MOLECULAR COMPLEXATION AND PHASE DIAGRAMS OF
UREA/POLYETHYLENE GLYCOL MIXTURES

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MOLECULAR COMPLEXATION AND PHASE DIAGRAMS OF
UREA/POLYETHYLENE GLYCOL MIXTURES

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ABSTRACT

Polyethylene glycol (PEG) is a common polymer that is widely used in food and pharmaceutical industries, whereas urea is an organic molecule that is abundant in human body. As PEG can easily enter the body by food digestions, there is a possibility of PEG/urea complexation resulting in stable crystal formation, which might raise some health concerns such as kidney or urinary stones. Therefore, it is of paramount importance to understand the phase behaviors and the mechanisms of formation of stable compounds of the PEG/urea complexes.

In this study, detailed investigations on phase diagrams of various molecular weights PEG/urea mixtures have been presented. Different characterization techniques (Differential Scanning Calorimetry, Polarized Optical Microscope, and Fourier Transform Infrared Spectroscopy) were utilized to determine the phase transitions such as the crystal-liquid and crystal-crystal transition. Various coexistence regions involving induced crystalline phases were investigated by Wide angle X-ray diffraction, FTIR and POM. Phase diagrams of each PEG/urea system were calculated by self-consistently solving the combined free energy of Flory-Huggins for liquid-liquid separation and the phase field free energy for crystal solidification. It was found that the blends of varying molecular weight PEG (8k,1k and 400) with urea show different types of phase diagrams. The phase diagram of PEG8k/urea is a
combination of azeotrope and eutectoid reactions, covering the metastable submerged phases such as induced $\alpha$ phase and metastable $\beta$ phase. However, the phase diagram of PEG1k/urea is of peritectic type, whereas PEG400/urea exhibits eutectic character. Of particular interest is that only very small urea amount (2 wt%) is needed to form stable $\alpha$ inclusion crystal via complexation with PEG. If such crystals form in blood stream, it may be of health concern, especially diabetes patients. However, such a risk may be alleviated by drinking a lot of water, because the $\alpha$ crystal is water soluble and is expected to dissolve in body serum.
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TABLE OF CONTENTS

LIST OF FIGURES........................................................................................................... ix

CHAPTER

I. INTRODUCTION.......................................................................................................... 1

II BACKGOUND AND LITERATURE SURVEY ............................................................ 3

2.1 Thermodynamics of Polymer Blends .................................................................... 3

2.2 Kinetics of Phase Separation ............................................................................... 10

2.2.1 Nucleation and Growth (NG) ........................................................................ 10

2.2.2 Spinodal Decomposition (SD) ........................................................................ 11

2.3 Crystallization of Polymer Blends ........................................................................ 12

2.3.1 The Mechanism in Polymer Crystallization ................................................... 12

2.3.1.1 Kinetics of Nucleation .......................................................................... 12

2.3.1.2 Kinetics of Crystal Growth .................................................................... 14

2.3.2 Crystallization in polymer blends ................................................................. 20

2.3.3 Phase Diagrams of Binary Crystalline Polymer Blends ................................ 21

2.3.3.1 Phase Field Model of Crystallization to a Homopolymer .................. 21

2.3.3.2 Phase Field Model of Crystallization to Polymer Blends ............... 23

2.4 Overview of PEG/Urea system ............................................................................ 27

III MATERIALS AND EXPERIMENTAL TECHNIQUES ...................................... 31
3.1 Material ................................................................................................................... 31
  3.1.1 Polyethylene glycol (PEG) ................................................................. 31
  3.1.2 Urea ................................................................................................. 33

3.2 Samples Preparation ............................................................................................. 35

3.3 Samples Characterization ..................................................................................... 35
  3.3.1 Differential Scanning Calorimetry (DSC) ........................................... 35
  3.3.2 Polarized Optical Microscope (POM) ........................................... 36
  3.3.3 Thermogravimetric Analysis (TGA) ........................................... 36
  3.3.4 Fourier Transform Infrared Spectroscopy (FTIR) ................................ 37
  3.3.5 Wide angle X-ray diffraction (WAXD) ........................................... 37

IV. MISCIBILITY CHARACTERIZATION, PHASE DIAGRAM AND
MORPHOLOGY DEVELOPMENT IN HIGH MOLECULAR WEIGHT
PEG/UREA BLENDS ............................................................................................ 38
  4.1 Introduction ................................................................................................... 38
  4.2 Experiment Section ...................................................................................... 40
  4.3 Results and discussion ............................................................................... 41
  4.4 Conclusions .............................................................................................. 59

V. PHASE DIAGRAM OF LOW MOLECULAR WEIGHT PEG/UREA BLENDS
............................................................................................................................ 61
  5.1 Introduction ............................................................................................... 61
  5.2 Experiment Section ..................................................................................... 62
  5.3 Results and Discussion ............................................................................. 63
  5.4 Conclusions ............................................................................................ 77
VI. EFFECTS OF POLYMER MOLECULAR WEIGHT ON PHASE DIAGRAM AND MORPHOLOGY DEVELOPMENT IN BLENDS OF PEG/UREA SYSTEMS ................................................................................................................. 79

6.1 Introduction ......................................................................................................... 79

6.2 Experiment Section ............................................................................................. 80

6.3 Results and discussion ....................................................................................... 81

6.4 Conclusions ......................................................................................................... 94

VII. SUMMARY .......................................................................................................... 95

REFERENCES ........................................................................................................... 97
<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Schematic relation between phase stability and free energy of mixing in polymer blends</td>
<td>8</td>
</tr>
<tr>
<td>2.2 Schematic representation of typical phase diagrams in polymer blends</td>
<td>9</td>
</tr>
<tr>
<td>2.3 Dependence of free energy ($\Delta G$) on nucleus size (R)</td>
<td>13</td>
</tr>
<tr>
<td>2.4 Schematic phase diagram of a crystalline-amorphous polymer blend</td>
<td>18</td>
</tr>
<tr>
<td>2.5 The variation of free energy of crystallization as a function of crystal order parameter, $\psi$ of a pure homopolymer</td>
<td>23</td>
</tr>
<tr>
<td>2.6 Phase diagrams dependence on anisotropic interaction parameter $c_\omega$ (a) ideal crystal solution, $c_\omega=1$; (b) eutectic in solid solution, $c_\omega&lt;1$; (c) azeotrope in solid solution $c_\omega&gt;1$.</td>
<td>27</td>
</tr>
<tr>
<td>2.7 Schematic structure of inclusion compounds</td>
<td>30</td>
</tr>
<tr>
<td>3.1 Chemical structures of (a) polyethylene glycol and (b) urea</td>
<td>34</td>
</tr>
<tr>
<td>4.1 DSC thermograms of 70/30 PEG8k/urea blends at various heating rates (a) DSC curves (b) melting point depression</td>
<td>42</td>
</tr>
<tr>
<td>4.2 DSC thermograms of PEG8k/urea obtained at a heating rate of 2°C/min</td>
<td>43</td>
</tr>
<tr>
<td>4.3 (a) DSC thermogram of PEG8k/urea blends (I) 23/77; (II) 25/75; (III) 28/72 (b) I: first heating curve of 52.5%; II: second heating curve of 52.5%</td>
<td>44</td>
</tr>
<tr>
<td>4.4 Optical micrographs showing the morphologies of 60/40 PEG8k/urea blends as a function of temperature</td>
<td>48</td>
</tr>
<tr>
<td>4.5 WAXD 2θ-scans of PEG8k/urea mixture at various compositions</td>
<td>49</td>
</tr>
<tr>
<td>4.6 FTIR spectra of PEG1k,urea, 60/40 PEG8k/urea acquired at 105°C</td>
<td>52</td>
</tr>
</tbody>
</table>
4.7 (a) FTIR spectra of 60/40 PEG8k/urea mixture as a function of temperature
   (b) FTIR spectra of 80/20 and 40/60 PEG1k/urea mixtures at various temperatures

4.8 Temperature vs. composition phase diagram of PEG8k/urea blends. The solid line was calculated based on the phase field model of crystal solidification, but the dish line was drawn by hand. Two vertical dish lines were corresponding to the molar ratio of α and β corresponding

5.1 TGA therograms of two different molecular weight PEG

5.2 (a) DSC thermograms of PEG400/urea blends with a heating rate of 2°C/min
   (b) Plots of melting points vs. composition of PEG400/urea blend

5.3 (a) Time-evolution of crystal morphology of 10/90 PEG400/urea blends at an isothermal temperature of 100°C
   (b) Time-evolution of crystal morphology of 90/10 PEG400/urea blends at an isothermal temperature of -10°C

5.4 Optical micrographs showing morphology variations of PEG400/urea blends at various temperature
   (a) PEG400/urea 30/70 at 30°C and 100°C
   (b) PEG400/urea 70/30 at 70°C and 100°C

5.5 WAXD 2θ scans of PEG400/urea mixture at various composition

5.6 FTIR spectra of 65/35 PEG8k/urea mixture at various temperatures in comparison with neat PEG400 and urea at room temperature

5.7 Temperature vs. composition phase diagram of PEG400/urea blends. (a) The calculated phase diagram based on combined free energies F-H theory and the phase field model of crystal solidification assuming the binary mixture a crystal and urea crystals (b) Complete phase diagram, the dish line was drawn by hand based on the experimental results and phase rules

6.1 (a) TGA therograms of various molecular weight PEGs
   (b) DSC therograms of various molecular weight PEGs and urea

6.2 (a) DSC thermograms of PEG1k/urea blends with a heating rate of 2°C/min
   (b) Plots of melting points of PEG1k/urea blends

6.3 WAXD 2θ scans of PEG1k/urea mixture at various compositions
6.4 FTIR spectra of urea and PEG1k/urea mixture at various compositions ............... 88

6.5 Temperature vs. composition phase diagram of PEG1k/urea blends. (a) The calculated phase diagram based on the phase field model of crystal solidification (b) Completed phase diagram, the dish line was drawn by hand based the experimental results and phase rules ................................................................. 89

6.6 Comparison among calculated phase diagrams of various molecular weight PEG/urea blends.(a) PEG400/urea (b)PEG1k/urea (c)PEG8k/urea ......................... 93
Polyethylene glycol (PEG) is a very common polymer that is widely used in food and pharmaceutical industries, and urea is an organic molecule that is abundant in human body. When PEG enter the body by food digestions, there is a possibility of PEG/urea complexation resulting in stable crystal formation, which might cause some health problems, like kidney stones. Therefore, it is important to understand the phase behavior and the mechanisms of formation of stable compounds of the PEG/urea complexes.

Both PEG and urea are crystalline material and it is well documented that the molecular complexation of PEG/urea mixture tends to form a stable compound, called $\alpha$ crystal,\textsuperscript{1,2} due to the strong specific interaction. $\alpha$ crystal is a kind of inclusion compound that is very stable due to the inter-species hydrogen-bonding. There is another $\beta$ compound formed in PEG/urea mixture at a lower temperature. The $\beta$ compound is metastable and can transform to $\alpha$ compound under certain thermal conditions.

In literature, there is a disagreement on the formation of $\beta$ crystal. Pellerin et al. reported that the metastable $\beta$ crystal formed in the blends of PEO/urea that transformed to the stable $\alpha$ phase upon increasing temperature above 90°C.\textsuperscript{3} However,
Guenet et al, who investigated the phase behavior of PEG/urea mixtures, were unable to confirm the $\beta$ crystal and thus their phase diagram is at variance with that of Pellerin et al. This is the source of our motivation to investigate the effect of molecular weight of PEG on the phase diagrams of its blends with urea.

To describe phase diagrams of crystalline polymer blends, Matkar and Kyu modified the free energies of Flory-Huggins free energy for amorphous-amorphous isotropic mixing by combining it with the Landau-type free energy of crystal solidification. This thesis employs this combined Flory-Huggins and phase field model to calculate the phase diagrams of various molecular weight PEG/urea blends.

