LIQUID-LIQUID PHASE SEPARATION IN AN ISOREFRACTIVE POLYETHYLENE BLEND MONITORED BY CRYSTALLIZATION KINETICS AND CRYSTAL-DECORATED PHASE MORPHOLOGIES

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ABSTRACT

A series of polyethylene (PE) blends consisting of a linear high density polyethylene (HDPE) and a linear low density polyethylene (LLDPE) with a hexane-chain branch density of 120/1000 was prepared at different concentrations. This set of blends possessed isorefractive indices and thus, was difficult to detect their liquid-liquid phase separation via scattering techniques. The LLDPE only crystallized below 50 °C; therefore, above 80 °C and below the melting temperature of HDPE, we had a series of crystalline-amorphous PE blends. Above the melting temperature of HDPE, this series of blends were in liquid state. A specifically designed two-step isothermal experimental procedure was utilized to monitor the liquid-liquid phase separation of this set of blends. The first step was quench the system from temperatures of known miscibility and isothermally anneal the blend at a temperature higher than the equilibrium melting temperature of the HDPE for the purpose of allowing the phase morphology to develop via a liquid-liquid phase separation. The second step was to quench the system to a temperature at which the HDPE could rapidly crystallize. Monitoring the overall crystallization kinetics via the time for developing 50% of the crystallinity ($t_{1/2}$) provided an experimental approach to identify the liquid-liquid phase separation binodal curve of the system because phase separation results in HDPE-rich domains exhibiting increased
crystallization rates and thus shortening the $t_{1/2}$. The annealing temperature in the first step at which the $t_{1/2}$ of the system exhibits an onset of the decrease is the temperature of the binodal point for that blend composition. In addition, the HDPE-rich domains crystallized to formed spherulites which decorate the liquid-liquid phase separated morphology. Therefore, the crystal dispersion indicates whether the phase separation followed a nucleation-and-growth process or a spinodal decomposition process. These crystal-decorated morphologies enabled the spinodal curve to be experimentally determined in this set of blends with isorefractive indice.
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CHAPTER I
INTRODUCTION

Single-site catalysts allow one to precisely control the structure of molecules including the regular incorporation of short-chain branches during synthesis of polyolefins.\textsuperscript{1-4} The commercial success of polyolefins sometimes requires the use of binary blends to improve and optimize targeted properties.\textsuperscript{5-7} It is typical to blend two different polyethylenes (PE): a high density PE (HDPE) with either no branch or a very low short-chain branch concentration that can crystallize, with another linear low density PE (LLDPE) with high short-chain branch concentrations that either crystallize at much lower temperatures or that is a rubbery elastomer. The LLDPE increases the toughness and impact strength of the blends in the solid state as well as improves their melt processability, while the HDPE enables the blends to maintain good tensile properties.

Even though the two components possess identical chemistries, it is known that HDPE and LLDPE are not always miscible. The miscibility of the two components is critically dependent on molecular characteristics such as molecular weight, short-chain branch concentration, branch type, composition, and processing conditions.\textsuperscript{19-32} Recent researches show that most PE blends exhibit an upper critical solution temperature (UCST).\textsuperscript{19,24-32} The interaction between molecular chains
increases with temperature cooling down. At high temperature, blends could be miscible, while the phase separation occurs during cooling. On the other side, since at least one component (HDPE) is crystallizable, phase separation starts to interplay with crystallization when temperatures cool below the melting temperature of crystallizable component.

One recent investigation on the interplay of liquid-liquid phase separation and crystallization in a PE blend involved PE components that had hexane and butane branches at different compositions. In the hexane branched PE, the hexane branch concentration was 9 per 1000 carbon atoms with a molecular weight of 112k g/mol, while the butane branched PE had a branch concentration of 77 per 1000 carbon atoms with a molecular weight of 77k g/mol. The hexane branched PE crystallized at high temperatures, and the butane branched PE only crystallized at much lower temperatures. Using scattering and optical microscopy techniques, a UCST liquid-liquid phase separation phase diagram was obtained. The binodal curve and its intersection with the melting temperature depression curve of the hexane branched PE crystals was experimentally determined. Within the phase separated region, the extrapolated melting temperatures were found to be invariant with respect to the concentration. This implies that the crystallization started after the concentration evolution of the liquid-liquid phase separation process was complete. The main difficulty in studying this type of PE blend lies in how to precisely identify and measure the crystallization and liquid-liquid phase separation kinetics. In the same series of PE blends described above at a 50/50 composition, the crystal growth
rates were measured after quenching the samples from the homogeneous melt to different crystallization temperatures using polarized light microscopy (PLM). The growth rates of the liquid-liquid phase separation in the coarsening stage were monitored utilizing a small-angle light scattering technique.\textsuperscript{54} It was found that a kinetic cross-over temperature for the phase separation and crystallization rates takes place at 118 °C. When the crystallization temperature is below 118 °C, the crystallization rate is faster than the phase separation rate, and so, crystallization dominates the final phase morphology. Significantly above this temperature, the phase separation process dominates the final phase morphology. Near 118 °C, the two processes compete with each other.

The earliest recognition of the inter-dependence between liquid-liquid phase separation and crystallization in polymer blends was reported more than 20 years ago.\textsuperscript{75,76} Since then, a number of different crystalline-amorphous polymer blend systems have been investigated. Because the equilibrium crystalline and morphological states are never reached on the experimental time scales in polymer blends, the interplay of these two processes in polymer blends is obscured by metastable states. Therefore, we need to take these temperature and time dependent metastable states into account.\textsuperscript{58,117,118}

Our interest is in monitoring the liquid-liquid phase separation in a crystalline-amorphous blend via crystallization kinetics and phase morphology. An experimental procedure was specifically designed such that liquid-liquid phase separation occurs before crystallization. This experimental procedure is a two-step
An isothermal process. The first step is to isothermally anneal the blend to concentration equilibrium at temperatures around the binodal curve boundary yet above the melting temperature of the crystalline phase to prevent crystallization. This leaves the phase morphology in a metastable state.\textsuperscript{58} In the second step, the sample is isothermally crystallized by quenching it to a lower temperature where crystallization occurs rapidly. Further concentration changes in the phase domains in the polymer are minimal because of the rate of crystallization. Additionally, the phase morphology of the domains is also preserved by crystal decoration.

In order to test this experimental approach, a series of PE blends were prepared for study. They consist of a linear, highly-crystallizable HDPE component and one less-crystallizable LLDPE component that possesses randomly distributed octane branches at a concentration of 120 branches per 1000 carbon atoms. Utilizing the two-step isothermal process described above, the crystallization kinetics was monitored and the phase morphology of these binary blends was observed to determine the binodal and spinodal curves of the liquid-liquid phase separation.

In this dissertation, the first part of Chapter 2 is a general overview of categories of PE and its blends. At the beginning, a brief history of the synthesis and commercialization of PE will be reviewed. Next, we will focus on the phase behavior of PE blends and the dependence of miscibility on molecular characteristics such as molecular weight, short-chain branch concentration, branch type, composition. Since this project is about a new method to determine the phase diagram, the various measurements for determining miscibility are briefly reviewed. Some emphasis will
be put on overcoming the experimental barrier of the close refractive indices of PE blends.

In the second part of Chapter 2, the complete understanding of the physics behind the liquid-liquid phase separation is a prerequisite to perform our experimental approach; therefore, the liquid-liquid phase separation thermodynamics and dynamics generalized to all polymer blends are reviewed.

In the followed part of Chapter 2, the focus is transferred to liquid-liquid phase separation coupling with crystallization, which is another experimental limit we are facing, irrespective of the one from the close refractive indices. Thus the good understanding the coupling between crystallization and liquid-liquid phase separation is necessary. This part introduces the coupling between the crystallization and liquid-liquid phase separation in detail, from the proposed thermodynamics model, to the prediction of the phase diagram, to the concrete examples of the different interplay scenarios.

The final part of Chapter 2 reviews how crystallization takes place in the crystalline-amorphous polymer blends, including the selection process or “poisoning” process during the crystallization, melting temperature depression of crystals in the miscible blends, and also some reported results of the effect of phase separation behavior on the nucleation.

Chapter 3 is the conceptual experimental design, detailed procedure, and experimental conditions. Our project core experimental design, two-step isothermal annealing, is clearly illustrated in this part.
Chapter 4 is the results and discussion for the determination of the binodal curve utilizing crystallization kinetics. It elaborates the changes in crystallization kinetics as well as in crystallinity under the phase separation effect for the blends with different HDPE volume fractions. Through our two-step annealing process, the binodal point could be determined by the sudden change in crystallization kinetics in terms of different first-step annealing temperatures at a fixed HDPE volume fraction. In this chapter, it also shows the result of the time phase separation consumes to reach equilibrium under isothermal condition.

Chapter 5 is the results and discussion for the determination of the spinodal curve using the crystal decorated phase morphology. Phase separation morphology is preserved through two-step annealing process. Crystal-decorated dispersed droplet phases, bicontinuous phases, and reversed matrix phases are illustrated in the experimental results. At each fixed HDPE volume fraction, the spinodal point could be determined by the changes in crystal-decorated morphologies which reflect the kinetic pathway altering from nucleation growth to spinodal decomposition.

Since most industrial investigations in the effect of phase separation on the crystallization use non-isothermal method, Chapter 6 explains the inaccuracy brought by the non-isothermal method and compares it with the two-step isothermal annealing process. The advantage of our two-step annealing process is proved again in this chapter.

Chapter 7 comes to a summary of research highlights.
CHAPTER II
BACKGROUND

2.1 Introduction of Polyethylene

Polyethylene (PE) is the most widely used consumer commodity polymer due to its low price, light weight and high chemical resistance. It has many applications, such as used in films, sheets, fibers, pipe and many types of molding. The wide range of applications is possible because of the variety of PE in the category of either homo or copolymers which are different from the molecular weight, type of branches, or composition of branches. In fact, convention ‘polyethylenes’ include any polymer for which ethylene is the main comonomer and that has some degree of crystallinity at room temperature. The first part of this chapter, a brief introduction of the various types of PE is given in the order of commercial availability.

A. Low Density Polyethylene (LDPE)

The first form of PE to become commercially available was discovered by Fawcett et al. at ICI in 1933, and developed into practically reproducible procedure by another ICI chemist, Michael Perri in 1935. Although this was an unintentional consequence of research on general chemical reactions at high pressure, the value of the new material was quickly realized and exploited, for example, in cable insulation for radar in World War II. In the sixty years of its history, its uses have grown and its
production techniques have been advanced until its production is now one of the largest of any material in the world.

The basic synthetic process is the free radical polymerization of supercritical ethylene. Most reactions are done at high pressure (over 150 MPa) and temperatures at 150 °C to 350 °C. Oxygen or peroxide is commonly used as the initiator. Even though the basic technology is sixty years old and there have been many developments and even “revolutions” in LDPE production, and new plants continue to be built for these products.

The polymers made in this process are characterized as having a highly branched structure. This is believed to come about from two main processes, backbiting and chain termination reaction.

