effect of molecular weight on PEO/DA 10/90 blends (a) PEO(LM), (b) PEO(IM), (c) PEO(HM) and (d) PEO(HMPD) by four-wave photo patterning using an axicon under UV laser (100 mW/cm²) irradiation at 55 °C for 10 min then quenching to the room temperature to observe the PEO crystal in the confined regions.
Figure 10.5 The optical microscopy images to investigate the effect of compositions on PEO(LM)/DA 10/90 blend, which has a $M_n$ of PEO as 5000. (a) 5/95, (b) 10/90, (c) 20/80 and (d) 30/70 by four-wave photo patterning using an axicon under UV laser (100 mW/cm$^2$) irradiation at 55 °C for 10 min then quenching to the room temperature to observe the PEO crystal in the confined regions.
Figure 10.6 PEO(LM)/DA 10/90 by four-wave photo patterning using an axicon under UV laser (100 mW/cm²) irradiation at 55 °C for 10min then quenching to room temperature to observe the PEO crystal in the confined regions examined by (a) optical microscopy image, (b) SEM image and (c) enlarged section from (b).
Figure 10.7 PEO(LM)/DA 30/70 by four-wave photo patterning using an axicon under UV laser (100 mW/cm²) irradiation at 55 °C for 10min then quenching to room temperature to observe the PEO crystal in the confined regions. (a) is the optical microscopy image. (b) and (c) are the enlarged SEM images showing the PEO crystal confined in the patterns.
Figure 10.8 PEO(HM)/DA 10/90 by four-wave photo patterning using an axicon under the UV laser (100 mW/cm²) irradiation at 55 °C for 10min then quenching to room temperature examined by (a) optical microscopy image and (b) AFM images showing the PEO crystal overgrows the patterns.

Figure 10.9 PEO(HM)/DA 20/80 by four-wave photo patterning using an axicon under UV laser (100 mW/cm²) irradiation at 55 °C for 10min then quenching to room temperature examined by (a) optical microscopy image, (b) followed enlarged SEM image showing the PEO crystal overgrows the patterns.
Figure 10.10 PEO(HM)/DA 20/80 by four -wave photo patterning using an axicon under UV laser (100 mW/cm²) irradiation at 55 °C for 10min then slow cooling to room temperature. The sample was heated at 1 °C/min then cooled 1 °C/min to distinguish the PEO crystal from the patterns. The overgrowing PEO crystal once melted away then came back when the sample cooled to 25 °C.
Figure 10.11 PEO(HM)/Tetraacrylate 10/90 by four-wave photo patterning using an axicon under the UV laser (100 mW/cm²) irradiation at 55 °C for 10 min then quenching to room temperature. The overgrowing PEO crystal observed in (a) parallel mode coexisted with grid pattern (b) cross polarized image shows the PEO crystals.
11.1. Concluding Remarks

In this dissertation, detailed investigations of phase diagram and photopolymerization-induced phase separation or crystallization dynamics of multifunctional acrylate(s)/PEO mixtures have been presented. In Chapters IV, V and VI, the phase diagrams before polymerization were obtained for polydisperse PEO and multifunctional acrylate(s) systems, viz., crystalline-amorphous and crystalline-crystalline blends along with the morphology investigation. Furthermore, the effects of PEO molecular weight and acrylate arm topologies on the phase diagrams were studied. The phase diagrams of multi-functional acrylate(s)/PEO were displayed isotropic liquid, isotropic liquid+ crystal coexisted regions, single crystal and crystal (PEO)+crystal (diacrylate). The phase diagrams moved upward as functionality of acrylates increased in the case of low molecular weight of PEO due to the solubility effect. However, the functionality exerts little or no effect on the phase diagram once the PEO molecular weight reaches a certain level. In the morphological point of view, the distinguishing of
phase regions in each composition with various molecular weights of PEO and multifunctional acrylate(s) is critical for verification, which has been demonstrated in Chapter IV and V.

In Chapter VII, the kinetics of photopolymerization and the influence of several parameters (functionality, temperature, intensity, photoinitiator amount and PEO concentration) were investigated by using PDSC and FTIR techniques. The lumped kinetic constant \( k \) drastically decreased as PEO content increased. PEO molecules seemingly act as obstacles, thereby changing the amount of light absorbed by the photoinitiator due to the light scattering effect. From these photopolymerization kinetics studies, the optimum condition was guided for the photopolymerization-induced crystallization or phase separation.

In Chapter VIII and IX, snapshot phase diagrams during and/or after UV irradiation were established for the multi-functional acrylate(s)/PEO mixtures. Morphology development of these systems was probed by means of optical microscopy to elucidate photopolymerization-induced crystallization or phase separation at given temperatures which is higher than melting points of original PEO/multi-functional acrylate(s) blend before any photo curing. The present study also explored various directionally solidified interface morphologies of polymer crystals subjected to a photointensity gradient.

Finally, with the guidance of phase diagram, several compositions of multifunctional acrylate/ PEO mixtures were studied for the photopatterning techniques. The holography setup allows the micron size channels by using axicon and nano size periodicity by wave interference. The confined areas created by photopatterning technique restricted the growth of PEO crystal in the case of low molecular weight. However, the high molecular
weight PEO crystals tend to out grow the patterned area after quenching to room temperature. In the case of low molecular weight of PEO in diacrylate, the PEO crystal is trapped in the confined region due to the slow crystal growth unlike the high molecular weight of PEO. These 3D-patterns which contain the PEO crystals can be used for many interesting, novel applications.

11.2. Recommendations

There have been a very large number of studies on the phase behavior of LC/monomer systems in photopolymerization induced phase separation. This work represents the first detailed study in photopolymerization induced crystallization. The spontaneous and simple method investigated in this study is recommended as one of the most effective candidates for the crystalline behavior and application in polymer blends during photopolymerization. The in-situ morphology development of photopolymerization-induced crystallization in the PEO/multi-functional acrylate(s) mixtures was also monitored for the first time. The results of this investigation should have substantial benefits and potential to be utilized as a basis in many areas such as nanostructure membranes, nanotemplates, photonic crystals, thermal swither and high-density information storage media owing to its thermal sensitivity and molecular weight dependency of highly ordered patterns.

Patterning with the laser interference in PEO/acrylate monomer mixtures using selective curing in nanostructures as templates in this way opens the door for future works
towards a variety of nanotechnological applications. To perform in-situ monitoring of the crystal morphology during the photo patterning, it is recommended that an optical microscope or AFM should be hooked up on the laser interference set up for interesting nanotechnology study in the future.


90. T. Scherzer and U. Decker, *Kinetic investigations on the UV-induced photopolymerization of a diacrylate by time-resolved FTIR spectroscopy: the