The present thesis is organized as follows. Chapter I gives a brief introduction and objectives of the completed research. Chapter II contains the fundamental knowledge and background to conduct the research. Chapter III describes experimental material and methods used in this work. Chapter IV reveals the phase diagram and morphology for binary crystalline blends a high molecular weight PEG8k/urea mixture. Chapter V demonstrates the phase diagram of a low molecular weight PEG400/urea mixture. Chapter VI investigate the phase diagram of intermediate molecular weight PEG1k/urea blend. Finally, the phase diagrams of three different molecular weights PEG/urea blends were compared. Chapter VII serves as the summary of this thesis.
2.1 Thermodynamics of Polymer Blends

Polymer blends consisting of dissimilar polymers have gained increasingly attention due to their multiple usages which can solve the design problems as well as reduce the production cost. Typically, different polymers can be combined into a single material in a number of ways. The miscibility of polymer blends can lead to a wide range of phase behaviors that directly influence the associated physical properties and ultimate applications.\(^5\) The phase behaviors or the miscibility between different polymer components is the key factor in polymer blends because polymer blends systems have partial or incomplete miscibility under most conditions.\(^6\)

In order to determine or predict the blend miscibility, the thermodynamic principle is required. Flory and Huggins independently developed their thermodynamic approaches and reached the same theoretical expression, known as Flory-Huggins theory.\(^7\text{--}^{10}\) The effect of thermodynamic parameters, like Flory-Huggins interaction parameter, on the binary phase diagrams has been investigated by many researchers.\(^11\text{--}^{16}\) The properties of the blending materials depend on the phase behaviors between the constituents, which are primarily governed by the
thermodynamic variables (temperature, pressure, number of statistical segments or molecular weight and its distribution, etc.).

The stability of polymer blend under constant temperature $T$ and pressure $P$ can be expressed by the Gibbs free energy of mixing, $\Delta G_m$. The thermodynamic criterion for stable homogenous mixture are as follows:

(i) the Gibbs free energy of mixing is negative;

(ii) the second derivative of the Gibbs free energy with respect to composition should be positive.

which means:

$$\Delta G_m < 0 \quad (2.1)$$

and

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right) > 0 \quad (2.2)$$

where $\phi_i$ is the volume fraction of either component.

The Gibbs free energy of mixing, $\Delta G_m$, can be defined as

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.3)$$

where $\Delta H_m$ and $\Delta S_m$ is the enthalpy and entropy of mixing and $T$ is the absolute temperature. Based on equation (2.3) Flory and Huggins developed the free energy of mixing for polymer mixture independently in 1942, but obtain the same theoretical expression. \cite{20,21}
According to the Flory-Huggins theory, the entropy of mixing, $\Delta S_m$, is expressed in the terms of volume fraction of each component as

$$\Delta S_m = -k_B(N_1 \ln \phi_1 + N_2 \ln \phi_2)$$  \hspace{1cm} (2.4)

where $k_B$ is the Boltzman constant, $N_i$ is the number of molecules of component ‘$i$’. The volume fraction ‘$i$’ can be defined as the number of each polymer-occupied lattice, which is equal to the chain length, $r_i$

$$\phi_i = \frac{N_i r_i}{N_i r_i + N_j r_j}, \quad i \neq j$$  \hspace{1cm} (2.5)

Therefore, the entropy of mixing in the incompressible system can be expressed in the term of volume fraction (i.e., $\phi_1 + \phi_2 = 1$) as

$$\Delta S_m = -N k_B \left( \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right)$$  \hspace{1cm} (2.6)

The enthalpy of mixing, $\Delta H_m$, can be expressed as:

$$\Delta H_m = N k_B T \chi_{FH} \phi_1 \phi_2$$  \hspace{1cm} (2.7)

Combined with equations (2.6) and (2.7), equation (2.3) can be rewrite as

$$\frac{\Delta G_m}{N k_B T} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi_{FH} \phi_1 \phi_2$$  \hspace{1cm} (2.8)

where $\chi_{FH}$ is Flory-Huggins interaction parameter that represents the interaction between polymer and solvent. Typically $\chi_{FH}$ reciprocal depends on absolute temperature

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^2$$  \hspace{1cm} (2.9)

Because of the assumption in Flory-Huggins theory that no volume change in mixing, $V_1$ is the lattice size that is defined by the solvent size. $\delta_1$ is the solubility parameter.
of each constituent. However, when the predicted value of $\chi$ is less than 0.3, the solubility method does not work well. In this case, an empirical equation is modified to

$$\chi = 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2$$  \hspace{1cm} (2.10)

Note that equations (2.9) and (2.10) are incapable of predicting on LCST (lower critical solution temperature) phase diagram, and thus the $\chi$-$T$ relation is further modified to an empirical form\textsuperscript{23}

$$\chi = A + \frac{B}{T}$$  \hspace{1cm} (2.11)

where $A$ and $B$ are constants. Experimentally $\chi$ depends not only on temperature, but also composition and microstructure.\textsuperscript{10,25,26}

From equation (2.8), it is apparent that the sign of $\chi$ determines the sign of $\Delta G_m$. If $\chi$ is negative, all the three terms on the right side of the equation are negative. In this case the polymer system is miscible at all compositions and temperature. For a positive $\chi$, the miscibility is not favored at all temperature.

Based on the Gibbs free energy of mixing, the phase diagram can be constructed. Figure 2.1(a) shows the variation of free energy of blends with composition at certain temperature $T_0$. Figure 2.1(b) is the phase diagram measured as a function of composition and temperature.

For a binary system in equilibrium, the chemical potentials of each component in two phase must be equal. From figure 2.1 the two points $\alpha$ and $\beta$ represent two phase coexist in equilibrium state,

$$\mu_1^\alpha = \mu_1^\beta$$  \hspace{1cm} (2.12)
\[ \mu_2^a = \mu_2^\beta \]  \hspace{1cm} (2.13)

where the superscripts denote the two equilibrium phases.

Solving equations (2.12) and (2.13) at a given temperature, the binodal curve can be obtained. Similarly, the spinodal curve can be calculated by the second partial derivatives of the Gibbs free energy of mixing

\[ \frac{\partial^2 G}{\partial \phi^2} = 0 \]  \hspace{1cm} (2.14)

The region between binodal curve and spinodal curve is the metastable area whereby the mixture is stable to small concentration fluctuation, but unstable against large fluctuation. The region under the spinodal is the unstable region where any fluctuation can cause a decrease of free energy.

The binodal curve and spinodal curve meet at the critical point which is determined by the third order partial derivatives of the Gibbs free energy of mixing

\[ \frac{\partial^3 G}{\partial \phi^3} = 0 \]  \hspace{1cm} (2.15)

Using equations (2.12), (2.13), (2.14) and (2.15), the critical volume fraction \( \phi_c \) and critical interaction parameter \( \chi_c \) can be calculated as follows:

\[ \phi_c = \frac{\sqrt{r_2}}{\sqrt{r_1} + \sqrt{r_2}} \]  \hspace{1cm} (2.16)

\[ \chi_c = \frac{(\sqrt{r_1} + \sqrt{r_2})^2}{2r_1r_2} \]  \hspace{1cm} (2.17)

Figure 2.2 displays several types of phase diagram based on the theory. Figure A represents the completely miscible system. Figure B and C are most common types of phase diagrams, upper critical solution temperature (UCST) and lower critical solution temperature (LCST). Figure D is the closed loop. Figure E is the combined UCST and LCST.
Figure 2.1 Schematic relation between phase stability and free energy of mixing in polymer blends
Figure 2.2 Schematic representation of typical phase diagrams in polymer blends
2.2 Kinetics of Phase Separation

Phase separation takes place via two different mechanisms.\textsuperscript{25} One is the nucleation and growth (NG)\textsuperscript{27} and the other is the spinodal decomposition (SD).\textsuperscript{28}

2.2.1 Nucleation and Growth (NG)

The nucleation and growth mechanism usually happens in the liquid-solid transition, liquid-vapor transition and crystallization. In metastable region, the mixture is stable to the infinitesimal fluctuations. The system need excess energy to overcome certain energy barrier, therefore a finite fluctuation is necessary to obtain a phase transition. Nucleation and Growth refers to the process that the new phase starts as a small nuclei and then grows and extends.

The activation energy of the NG process can be expressed as

\[
\Delta G^* = -\frac{4}{3} \pi r^3 \Delta G_t + \pi D^2 \sigma
\]  

(2.18)

where the first term is the free energy contribution of the volume created by the nuclei which represents the stage that the concentration fluctuations produce the new nuclei phase; Second term is the free energy contribution of the interface between the nuclei and the mother phase which represents the coalescence process. $\Delta G_t$ is the free energy difference between the nuclei and mother phase. $\sigma$ is the interfacial energy per unit area. $D$ is the average diameter of the nuclei. Based on the Lifshitz-Slyozov-Wagner asymptotic law\textsuperscript{29}, $D$ can be expressed as:

\[
D^3 - D_0^3 = \gamma (t - t_0)
\]  

(2.19)

where $D_0$ is the diameter of the particle at initial and $\gamma$ is the rate constant.
2.2.2 Spinodal Decomposition (SD)

The spinodal decomposition (SD) plays a major role in the second order phase transition in metal alloys and phase separation of polymer blends which has been well studied by Cahn.\textsuperscript{30–34}

In SD, Cahn considered the decomposition process as a pure diffusion process. The diffusion which results spontaneously from the chemical potential gradient is to reduce the free energy. Also, the SD can occur at infinitesimal concentration fluctuations without requiring any activation energy.

The initial stages of phase separation can be described by the Cahn-Hilliard diffusion equation

\[
\frac{\partial c}{\partial t} = D \nabla^2 (c^3 - c - \gamma \nabla^2 c)
\]  \hspace{1cm} (2.20)

where D is the diffusion coefficient, \( \sqrt{\gamma} \) is the length of the transition regions between the domains. The equation describes the process of phase separation, by which two components of a binary mixture spontaneously separate and form pure domains in each component.\textsuperscript{30} Then the phase boundary is initially diffused, but it becomes sharp, which resulting in the formation of interconnected morphology. The difference between SD and NG is the composition of the domains. In SD, both size and composition depend on time as it is a diffusion process and in NG the composition for each domain is constant only the size and size distribution of the nuclei depend on time.
2.3 Crystallization of Polymer Blends

2.3.1 The Mechanism in Polymer Crystallization

Crystallization is the process of formation of solid crystals precipitating from dilute solution or melt. Under rare circumstances, crystals can be deposited directly from a gas.\(^{35}\) For polymer, crystallization can occur from mechanical stretching besides cooling from the melt or solvent evaporation. Generally, the crystallinity in polymer enhance mechanical strength, resistance to degradation and barrier performance.\(^{22}\)

Crystallization is a non-equilibrium phase transition process which is a first-order phase transition. Crystallization proceeds by the mechanism of nucleation and growth, that is, nuclei of new crystal phase appear and then grow in size by incorporation of more chains from the surrounding amorphous melt.