![Figure 2.1.1 Backbiting reaction.](image)

In the backbiting process, the free radical on the growing end of a chain can loop back to some other portion of the chain and reacts. The loop breaks at the point of reaction, and the radical is transferred to a section in the middle of the chain. The loop then becomes a branch of the chain, which continues to propagate chain growth.
at the reaction point, as shown in Figure 2.1.1. This backbiting reaction mainly leads to short branches with a few repeat units long.

Much longer branches are produced from the second mechanism, chain termination reaction, in which the growing end of a chain terminates on another molecule, as shown in Figure 2.1.2.

\[ \text{Figure 2.1.2 Chain termination reaction.} \]

Several other mechanisms have also been proposed, while the results of chain structures are very complicated. For instance, a tree-like architecture with both short and long chain branches can be found, but the complete mechanism has not been firmly elucidated.

LDPE is defined by a density range of 0.910 - 0.940 g/cm³, named due to its low density. The reason for its low density is that it has lower crystallinity. Only long ethylene sequences can participate in the crystal lattice of PE, and the side branches are excluded out. This exclusion serves to lower the crystallizability of LDPE. Since the density of these branches can be controlled by various processing variables (temperature, pressure, initiators), the density and crystallinity of the PE can be controlled.

LDPE has applications in a wide variety of markets (see Figure 2.1.3). The mechanical properties of each of these materials can be varied by controlling the
density and molecular weight of the polymer. In general, they are not as tough as those made from linear PE without long side branches. On the other hand, these long branches are advantageous to ease the processing of LDPE as compared to its linear counterparts. Thus this factor has helped maintain its use as an important product.

B. High Density Polyethylene (HDPE)

The next major advance in PE production was the discovery of catalysis that allows the synthesis of a linear version of PE by Ziegler in 1953. The new linear polymers were more crystallizable than LDPE, and given the name ‘high density’ PE (HDPE). Because of this, the new material had a very different set of mechanical properties, showing stronger intermolecular forces and tensile strength than LDPE. It has become one of the largest produced materials around the world.

Although HDPE can be made in a homogeneous catalytic process such as bulk or solution, the majority is made with supported, heterogeneous catalysts. This is
mainly because of the easy separation the catalyst from the polymer. The catalysts are typically titanium chlorides supported on silica. The activity of these catalysts has increased greatly over the years, so that achieving currently rates of 1000,000 gram of PE per gram of catalysis, or even more\textsuperscript{12}

The molecular weight of the HDPE is controlled by the addition of chain transfer agents, typically via hydrogen. As a result, a wide range of molecular weights is produced. The density of PE products varies slightly with molecular weight, i.e., the density is a bit less for very high molecular weights. The main way to control density is by adding a small amount of a comonomer such as butane. This breaks up the ethylene sequences and so reduces crystallinity.\textsuperscript{11} Because of the variability in properties, modern HDPE plants have a great deal of flexibility in the kinds of products they can make.

HDPE can be used in a great variety of applications as well (shown in Figure 2.1.3), such as milk bottles, pails, detergent bottles, stadium cups, and lubricating oil bottles. In addition, a large number of the piping used for water distribution and sewage is now made from HDPE. It is also increasingly used for gasoline tanks on motor vehicles. There are some high technology applications as well, such as medical prostheses and high strength fibers. The latter ones are made from HDPE of extremely high molecular weight, and used for sails and bullet-proof vests as well.\textsuperscript{1,4}

C. Linear Low Density Polyethylene (LLDPE)

LLDPE is a substantially linear PE, with significant numbers of short branches, commonly made by copolymerization of ethylene with longer-chain olefins. The
structure of LLDPE differs from that of conventional LDPE because of the absence of long chain branching. The linearity of LLDPE results from the different manufacturing processes of LLDPE and LDPE. In general LLDPE is produced, at lower temperatures and pressures, by copolymerization of ethylene with \( \alpha \)-olefin comonomers as butene, hexene, or octene. The copolymerization process produces an LLDPE polymer that has a narrower molecular weight distribution than conventional LDPE.

The first method to produce LLDPE is through a solution processing. This method is fairly expensive due to the need to remove the polymer from the solution, Karol and coworkers at Union Carbide developed a cheaper process in the 1970’s,\(^{13}\) which is a gas-phase process. Therefore, LLDPE from Unipol process become the most widely used today. Several other companies have also developed successful gas-phase technology to make LLDPE. However, one of the main limitations of this gas-phase technology is that the monomer must be kept volatile in the gas-phase, thus only propylene and butene can be used as comonomer when using Ziegler-Natta catalysts, except 1-octene which costs energy too high to be feasible when kept into gas-phase.

In terms of volatility of comonomer, the solution processes for LLDPE are able to produce octene or other large \( \alpha \)-olefins copolymer with PE. Although ethylene-octene copolymers are more expensive to produce than ethylene-butene ones, they have superior mechanical performance, such as tear strength when made into films.\(^{14}\)
The largest use of LLDPE is for film applications similar to LDPE. LLDPE has no long branches, thus, it has mechanical properties superior to LDPE, especially in terms of toughness attributes such as puncture or tear resistance. Compared with HDPE, the branches of LLDPE give superior processing characteristics; while compared with the long branches of LDPE, LLDPE has less superiority in terms of processing characteristics. In many regions, film extruders are very low-powered and need to use blends of LDPE with LLDPE. As a result LLDPE has not completely replaced LDPE as was expected upon its introduction in the 1970’s.

D. Plastomers

This is a class of ethylene copolymers that stand between LLDPE and the completely amorphous elastomers, so they haven been dubbed ‘plastomers’, also called ‘very low density PE’ or VLDPE. This type of ethylene copolymer has a large amount of comonomer, and there is only a very small amount of crystallinity left. The crystalline phase in these plastomers is so small that the domains can not order into periodic lamellae, but more likely are arranged like physical cross-linking. Therefore, they are more elastic and less stiff than LLDPE. With the advance of metallocene catalysts, there has been more controbility to adjust branch structure or density by incorporating various types or amounts of comonomers. VLDPE has its use as a sealing layer in film applications and controlled permeation packaging for fruits and vegetables. VLDPE is a good example of how the various categories of polyolefins are merging into one another. Also, it shows the remarkable diversity of uses for polyolefins.
E. Impact of New Catalysts

In the last two decades, the most important developments in polyolefin technology are the improvements in catalysts.\textsuperscript{2} A great number of new catalysts have been found. The most prominent milestone is the metallocene catalysts. The key advancement came in 1978 when Sinn and Kaminsky discovered the efficiency of methyl alumoxanes as cocatalysts for zirconocenes.\textsuperscript{15} They had high polymerization activities, but required excessively high levels of alumoxane to be commercially feasible. However, this led to more efforts in many industrial labs, finally leading to commercialization of metallocene-produced PE, first by Exxon in 1991, then by Dow in 1993, and now by many polyolefin producers.\textsuperscript{4}

The main advantage that metallocenes bring is that they are single-site catalysts which allow much greater control of parameters such as molecular weight distribution and branch density distribution. For PE, single-site catalysts allow greater ability to incorporate comonomer, which results in more new products such as ethylene-hexene and ethylene-octene copolymers made in more efficient processes. It also provides the ability to introduce long branches in the linear polymers.\textsuperscript{3} Furthermore, metallocenes catalysts allowed the production of polymers that were not commercially feasible before, such as syndiotactic polystyrene, so-called cyclic olefin copolymers.\textsuperscript{16}

The success of metallocene catalysts has led organometallic chemists to examine the catalytic activity of other compounds. Chemists at the University of North Carolina and Dupont have found that nickel and palladium complexes with diimine ligands polymerized ethylene and other olefins.\textsuperscript{17} The interesting part is that
under certain conditions the homopolymers of ethylene contain many short branches; while, homopolymers of an olefin such as 1-hexene can be made to contain fewer branches than the number of monomers, which means that some of the monomers have been incorporated end-to-end. There have also been reports of olefin catalysis with other late-transition-metals such as aluminum.\textsuperscript{18} The success of such catalysts is significant, as they are more tolerant of polar impurities that can poison polymerization. In fact, such compounds can copolymerize monomers such as acrylates. As more systems are examined, it is likely that many more advances in polyolefins will be found.

2.2 Polyethylene Blends

Even with the large range of PE available, it is difficult to choose a single type of PE with the best properties. Blending is usually the solution to property optimization. PE blends have been used to provide desired range of properties.\textsuperscript{5-7}

2.2.1 Miscibility of Polyethylene blends

Although most polymer blends are immiscible, PE blends have a high degree of miscibility due to similar chemical structures. PE can be blended within its own polyolefin family, as well as with other polymers. In this dissertation, we only focus on the one blended within its own PE family. Phase behavior is caused by the molecular structure, such as molecular weight, branch type, and branch density.\textsuperscript{19-32}

The blends of PE are regarded as “nearly miscible”, but their miscibility has been studied extensively. The results show that PE blends are not truly completely miscible; in fact, most of these blends possess the upper critical solution temperature
Some of them even have exhibited an lower critical solution temperature (LCST) phase behavior. The reason for the difficulty in differentiating their phase behavior is the close refractive index from the same base chemical component. Because of the refractive index similarity, the conventional techniques for measuring the phase miscibility failed in the case of PE blends, such as phase contrast microscopy, or the cloud point light scattering. The details will be elucidated in the latter part of this chapter. The results of miscibility for the PE blends were mainly obtained by the small-angle neutron scattering (SANS). Wignall and Alamo et al. investigated the melt-miscibility of both HDPE/LDPE and HDPE/LLDPE, and the results confirms that the mixture are homogeneous in the melt for all compositions when the branch content is low, i.e. $< 4$ branches/100 backbone carbon atoms for a molecular weight of $M_w \sim 100k$ g/mol. However, when the branch content is higher, i.e. typically $\geq 8$ branches/100 backbone carbons the blends phase separate in the melt. Crist and co-worker have also used SANS to determine the phase behavior of 50/50 blends of HDPE and hydrogenated polybutadiene (HPB) that are structurally analogous to ethylene-butene-based LLDPE (although the former have narrower molecular weight and composition distribution than those of LLDPE synthesized by the metallocene or Ziegler method). Their results also confirmed that the blends are homogeneous in the melt when the branch content is low. The miscible blends in the melt were found to have $\chi$ values on the order of $10^{-4}$. If combined other measurements results, the following conclusions are regarding the miscibility of polyethylene blends. The branch content is the most
important factor to control the miscibility. The miscibility decreases with increase of branch content.\textsuperscript{24-27} The branch type also affects the miscibility. The miscibility decreases with increase of branch length. For example, LLDPE with 4.4 butene branches / 100 backbone carbons is miscible with HDPE at all composition.\textsuperscript{29} However, LLDPE with 4 hexene branches / 100 backbone carbons is immiscible with HDPE when the volume fraction of HDPE is less than 60\%,\textsuperscript{32} and LLDPE with 2.1 octene branches/100 backbone carbons is claimed immiscible with HDPE when HDPE volume fraction is less than 50\%.\textsuperscript{31} It is hard to deduce the effects of long branch chains in LDPE. Furthermore, decreasing molecular weight increases the miscibility. For example, in the study of Hill \textit{et al.}, HDPE with molecular weight 100k g/mol shows phase separation with the LDPE with 5.2 branches/100 backbone carbons when the HDPE volume fraction is lower than 50\%. However, HDPE with molecular weight of 2553 g/mol is miscible with LDPE at all HDPE composition.\textsuperscript{30} Most of blends possessed an UCST type phase behavior within the temperature range between the processing temperature and application temperature. Thus, the blends become more miscible with increasing the temperature. Usually, the blends become more miscible with the increase of linear polyethylene content.

In summary, the miscibility of PE blends is dependent on molecular structures (molecular weight, branch density and type), temperature, and composition. Therefore, phase diagrams based on the composition and the temperature are necessary to characterize the miscibility of specific PE blends.
2.2.2 Experimental Techniques for Miscibility Determination In PE Blends

The similarity in physical and chemical structures among PEs makes the experimental determination of two components’ solubility more difficult than for other polymer families. The large varieties of PE are nearly identical in melt density and refractive index and sometimes in glass transition temperature as well. Therefore, many of the conventional experimental techniques for determining miscibility boundaries are hard to exploit in PE blends. As well reviewed by Crist and Hill, considerable progresses have been made during the past decade in measuring the miscibility of polyolefin blends (including PE blends). Here, a brief review on how these measurements are made is presented.

The major advances come from small-angle neutron scattering (SANS) measurements in single-phase mixture region containing one deuterium-labeled component, which provides direct information on the thermodynamic interactions that govern phase behavior. Nuclear reaction analysis (NRA), which also needs deuterium labeling, has been used to evaluate the composition of coexisting liquid phases. Finally, light scattering techniques and measurements of the pressure-volume-temperature (PVT) properties of pure components provide less direct, but still useful information about PE mixing characteristics.

A. Small-angle Neutron Scattering

Wignall et al. were the first to study the miscibility of polyolefins using SANS. In 1981, they showed that PP (polypropylene) and PE are not miscible in the melt. Soon after, they examined blends of various types of PE. Then in 1990, Crist
first accomplished this quantification of interactions in the blends,\textsuperscript{24,35-37} and was shortly followed by the groups in Princeton and Exxon.\textsuperscript{38-40} More recently, with the progress in the metallocene produced PE copolymers, SANS also has been used for the determination of interaction in this new specie of PE.\textsuperscript{41} There is now a large number of SANS-derived data on around 200 blends involving more than 50 polyolefin species.\textsuperscript{5}

With SANS the interaction strength can be directly determined through the random-phase approximation. Assuming the $\chi$ of the Flory-Huggins theory is independent of the volume fraction, one can derive the following expression for $S(q)$, the static structure factor for a single-phase blend:

$$\frac{1}{S(q)} = \frac{P_1}{M_1 \phi_1 P_1(q)} + \frac{P_2}{M_2 \phi_2 P_2(q)} - 2 \frac{\chi}{RT}$$  \hspace{1cm} \text{Equation 2.1.1}

In this equation, $P_i(q)$ is the form factor of component $i$, which is generally given by the Debye formula for monodisperse random coil polymers. For polydisperse materials, more general expressions are available that take the molecular-weight distribution and long-chain branching into account.\textsuperscript{42} The SANS experiment provides $S(q)$, and when both deuterated and hydrogenated versions of each component are available, each $P_i(q)$ can be obtained by independent SANS experiments,\textsuperscript{38} so for the blend the only unknown in Equation 2.2.1 is $\chi$. Values of $\chi$ as a function of $T$ have been determined in this way for many polyolefin blends. However in some cases, the dependence on the volume fraction can not be neglected, thus the primitive assumption is invalid. Furthermore, because of the deuteration of one component,
some controversies in the miscibility arise due to the change in the intrinsic molecular interactions between the deuterated and hydrogenated components.\textsuperscript{36,39,43}

B. Nuclear Reaction Analysis

The use of NRA to determine polyolefin (including polyethylene blends) phase behavior was pioneered by Klein and coworkers.\textsuperscript{44,45} The basic physics of NRA is the nuclear reaction of $^3\text{He}$ with a deuteron to produce $^4\text{He}$ and a proton with a combined kinetic energy of 18.4 MeV. When passing through matter, the product $^4\text{He}$ loses kinetic energy in proportion to the distance traveled. Thus, when a monochromatic beam of $^3\text{He}$ is shined on a polymer sample containing some deuterium, the energy of the emerging $^4\text{He}$ can be related to the depth at which the reaction took place. The energy spectrum of $^4\text{He}$ translates accordingly into a depth profile of deuterium in the sample.

This method can be used to determine the amounts and compositions of the phases on the coexistence curve of a blend. Two polymers are made into a bilayer, with one labeled with deuterium, and then allowed to equilibrate to the maximum mixing level at a chosen temperature. If the mixture is phase separated at this temperature, the final state will consist of a layer at the top composed of one of the phases, an interfacial region of various compositions, and a layer at the bottom composed of the other phase. The deuterium depth profile from NRA thus gives the composition of each equilibrium phase on either side of the interface, and a material balance gives their amounts. If the mixture is miscible at this temperature, the final state will reach one layer with both top and bottom having same composition. Such
measurements at other temperatures then provide the coexistence binodal curve for the blend. The NRA and SANS techniques can be complementary, in that they can be run on the same polymer pair, one providing data in the two-phase region and the other in the one-phase region. However, it still can not solve the ambiguity from the intrinsic isotope interaction. Furthermore, there is the possibility of that the $^{3}$He beam shining may break down the real shape of phase morphology. Regardless of the intrinsic isotope effect and $^{3}$He beam shining damage, SANS and NRA are still two major convincing techniques to study the miscibility of polyolefin blends at the current stage.

C. Miscibility Study form Crystal Morphology

Studies in liquid-liquid phase separation in blends of homopolymer with branched copolymer through crystallization had been preceded at Bristal for some years. When crystallization occurs from the immiscible blend, each phase must crystallize independently. The different crystallization condition in two phases will lead to the different crystallization temperatures, separated melting endothermic peaks and double crystallization morphologies. Therefore, investigations were done with differential scanning calorimetry (DSC), and transmission electron microscopy (TEM) on a set of quenched PE blends at different conditions.46 Two types of crystals, separated on a scale of micrometer, were observed by surface replica TEM after quenching blends at various compositions from some temperatures; while two crystal melting peaks were observed by DSC after quenching at the same conditions. If only one crystal type was observed by TEM, which indicates blend miscible, there is only
one melting peak recorded. However, the separation of melting peaks is more sensitive to composition changes than to changes in initial quenching temperatures. Thus when blends were quenched form relatively higher temperatures, the DSC melting peaks were not as well separated as the TEM results.46,47

Bristol group proposed a phase diagram through the morphology map, in which two-well separated crystal populations found on quenching were designated “separated” at the quenching temperature, and a single crystal population found on quenching was assigned “mixing”.46,47 The phase diagram revealed an unusual shape that the two-phase region formed a close loop located at the low linear PE contents,48 These observation arose the arguments that the separation seen in quenched blends was not the genuine result of liquid-liquid phase separation in melt, but the result of separation during crystallization.25,49

D. Light Scattering

Because the density and refractive index differences between pairs of PE molecules are usually quite small, it is difficult to use light scattering on PE blends (even polyolefins) to determine the cloud-point curve of these materials. To the eye, both miscible and immiscible blends will look clear for nearly all pairs. However, light scattering can still be used to determine the late stage of phase separation already at large scale for certain types of PE blends due to the increases in scattering from phase separation. It should be noted that this increase in scattering has great dependence on the extent of phase separation and the molecular chain structure (the differentiation of molecular chain structures may be large enough to provide relatively
large difference in refractive index). The technique is particularly effective to study the late stage of phase separation with the already-known miscibility boundary in the phase diagram. A great deal of work has been done on blends of the various forms of PE.50-54 As light scattering does not require deuterium labeling, if combined with SANS, hence, it is useful for evaluation the isotope effects in deuterated system. At certain level light scattering is still very useful in confirming the phase behavior of polyolefin blends.

E. Other methods

Some work has also been done using other experimental techniques, such as thermal analysis,55 and rheological analysis.56 There is a large number of published works on the microscopy of polyolefin blends, but these studies are nearly always for blends that have crystallized, therefore provide no direct evidence of the state of the melt.57

Thus, so far there is none perfect technique to provide the direct evidence for the true phase behavior of the PE (also polyolefin) blends. Multiple techniques are still being developed to deal with the various pitfalls to arrive at a major solution.

2.3 Liquid-Liquid Phase Separation

Since the focus is on the miscibility and phase behavior of liquid-liquid phase separation of PE blends, this section will discuss the thermodynamics behind the phase separation behavior.
2.3.1 Thermodynamics of Liquid-Liquid Phase Separation

The thermodynamics of mixing is the principle for all blends. When mixing two components with equal or different molecular sizes, liquid-liquid phase separation may occur. This relies on the difference in the Gibbs free energy between mixed and unmixed state, $\Delta G_{\text{mix}}$, which is the driving force of phase separation. The relationship between the differences in the Gibbs free energy of mixing verses the concentration of a specific component in a binary mixture is schematically shown in Figure 2.3.1, which illustrates free energy changing with three-temperature routes.

![Figure 2.3.1 Differences in the Gibbs free energy of mixing, $\Delta G_{\text{mix}}$, with respect to concentration for a binary mixture. (a) Both liquids are completely miscible forming one liquid phase; (b) this mixture is at the critical point; and (c) liquid-liquid phase separation occurs. Note that these three cases are at three different temperatures.][1]

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[1]: Figure 2.3.1 Differences in the Gibbs free energy of mixing, $\Delta G_{\text{mix}}$, with respect to concentration for a binary mixture. (a) Both liquids are completely miscible forming one liquid phase; (b) this mixture is at the critical point; and (c) liquid-liquid phase separation occurs. Note that these three cases are at three different temperatures.58
It elucidates the dependence of liquid-liquid phase separation on the
temperature at a constant pressure. In Case (a) of Figure 2.3.1, blends are miscible
across over all concentrations. The criterion for the complete miscibility is that the
second derivative of the Gibbs free energy with respect to the concentration
\( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x^2} \) has to be larger than zero for all compositions at a given temperature
and pressure as shown in the figure. The concave upward shape of the line is an
indication that the derivative will be positive over all compositions. With a change in
the temperature at a constant pressure, [Case (b) and Case (c) in Figure 2.3.1], the
Gibbs free energy profile of the mixture changes.58

Case (b) of Figure 2.3.1 represents the mixture at the critical point. At the
critical point, both the second derivative \( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x^2} \) and the third derivative
\( \frac{\partial^3 \Delta G_{\text{mix}}}{\partial x^3} \) of the Gibbs free energy are required to be equal to zero. It further
indicates that the miscibility of the mixture has reached the maximum stability above
which the sign of \( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x^2} \) becomes negative, and thus leads to the onset of the
liquid-liquid phase separation.58