2.3.1.1 Kinetics of Nucleation

Polymer crystallization starts with the primary nucleation which can be defined as appearance of small amounts of crystalline phase that are sufficiently large to become stable. There are three physical mechanisms in nucleation: spontaneous homogeneous nucleation which occurs in a supersonic cooled homogeneous melt orientation induced nucleation, and heterogeneous nucleation on surface of a foreign phase such as nucleating agent and residual catalyst.\(^{36}\)

In order to form stable nuclei, the free energy barrier to crystallization needs to be overcome. Recalling the discussion of NG in section 2.2.1, the free energy of spherical droplet with radius \(R\), \(\Delta G\), can be written as the sum of a surface term and a
Figure 2.3 Dependence of free energy ($\Delta G$) on nucleus size (R)
volume term (see Equation 2.18):

\[ \Delta G(R) = -\frac{4}{3} \pi r^3 \Delta G_V + \pi D^2 \sigma \]  \hspace{1cm} (2.21)

where \( \sigma \) is the surface energy and \( \Delta G_V \) is the free energy change per unit volume which is negative when \( T < T_m \). Figure 2.3 illustrates the variation of free energy with nucleus size based on equation (2.21). The critical nucleus \( R^* \) can be obtained, when \( \Delta G \) reaches the maximum positive value. In order to form a new phase, the radius of nuclei needs to grow larger than \( R^* \), and thus decreasing the free energy during further growth. Also, the growth is spontaneous once the nuclei exceeds the critical nucleus. Based on equation (2.21), the expression for \( R^* \) and \( \Delta G^* \) can be shown:

\[ R^* = -\frac{2\gamma}{\Delta G_V} \] \hspace{1cm} (2.22)

\[ \Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta G_V^2} \] \hspace{1cm} (2.23)

The \( \Delta G_V \) can be substituted with a term involving the enthalpy of fusion and the super cooling:

\[ \Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta H_V} \left( \frac{T_m^0}{T_m} \right)^2 \] \hspace{1cm} (2.24)

2.3.1.2 Kinetics of Crystal Growth

Crystal growth is achieved by the further addition of folded polymer chain segments. After realizing the ‘equilibrium theory’\(^{37} \), which does not include the folding mechanisms, Price, Lauritzen and Hoffmen developed the kinetic approach to describe the process of crystal growth.\(^{38,39}\) The kinetic theory assumes the growing phase has a variation of thickness correlating to the growth rate and supercooling rate.
According to Hoffman’s theory\textsuperscript{40}, the growth rate can be expressed as follow:

\[ I = N_0 \exp \left( \frac{-E_d}{RT} - \frac{\Delta G^*}{RT} \right) \]  \hspace{1cm} (2.25)

where \( N_0 \) is the number of molecules in a unit volume of the liquid. \( E_d \) is the activation free energy for diffusion of chain segments to the phase boundary.

### 2.3.2 Crystallization in polymer blends

Compared to the crystallization in homopolymer (or pure polymer), the crystallization in polymer blends is more complex in many ways. The crystalline and amorphous (solvent) components can be miscible or immiscible, even immiscible in the melt. A second species may modify the crystallization process in several different ways. Based on how to combine the influence of melt or crystallization of the crystal component with the phase separation behaviors in the polymer blends, the theory or model of the crystallization in polymer blends do not agree with each other.\textsuperscript{41–44}

For the crystallizable polymer blends, the presence of a miscible amorphous component can alter the crystallization behavior of the crystalline component. This behavior was interpreted in terms of kinetic theory of crystallization, and have been modified for the composition of the blends and the variations in glass transition temperature.

Two kinds of phase separations in semicrystalline polymer blends exist: liquid-liquid phase separation due to the immiscibility of amorphous phases and solid-liquid phase separation due to crystallization of the crystallizable components.
In the case that one or both components of polymer blends are crystalline, there can be mutual interference of phase separation and crystallization. Tanaka and Nishi are the first to indicate the possibility that the phase separation process is coupled with crystallization. These types of coupling between nonequilibrium phenomena have been studied from neither the theoretical nor the experimental viewpoint before. The phase diagram of a crystalline and amorphous polymer is shown in Figure 2.4

Strictly, a binodal line cannot be defined below the melting curve in an equilibrium phase diagram. However, various phase structures are formed in reality by the competition between two nonequilibrium processes. In literature the melting curve and the binodal and spinodal lines are expressed independently. When two or more nonequilibrium phenomena take places simultaneously, the final phases strongly depend on their dynamics and cannot be determined by an equilibrium phase diagram. When the system is quenched from the isotropic region to a crystallization temperature, four regions can be specified:

Region A: The crystallization and spinodal decomposition phase separation processes take place simultaneously.

Region B: The crystallization and NG-type phase separation processes take place and a droplet-like structure will appear.
Region C: The crystallization can induce phase separation because the amorphous polymer is removed by crystallization and regions whose composition is within the binodal line are formed.

Region D: The phase separation at $T > T_m$ can induce crystallization because it forms a crystalline polymer-rich region where the melting point at the composition is higher than $T$. The final structures under this process are grouped into several types by the relationship between the degree of undercooling for crystallization $\Delta T_m = T_m - T_c$ and the depth of the quench into the ordered two-phase state $\Delta T_p = T_p - T_c$; $T_p$ is the phase separation temperature. When the crystallization process is faster than the phase separation process, the scale of the crystal 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 scale of the macroscopic phase separation is larger than the radius of the spherulite.
Figure 2.4 Schematic phase diagram of a crystalline-amorphous polymer blend
Tanaka and Nishi discussed the case A and C for a binary mixture of poly(ε-caprolactone) (PCL) and polystyrene (PS). In case A, the coarse spherulite result includes PS droplet, while in case C the spherulite are separated and show large droplets on its surface. Also a nonlinear growth of spherulite and a shape instability have been found in this system. Li, Stein and Jungnickel kept on investigating the PCL/PS binary system. They suggested that demixing-induced crystallization as well as crystallization-induced demixing can occur depending on the composition of the blend and on the relative position of the crystallization curve and the miscibility gap in the phase diagram. Also, these two kinds interaction of phase transition can affect the growth rates of adjacent spherulite. This results in anisotropic concentration distribution or phase-separation morphology around their surfaces.

Briber and Khoury investigated the system of poly(vinylidene fluoride) and poly(ethyl-acrylate). They used the cloud point measurement to establish the phase diagram. The blend exhibits overlapping phase separation and crystallization behavior with the intersection of the cloud point curve (binodal). However, it is hard to establish the phase diagram only by the cloud point measurement when crystallization and liquid-liquid phase separation mutual affect strongly. Tomura et al. used light scattering to analysis upper critical solution temperature (UCST) behaviors in a poly(vinylidene fluoride)/ poly (methyl methacrylate) blends. Svoboda and Kressler studied the UCST behaviors in system of PCL and poly(styrene-ran-acrylonitrile)(PSAN) using the TEM micrographs to confirm the changes in morphology during the quenching. In order to study the interactions in
this miscibility window in detail, Svoboda and Kressler also used FTIR to determine the phase behavior in PCL/PSAN system. They presented that the shifts of spectral peaks in FTIR is a proof of presence of specific interactions.

There have also been several attempts to theoretically explain phase diagrams for polymer blends, which exhibit both crystallization and liquid-liquid phase separation. Flory first showed the liquid-liquid phase transition above the melting transition of polymer/solvent system. Burghardt extend the Flory-Huggins polymer solution thermodynamic theory to compute the phase diagram for polymer mixtures exhibiting both crystallinity and limited liquid-liquid miscibility. The interaction of crystallization and liquid demixing results in a monotectic phase structure. Blow the monotectic point, the binodal curve has no equilibrium significance, since at that stage crystallization is preferred to dominate. Consideration of the free energy of mixing curve indicates that liquid-liquid phase separation may play a role in determining crystal morphology, even when there is no liquid-liquid equilibrium in the phase diagram.

Matkar and Kyu recently modified the Flory-Huggins free energy for both amorphous-amorphous isotropic mixing by combining it with the phase field free energy of crystal solidification. The predictive capabilities of their theory are summarized below.
2.3.3 Phase Diagrams of Binary Crystalline Polymer Blends

Eutectic crystallization received little attention in binary crystalline polymer blends,\textsuperscript{56,57} although it has been extensively explored in metal alloys and small molecule systems. In general, the eutectic crystal is characterized by a eutectic point in the phase diagram where two solid phases are in simultaneous equilibrium with the isotropic liquid phase. In 1977, Wittmann and Manley reported the eutectic crystallization in blends of polycaprolactone and trioxane.\textsuperscript{58} The observed eutectic curves were analyzed in the framework of the Flory diluent theory. However, there is one major deficiency in the original Flory diluent theory that is incapable of explaining the solidus line in the phase diagram because of the inherent immiscibility assumption between the amorphous liquid and the neat solid crystal. In other words, the chemical potential of the liquid solution was equated in the derivation to that of pure polymer crystal.\textsuperscript{10}

By using the solid solution concept that has been known to exist in other binary systems such as metal alloys, organic molecular solutions, and liquid crystalline mixtures,\textsuperscript{59–62} Matkar and Kyu elucidated the phenomenon of eutectic, peritectic, or azeotropic crystallization in polymer blends.\textsuperscript{4,54} They established the phase diagrams of polymer mixtures as a function of anisotropic interaction parameter and also of the amorphous-amorphous interaction parameter.
2.3.3.1 Phase Field Model of Crystallization of a Homopolymer

The free energy density of crystal solidification pertaining to the crystal phase order parameter \( \psi \) may be described in the context of the Landau-type asymmetric potential as shown in figure 2.5.

\[
f(\psi) = W \int_0^\psi (\psi - \zeta)(\psi - \zeta_0) d\psi = W \left[ \frac{\psi^4}{4} - (\zeta - \zeta_0) \frac{\psi^3}{3} + \zeta \frac{\psi^2}{2} \right]
\]  

(2.26)

where the coefficients of the Landau free energy expansion in terms of a crystal order parameter \( \psi \) are treated as temperature dependent in polymer crystallization in order to account for the imperfect nature of polymer crystals. The crystal phase order parameter may be defined as follow

\[
\psi = \frac{l}{l_0}
\]  

(2.27)

where \( l_0 \) is the lamellar thickness of a perfect polymer crystal and \( l \) is the lamellar thickness the polymer crystals. In equation (2.26), \( \zeta \) represents the unstable hump for the crystal nucleation to overcome the barrier and \( W \) is the energy barrier to crystallization. Model parameters \( W \) and \( \zeta \) are intimately related to the material properties of the individual components. This \( \zeta_0 \) represents the crystal order parameter at the solidification potential for crystallization that may be treated as supercooling or crystal melting temperature dependent.
Figure 2.5 The variation of free energy of crystallization as a function of crystal order parameter, ψ of a pure homopolymer\textsuperscript{44}
As shown in figure 2.5, at melting temperature, there is no free energy difference between melt and solid, which implies the coexistence of crystal and melt. When temperature is lower than the melting temperature, the free energy density has a global minimum at $\zeta_0 < 1$, which means the linear crystallinity is less than unity. When the melt quench to the temperature lower than melting point some amorphous materials are entrapped in the solidus phase which leads to the defective crystals. This kind of incomplete crystallization is due to the metastable nature of the polymorphous crystals. As the supercooling increases, $\zeta_0$ moves to a lower value, which implies the imperfect crystal containing a sizable amount of entrapped amorphous chains or defects.

2.3.3.2 Phase Field Model of Crystallization of Polymer Blends

The total free energy density of mixing of a binary crystalline polymer blend can be expressed as the sum of the free energy density pertaining to crystal solidification of the crystalline constituent with its volume fraction ($\phi$) and the free energy of liquid-liquid mixing as described by the Flory-Huggin’s theory of isotropic mixing with the addition of the anisotropic interaction terms including crystal-amorphous, amorphous-crystal, and crystal-crystal mixing.

$$f_{\text{overall}}(\phi, \psi_1, \psi_2) = f_{\text{crystal}} + f_{\text{mixing}} + f_{\text{interaction}}$$

The phase field free energy of crystallization is given by a Landau-type asymmetric potential as shown in equation (2.26) and figure 2.5
\[ f_{\text{crystal}} = \phi f(\psi_1) + (1 - \phi)f(\psi_2) \]  

(2.29)

The Flory-Huggins free energy of mixing of a crystalline-crystalline polymer blend can be written as

\[ f_{\text{mixing}} = \frac{\phi \ln \phi}{r_1} + \frac{(1 - \phi) \ln(1 - \phi)}{r_2} + \chi_{aa}\phi(1 - \phi) \]  

(2.30)

The interaction term can be expressed as follow:

\[ f_{\text{interaction}} = (\chi_{ca}\psi_1^2 - \chi_{cc}\psi_1\psi_2 + \chi_{ac}\psi_2^2)\phi(1 - \phi) \]  

(2.31)

The anisotropic interactions such as crystal solid-amorphous liquid or amorphous liquid-crystal solid interactions may be defined as \( \chi_{ca} \) and \( \chi_{ac} \), respectively. These anisotropic interactions of separate crystals and \( \chi_{cc} \) of cocrystals are complimentary to \( \chi_{aa} \) representing isotropic interaction of amorphous materials. The crystal-crystal interaction may be expressed as a geometric mean of the crystal-amorphous and amorphous-crystal interactions to account for the nonideal rule of the crystalline mixture.

\[ \chi_{cc} = c_\omega \sqrt{\chi_{ca}\chi_{ac}} \]  

(2.32)

The parameter \( c_\omega \) represents the anisotropic interaction, which signifies any departure from ideality. \( c_\omega \) is associated with the anisotropic interactions only which are intimately related to the heat of fusion of these individual crystals as well as of the cocrystals and thus it is not directly connected to \( \chi_{aa} \). This \( c_\omega \) parameter is analogous
to the “c” anisotropic interaction parameter defined for the cases of smectic and nematic liquid crystal mixtures.\textsuperscript{63,64}

When the crystalline mixture is completely immiscible in the solid crystalline state and forms separate crystals, the interaction parameter can be taken as zero, $c_0=1$, and thus the crystal order parameters develop independently of each other, which is a typical characteristic of a completely nonideal solid solution. On the other hand, if the system is a completely ideal solid solution, the crystalline mixture would be completely miscible at all concentrations, $c_0=1$. Figure 2.5(b) illustrates the self-consistent solution with $c_0=1$ showing an ideal solid solution phase diagram with a crystal-liquid coexistence region bound by the liquidus and solidus lines. The value of $c_0<1$ implies that the crystallization is favored to occur as separate individual crystals. The phase diagram is shown as figure 2.6 (a). The liquidus and solidus lines intersect and form a tricritical point which is also known as the eutectic point. When the crystal solid solution (cocrystal) in a blend is more favored in the mixed state than in their individual pure states (separate crystals), the azeotrope occurs. Figure 2.5(c) shows the development of the azeotrope as a consequence of increasing the miscibility between the two-crystal solid solution ($c_0>1$), which leads to the formation of a tricritical point higher than the melting transition of either component.
Figure 2.6 Phase diagrams dependence on anisotropic interaction parameter $c_{\omega}$:

(a) ideal crystal solution, $c_{\omega}=1$; (b) eutectic in solid solution, $c_{\omega}<1$;

(c) azeotrope in solid solution $c_{\omega}>1$. 
2.4 Overview of PEG/Urea system

It is well documented that PEG and urea can form very stable inclusion compounds due to the inter-species hydrogen-bonding. It is of crucial importance to understand the mechanisms on complexation between PEG and urea molecular leading to formation of stable on metastable compounds.

Inclusion compounds are formed between two substances linked intimately, but without or with covalent bonds. One substance is regarded as the host and the other as the guest. In general the guest is spatially confined within host. It is convenient to divide inclusion compounds into two classes. In one class, the host is a molecule possessing an appropriate cavity or binding site within which appropriate guest molecules may be infused. For such molecular hosts, the host-guest complex can generally exist as an ‘associated’ entity both in the solid state and in dispersed phases (e.g. in solution). For the other class of inclusion compound, however, the association of host and guest is strictly a solid-state phenomenon, with the guest species located within the crystalline framework of a solid host material.

The crystalline inclusion compounds formed from spontaneous assembly of polymers and small molecules provide a method for observing the behaviors of isolated nanoconfined polymer chains. It has been known for many years that certain small molecules such as urea, thiourea, perhydrotriphenylene (PHTP), and cyclodextrin form crystalline inclusion compounds with semicrystalline polymers via a so-called co-crystallization process. As shown in figure 2.7 each chain of the
guest is forced into an extended conformation by the confines of the channel and is completely isolated from neighboring chains, which is possible to make some difference with the pure guest material. The scientific interest in these materials is motivated by the desire to compare the structural, dynamic, and chemical properties of organic ‘guest’ molecules embedded within different crystalline environments, and to investigate how the properties of the guest molecule may be influenced by the structural characteristics of its surrounding.

Urea can form crystalline inclusion compounds with polymer guests by crystallizing into an extensively hydrogen-bonded hexagonal matrix, isolating each guest molecule into parallel channels as shown in Figure 2.5.\textsuperscript{69–72} The urea inclusion compounds were first discovered by Bengen and Capchlenk in 1940s.\textsuperscript{73} They found that urea is capable of forming addition products with a great number of aliphatic compounds of various kinds. The partners must have a chain structure the chain being straight or branched within certain limits. At that time the classic theory of the complex chemistry cannot explain the crystal structure. At 1952 Smith obtained the crystal structure of this kind of urea-hydrocarbon complexes by X-ray examination.\textsuperscript{74} Monobe and Yokoyamo determined the molecular interaction and the morphology of urea-polyethylene complex at 1973.\textsuperscript{75} Later on, many research has investigate different urea/polymer inclusion compound, and different models used to describe the crystal structure and molecular interaction in urea/polymer system.\textsuperscript{69,70,72}
Figure 2.7 Schematic structure of inclusion compounds of urea \textsuperscript{67}
CHAPTER III
MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 Material

3.1.1 Polyethylene glycol (PEG)

The polymeric derivatives of ethylene oxide are divided into two classes defined by their molecular weights. PEG refers to the oligomers and polymers with a molecular weight below 20,000 g/mol, while polyethylene oxide (PEO) is the polymeric analog with \( M_n \) larger than 20,000 g/mol.

PEG is a crystalline, thermo-plastic and water-soluble polymer with the chemical formula depicted in figure 3.1(a). The melting temperature of PEG depends on the molecular weight. In table 3.1, are shown the melting temperature, density and physical appearance of PEG.

Single crystals of PEG are flat platelets\(^7\) with c-axis normal to the basal plane. Single crystal lamellae can be grown from dilute solution. Investigation by electron microscopy has shown the existence of lamellar structure. Hedrites and spherulites are typical crystals formed from solution. Melt-crystallization of PEG results in multilevel crystal lamellae whose growth rates are related to molecular weight and supercooling.
Table 3.1 Summary of physical properties of Polyethylene glycol

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Melting Point (°C)</th>
<th>Form</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4</td>
<td>viscous liquid</td>
<td>1.128</td>
</tr>
<tr>
<td>1000</td>
<td>38</td>
<td>waxy solid</td>
<td>1.13</td>
</tr>
<tr>
<td>8000</td>
<td>60</td>
<td>powder</td>
<td>1.13</td>
</tr>
</tbody>
</table>
For investigating the influences of PEG molecular weight on the phase behaviors of PEG/urea system, various PEG has been selected. The summarized PEG material properties due to the molecular weight are given in table 3.1.

3.1.2 Urea

Urea is an organic compound with chemical structure that two \( -\text{NH}_2 \) joined by a carbonyl functional group. The studies of urea by microwave spectroscopy indicate that urea is almost planar but that the amino groups are somewhat pyramidal.\(^7\) Urea molecules are extensively bonded through hydrogen bonds and the crystal geometry of the molecule is influenced by such neighbor interactions.\(^8\) Based on the concept of inclusion compounds, urea molecules can form an extensively hydrogen-bonded arrangement densely packed along these tunnels and the long-chain molecules are packed inside these tunnels.

Urea was supplied by Sigma-Aldrich Chemical Company, having the density of 1.135g/cm\(^3\). The structure of urea is shown in figure 3.1(b).
Figure 3.1 Chemical structures of (a) polyethylene glycol and (b) urea
3.2 Samples Preparation

PEG sample with weight-average molecular weight of 400 and 1000 were obtained from Aldrich Chemical Co. PEG in powder form with $M_w$ 8000 was purchased from Polyscience, Inc. The urea sample was also purchased from Aldrich Chemical Co. All samples were dried overnight before use. The samples having different PEG/urea blending ratios were prepared by dissolving in a methyl alcohol (Fisher Scientific) to form a 5 wt% solution. In order to fully dissolve PEG and urea, the solution was heated to 65°C. The PEG/urea mixture formed after a few hours contact.

The solid complexes with different PEG/urea composition were extracted from their solutions. In order to remove residual solvent completely all the solid compounds were dried in a vacuum oven for 24 hours at room temperature.

The samples were prepared for the FTIR by depositing on the KBr substrate. The solutions of the PEG/urea blends were cast onto the KBr disk, and the solvent was removed by drying in the vacuum oven at room temperature for 24h. The way to prepare the POM sample is similar to the KBr method, except that solution was cast onto the microscope glass sides.

3.3 Samples Characterization

3.3.1. Differential Scanning Calorimetry (DSC)

The melting point of pure PEO, urea and their blends were determined using DSC (Model 2920, Thermal Analysis instruments, TA). Samples were sealed in aluminum
hermetic DSC pans with the aid of an encapsulating press. An empty aluminum pan was used as a reference. Nitrogen gas was purged to the unit to maintain the inert atmosphere. Different heating rates (2°C/min, 5°C/min and 10°C/min) were employed for all PEG/urea compositions. All the samples underwent heating runs twice.

3.3.2. Polarized Optical Microscope (POM)

In order to confirm the coexistence regions, POM (BX60, Olympus) was employed. The blend samples were heated in the hot stage (TMS 93, Linkam) from room temperature to desired experimental temperature at 2°C/min. The microstructures were photographed as a function of temperature using a digital camera (EOS 400D, Canon) under suitable magnifications (i.e., 500x) and the POM images were taken under the crossed polarization.

3.3.3 Thermogravimetric Analysis (TGA)

TGA is a method of thermal analysis in which changes in physical and chemical properties are measures as a function of increasing temperature. The mass loss with increasing temperature was measured by TGA(Model 2950, Thermal Analysis instruments, TA). Sample for thermogravimetric measurements were prepared by introducing approximately 5-10 mg of material into the pan. Nitrogen gas was purged to the unit to maintain the inert atmosphere. The heating rate of all the tests was 20°C/min.
3.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was recorded on a FTIR spectrometer (Nicolet 380, Thermo Electron) by signal averaging over 32 scans in wavenumbers ranging from 525 to 4500 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). The blend samples cast on the KBr disks were placed in a sample hot stage in order to hold the samples at the desired experimental temperature. A heating chamber was used to analysis the molecular interactions at various temperature.

3.3.5. Wide angle X-ray diffraction (WAXD)

The samples for the WAXD study were the powder form prepared from solid complexes. Amorphous tapes were used to stick the powder samples on the holder, and tapes scattering were collected first as background and subtract it from the actual data in order to remove the tape’s effects. WAXD scans of powder samples were obtained on Bruker AXS D8 Discover apparatus. The operating voltage and current were set to 40 kV and 40 mA, respectively.
4.1 Introduction

Blending polymer is one of the most common techniques to enhance certain properties of materials. The material performance is largely affected by the miscibility of the blend. Therefore, it is very important to investigate the miscibility and phase behaviors of the blends. If the two components in a polymer blend are all crystallizable, the crystal-melting transition will occur in addition to the liquid-liquid phase segregation, which makes the system too complicated to investigate. Therefore, the crystalline polymer blends received little attention compared to the amorphous polymer blends.\textsuperscript{79–81} Only a small amount of works have been reported on the crystalline polymer blends. Recently, with the help of Flory-Huggins theory and some concepts from other fields like metal alloys and liquid crystals, crystalline polymer blends is attracting greater attention from researchers.\textsuperscript{82–84}

It has been known for many years that certain small molecules can form crystalline inclusion compounds with semicrystalline polymers via a cocrystallization process. Urea has this kind of ability to form complexes with linear aliphatic chains. As in most urea inclusion compounds, the guest chains are packed inside narrow
channels constructed from an infinite network of hydrogen-bonded urea molecules.