For Case (c) in Figure 2.3.1, the curve changes to have a central concave
downward section with two inflexion points, \( x_1^A \) and \( x_2^A \), at which \( \partial \Delta G_{\text{mix}}/\partial x \) are
equal (If the two molecular sizes and weights are equal , then \( \partial \Delta G_{\text{mix}}/\partial x \) are equal to
zero) and \( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x^2} \) is larger than zero. When the concentration of the initial
mixture is between \( x_1^A \) and \( x_2^A \), after quickly quenched to the one corresponding to the
Case (c), in order to decrease the \( \Delta G_{\text{mix}} \) to the minimum Gibbs free energy of the
system, the mixture separates into two distinct liquid phases. Concentration of
component A will then reach $x_1^A$ and $x_2^A$ within each phase. Therefore, liquid-liquid phase separation takes place within this concentration range. If the concentration of the initial mixture is beyond the range of $x_1^A$ to $x_2^A$, at the specific temperature of Case (c), the secondary derivative of the Gibbs free energy ($\partial^2 \Delta G_{\text{mix}}/\partial x^2$) is still larger than zero, which means the stability of the miscible mixture can be maintained. Here liquid-liquid phase separation does not occur.\(^{58}\)

Case (c) in Figure 2.3.1 could provide a deeper analysis of the miscibility of the two components. According to it, expanded as Figure 2.3.2, a system with an upper critical solution temperature is plotted. Above the critical temperature, both components are completely miscible in the liquid state, forming a single liquid phase. When the temperature is slightly below the critical temperature, $\Delta G_{\text{mix}}$ curve exhibits two minima (the lowest point in the concave curve) on either side of the critical concentration. Further decrease in the temperature leads to a much wider concentration separation between these two minima, meanwhile the $\Delta G_{\text{mix}}$ barrier between these two minima (central downward concave) increases. As mentioned in the last paragraph, these two minima have identical chemical potentials.\(^{58}\)

Furthermore, in Figure 2.3.2, two inflexion points can be found between each local minima and the center maxima, at which $\partial^2 \Delta G_{\text{mix}}/\partial x^2$ is equal to zero. Between the minima and inflexion points, $\partial^2 \Delta G_{\text{mix}}/\partial x^2$ is larger than zero. Here, the system is able to maintain certain stability. However, between the two inflexion points, $\partial^2 \Delta G_{\text{mix}}/\partial x^2$ is smaller than zero leading to an unstable region.
If connecting the local Gibbs free energy minima at all temperatures, the binodal curve can be obtained; the spinodal curve can be obtained by connecting the inflexion points, as shown in Figure 2.3.2. This is the upper critical solution temperature (UCST) phase diagram for the liquid-liquid phase separation.

![Diagram showing Gibbs free energy for mixing, $\Delta G_{\text{mix}}$, with respect to concentration for a binary mixture with an upper critical solution temperature at different temperatures. The × points are the minima at which $\partial \Delta G_{\text{mix}}/\partial x$ values are equal to zero. The ○ points are the inflection points at which $\partial^2 \Delta G_{\text{mix}}/\partial x^2$ values are equal to zero. The curve formed by the minima points is the binodal curve; while, the curve created by the inflexion points is the spinodal curve.](image)

Figure 2.3.2 Gibbs free energy for mixing, $\Delta G_{\text{mix}}$, with respect to concentration for a binary mixture with an upper critical solution temperature at different temperatures. The × points are the minima at which $\partial \Delta G_{\text{mix}}/\partial x$ values are equal to zero. The ○ points are the inflection points at which $\partial^2 \Delta G_{\text{mix}}/\partial x^2$ values are equal to zero. The curve formed by the minima points is the binodal curve; while, the curve created by the inflexion points is the spinodal curve.  

Note that the symmetry of the binodal and spinodal curves in the figure is caused by the comparability of different molecular size and volume fraction of the two components. If the two liquid components have large difference in molecular sizes, such as a polymer in solution with a small molecule solvent, then the asymmetry of binodal and spinodal curve will appear because of the large discrepancy in the segment volume size. In the asymmetric case, the identical chemical potentials
may not be located at the minima of the free energy wells. Instead, the concentrations in two phases coexist on a tangential line with a non-zero slope touching both free energy wells, which may slightly shift a little off the minima.\textsuperscript{58}

When a binary system is quenched with a fixed concentration of x along the vertical line to the region under the binodal curve, as shown in the Figure 2.3.3, phase separation takes place. At this temperature, a tie line connects the two points, $x_1^A$ or $x_2^A$. If the quench temperature is located along this line, the phase separation will reach equilibrium concentrations of $x_1^A$ and $x_2^A$. As the quenching temperature decreases, the two concentrations $x_1^A$ and $x_2^A$ correspondingly move along the binodal line to the values that correspond to the appropriate tie line.\textsuperscript{58}

![Figure 2.3.3 Liquid-liquid phase separation at two different concentrations ($x_1$ and $x_2$) in an upper critical solution temperature system. The solid line is the binodal curve, and the dashed line is the spinodal curve. The quench along $x_1$ is an off-critical quench, while that along $x_2$ is a critical quench.\textsuperscript{58}](image-url)
The path of the quenching process determines the mechanism of phase separation. When quenching into the metastable region between the binodal and spinodal curves, as in the case along concentration $x_1$, it is called an off-critical quench.\textsuperscript{59} If the system is quenched along concentration $x_2$, which passes through the critical point located at the top of the curve, a critical quench occurs,\textsuperscript{60} also shown in the Figure 2.3.3. In the latter case, the system enters the spinodal decomposition region without passing through the metastable region. Although the criterion differentiating these two types of quenches is not absolutely rigid, generally speaking, critical quench requires the phase separation to take place at or around the critical concentration of the two liquid components.

The off-critical and critical quenches lead to the nucleation growth or spinodal decomposition mechanism, respectively. Through the nucleation growth mechanism, free energy and concentration fluctuations need to overcome the nucleation barrier to initiate the phase separations.\textsuperscript{59} Through the spinodal decomposition, the single-phase system is unstable and spontaneously separates into two equilibrium concentrations.\textsuperscript{60} Therefore, based on the thermodynamics, at one specific temperature, the final phase concentrations ($x_1^A$ and $x_2^A$) are identical in both types of mechanism, because they develop along the same tie line, shown in Figure 2.3.3. In the following section, a more detailed look at the liquid-liquid phase separation kinetics will be discussed.
2.3.2 Kinetics of Liquid-Liquid Phase Separation in Binary Mixtures

Considerable attention has been given to both the theoretical and experimental aspects of liquid-liquid phase separation kinetics in binary mixtures. The phase separation processes can generally be divided into three stages: early; intermediate, and the late stages. In the early stage, the new phase is small and the boundary is diffuse, while the concentration begins to develop into equilibrium values. The late stage is defined by fixed phase concentrations and sharp interfacial boundaries. During the intermediate stage and late stage, the phase morphology coarsens via consuming small micro-domains to form the final large stable phase domains, and the total volume of each phase is conserved.

At the initial stage of phase separation, in regards to the concentration of a binary mixture and the phase diagram, liquid-liquid phase separation is bound by the binodal curve and spinodal curve. When the mixture is directly quenched from a single liquid phase region into the metastable region in an USCT system like the one shown in Figure 2.3.3, the phase separation is a nucleation growth process. When the system is critically quenched into the unstable region bound by the spinodal curve, also shown in Figure 2.3.3, a spinodal decomposition process takes place. Therefore, the difference between the nucleation and the spinodal decomposition recesses in an ideal “mean-field” system must be clearly understood.

The difference between two kinetic mechanisms in the early, intermediate, and late stages is schematically illustrated in Figure 2.3.4, as composition verses the local linear distance. The upper and lower limits of the concentration are given by the
tie-line limits intersecting the binodal curve when temperature is constant at one certain value (see Figure 2.3.3). At the early stage, nucleation growth forms sharp interfacial boundary, while spinodal decomposition develops the diffuse boundary, both of which are at the small scale. Following the early stage, the process continues into the intermediate stage, a series of coalescence steps that is defined as Ostwald ripening; at the late stage, phase separation ends with the gravitational or divergent coalescence that leads to the formation of large size separate domains, fix concentration and sharp interfacial boundary.\textsuperscript{61}

Figure 2.3.4 Schematic representation of the density fluctuations during the spinodal decomposition mechanism (SD, left) and the nucleation-limited growth (NG, right) mechanism. Three steps are shown: first, where in SD the wavelength is constant but the amplitude increases, second where both the wavelength and the amplitude change, and third, where the concentration amplitude is at maximum and the wavelength increases due to coarsening processes.\textsuperscript{62}
From the perspective of kinetics, the nucleation growth process is a process during which a metastable state relaxes toward an equilibrium state. A very small droplet with one major component forms a nucleus out of the binary mixture despite the higher free energy it generates. Therefore, a phase nucleus must grow in size to overcome the free energy barrier and stabilize itself. The height of this barrier depends on the system’s degree of metastability, which is determined by the amount of supercooling at a constant pressure. In the nucleation growth case, the activation energy comes from the localized density fluctuations of large amplitude,\textsuperscript{62} which drives the metastable state to gradually relax to equilibrium.

On the other hand, the spinodal decomposition process involves no free energy barrier, only the growth of concentration fluctuations of small amplitude that exceed a critical wave length. When an optimal fluctuation of small amplitude exceeds a critical wavelength, the fluctuation develops too slowly because the molecules need to diffuse over long distance. Below this critical value, the fluctuations generate large interfaces which cost too much energy. Therefore, the interfaces are not sharp, revealing that an unstable state relaxes by the spontaneous growth of long-wavelength fluctuations of small amplitude.\textsuperscript{62}

From the phase morphology perspective, nucleation growth and spinodal decomposition generate completely different micro-domain structures before they reach the ultimate equilibrium state. In a nucleation growth process, the new phase in the binary mixture forms the morphology of discrete small droplets embedded in a
matrix. While in a spinodal decomposition process, the bicontinuous morphology develops with a characteristic length scale that is determined by the fluctuation wavelength of the fastest growth,\textsuperscript{61,62} as shown in Figure 2.3.5. Hence, in most practical cases of liquid-liquid phase separation, a phase morphological change is taken as the evidence of a change in the phase separation mechanism, especially accurate at the early stage of phase separation.

![Morphologies of phase separation](image)

Figure 2.3.5 Morphologies of phase separation: (a) Morphology of nucleation growth phase separation; (b) Morphology of spinodal decomposition of phase separation.\textsuperscript{123}

On the other hand, from the growth rate of phase domain perspective, two kinetic mechanisms could be possibly differentiated as well. As shown in Figure 2.3.6, there is a significant difference in the scattering pattern evolution for nucleation growth and spinodal decomposition mechanisms, especially during the early stages of phase separation. Spinodal decomposition follows the semi-logarithmic dependence, whereas nucleation growth follows a linear one. But this method of differentiation has large composition dependence, only applicable at a range of certain compositions.
When the composition of the minor phase is above 15%, the spinodal decomposition occurs by rapid growth of the regularly spaced concentration waves, while nucleation growth is a slower and random process. In the followed sections, details of each mechanism and stage will be reviewed.