This chapter is mainly focused on the high molecular weight PEG (M_w=8000)/urea inclusion compounds. PEG having molecular weight 8000 (PEG8k) is solid powder and often used to make tablets in pharmaceutical industries. The polymer chains of PEG are compelled to adopt an extended structure by forming inclusion compounds with the small-molecule urea. Then two different new crystal phases (α-phase and β-phase) form in the urea/PEG mixture, which attract considerable interests. In this chapter, the phase behaviors in PEG8k/urea system were investigated by means of POM and DSC. The morphology evolution of both pure components and the new-form cocrystals were examined under various temperature conditions. Finally, the phase diagram was constructed experimentally and theoretically via self-consistent solution to the combined Flory-Huggins and phase field free energy.

4.2 Experiment Section

The experimental phase diagram of the PEG8k/urea was established by means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Blends for the establishment of the phase diagram were prepared by weighting the appropriate amounts of PEG8k and urea mixing small vial with methanol. The powder form blends can be obtained by the solvent casting method given in Chapter III.

As described above there are two different cocrystals in PEG/urea system. To characterize the cocrystals, the pure cocrystals, α and β, need to be prepared first. The
A pure α compound was prepared by the solution casting method described above, whereas the pure β compound was obtained by the so-called melt-quenched method by heating the α compound to 150°C (above the melt point of the pure α compound) and cooling it to room temperature immediately. However, the melt-quenched sample is a mixture rather than the pure β compound, which will be discussed later.

The thermal phase behaviors experiments like crystal-crystal transition and crystal-liquid transition were carried out by DSC and POM. Various temperatures and heating rates were employed for the PEG8k/urea mixture. The interactions between each component in the blends were examined by the FTIR. FTIR is carried out at different coexistence regions of the phase diagram. As a supplemental method, the WAXD was used to determine the crystal structure and miscibility of the polymer blends at certain compositions.

4.3 Results and Discussion

DSC was utilized to study the thermal behavior. Melting point depression is widely used to determine whether the system show blend miscibility. Theoretically, the melting points need to be measured under the equilibrium condition, because the heating rate can affect the melting transition. For convenience, equilibrium melting points are customarily evaluated from the experiments. Typically the equilibrium melting points can be determined by suitable extrapolating the Tm data to the zero heating rate.

Figure 5.1 depicts the DSC thermograms of the 70/30 PEG8k/urea blend at
various heating rates. The melting peaks of PEG8k crystal and crystal do not shift. The melting peak around 90°C is strongly influenced by heating rate, where the melting peak shifts to a higher temperature with increasing temperature. It appears that the fast heating rate might miss the equilibrium melting, and a very slow heating rate might suffer the annealing effect. On the other hand, the melting peak shift is the presentation of thermodynamical metastability of β crystal, which will be discussed later.

Figure 4.2 exhibits the DSC thermograms of PEG8k/urea blends obtained at a heating rate of 2°C/min. The melting transition of neat PEG8k and urea are in the vicinity of 60°C and 135°C, respectively. The endothermic peak at around 141°C which is higher than the melting points of both component is the melting peak of the inclusion crystal, α compound, formed by PEG and urea.$^{3,88}$
Figure 4.1 DSC thermodiagrams of 70/30 PEG8k/urea blends at various heating rates

(a) DSC curves (b) melting point depression
Figure 4.2 DSC thermograms of PEG8k/urea obtained at a heating rate of 2°C/min
Figure 4.3 (a) DSC thermodiagram of PEG8k/urea blends (I) 23/77; (II) 25/75; (III) 28/72 (b) I: first heating curve of 52.5/47.5; II: second heating curve of 52.5/47.5
The phase α crystal develops once PEG8k added into urea. As mentioned above, the urea molecules can form self-hydrogen bonding into a tunnel host structure. When the long-chain polymer PEG8k is added, the polymer chains enter the “tunnels” and form the inclusion compound α. At first the number of “tunnels” is larger than the number of polymer chains, therefore the system is separated into two phases, α phase and urea phase. With the PEG added gradually, all the “tunnels” are occupied by PEG chains. The excess PEG that cannot enter the tunnels will organize among themselves into the PEG crystal phase. Therefore the pure α compound can be obtained when the molar space (volume) available in the “tunnels” is equal to that occupied by polymer chains.

In order to draw a completed phase diagram, determination of the molecular composition of the inclusion crystal α become critical. Chenite and Brisse showed that its stoichiometry is \((EO)_4\text{-}(\text{urea})_9\).\(^2\) As shown in the Figure 4.3 (a), the 23/77 PEG8k/urea mixture has two exothermic peaks. The first transition peaks in the vicinity of 135°C are the melting peaks of the urea crystalline phase. The area of the urea melt peak is much smaller than those in the 10/90 PEG8k/urea sample and the DSC thermograms of neat urea, indicating that most of the urea molecules have formed the α phase with PEG8k as the PEG8k composition increases. On the other hand, when the composition of PEG reaches 28/72, the peak at 135°C disappears, and a tiny exothermic peak shows up around 60°C, i.e., the typical melt temperature of PEG8k. This curve suggests the latter situation mentioned in the previous paragraph that the excess PEG that cannot enter the tunnels forms the PEG crystal phase. Based
on the DSC curves, the composition of pure α compound lies between of 23% and 28% of PEG. Upon thorough inspection, the composition of pure α compound was found to be approximately 25/75, which is very close to the composition reported in the literature.\(^1\)

Figure 4.2 shows a series of exothermic peaks appearing around 85°C when PEG8k composition is greater than 50%. Some literatures claimed this is due to the crystal-crystal transition in the PEG/urea system.\(^{88,89}\) Besides the inclusion compound α, PEG and urea can also form another metastable compound called β phase crystal. Because of the challenge of preparing a large quantity of the β complex in a pure state (without residual urea), its structure and even its stoichiometry have not been established firmly yet. However, by taking into account the crystal dimension and the hydrogen bonding interactions between the amino groups of urea and the ether groups of PEG, the sandwich-like structure model can be established.\(^3,90,91\) In the sandwich model the PEG chains form a series of plains which are separated by the layers composed of urea molecules.

Figure 4.3(b) shows the melt-quenching methodology used to prepare β compound. It was reported that the stoichiometry of the β complexes occur when PEG:urea molar ratio is 3:2.\(^{92}\) The molar mass of the PEG repeat unit and urea are 44 and 40, respectively. Therefore the sample quenched into the β compound is equivalent to the 52.5/47.5 of PEO weight. The first heating DSC curve(I) of the 52.5/47.5 mixture shows two exothermic peaks at 60°C and 141°C, which are the typical melting points of PEG8k and α crystal. Then the melt sample was directly
quenched to room temperature. The second heating curve (II) is completely different with the first one. The peak around 85°C implies the development of β crystal.

Figure 4.4 exhibits the crystalline morphology in the mixture of 60/40 PEG8k/urea. At room temperature, the spherulitic structure of metastable β crystals formed with the PEG8k small crystals forming inside the β crystal spherulites. When temperature is raised to 60°C, the tiny crystals melt and become isotropic. It is reported that β crystals can convert back to the stable α form by heating to 90°C. ³ From the DSC curve, the peak at 90°C can be regarded as an overlap of the endothermic melting of the β crystals with the exothermic crystallization of the α complex. In order to make clear how the metastable β complex convert back to the stable α form at around 90°C, the polarized optical micrographs was employed to confirm this β-α transition process. Under the POM, the evolution of needle-like structure can be detected at 90°C following the melting of β crystals. This phase behavior can be regarded as β-α transition. The needle-like crystals finally melted around 140°C, which is the typical melting temperature of the α compound.
Figure 4.4 Optical micrographs showing the morphologies of 60/40 PEG8k/urea blends as a function of temperature.
Figure 4.5 WAXD 2θ-scans of PEG8k/urea mixture at various compositions
To demonstrate the composition of the crystal coexisting phases, wide angle X-ray diffraction was performed on the PEG8K/urea as a function of concentration. The WAXD patterns are shown in Figure 4.5. As described above the PEG8k mass fraction of α compound is 25 wt%. The WAXD pattern also show that the pure α compound can form at 25/75 PEG8k/urea samples, which are quite different from those of pure PEG8k or urea crystals. 10/90 PEG8k/urea pattern shows a coexist of pure urea crystals and α crystal. The peaks at 24.5° and 29° are signs of PEG crystal, and then peaks at 26° and 27° is due to the existence of α the crystal.

On the other hand, new distinct diffraction peaks appear after quenching the 52.5/47.5 PE8k/urea sample. These peaks are drastically different from those of pure PEG8k, pure urea, and the α compound. Together with the figure 4.3 (b), this diffraction pattern can be assigned to the form β crystal. This specific composition corresponds to the PE8k: urea molar ratio of 3:2.

In figure 4.5, the characteristic peaks of PEG8k crystal at 19.5° and 24° show up in 80/20 curve, which imply the existence of pure PEG8k crystal. The peak at 21.5° is caused by the diffraction of β crystal. For the blends rich in PEG8k, the system can be considered as a mixture of PEG8k and β crystal.

In the middle region of phase diagram, when the concentration of PEG8k is larger than 25 wt% (such as 40/60), the diffraction pattern is primarily contributed by a combination of α compound and β compound. The peaks at 26° and 27° indicate the existence of α compound, but it may also contain some pure PEG8k crystals, as revealed by the DSC diagram. This observation implies that the samples prepared at
middle region (from 25/75 to 52.5/47.5) PEG8k/urea are phase segregated. This concentration range is very close to the demarcation line (or border) between the \( \alpha + \beta \) coexistence phase and the \( \beta + \) Crystal PEG(Cr\textsubscript{PEG}) coexistence phase. Thus any heterogeneity in the sample can lead to the revelation of the above three crystalline phases. This may be due to the difficulty of preparing the uniformly dispersed sample in the phase separated region and the PEG8k crystal in this region is probably thermodynamically unfavorable.
Figure 4.6 FTIR spectra of PEG8k, urea, 60/40 PEG8k/urea acquired at 105°C
Figure 4.7(a) FTIR spectra of 60/40 PEG8k/urea mixture as a function of temperature
(b) FTIR spectra of 80/20 and 40/60 PEG1k/urea mixtures at various temperatures
Figure 4.6 shows the FTIR spectra obtained for urea, PEG8k, and PEG8k/urea inclusion compound. The inclusion compound is obtained by heating the 60/40 PEG8k/urea sample to 105°C that is higher than the β−α transition temperature. The urea FTIR spectrum shows bands at 1672 cm$^{-1}$ due to C=O stretching, at 1611 cm$^{-1}$ due to N-H bending vibrations, and at 1466 cm$^{-1}$ due to the N-C-N antisymmetric stretching vibration. The bands due to urea are greatly affected by the formation of inclusion compound. The bands due to PEG8k are not much affected by the formation of the complex. The bands at 1672 and 1466 cm$^{-1}$ due to urea are shifted to 1682, 1637 and 1442 cm$^{-1}$, respectively, in PEG8k/urea inclusion compound.

Two different bands at 1694 and 1658 cm$^{-1}$ for C=O stretching vibrations suggest that urea molecules are found in two different environments in the inclusion complex. The single-crystal diffraction studied by Chenite and Brisse$^2$ suggested that two-thirds of the urea molecules form the matrix that are strongly hydrogen-bonded to each other and one-third of the urea molecules reside in the channels. The urea molecules residing in the channels are also hydrogen-bonded to the oxygen atoms of the PEG8k chains as well as the channel-forming urea. The strength of hydrogen bonding is probably weaker than the strength of hydrogen bonding within the matrix. The literature is consistent with our FTIR results shown in figure 4.6 that shows two vibrations for carbonyl stretching. On the other hand, it can clearly be seen that the vibrations due to C-O stretching (960 cm$^{-1}$) are shifted to lower wavenumbers (946 cm$^{-1}$) in the PEG8k/urea inclusion compound. These shifts can be explained in two scenarios: first, the shifts are due to bond weakening when the hydrogen bond
formed between the urea N-H and the oxygen atom in the PEO chain. The other reason is the difference between the structural environments of the PEG chain in bulk and inclusion compound.

The temperature dependence FTIR is measured at different composition. Figure 4.7(a) exhibits the IR spectrum of 60/40 PEG8k/urea sample at different temperatures. The \( \beta \rightarrow \alpha \) transition can be confirmed by the red shift of C-O stretching. The vibration of C-O stretching at 952 cm\(^{-1}\) at room temperature shifts to 946 cm\(^{-1}\) when sample is heated to 105°C. The red shift is due to the conformational change of PEG chains. In \( \beta \) compound, the PEG chains and urea networks are separated in different layers forming a sandwich structure. The interactions between the PEG layer and urea layer are van der waals forces or very weak hydrogen bonds. In \( \alpha \) compound, the oxygen atom in the PEG chain form hydrogen bond with the N-H of urea when PEG chains enter the tunnels formed by urea. This H-bonding is much stronger as compared to the hydrogen bond between PEG and urea in \( \beta \) sheet compound. Figure 4.7(b) show the a similar shift of C-O stretching vibrations in 40/60 and 80/20 samples due to the heating.
Figure 4.8 Temperature vs. composition phase diagram of PEG8k/urea blends. The solid line was calculated based on the phase field model of crysal solidification, but the dish line was drawn by hand. Two vertical dish lines were corresponding to the molar ratio of $\alpha$ and $\beta$ compounds.
Considering all the analyses above, it is now possible to draw a complete phase diagram of the PEG8k/urea mixture. Figure 4.8 is obtained by the DSC thermograms of samples with various PEG8k:urea mass ratios. The nature of the different α and β phases have been confirmed by WAXD, FTIR and POM.

The phase diagram can be separated in three main composition ranges. When the mass fraction of PEG8k is less than 25 wt%, the samples consisted of a mixture of solid urea and α compound that sequentially melt at 135°C and 141°C. When the mass fraction of PEG8k is larger than 52.5 wt%, samples consisted of a mixture of PEG with the β complex. The middle region between 25/75 and 52.5/47.5 is rather complex. First, this range should be the mixture of the solid α and β compounds from the theoretical perspective (or phase rules). However, the results of DSC and WAXD suggest the possible existence of pure PEG8k. In addition, a little amount of β compounds can be detected in this region unless the composition is closed to 52.5/47.5. This is due to thermodynamically instability in the middle region. Relative crystallization kinetics for the different species should be taken into consideration. Crystallization of α compound is much faster than that of β compound. The PEG8k/urea molar ratio of the two compound are 4:9 and 3:2, which means α compound is rich in urea as compared to β compound. At low PEG8k compositions, more α crystals are formed than expected under equilibrium conditions. Therefore, more urea is consumed to make more α crystals, which leads to the decrease of β compound. Because of the increase of α crystals that contain less PEG8k, Some pure PEG8k crystals were left in the system. Taking into consideration of non-equilibrium
nature of the crystallization, it is possible that a weak PEG8k melting transition can systematically show up. In order to balance the phase diagram, we may predict there is a pure PEG phase show up when the PEG8k concentration of mixture is close to pure PEG8k (>98wt%).

The phase diagram can be regarded as a combination of azeotrope and eutectoid systems. The elevated temperatures corresponding to the upper part of this diagram are azeotrope type, where the $\alpha$ co-crystal is favored to form and more stable due to the strong complexation. This type of azeotrope phase diagram may be modeled theoretically in the framework of the phase field theory of crystal solidification.$^{54}$

The phase field model has been introduced in Chapter II. The coexistence regions have determined by DSC, WAXD, FTIR and POM. In addition, there are too many different crystals interacting with each other that makes it hard to calculate by the phase field model. The upper part of the phase diagram, it is a typical crystal-isotropic transition of solid solution ($\alpha$ crystal). Therefore, the phase field model was utilized to describe this crystal-isotropic transition. To demonstrate the role of phase interaction in the phase diagram, the critical interaction parameters were taken as: $r_1=80$, $r_2=2$ and $c_\omega=1.055$. The anisotropic interaction parameter $c_\omega$ is larger than 1, which means a formation of a azeotrope point higher than the melting transition of either component. The development of azeotrope is due to the increasing miscibility between two components. Another notable feature of the simulated phase diagram is that the predicted trends have solidus and liquidus lines, whereas the experimental melting transition only has single DSC peaks. Because of the deficiency of original Flory
diluent theory that predicts only a single liquidus line, the present predicted trends were consistent with other binary system such as metal alloys or liquid mixture.

The calculated phase diagram exhibits the coexistence of the isotropic liquid + stable complex crystal (i.e., the $\alpha$ crystal). This coexisting region has the convex curvature implying that the complexed co-crystal is more stable than the individual parent crystals. With the descending temperature, the stable $\alpha$ phase crystal undergoes solid-solid phase transitions by separating into two solid crystals (i.e., urea crystal + $\alpha$ phase crystal and PEG8k crystal + $\beta$ phase crystal), which is known as a eutectoid system. The signature of the eutectoid reaction is the occurrence of a V-shaped junction in the two solid-solid transitions converging at a common concentration.

4.4 Conclusions

The phase diagram of PEG8k and urea was found to consist the azeotrope at a high temperature followed by the eutectoid behavior, in which the stable $\alpha$ crystal is transformed into the urea crystal + $\alpha$ crystal and the $\beta$ crystal + PEG crystal coexistence phases. The phase behavior of the urea crystal + $\alpha$ crystal is straightforward: when the urea crystal melts, it transforms to the isotropic + $\alpha$ crystal coexistence phase before reaching the isotropic liquid with increasing temperature. The phase behavior at the higher PEG concentration is complicated by the fact that the UCST is presumably protruded above the $\beta$ crystal + PEG8k crystal boundary as PEG8k crystals melt. Subsequently the $\beta$ phase melts into the $\alpha$ phase through complexation with urea. The experimental finding of possible existence of PEG8k
crystals may be due to inhomogeneity of concentrations during sample preparation. The boundary line between urea crystal + α phase at 25/75 corresponds to the PEG:urea molar ratios of 4:9, whereas that of the PEG crystal + β phase crystal corresponds to the PEG:urea molar ratios of 3:2. It is reasonable to infer that the stoichiometric ratios (i.e., 4:9 and 3:2) of PEG and urea crystal complexes is the reason of unique eutectoid phase diagram, although an ideal eutectoid system should exhibit only the Cr_{urea} + Cr_{PEG} only in the intermediate concentrations instead of the observed α + β coexistence region. This combined azeotrope and eutectoid phase diagram is consistent with that our previous PEO/urea system.
CHAPTER V

PHASE DIAGRAM OF LOW MOLECULAR WEIGHT PEG/UREA BLENDS

5.1 Introduction

The phase diagram and morphology development in blends of PEG8k and urea has been investigated in Chapter IV. It has been well documented that molecular weight can affect the phase behaviors in polymer blends.\textsuperscript{93,94} It is our continued interest to investigate the effect of the molecular weight of PEG and urea on the melt/crystallization transition and morphology development in their blends.

In this chapter, the influence of the polymer molecular weight on phase diagram and morphology will be demonstrated. We will utilize the theories and experiments to investigate the equilibrium thermodynamics of polymer mixture, which are described in terms of experimentally accessible parameters determined in previous chapters.

The phase diagram involving solid-liquid phase transition has been examined via determining the depression of melting point by DSC. Crystal-crystal transitions are observed by the polarized optical microscopy (POM). The morphology of various coexistence regions have been determined by POM with thermal controller. The crystal structures and the interactions between molecules have been determined by WAXD and FTIR. To determine the effect of molecular weight on melting transition and coexistence regions, a molecular weight PEG has been investigate as compared to
the PEG (8000) using in last chapter.

5.2 Experimental section

The experimental phase diagram of PEG400/urea was established by means of POM and DSC. Blends of PEG400 and urea were prepared by weighing the desired amounts of PEG400 and urea mixing small vial with methanol. The blend films were obtained by the solvent casting method described in Chapter III.

The development of crystalline structure and phase morphology was examined by POM with the aid of a hot stage. The solvent-casting blend samples for POM were heated until they were optically transparent. Because both PEG400 and urea are moisture sensitive, the hostage of POM is under nitrogen flow to isolate from water in the air.

The melting transitions of PEG400/urea blends were determined using DSC. Sample for calorimetric measurement were prepared by introducing 5-10 mg of solvent casting blends into aluminum hermetic DSC pans. Nitrogen gas was purged into the unit to maintain an inert atmosphere. Various heating rates were used for whole PEG400/urea mixtures.

FTIR and WAXD were carried out in various coexist region. In order to analyses the molecular interaction without the influence of water in the blends system, a sample hot stage was used for FTIR measurement. The blend samples were heated to desired temperature and hold for 10 min to equilibrate the blends system. Then the IR spectra at different temperature and compositions were examined. WAXD was carried
out on the solid state blend samples to examine the crystal structures within the crystal coexistence regions.

5.3 Results and discussion

Figure 5.1 depicts the TGA thermograms of PEG8k and PEG400. PEG400 starts to decompose at 180°C. The decomposition temperature of PEG8k is 30°C higher compared to PEG400. This is due to the stabilization by the macromolecular chain length. PEG chain decomposed by random scission of the chain links without chain-end-initiated depolymerization. That implies that the longer polymer chain, the higher energy for the decomposition needs. Based on figure 5.1, It is reasonable to infer that increasing molecular weight enhances the thermal stability of PEG.

Figure 5.2(a) exhibits the DSC thermograms of PEG400/urea blends covering the whole range of composition at a heating rate of 2°C/min. The melting peak of urea shifts from 135°C to a lower temperature when PEG400 concentration increases. The peaks above 110°C vanish at the PEG400 rich region, which suggests that no pure urea crystal phase exists at high PEG400 concentrations. We can witness there are a series of exothermic peaks show up around 90°C for the entire compositions. We suppose that these are the melting peaks of PEG400 cocrystals with urea. The peaks around 0°C at high PEG400 concentrations are typical melting peaks of PEG400. In addition, because PEG400 is liquid at room temperature, the high PEG400 samples may phase separate during the sample preparation. In solvent casting process the samples may undergo a non-equilibrium crystallization and phase separate. To avoid this no-equilibrium effect, only the second DSC heating runs were used in analysis.
Figure 5.1 TGA therograms of two different molecular weight PEG
Figure 5.2 (a) DSC thermograms of PEG400/urea blends with a heating rate of 2°C/min (b) Plots of melting points vs. composition of PEG400/urea blend
Figure 5.3(a) displays the time evolution of crystalline morphologies in blend PEG400/urea 10/90 at 100°C. The sample was heated to 100°C, and then isothermal measurement was taken. The photos were taken as a function of time. During the isothermal process, one kind of crystal melted at 100°C. The other crystal would not melt until the sample heated to the melting point of urea. Therefore, this region is suggested as a coexist region of urea crystal and \( \alpha \) crystal.