Figure 2.3.6 A semi-logarithmic plot of the scattering intensity function vs. time for PBD blends with PS at wave vector $q = 2750 \text{ nm}^{-1}$; filled circles are for spinodal decomposition and open circles are for nucleation growth.

2.3.2.1 The Early Stage of Phase Separation

The following section will describe the details of two different kinetic paths, nucleation growth and spinodal decomposition, at the early stage of phase separation, then followed by the intermediate stage and the late stage.
2.3.2.1.1 Nucleation Growth Process

The classical theories on nucleation, dating back to the work of Gibbs,\textsuperscript{64} assume that the nuclei formed during the initial stages of nucleation reach the stable phase with a well-defined interface. This enables the calculation of the smallest size of nucleus as long as the free energy difference between initial and stable phases and the interfacial free energy are known. Most experiments have not been able to probe the initial stages of nucleation. Instead, they measured the rate of the phase transformation at later times and inferred what must have happened during the initial stages of nucleation.\textsuperscript{62} The results from these experiments have been well described by the classical nucleation theory. Thus, this led to the belief that the assumptions of the classical nucleation theory must have been satisfied during the initial stage.

For the case of liquid-liquid phase separation, nucleation theory was proposed many years ago by Cahn and Hilliard.\textsuperscript{60} During the off-critical quench, at a given shallow quench depth, phase separation follows the classical nucleation theory. The single phase system gets into a metastable state which evolves towards the stable equilibrium state via localized droplet fluctuation of a critical size. The critical energy for the formation of a droplet is determined by a competition between a bulk volume free energy term which favors growth of the droplet, and a surface free energy term which dissolves the droplets. Because of this excess surface energy induced energy barrier. The activation energy, $\Delta G^*$, required to initiate the nucleation growth process is expressed as
\[ \Delta G^* = -\frac{4}{3} \pi R^3 \Delta G_v + 4\pi R^2 \sigma \]  

Equation 2.3.1

Where the first term is a bulk volume free energy of the nucleus and the second term is the surface free energy between the nucleus and the matrix phase. \( \Delta G_v \) is the free energy difference between a nucleus and the matrix phase, where \( \sigma \) is the surface energy per unit area and \( R \) is the radius of the nucleus that can be calculated by minimization of the activation energy with respect to \( R \), leading to the critical radius \( R_c \), \( R_c = \frac{2\sigma}{\Delta G_v} \). During these free energy competition, the nucleus size \( R \) is larger than \( R_c \), it grows, while \( R \) is smaller than \( R_c \), it shrinks. When nuclei form, the system decomposes with a decrease in the free energy causing nucleus growth resulting in droplet domains.

Cahn and Hilliard also proposed that, at deep quench depths gradually close to the vicinity of the spinodal, the nucleus begins to differ from the classical nucleus.\(^{60}\) The pressure and composition at the center of the nucleus are less than those of a classical nucleus; at first, the radius remains less than that of a classical nucleus, but eventually it passes through a minimum and afterwards increases; and the thickness of the interface is greater that that of a flat interface between the equilibrium phase. Until quench to supersaturation near the spinodal, all the characteristic of a classical nucleus is lost. Particularly, the energy barrier approaches zero; the composition at the center is still same as the one at initial state; and the radius becomes infinite; finally, none of the nucleus is even approximately homogeneous. This is the case of the spinodal decomposition, detailed described in Section 2.3.2.2.
As most described here is more about the thermodynamic terms. For the kinetic point of views, the early stage kinetics of nucleation in liquid-liquid phase separation has not been clearly understood, while the intermediate and late stages kinetics could be regarded to follow Ostwald ripening rule that will be discussed in a later section.

2.3.2.1.2 Spinodal Decomposition Process

For the spinodal decomposition process, the early stage kinetics has been described by the Cahn-Hilliard-Cook theory originally developed for metal alloys. After the system is critically quenched into the region below the spinodal curve in a UCST system, the amplitude of the concentration fluctuations is sufficiently small compared to the difference between the initial and final equilibrium concentration. The growth of concentration fluctuations of small amplitude eventually exceeds the critical value. Most studies in the spinodal decomposition use scattering method. The time evolution of the structure factor $(S)$ is a function of the scattering vector $(q)$ and time $(t)$, such that $S(q,t)$ can be written:

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2 \left[ (\frac{\partial^2 \Delta G_{mix}}{\partial \chi^2}) + 2\kappa q^2 \right] S(q,t) + 2MKTq^2$$

Equation 2.3.2

where $M$ is the mobility defined as the proportionality constant in the relationship between the inter-diffusion current density and the chemical potential gradient. The inter-diffusion coefficient can be defined as $D_{\text{inter}} = M(\partial^2 \Delta G_{mix}/\partial \chi^2)_0$. The parameter $\kappa$ is an interfacial free energy coefficient defined as the proportionality constant in the...
relationship between the interfacial free energy density and the square of the concentration gradient. The last term on the right side of Equation 2.3.2 is the thermal noise (associated with $kT$), with the amplitude that is observed in fluctuation-dissipation theory. The solution of the differential Eq.2.3.2 is given by:

$$S(q,t) = S_{\infty}(q) + [S_0(q) - S_{\infty}(q)] \exp\{2R(q)t\} \quad \text{Equation 2.3.3}$$

The $S_{\infty}(q)$ here is the virtual structure factor, and it can be written as:

$$S_{\infty}(q) = \frac{kT}{(D_{\text{inter}}/M + 2\kappa q^2)^{1/2}} \quad \text{Equation 2.3.4}$$

and the characteristic length becomes

$$R(q) = -\left(D_{\text{inter}}q^2 + 2\kappa Mq^4\right) \quad \text{Equation 2.3.5}$$

Therefore, within the spinodal decomposition region, any concentration fluctuation grows exponentially at a scattering vector $q$ with a characteristic length $R(q)$. The optimal growth wavelength of $R(q)$ sets the length scale of the phase separation of the spinodal decomposition. When we plot $R(q)/q^2$ verses $q^2$ based on Equation 2.3.5, the intercept is the inter-diffusion coefficient, $D_{\text{inter}}$. This is usually called a Cahn plot. Note that this coefficient is negative when we study fluctuation growth, and it is positive when we study diffusion. 67

2.3.2.2 The Intermediate Stage of Phase Separation

Specifically for spinodal decomposition, the intermediate stage has also been studied. As time passes, the amplitude of the concentration fluctuation increases, and the characteristic length grows. In scattering experiments, the spinodal peak
continuously sharpens and gradually shifts to smaller scattering vectors. The system thus enters the intermediate stage, and this stage is then followed by the late stage of the spinodal decomposition process.\textsuperscript{59} A universal scaling of the reduced characteristic length verses time can be observed in this stage. Experimentally, one plot the maximum-intensity reduced scattering vector, $S(q_m, t)$, represented by $Q_{\text{max}}$, with respect to reduced time. Here, the reduced time is defined as:

$$\tau = \frac{t}{t_c}, \text{where } \frac{1}{t_c} = (D_{\text{int}} q^2) \text{ at } t = 0$$

Equation 2.3.6

The reduced scattering vector is thus:

$$Q_{\text{max}} = \frac{q_m(t)}{q_m(t = 0)}$$

Equation 2.3.7

A more insightful analytical solution for the mode coupling calculation is also available\textsuperscript{68} for the time-dependent scattering structure factor of binary mixtures.

2.3.2.3 The Late Stage of Phase Separation

Compared with the early stage, the late stage of phase separation is easy to measure with experimental techniques. During last two decades, more kinetic theories at this stage were established. The major ones are the coarsening theory and the structure similarity studied through the scaling law.

2.3.2.3.1 Scaling Law in the Late Stage of Phase Separation

Generally, during the late stage of liquid-liquid phase separation in binary mixtures as the system coarsens, the scaling law is used to describe the experimental scattering data. If $q_m$ represents the scattering vector of the scattering structure factor
Equation 2.3.8

\[ q_m \propto t^{-\alpha} \quad \text{Equation 2.3.8} \]

and

\[ S(q_m, t) \propto t^\beta \quad \text{Equation 2.3.9} \]

where \( \alpha \) and \( \beta \) are the scaling exponents characterizing the phase evolution with time. In the intermediate stage of spinodal decomposition, the relationship between \( \alpha \) and \( \beta \) follows the inequality:79

\[ \beta > 3\alpha \quad \text{Equation 2.3.10} \]

The characteristic wavelength and amplitude of the concentration fluctuation increase with time. However, in the late stage of spinodal decomposition, the amplitude of the concentration fluctuations reaches the equilibrium value determined by the coexistence curve in Figure 2.2.4 and the relationship of \( \alpha \) and \( \beta \) becomes

\[ \beta = 3\alpha \quad \text{Equation 2.3.11} \]

for a three-dimensional system.

2.3.2.3.2 Self-Similarity of Domain Morphology in the Late Stage of Phase Separation

The growth of amplitude of dominant concentration fluctuations, at the very early stage, continuous with no change in the size, as the Cahn theory predicted;79 at the intermediate stage, both the size and amplitude of concentration fluctuations grow; and at the late stage, the morphology of the micro-phase keeps “self-similarity”, which means that only the change in the growth of size with time is involved, but the
amplitude of concentration fluctuations and morphology shape remains invariant. This can be reflects by the scaling law associated with real time scattering method experiments in which the peak scattering vector should be proportional to the reciprocal of the characteristic size, $R(t)$. In this case, the scattering structure factor should also be self-similar:

$$S(q,t) = (q)^{-d} f\left(\frac{q}{q_{\text{max}}}\right) = (q)^{-d} g\left(\frac{t}{t_{\text{max}}}\right)$$

Equation 2.3.12

Therefore, we can plot $S(q,t)(q)^d$ verses $q/q_{\text{max}}$ at different times, or $S(q,t)(q)^d$ verses $t/t_{\text{max}}$ at different wave numbers. Doing so will result in a universal structure factor.

A well-known experiment studying the spinodal decomposition with the scaling law for a simple binary mixture near the critical temperature (only 0.6 micro\(^\circ\)C away) is the mixture of 2,6-lutidine and water.\(^70\) Figure 2.3.7 shows the light scattering results for this system around the late stage of the spinodal decomposition process. In this figure, scattering intensity is plotted against wave number, $q_{\text{max}}$. As the phase morphology grows and coarsens, the maximum wave number, $q_{\text{max}}$, decreases with time but the phase morphological shape does not change, only the length scale. Therefore, the experimental data in Figure 2.3.7 can be reduced with respect either to the maximum length scale or to maximum wave number at different times to construct a universal master scattering curve for time, $t$ shown in the Figure 2.3.7(b). This data indicates that during the phase separation in the late stage of the spinodal decomposition process, the morphological change is self-similar. In these
Figure 2.3.7 Light scattering results for liquid-liquid phase separation in a simple binary mixture of 2,6-lutidine and water: (a) data plotted for the scattering intensity versus wave number at different times, and (b) scaled universal scattering curve from the experimental data of (a) after plotting the structure factor, $S$, versus reduced wave vector.\textsuperscript{70}

phase-separated bicontinuous domains, the equilibrium concentrations have been reached.

Until now, the main way to study spinodal decomposition process is mostly using the scattering methods, especially light scattering. However, for those polyolefin blends with isorefractive indices, none of techniques are really efficient to detect the spinodal decomposition process.

2.3.2.3.3 Coarsening Process

For late stage of coarsening, a simple treatment of coarsening kinetics was proposed by Ostwald, so being called “Ostwald’s ripening”.\textsuperscript{71} During phase separation, if a system has two liquid phases with sharp interfacial boundaries, the newly formed
minority liquid phase domains are dispersed in the majority liquid matrix. Since there is more interfacial surface for smaller the dispersed droplet, a greater surface energy cost is needed to maintain their size. Thus, these droplets are not yet in thermodynamic equilibrium. The total free energy associated with the interfaces can be decreased by having droplets coalesce, increasing the size of the minority liquid phase domain. Statistically, if a variety of sizes occurs in the droplets, the large droplets will grow by consuming the small droplets.⁷¹

Ostwald’s ripening consists of two processes: a mass transport process between the droplets via diffusion, and attachment-detachment growth of the minority liquid phase. The former one is governed by a diffusion field in the dominant matrix liquid phase, thus it’s a diffusion-limited process. On the other hand, the attachment-detachement process is the slowest, which is a rate-limiting step. The coarsening is then reaction-limited. These reaction-limited processes have similar characteristics to the nucleation-limited processes.⁷¹

There have been extensive researches studying the kinetics of diffusion-limited Ostwald’s ripening. When a binary mixture is in an off-critical quench, and the minority phase forms the droplet phase domain, theoretical calculations indicate that, the growing droplet size of the minority phase should follow the equation:

$$\langle R(t) \rangle = (K_t t)^{1/3}$$  \hspace{1cm} \text{Equation 2.3.13}
where $<R(t)>$ represents the average droplet size and $K_1$ is the coarsening rate constant that depends on the diffusion constant and the surrounding environment. This calculation is based on two assumptions: First, the droplet size grows along with its radius, $R(t)$; Second, the volume fraction of this dispersed phase is small so that the phase boundaries are not in contact and nor correlated. Furthermore, the droplet size distribution reaches a universal scaling form which is material independent. On the other hand, the 1/3 power in Equation 2.3.15 can be obtained by general dimensional arguments by using a mean-field approximation $^{71,72,73}$ This is the well-known Lifshitz-Slyozov-Wagner law in the case of a three-dimensional bulk system.

On the other hand, in the reaction-limited process, the average droplet size follows: $^{74}$

$$
<R(t)> = (K_2 t)^{1/2}
$$

Equation 2.3.14

Now $K_2$ is the coarsening constant that now relies on the reaction constant and the surrounding environment. At this stage, phase boundaries have been in contact or correlated, and the attachment-detachment process is very slow, and the power proposed by general dimensional arguments becomes 1/2.

Many studies of the kinetics of the bulk liquid-liquid phase separation with the concept of Ostwald’s ripening process are still ongoing, and many recent reports have appeared concerning the coarsening process of two-dimensional phase-separated system.
2.4 Liquid-Liquid Phase Separation Coupled with Crystallization

The dynamics of the phase separation behavior in various systems has been studied extensively, such as polymer blends, liquid mixtures and metallic alloys. However, when the phase separation process is coupled with other ordering process, i.e., crystallization, this will bring complexity into the investigations, especially due to the resultant difference of structures and morphology which is important from both a scientific and industrial points of view.

Here we are focusing on the coupling of liquid-liquid phase separation with crystallization in polymer blends. The phase separation of polymer blends carries out relatively slowly due to the sluggish diffusion on account of the large size. In addition, blending of polymers with different compositions, molecular weights and architectures is an important strategy to optimize the properties and applicability of the final product. Meanwhile, most of these polymers are semi-crystallizable. In many cases, during processing, miscibility gaps inevitably interfere with the solidification of crystallization. Therefore, there is a great necessity to understand the fundamental physics of coupling phenomenon between phase separation and crystallization.

Many researchers have studied different aspects related to phase separation coupled with crystallization. It can take place either in blends with two crystalline components or with crystalline and amorphous components. Here we are interested in the case where at least one component in the blend is crystallizable. About thirty years ago, Tanaka and Nishi already proposed all possible types of coupling
between phase separation behavior and the crystallization process in polymer binary
blends with one crystalline and one amorphous component.\textsuperscript{75,76}

Figure 2.4.1 illustrates both UCST and LCST phase diagrams coupled with a melting point depression curve which could intersect with, tangentially crossover, or exist either above or buried beneath the phase diagram. Depending upon the relative positions of the binodal curve and melting temperature depression line, the phase separation would become metastable. On the other hand, it should be noted that the melting point depression curve is composed of equilibrium melting temperature points instead of solidification points. The true solidification of crystallization is degree of supercooling dependent, which includes kinetic factors. In most cases, the
consequence of involving kinetics factors leads to crystallization falling into the metastable state. Therefore, the melting points depression curve is not equal to a solidification curve; the former is thermodynamics-oriented, while the later is more kinetics-oriented.

Except in Cases (e) and (f) in Figure 2.4.1, all others are experimentally hard to investigate in the coupling regions, because within each of these processes, metastable states exist with their own origins. Especially, on larger scales among these processes, they also either intersect each other or one overrides the other. Although it is experimentally difficult to approach the thermodynamic equilibrium state, modified thermodynamic theories have been proposed to predict the hypothetical phase diagram in crystalline-amorphous polymer blends

2.4.1 Thermodynamics of Binary Crystalline-Amorphous Polymer Blends

The Flory-Huggins (FH) theory has been employed to establish a phase diagram of binary liquid-liquid polymer blends based on the incompressibility assumption,\textsuperscript{77}

\[
\frac{\Delta G^m(\phi)}{N_A k_B T} = \frac{\phi}{r_1} \ln(\phi) + \frac{(1 - \phi)}{r_2} \ln(1 - \phi) + \chi_{ab} \phi (1 - \phi) \tag{2.4.1}
\]

where $\Delta G(\phi)$ is the free energy of mixing. The volume fraction may be expressed as $\phi = n_1 r_1/(n_1 r_1 + n_2 r_2)$, where $n_1$ and $n_2$ are moles of each polymer, $r_1$ and $r_2$ are the characteristic segment length of each polymer respectively. The total number of polymer chain segments is given as $n = (n_1 r_1 + n_2 r_2)$. Moreover, $\chi_{ab}$ is the FH interaction parameter determining the enthalpy contribution toward mixing,\textsuperscript{77} which is
proportional to the interchange energy, and inversely proportional to absolute temperature.

In order to account for the non-ideal free volume effects, it expresses $\chi_{ab}$ in an empirical expression in the following:

$$\chi_{aa} = (A + B/T + C \ln T)(D\phi + E\phi^2 + F\phi^3 + \cdots) \quad \text{Equation 2.4.2}$$

where items in the first bracket represents athermal and thermal dependencies, and items in the second bracket term reflect concentration dependencies.\(^{78}\) This modified model has been used extensively to determine a variety of phase diagram such as UCST, LCST, a combined UCST-LCST, a closed loop, or an hour-glass phase diagram. As mentioned in Section 2.3.1, a phase diagram can be established by applying a common algorithm via free energy minimization of the blends. The binodal curve is determined with the equal chemical potential and the minimum free energy principle.

$$\frac{\partial \Delta G_{mix}}{\partial \phi_a} = \frac{\partial \Delta G_{mix}}{\partial \phi_b} \quad \text{Equation 2.4.3}$$

Though FH theory may be sufficient enough to elucidate the empirical phase diagram of liquid-liquid polymer blends, for crystalline-amorphous polymer blends, a considerable modification is required by incorporation with a solidification potential for the crystallization of crystalline component. Although the FH theory is a classical example of them,\(^{78,79}\) one shortcoming of the FH theory is the assumption that it regards the complete rejection of the solvent from the crystalline phase, thus, the
crystal phase in the blend is completely pure. This assumption has its own advantage because one can take the chemical potential of the pure crystal phase as equal to the one of the crystalline component, which facilitates the analysis, such as the Flory melting point depression equation. However, the Flory diluent equation meets several limitations when applied to some systems that exhibit complex coupling between crystallization and liquid-liquid phase separation,\cite{76,80-82} it is necessary to take into account the crystal-amorphous interaction in addition to the conventional liquid-liquid amorphous FH interaction.\cite{83,84} Kyu’s group introduces a phase field model of solidification from crystalline polymer blends undergoing the crystal-melt phase transition. Then they use self-consistent solutions to establish the coexistence phase boundaries of a hypothetical phase diagram of the crystal-amorphous blend.\cite{84}

Polymer crystallization has been described in the framework of a phase field free energy having a crystal order parameter $\psi$, in which $\psi=0$ defines the melt and $\psi=l$ or close to unity, assumes in the metastable crystal phase, at the equilibrium limit.\cite{84,85} The crystal phase order parameter, $\psi$, may be defined as the ratio of the lamellar thickness ($l$) to the lamellar thickness of the equilibrium perfect crystal ($l^0$), i.e. $\psi=l/l^0$, and thus it represents the crystallinity in one dimension.

The free energy density of a polymer blend containing one crystalline component may be expressed as

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

Equation 2.4.4
where \( f(\psi) \) is the free energy of crystallization of the crystalline component expressed as a Landau expansion in \( \psi \) that is determined by its concentration or volume fraction in the blend. This ensures the free energy of the blend to approach its pure crystal limit, which is \( f(\psi, \psi \rightarrow \psi) \rightarrow f(\psi) \) where \( \psi \rightarrow 1 \). The natural log items represent the entropic contribution, while \( \chi_{aa} (1-\psi) \) is the enthalpic contribution to the FH free energy of liquid-liquid phase separation. The \( \chi_{ca} \psi^2 (1-\psi) \) represents the solid-liquid interaction, and the \( \chi_{ca} \) is called the crystal-amorphous interaction parameter that is repulsive and may be evaluated from the heat of fusion of the crystalline component. Furthermore, when the one-dimensional crystallinity \( \psi \) is multiplied by the volume fraction, their product \( \psi \psi \) reflects the bulk crystallinity, and \( \psi(1-\psi) \) represents the amount of the noncrystalline component interaction with the crystal phase. One should note that this modification in terms of the FH diluent theory is still within the limit of complete rejection of the polymeric solvent from the crystal phase, which means \( \chi_{ca} \) is repulsive and a pure crystal phase is formed in the blend without interference by the amorphous polymeric solvent.83,84

The free energy density of the crystal solidification, \( f(\psi) \), is expressed by the asymmetric Landau expansion in their model. This kind of asymmetric Landau potential has been utilized in the phase field model for the elucidation of solidification phenomena such as metal alloys or polymer crystallization.84,85