Figure 5.3 (b) represents the time evolution of crystalline morphologies at high PEG400 composition (PEG/urea 90/10). The blends sample is liquid state with little crystal in it. When temperature was below the melting temperature of PEG400, around -10°C, some birefringent entities developed that indicates of PEG400 crystal formation.
Figure 5.3(a) Time-evolution of crystal morphology of 10/90 PEG400/urea blends at an isothermal temperature of 100°C
Figure 5.3 (b) Time-evolution of crystal morphology of 90/10 PEG400/urea blends at an isothermal temperature of -10°C
Figure 5.4 Optical micrographs showing morphology variations of PEG400/urea blends at various temperature
(a) PEG400/urea 30/70 at 30°C and 100°C
(b) PEG400/urea 70/30 at 70°C and 100°C
Similar experiments have been performed for various compositions. The POM images (Figure 5.4) reveal that the crystal structure is the needle-like or sheaf-like structure and the melting point corresponds to that measured by DSC.

To clarify the crystal-crystal coexistence region, WAXD is employed to determine the crystal structure of various PEG400/urea compositions. Figure 5.5 shows the WAXD patterns for different PEG400/urea compositions. Recalled the discussion about the WAXD patterns of PEG8k/urea system in Chapter IV, the XRD curve of 15/85 sample reveals a the similar pattern of $\alpha$ crystals. In addition the peaks at 22° is due to urea crystal, indicating the coexistence of the $\alpha$ crystal and urea in this region. When the concentration of PEG400 is higher than 50wt%, the patterns were dominated by $\alpha$ crystal. Based on the DSC thermodiagram shown in figure 5.2(a), the region where concentration of PEG400 is higher than 50wt% is the coexistence region of $\alpha$ crystal and isotropic PEG400 liquid at room temperature.

Figure 5.6 shows the FTIR spectra of pure PEG400, pure urea and PEG400/urea 65/35 blends at different temperatures. PEG400/urea 65/35 blends at room temperature can be regarded as a mixture of $\alpha$ crystal and PEG400 liquid. The 65/35 blends at 120°C is the melt mixture of urea and PEG400. The urea spectrum shows a band at 1466 cm$^{-1}$ attributable to the N-C-N antisymmetric stretching vibration. As Compared with the blending samples, the band at 1466 cm$^{-1}$ of urea shifts to 1447 cm$^{-1}$ in the 65/35 PEG400/urea mixtures.

The bands of PEG400 are also affected by the formation of inclusion crystals. The absorption peak at 950 cm$^{-1}$ can be assignerd to C-O stretching in neat PEG400.
When the PEG400 is blended with urea, this band shift to a lower wavenumber (945 cm\(^{-1}\)), which implies that the configurations of PEG400 chain may change due to the formation of inclusion crystals. This red shift is similar to the shift in PEG8k/urea blends. The red shift is due to the fact that the oxygen atom in PEG chain can form hydrogen bonds with amino groups of urea that lower the energy of PEG chains. When the mixture heated above the melting point of \(\alpha\) crystal, C-O stretching absorption peak stay at the same position of neat PEG400, which implies that the inclusion compound is vanished and the remaining urea networks is same as the conformation of pure urea.
Figure 5.5 WAXD 20 scans of PEG400/urea mixture at various composition
Figure 5.6 FTIR spectra of 65/35 PEG400/urea mixture at various temperatures in comparison with neat at room temperature
Figure 5.7 Temperature vs. composition phase diagram of PEG400/urea blends. 
(a) The calculated phase diagram based on combined free energies F-H theory and the phase field model of crystal solidification assuming the binary mixture a crystal and urea crystals (b) Complete phase diagram, the dish line was drawn by hand based on the experimental results and phase rules
To substantiate the solid crystal-liquid melt coexistence regions, the melting temperatures were plotted against composition in figure 5.2. Based on figure 5.3 and 5.4, the crystal morphologies give guidance to crystal appearance in the PEG400/urea. The phase boundary displays different distinct regions: isotropic (I), co-existence of crystal-isotropic liquid (Cr$_{\text{urea}}$+I and Cr$_{\alpha}$+I) and crystal-crystal(Cr$_{\text{urea}}$+Cr$_{\alpha}$).

A calculated phase diagram figure 5.7(a) was drawn based on Flory-Huggins free energy theory the phase field model. The phase diagram can be separated into three parts according to PEG400 concentration. When the composition of mixture is closed to neat urea, a single phase crystal Cr$_{\text{urea}}$ can be discerned. On the other hand, when the composition of mixture is closed to neat PEG400, the blends can be regarded as a single phase of $\alpha$ crystal. When temperature of the sample falls below the melting point of PEG400, tiny PEG400 crystals show up according to POM observation. The phase diagram involving PEG400 crystal will be discussed latter in the completed phase diagram.

In most region of the phase diagram, only one crystal-crystal coexistence region can be found. The blends in this region consist of a mixture of urea crystal and $\alpha$ crystal. The melting temperature of $\alpha$ crystal is nearly constant. The depression of melting transition of urea phase is noticeable. This kind of phase behavior is very similar to the eutectic system, where the liquid mixture compound solidifies and separated into two solid solution. One is the urea+ isotropic and the other is the $\alpha$ crystal+ isotropic.
The phase field model was used to describe this kind of eutectic behavior. The critical interaction parameters were taken as: $r_1=2$, $r_2=4$ and $c_0=0.9$. Compare to the PEG8k/urea system discussed in Chapter III, $r_1/r_2$ ratio reduce from 80/2 to 4/2, which corresponds to the molecular weight ratio. $c_0$ is smaller than 1 meaning that the system is destabilized and forms separate individual crystals instead of a homogeneous solid solution at lower temperature. This eutectic system implies that the mixture has a single composition that solidifies at a lower temperature than any other compositions made of the same ingredients. This composition is known as the eutectic point. In figure 5.7, we can see the eutectic point at 0.8 where the blend has a lower melting temperature than other compositions.

Consider the neat PEG400 crystal that only exists at low temperatures, a complete phase diagram can be established. As shown in figure 5.7, there are two notable differences between the calculated phase diagram and completed phase diagram. The calculated phase diagram was calculated as a function of PEG400 volume fraction, while the experimental was drawn as a function of weight fraction. The density of urea is 1.135g/cm$^3$ and PEG400 is 1.128g/cm$^3$, which are very close. The difference between volume fraction and weight fraction is neglectable. The other difference is that solidus line and liquidus line touch the neat PEG400 boundary in figure 5.7 (a). Note that the calculation is based on the competition of pure urea and $\alpha$ crystal rather than pure PEG. The calculation was not carried out for pure PEG400 as there are only pure urea or $\alpha$ crystals in the temperature range calculated. In reality, the liquidus line and solidus cannot touch the neat PEG 400 boundary.
Compare with the phase diagram of PEG8k/urea blends (figure 4.8), we can witness some similarities and differences between the two systems. The inclusion cocrystals exist in both blends system, but the thermal behaviors of these two cocrystals are quite different. In high molecular PEG/urea system, the melting temperature of $\alpha$ crystal is 141°C that is higher than the melting points of both two neat materials. This phenomenon leads to azeotrope at high temperature. In the low molecular PEG/urea system, the melting point of $\alpha$ crystal is around 90°C that is lower than the melting point of pure urea crystal. The melting transition of $\alpha$ cocrystal product a “eutectic point” where the liquid (I) and two solid solution (Cr$_{\text{urea}}$ +I, Cr$_{\alpha}$ +I) all coexist at the same time and are in chemical equilibrium.

5.5 Conclusions

In order to determine the effects of PEG molecular weight on melting transitions of PEG/urea blends, the low molecular weight PEG/urea system were investigated. It was found that the melting points of PEG and $\alpha$ cocrystal affected by the molecular weight. The low molecular weight decreases the transition temperature significantly, which change the configuration of phase diagrams. The phase diagram of high molecular weight PEG/urea blends is considered as a combination of azeotrope at high temperature. The eutectoid behavior reveals the stable $\alpha$ crystal is transformed into the urea crystal + $\alpha$ crystal and the $\beta$ crystal + PEG crystal coexistence phases. In PEG400/urea blends, the melting point of $\alpha$ crystal is lower than the melting temperature of pure urea crystal, which leads to a transformation of phase diagram.
The temperature depression of α crystal melting transition leads to eutectic type phase diagram where the liquid (I) is favor to separate into two solid solution (Cr_{\text{area}} + I, Cr_{\alpha} + I) with the descending temperature.
CHAPTER VI

EFFECTS OF POLYMER MOLECULAR WEIGHT ON PHASE DIAGRAM AND MORPHOLOGY DEVELOPMENT IN BLENDS OF PEG/UREA SYSTEMS

6.1 Introduction

The phase diagram and morphology development in blends of urea and high molecular PEG (PEG8k) as well as low molecular weight PEG (PEG400) have been investigated in Chapters IV and V. It has been well discussed that the molecular weight of PEG can affect the melting transition of the blends as well as the morphology development in their blends. In the high molecular weight PEG/urea system, the phase diagram can be regarded as a combination of azeotrope and eutectoid systems. The upper part of this diagram is azeotrope type in which the $\alpha$ co-crystal is favored to form due to the strong complexation. In the low molecular system, the phase diagram convert into a eutectic type on the top instead of azeotrope, because of the melting temperature depression of $\alpha$ crystal. These findings invoke our continued interests on how the molecular weight affect the phase diagram of PEG/urea blends.

In this chapter, the influence of polymer molecular weight on the phase diagram and morphology in PEG/urea blend is demonstrated. A medium molecular weight PEG, PEG1k, is used to test the assumptions made based on the difference between
high molecular weight and low molecular weight PEG/urea systems. We utilize the combined Flory-Huggins theory and phase field theories that deal with the equilibrium thermodynamics and non-equilibrium dynamics of polymer mixture to determine the phase diagram of PEF1k/urea system.

The binary phase diagrams for the two crystalline polymer blends were by taking into account all possible interactions into consideration such as crystal-amorphous, amorphous-crystal and crystal-crystal interactions. The theory combines Flory-Huggins free energy for amorphous-amorphous mixing and phase field free energy of crystallization of crystalline components. The model can be used to determine a phase diagram involving various coexistence regions like liquid-liquid, liquid-solid and solid-solid coexistence regions bound by liquidus and solidus lines.\textsuperscript{96–98} The details have been discussed in Chapter II.

The phase behaviors of the PEG1k/urea blends have been investigated. The miscibility determination, phase diagram and morphology development were observed by means of DSC and POM. To confirm the co-existence regions, WAXD and FTIR were performed and tested with those the region predicted by the theory.

6.2 Experimental Section

The experimental phase diagram of the PEG1k/urea was established by means of polarized optical microscope (POM) and differential scanning calorimetry (DSC). Blends for the establishment of phase diagram of PEG1k were prepared by solvent casting method mentioned in Chapter III. The experimental procedures and characteristics like WAXD and FTIR are same as those described previously.
Figure 6.1(a) TGA therograms of various molecular weight PEGs
(b) DSC therograms of various molecular weight PEGs and urea
6.3 Results and Discussion

Figure 6.1(a) depicts the thermogravimetric curves of various molecular weight of PEG. Two features can be discerned: first, the decomposition temperature increases with increasing molecular weight; second, PEG1k shows a slower decomposition rate than the others. The reason of thermal stability dependence on molecular weight has been discussed in Chapter V.

As described in Chapter III, the physical appearance of PEG is different at room temperature changes with the molecular weight. PEG400 is viscous liquid at room temperature. PEG1k is waxy solid and PEG8k is powder. Figure 6.1(b) shows the melting transition curves as a function of molecular weight of PEG. One obvious feature is that the melting temperature increases with the increasing of PEG molecular weight. The increase in melting transition with increase molecular weight is in line with the general perception of polymer crystallization. It is known that the melting point of ultrahigh molecular weight of PEG (or PEO) is around 65°C, which is a little bit higher than the melting point of PEG8k. It is possible that this increasing trend will level off asymptotically with continued increase in molecular weight. Another feature is that the melting peak gets sharp with increasing molecular weight at the same heating rate. As the molecular weight of PEG increases, the kinetic stability of folded chain forms increase. Kambe demonstrated that the large molecular weight of PEG exhibits only folded-chain crystals.\textsuperscript{99} Whereas the low molecular PEG is a mixture of the crystalline lamellae with different folding periods was formed after cooling down, which is dependent on the temperature and annealing time.\textsuperscript{100,101} Therefore, the
melting peak of low molecular weight PEG become wider. Kovacs even made it possible to separate the melting peaks for these lamellae with different thickness with the same molecular weight.\textsuperscript{101}

Figure 6.2 shows the DSC diagrams of PEG1k/urea mixture covering the whole range of composition with a heating rate of 2°C/min. The melting peak of urea phase shifts a little bit to lower temperatures when the PEG1k concentration increases. The melting peaks of PEG1k show up around 38°C when the concentration of PEG1k reaches 35 wt%. The melting peaks around 110°C are due to the melting of PEG1k/urea cocrystals. It should be noticed that $\beta$–$\alpha$ transition phenomenon does not occur in PEG1k/urea system. The DSC thermograms imply that there are only three crystalline forms (PEG1k, urea and $\alpha$) in the PEG1k/urea system.
Figure 6.2 (a) DSC thermograms of PEG1k/urea blends with a heating rate of 2°C/min
(b) Plots of melting points of PEG1k/urea blends
Figure 6.3 depicts the WAXD pattern of PEG1k/urea blends at various compositions. The characteristic peaks of urea crystal are located at 22° and 24.5°. The 15/85 PEG1k/urea sample shows the same diffraction peak as urea. This implies that there is only urea phase in the mixture at a low PEG1k concentration. As the PEG1k concentration increase, new peaks show up at 18.5°, 25° and 26.5°. These peaks are due to the existence of PEG1k+urea. The pattern of 35/65 samples can be regard as a combination of pure PEG1k crystals and the α cocrystals. The neat PEG1k crystal shows two peaks at 19.5° and 23.5°. Therefore, at high concentration of PEG1k (85/15), the blends are a mixture of α cocrystals and PEG1k crystal, and the 55/45 sample is a mixture of urea, PEG1k and α cocrystals. Base on the WAXD patterns, we can draw a conclusion on the crystals coexist region: at low PEG1k concentration there is only urea crystal phase; in the middle area the sample is a mixture of urea crystal and α crystal, but the sample may also contain some PEG1k crystal; at PEG1k high concentration the blends is a mixture of α crystals and PEG1k crystal.

Figure 6.4 shows the FTIR absorbance diagram of PEG1k/urea at various compositions. The urea spectrum shows bands at 1466cm⁻¹ due to the N-C-N antisymmetric stretching vibration. These bands due to urea are greatly affected by the formation of inclusion compound. At low PEG1k concentration (10/90), the peaks of urea show little or no shift (from 1466 to 1465cm⁻¹). However, when the concentration of PEG1k increases to 30/70, the N-C-N peak separates into two peaks. One peak shifts to a high wavenumber and the other shifts to a lower wavenumber. This separation implies that there are two kinds of urea conformation formed in the
mixture. Keep increasing the concentration of PEG1k, the N-C-N shift to 1450 cm\(^{-1}\) at 80/20. These red shifts are due to the formation of inclusion cocrystal \(\alpha\). Based on the analysis of FTIR results, we can get a brief idea about the crystals coexistence region. At low concentration of PEG1k, there is only urea phase in the mixture. As the concentration of PEG1k increases, inclusion cocrystal \(\alpha\) forms and coexists with urea crystal in the mixture.
Figure 6.3 WAXD 2θ scans of PEG1k/urea mixture at various compositions
Figure 6.4 FTIR spectra of urea and PEG1k/urea mixture at various compositions
Figure 6.5 Temperature vs. composition phase diagram of PEG1k/urea blends. (a) The calculated phase diagram based on the phase field model of crystal solidification (b) Completed phase diagram, the dish line was drawn by hand based the experimental results and phase rules.
Based on the melting points distribution obtained by DSC and the crystals coexist condition justified by WAXD, we can draw a phase diagram by using a phase field model. As depicted in figure 6.5 (a), the self-consistent solution reveals a solid-liquid coexistence region bound by the solidus and liquidus lines. The critical interaction parameters are taken as: $r_1=20$, $r_2=2$ and $c_{\omega_1}=0.985$. The rest parameters are the same as the previous two systems. The anisotropic interaction parameter $c_{\omega_1}$ is very close to 1, which means the mixture of PEG1k/urea is similar with the ideal solid solution. Solid solution refers to a solution rather than a compound the crystal structure of solvent remains unchanged by addition if the solutes. In a completely ideal solid solution, the crystalline mixture is completely miscible at all concentrations. In PEG1k/urea system, the blends can be regarded as a mixture of two solid solutions. One is the urea solution with PEG1k acting as the solute in a matrix of urea. The urea solution shows similar WAXD 2θ-peaks as those of neat urea crystal. Therefore, the urea solid solution is labeled “Cr$_{\text{urea}}$” in the phase diagram. The other solid solution is the α cocrystal, which is an inclusion crystal of urea and PEG1k. The detail information about the structure of the PEG/urea inclusion crystal compounds have been discussed in Chapter II and III. A binary phase diagram of a mixture of two substances, urea and PEG1k, can be established.

Consider the “undissolved” PEG1k crystal at high PEG1k concentration region, a completed phase diagram was drawn in figure 6.5(b). Notice that the density of urea is 1.135g/cm$^3$ and PEG1k is 1.13, the difference between volume fraction and weight fraction is neglectable.
Figure 6.5 shows the binary phase diagram of PEG1k/urea system. The close resemblance 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 phase diagram displays a peritectic type with several distinct regions: isotropic (I), coexistence of crystal-isotropic liquid (Cr\textsubscript{urea}+I, Cr\textsubscript{α}+I) and crystal-crystal (Cr\textsubscript{urea}+Cr\textsubscript{α}). At low PEG1k composition, a single phase crystal (Cr\textsubscript{urea}) can be discerned. At high PEG1k concentration, the blend is Cr\textsubscript{α} phase mixed with “undissolved” PEG1k crystal.

As demonstrated in the previous Chapters IV and V, the calculated phase diagrams of various molecular weights of PEG and urea have been compared in Figure 6.6. All the phase diagrams show a consistent trend that depends on the molecular weight of PEG. The melting temperature of α crystal increases with increasing molecular weight. The melting temperature of α crystal is 90°C in PEG400/urea system and 110°C in PEG1k/urea system. In PEG8k/urea blend the melting point is 141°C, even higher than the melting temperature of neat urea. These differences in melting temperature lead to diverse of phase diagrams.

The major influence of molecular weight on the calculated phase diagram is the effect on parameter $r_1$, $r_2$ and $c_ω$. It is easy to understand that the molecular weight can affect $r_1$ and $r_2$, because $r_1$ and $r_2$ are related to the molar volume in the blends. In PEG400/urea system the $r_1/ r_2$ ratio is 4/2, which means the PEG occupied more
molar volume in the blend than urea. In PEG1k/urea the ratio increases to 20/2 due to the increasing degree of polymerization. In PEG8k/urea system the ratio reaches 80/2.

Another important parameter influenced by molecular weight is the cross-interaction parameter $c_\omega$. When the crystalline mixture is completely immiscible in the solid crystalline state and forms separate crystals, the cross-interaction parameter can be taken as zero, i.e., $c_\omega=0$, and thus the crystal order parameters develop independently of each other, which is a typical characteristic of a completely nonideal solid solution. On the other hand, if the system is a completely ideal solid solution, the crystalline mixture would be completely miscible at all concentrations, i.e., $c_\omega=1$, and then the crystal order parameters must be coupled to each other so that the systems can undergo cocrystallization. The value of $c_\omega<1$ implies that the system is destabilized and crystallization is favored to develop as separate individual crystals, while $c_\omega>1$ indicates the formation of azeotropic cocrystals which have an azeotrope point higher than the melting transition of either component i.e., the system is stabilized. Compare the three calculated phase diagram in figure 6.6, we can see how the $c_\omega$ influence the phase diagram. The $c_\omega$ for PEG400/urea system is 0.9 which favors a formation of eutectic mixture. Eutectic system means that the mixture has a single composition that solidifies at a lower temperature than any other composition made us off the same ingredients. In PEG1k/urea system the value of $c_\omega$ is 0.985 which is very closed to the ideal solid solution. In the PEG8k/urea blends $c_\omega$ is 1.055 and leads to azeotropic type of phase diagram. The PEG8k/urea solid solution
Figure 6.6 Comparison among calculated phase diagrams of various molecular weight PEG/urea blends. (a) PEG400/urea (b) PEG1k/urea (c) PEG8k/urea
(α+cocrystal) is more stable than those of pure constituent crystals. The strong complexation of α cocrystal is the manifestation of the azeotropic.

6.4 Conclusions

In order to clarify the effects of PEG molecular weight on melting transitions of PEG/urea blends, the PEG1k/urea system were investigated. The phase diagram of PEG1k/urea blend was established based on the melting points measured from experiment and the calculation in the frame work of the combined Flory-Huggins theory and phase field model.

There are three crystal coexistence regions in the phase diagram: single urea solid solution, \( \text{Cr}_{\text{urea}}+\text{Cr}_\alpha \) and single \( \alpha \) crystal. The system shows a peritectic phase diagram which is similar as the PEG400/urea. There is no \( \beta \) crystals exist in the PEG1k/urea system.
CHAPTER VII
SUMMARY

In this thesis, the effect of molecular weight on the phase diagrams of PEG/urea mixtures have been investigated both experimentally and theoretically. The phase diagram of high molecular weight PEG (PEG8k) and urea was found to be of azeotrope type consisting of urea and \( \alpha \) inclusion crystal. With the decreasing temperature, the eutectoid behavior was observed, whereby the stable \( \alpha \) crystal was segregated into the urea crystal +\( \alpha \) crystal and the \( \beta \) crystal + PEG crystal coexistence phases. This observed phase diagram is consisted with those obtained by the Pellerin’s group for the PEO/urea system and also by us except that we are able to identify the azeotrope and eutectoid behaviors in this thesis.

Upon lowering molecular weight of PEG to PEG400, the melting point of \( \alpha \) cocystal was observable but the \( \beta \) crystal no longer existed. The lack of \( \beta \) crystal is consist with that reported by Guenet’s group. Of particular interest is that the PEG400/urea shows a eutectic type phase diagram in which the isotropic liquid (I) was found to separate into two solid solutions (\( \text{Cr}_{\text{urea}} + \text{I} \), \( \text{Cr}_{\alpha} + \text{I} \)).

In the case of blends of medium molecular weight PEG (PEG1k) with urea, a peritectic phase behavior was observed showing the solid-solid-liquid peritectic line. It is reasonable to conclude that upon increasing molecular weight of PEG, the phase
diagram transforms from eutectic to peritectic to azeotrope while the pure $\alpha$ phase region expands.

In the theoretical calculation, the changing trend from the eutectic, peritectic to azeotrope was captured by varying the cross interaction strength ($c_\omega$) from 0.9, 0.985 to 1.055. The relationship between molecular weight of PEG ($r_1$) and $c_\omega$ is presently unclear except that they are mutually dependent via total free energy description. It is also noticed that the melting temperatures of PEG as well as $\alpha$ crystals increase upon increasing PEG molecular weight. The lack of $\beta$ crystals in the lower molecular weight PEG may be attributed to increasing number of hydroxyl end group of PEG chain. It may be hypothesized the OH group affect the stability of $\alpha$ inclusion crystal and $\beta$ metastable crystal, since these crystals are formed by complexation through strong interspecies hydrogen bonding. The relationship between $c_\omega$ and molecular weight will be left to the scope of future study.
REFERENCES


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