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

Equation 2.4.5
where $W$ is a coefficient representing the energy cost to overcome the nucleation barrier $\zeta(T)$, and the $\zeta_0(T_m)$ represents the location of the nucleation barrier on the $\psi$ axis and the solidification potential, both of which are melting temperature dependent. It should be cautioned that the coefficient of the cubic order must be nonzero in order to apply the Landau potential into a first-order phase transition; otherwise, the potential is only applicable to a second-order phase transition or at equilibrium when the two minima are equivalent, as shown in Figure 2.4.2.84
In order to establish the hypothetical phase diagram using the phase field model of crystallization, the free energy of the blend has to be found at the minimum with respect to the order parameters. They minimize $f(\psi, \phi)$ with respect to $\psi$ in order to find the solution,

$$\frac{\partial f(\psi, \phi)}{\partial \psi} = W(\psi - \zeta)(\psi - \zeta_0) + 2\chi_{ca}(1 - \phi) = 0 \quad \text{Equation 2.4.6}$$

or

$$W(\psi - \zeta)(\zeta_0 - \psi) = 2\chi_{ca}(1 - \phi) \quad \text{Equation 2.4.7}$$

For the single crystal component, $\gamma = 1$, the lower right-hand side of equation 2.4.6 becomes zero, thus $\psi_c = \xi$ signifies the unstable potential barrier, while $\psi_c = \xi_0$ represents the solidification potential well of the neat crystal. In the blend, $\gamma \leq 1$, the solidification potential minimum $\psi_c = \psi_{\text{min}}$ will shift away from $\xi_0$. At a given crystallization temperature and a given concentration, $W$ represents the penalty for overcoming the unstable potential barrier. Subsequently, the binodal curves can be calculated based on equal chemical potential and the minimum free energy principle in the following form:\textsuperscript{84,85}

$$\left. \frac{\partial f(\psi, \phi)}{\partial \phi} \right|_{\psi = \psi_{\text{min}}, \phi^a} = \left. \frac{\partial f(\psi, \phi)}{\partial \phi} \right|_{\psi = 0, \phi^i}$$ \quad \text{Equation 2.4.8}

Based on this proposed thermodynamic model for crystal-amorphous blends, Kyu’s group\textsuperscript{84} has created various phase diagrams of a hypothetical crystal-amorphous polymer blend having a critical LCST temperature at 252°C and a critical UCST temperature at 202°C, with various melting temperature and crystal-amorphous
polymer interaction parameter. Figure 2.4.3 shows the influence of melting temperature on the phase diagram from top to the bottom, as well as the effect of crystal-amorphous interaction energy on the phase diagram from left to right.

In Figure 2.3.3, the coexistence of the LCST and UCST can be established in which the crystal solid-liquid transition can intersect with the UCST (Figure 2.4.3a), or move up to the region between UCST and LCST (Figure 2.4.3d), or even up to intersect with the LCST (Figure 2.4.3g). When intersecting with UCST (Figure 2.4.3a) a liquid-liquid and crystal-liquid coexistence region exists, and the neat crystal gap shown by the solidus line at the high concentration of crystalline component. With increasing repulsive crystal-amorphous interaction parameter, as horizontal changes shown in the figures, the solidus line moves toward the pure crystal component axis and at the same time the neat crystal gap becomes narrower suggesting that more solvent is rejected our from the solidus phase (Figure 2.4.3a-c).
Figure 2.4.3 Hypothetical phase diagrams for crystal–amorphous polymer blends exhibiting a combined LCST and UCST intersected by the crystal–melt transition gap bound by the liquidus and solidus lines, showing (a) effect of melting temperature of the pure crystal component increasing from top to bottom (182, 223, and 262 °C) and (b) the effect of repulsive crystal–amorphous interaction energy increasing from left to right. $\chi_{ca}$ parameter is varied from 0.01, 0.1, and 1 at the melting temperature by setting the UCST temperature to 182 °C and the LCST temperature to 262 °C. The melting enthalpy of the crystal component was taken as 1500 cal/mol.
With a continuous increase of the melting point, as vertical changes in the figures, when intersecting with LCST (Figure 2.4.3g), the solidus region increases as the solidus line moves up, therefore widening the crystal-liquid coexistence region like the hour-glass phase diagram. This kind of hour-glass phase diagram further transforms to almost a completely immiscible crystal-liquid amorphous gap with an increase in the repulsive crystal-amorphous interaction (Figure 2.4.3i).84

These theoretical predictions comprehensively cover all types of coupling between crystallization and liquid-liquid phase separation, especially encompassing the crystal-amorphous interaction, which emphasizes the viewpoints of crystallization-induced phase separation. However, there is still experimental difficulty in studying the coupling region within which the competition of two mechanisms always exists. The solidification of the crystalline phase may limit the mobility of the liquid amorphous phase, thus destroying the consistency of $\chi_{ca}$ in this model and resulting in locking the phase separation into the metastable state, rarely reach the thermodynamic equilibrium.

2.4.2 Examples of Experimental Study in Liquid-Liquid Phase Separation Coupled with Crystallization in Polymer Blends

All the cases in Figure 2.4.1 and Figure 2.4.3 represent the relationships between the liquid-liquid phase separation (either upper or lower critical solution temperature) and crystallization (one component can be crystallized) in polymer blends. There is a large collection of crystalline polymer blends available in literatures (see for example, Reference 86, 87). However, based on the experimental truth, our
focus here will only be on the cases where liquid-liquid phase separation intervenes in crystallization.

Several systems among many examples were chosen to illustrate the principles of interest we want to convey. The first system selected is a binary mixture of a poly(\(\varepsilon\)-caprolactone) with the average molecular weight of 10.7k g/mol and a low molecular weight polystyrene with average molecular weight of 840 g/mol. The report of this mixture was initially published by Tanaka and Nishi,\(^75,76\) The low molecular weight of polystyrene component is used for better mixing and fast diffusion. Figure 2.4.4 shows the phase diagram of this binary blend. At high temperatures, two components are miscible. With decreasing temperature, they undergo a liquid-liquid phase separation, investigated by direct observation with an optical microscopy in the hot stage and cloud points with a scattering technique. This is a prime example of a typical UCST system. Poly(\(\varepsilon\)-caprolactone) is the crystallizable component, as shown in Figure 2.4.4, its melting temperatures decrease with an increase in PS concentration: the solid crystal-melt phase boundary reflects the melting temperature depression in this binary blend. This melting temperature depression line intersects with the binodal curve. Crystallization can take place when the temperature is below this melting temperature depression line, depending upon the degree of supercooling. In this case, kinetics determines which one dominates.

In Tanaka and Nishi’s experiment, by quenching a sample with a concentration of 70/30 (poly(\(\varepsilon\)-caprolactone)/ polystyrene) to a lower temperature, the poly(\(\varepsilon\)-caprolactone) initially crystallized in the miscible region. The polystyrene
molecules were rejected from the growth front and only the poly(ε-caprolactone) molecules were allowed to crystallize. This is a case of “poisoning” as described in Section 2.5.2. Depending upon the diffusion rate of polystyrene, the crystal growth rate of poly(ε-caprolactone) became slower with diffusion-limited (non-linear growth rates). The competition between these two processes led to the local phase separation at the growth front of poly(ε-caprolactone) spherulites where the concentration of poly(ε-caprolactone) was the lowest.\textsuperscript{76} Furthermore, as the crystallization of poly(ε-caprolactone) in the system continued, the overall concentration of poly(ε-caprolactone) in the rest solution decreases, moving horizontally towards and passing through the binodal curve, finally entering the liquid-liquid phase separation region. At this point, phase separation will start. Coupling phenomena in the blend of poly(ε-caprolactone) with polystyrene was also studied by other researchers\textsuperscript{88,89} and similar results were achieved.

The second example we have chosen is PE blends. We focus on the blends where both polymer components have short chain branches but with different sizes and compositions, or one polymer component is linear without branches. As discussed in Section 2.2.2, there have been substantial investigations in the binary PE blends. Research contributions on these binary PE blends generated a tremendous amount of discussion regarding liquid-liquid phase separations and crystallization induced phase separations in these systems.\textsuperscript{19}
Figure 2.4.4 Temperature-concentration phase diagram of a binary blend of a poly(£-caprolactone) and polystyrene. Open circles are the cloud points observed experimentally; the solid and dash lines are the binodal and spinodal lines, respectively, fitted to the experimental data by the Flory-Huggins theory. The liquid-liquid phase separation is an UCST type. 76

A series of binary blends consisting of PEs with hexane and butane branches was recently studied. 53 The samples were specifically designed to have very different branch contents. In the PE with the hexane branches (PEH), the hexane branch content was 9 per 1000 carbons with a molecular weight of 112k g/mol, while in the PE with the butane branches (PEB), its branch content was as high as 77 per 1000 carbons with a molecular weight of 77k g/mol. The PEH sample crystallizes at high temperatures and the PEB only crystallizes at lower temperatures.
Figure 2.4.5 is the temperature-concentration phase diagram for the binary blend of these two different-chain-structures PE at atmospheric pressure. The similarity with Figure 2.4.4 is evident. Using scattering and optical microscopy techniques, the liquid-liquid phase separation can be observed as shown in Figure 2.4.5.

Figure 2.4.5 Temperature-concentration phase diagram of a binary blend of PEH and PEB. The liquid-liquid phase separation is an UCST type. The crystal-melt boundary line reflects the melting temperatures of the crystals formed by PEH, which decreases outside of the binodal curve with decreasing concentration, but remains invariant within the binodal curve. The binodal curve was obtained by modified light scattering technique, and the spinodal curve was calculated based on the Flory-Huggins formalism.53

In this figure, the melting temperatures were calculated through experimental data by Hoffman-Weeds method. They decrease with decreasing concentration of PEH outside the phase separation region; while within the phase separation region,
the melting temperatures are invariant with varying concentrations, which implies that the crystallization was started after completion of the liquid-liquid phase separation with two distinct concentrations.

Several interesting issues have been brought up and required to investigate further. For example, what would the crystallization behavior of PEH be if the liquid-liquid phase separation was at the initial, intermediate or late stage of phase separation. The different stages have been described in Section 2.3. Furthermore, if we could monitor the overall crystallization and growth rates throughout the liquid-liquid phase separation at different supercoolings, quantitative understanding of the interplay and competition between crystallization and phase separation could be achieved. It can be expected that the crystallization kinetics would also be affected by the phase separation morphology. This is particularly true when the phase separation is in the initial stage and the phase separated morphology has not grown to maturity. The reason is that when the crystallizable PEH is constrained within very small spaces such as in droplets, the growth rates slow down. Moreover, as long as the phase separated domains do not reach an unchangable concentration (in the late stage of phase separation), the crystal growth rate can not be linear.

Concerning on these interesting issues, further investigations continued with the same series of polyethylene blend samples. The major difficulties for these studies lie in how to precisely separate and identify the crystallization and liquid-liquid phase separation processes and individually measure their kinetics. In their study, the crystal growth rates were measured with optical microscopy by
quenching the samples from their homogeneous melt to different crystallization temperatures; while the liquid-liquid phase separation rates were measured at the coarsening stage with a small-angle light scattering technique. Figure 2.4.5 shows a plot which puts two sets of kinetic data together to illustrate the relationship between these two processes for a sample containing 50/50 PEH/PEB.

Figure 2.4.6 Crystal growth rates and liquid-liquid phase separation rates for a binary blend consisting of 50 % PEH and 50% PEB. The solid squares represent the crystal growth rates and the open diamonds are the growth rates of the characteristic length of the liquid-liquid phase separation in the coarsening stage. $T_B$ is the binodal temperature and $T_m$ is the melting temperature of the PEH crystals. The two rate lines cross over at 118 °C.54

When the temperatures are far below the cross-over temperature of 118 °C, the crystallization is faster, and it dominates the final morphological development. At temperatures above 118 °C, the phase coarsening process controls the final morphology. Near 118 °C, these two processes compete with each other.54
Another interesting example is the binary blend of poly(vinylidene fluoride) (PVDF) with poly(ethyl acrylate) (PEAc). In this case, the liquid-liquid phase separation occurs as LCST type, and the phase diagram intersects the solid crystal-melt phase boundary (reflecting the melting temperature curve). Figure 2.4.7 shows its phase diagram.\(^{90,91}\)

![Figure 2.4.7 Temperature-concentration phase diagram of a binary blend consisting of poly(vinylidene fluoride) (PVDF) and poly(ethyl acrylate) (PEAc) at atmospheric pressure. The liquid-liquid phase separation has a lower critical solution temperature and the solid crystal-melt phase boundary intersects the binodal and spinodal curves.\(^{90}\)](image)

Another more interesting example is the binary blend of poly(ε-caprolactone) (PCL) and polystyrene-block-polyacrylonitrile (SAN) binary blends, a closed miscibility loop with one lower and one virtual upper critical solution temperature was reported, shown in Figure 2.4.7. The crystallization process also intersected phase separation as evidenced by light-scattering and transmission electron microscopy.\(^{92}\)
Figure 2.4.8 Temperature-concentration phase diagram of a binary blend consisting of poly(ε-caprolactone) (PCL) and polystyrene-block-polyacrylonitrile (SAN). The phase diagram is a closed miscibility loop with one lower and one virtual upper critical solution temperature. Light scattering and TEM results proved that crystallization intersects with this miscibility loop, but crystal-melt curve is not plotted here.\textsuperscript{92}

The final example given out here is a series of binary blends of crystalline poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA). These blends were first found to have a LCST around 350 °C.\textsuperscript{93} Later, it was also found through light scattering and morphological observations that these blends might also exhibit an UCST phase diagram at low temperatures as shown in Figure 2.4.8.\textsuperscript{94} The evidence for the existence of an UCST is form the crystallization morphology. When PVDF crystallized from the miscible melt, a large spherulitic morphology was observed; while, when the blend was quenched into the binodal region, only a modulated morphology was found. This morphological transition occurred at the boundary of the binodal curve in the UCST as indicated in Figure 2.4.8.
Figure 2.4.9 Temperature-concentration phase diagram of a binary blend consisting of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA). The upper line is the binodal curve for the LCST liquid-liquid phase separation. Underneath the LCST is the crystal-melt phase boundary of PVDF, followed by another binodal curve for the UCST liquid-liquid phase separation.94

In this dissertation, the coupling phenomenon between crystallization and liquid-liquid phase separation we are focusing on is Case (a) in Figure 2.4.1, the melting point depression curve intercept with UCST phase diagram.

2.5 Crystallization Behavior in Crystalline-Amorphous Polymer Blends

Based on the introduction in Section 2.4, when facing the coupling of crystallization and liquid-liquid phase separation, the crystallization behavior becomes more complicated. The crystallization of miscible and immiscible polymer blends can differ remarkably from that of the pure crystallizable components. The presence of the amorphous component can disturb the normal crystallization process,
thus influencing melting temperature, crystallization kinetics, crystal growth rate, crystal morphology and phase morphology, etc.

2.5.1 Melting Temperature Depression

The melting behavior of a semi-crystalline component in a miscible blend strongly depends on the blend composition. The phenomenon of melting point depression was first described theoretically in a polymer-solvent system by Flory, which is widely known as Flory diluent theory.\(^7\) In his theoretical treatment, Flory assumed complete rejection of solvent from the crystalline phase. Nishi and Wang were the first to extend the Flory diluent theory from the crystalline polymer-diluent systems to the crystalline polymer-amorphous polymer systems, \textit{i.e.}, the blends of poly(vinylidene fluoride) (PVDF) and poly (methyl methacrylate) (PMMA).\(^9\)

The behavior results from the thermodynamic factors. Since the mixing makes the system more random, the entropy of mixing is larger than what it is for pure components. During the melting, the free energy of crystal equals to the free energy of melt, therefore

\[^{\text{2.5.1}}\]

\[
\Delta H - T_m \Delta S = 0 \quad \text{and} \quad T_m = \frac{\Delta H}{\Delta S}
\]

where \(\Delta H\) is the heat of fusion at melting, if regarding to the complete rejection of amorphous component, crystals formed in blends are completely same as the ones formed in the pure crystalline components. Thus, \(\Delta H\), the heat of fusion of the crystal at melting does not change in terms of mixing. Based on this point, due to the excess of entropy, the melting temperatures decrease. In another words of explanation, the
free energy of the crystallizable component will decrease from \( G^o_m \) to \( G^o_{mb} \), when the crystals are surrounded by a mixed melt phase due to the interaction between two components, The free energy of the crystalline phase, \( G_c \), is not affected by mixing. The melting temperature, defined as the cross section of \( G_c \) and \( G_m \) (when \( \Delta G=0 \)), may be depressed, as shown in Figure 2.5.1.\(^{96} \) It has to be noted that melting point depression is described only in miscible blends. Flory diluent theory, including modified the version, is only validated when the interaction parameter \( \chi_{12} \) is negative.

Miscible blends with at least one-crystalline component can exhibit melting point depression. However, miscible blending is not the only factor influencing the melting temperature decreasing. Sometimes, the experimental melting temperature turned out to be lower than the theoretical or calculated one, even in the single component system of pure crystalline polymer. This is the consequence of crystallization falling into the metastable state instead of equilibrium. At metastable state, crystal forms by overcoming a relatively lower energy barrier in the local range, without reaching the free energy minimum, at which the melting temperature is below the equilibrium melting point \(^{58} \) (this can be corrected by using Hoffman-Weeks plots to derive the equilibrium values).
Figure 2.5.1 Schematic diagram of the free energy of a crystalline phase ($G_c$) and the free energy of a melt phase of a homopolymer ($G_m^0$) and a miscible blend ($G_{mb}^0$) as a function of the temperature.

If regardless of the effect form metastable state, the melting point depression resulting from thermodynamic effects can be described by the following equation:

$$
\frac{1}{T_{mb}} - \frac{1}{T_m^0} = \frac{R V_u}{\Delta h_u V_{1u}} \left[ \ln \phi_2 + \left( \frac{1}{m_2} - \frac{1}{m_1} \right) \left( 1 - \phi_2 \right) + \chi_{12} \left( 1 - \phi_2 \right)^2 \right]
$$

Equation 2.5.2

$T_{mb}^0$ and $T_m^0$ are the equilibrium melting point of the blend and the pure crystallization component, respectively; $V_u$ is the molar volume of the repeating unit of the components ($1 =$ amorphous component and $2 =$ crystallizable component), $\Delta h_u$ is the heat of fusion per mole of the repeating unit; $m$ is the number of units in the molecule, i.e. the degree of polymerization; $\phi_i$ is the volume fraction, and $\chi_{12}$ is the polymer-polymer interaction parameter. Since, for polymers $m \to \infty$, then Equation 2.5.2 can be reduced to:
This melting point depression is only in regards to the miscible polymer blends. Once liquid-liquid phase separation occurs, then this theory is invalidated due to the change of volume fraction and interaction $\chi_{12}$.

### 2.5.2 Selection Process of Crystallization in Polymer Blends

When dealing with crystallization of polymer blends containing one crystalline and one amorphous component, the discussion of the exclusion of amorphous component in crystallizable polymer blends from the crystal growth leads to the introduction of the crystallization selection process. Many researches have proved the existence of a selection process during crystallization by blending two n-alkanes with identical chemical structure, but different conformations, specifically, once-folded and extended chain conformations, during the crystal growth.\textsuperscript{97,98} Their results showed that the crystal growth of longer n-alkanes was hampered by the deposition of shorter molecules onto the growth front, causing a rate minimum. This concept was extended to be introduced as a “poisoning” effect.\textsuperscript{99} to describe polymer blends with identical chemical structure but different molecular weights.\textsuperscript{100-102} As long as the molecular weight of one fraction is sufficiently low enough to not exactly fit in the crystal growth front, the deposition of the low molecular weight polymer onto the growth front poisons further growth and slows down the surface nucleation and growth rates.

In addition to blends with different molecular weights, one can also find many experimental reports of poisoning in blends with different chemical structures...
but miscible in the melt state, in which one component is crystallizable and another is not. In some miscible blending cases, the selection process ("poisoning") significantly decreases the crystal growth, because the non-crystallizable component would be recognized and selected on the crystal growth front, and then diffuse away. For instance, in the miscible blends of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA), the crystal growth rates of PEO are depressed by the addition of PMMA. The diffusion of PMMA eventually leads to the perturbation on the surface of PEO crystals by increasing the entropy of folding. Furthermore, due to the low diffusion coefficient of amorphous polymers, they are eventually accumulated at the crystal growth front, dramatically reducing the local concentration of the crystallizable component. Since which component deposits onto the growth front at any particular time depends on the local concentration of this component, it leads to few depositions of crystallizable chains onto the growth front. Thus, the non-crystallizable component is now "poisoning" the growth front and reducing the crystal growth rate, or even completely stopping the crystal growth. After crystallization of the crystallizable component, although initial two components are miscible in the melt, the accumulation of the other non-crystallizable component leads to the local phase separation. In this case, the phase separation is induced by the crystallization of the crystalline component.

On the other hand, if liquid-liquid phase separation takes place first, crystallization has to occur from immiscible state of the blends. Generally, the immiscible phases are actually composed of one non-crystallizable-component-rich
phase and one crystallizable-component-rich phase. The latter phase possesses higher concentration of crystallizable component than the initial single phase. During crystallization, because of the high local concentration, molecular chains of crystallizable component have more chances to deposit onto the crystal growth front in the crystallizable-component-rich phase, also less non-crystallizable chains are excluded at the crystal front, which leads to the relatively faster selection process, or less “poisoning”, compared with what happens in the crystallization from the miscible blends. As long as, the size of crystallizable-component-rich domain is large enough (usually larger in the 3 μm) to not affect the crystallization rates,\textsuperscript{108} based on the knowledge of crystallization selection process, phase separation enhances the crystallization in the crystallizable-component-rich phase.

2.5.3 Effect of Phase Separation on the Nucleation in Crystalline-Amorphous Polymer Blends

Whether crystallization takes place in the miscible or immiscible state of crystalline-amorphous polymer blends, the selection process during crystal growth is always present. Since crystallization includes crystal growth and nucleation processes, besides the effect on crystal growth, the question then becomes: how, if at all, the nucleation process will be influenced by the phase separation behavior, such as, concentration of crystallizable component, or the size of the phase domain.

From thermodynamic point of view, the nucleation process will be surely enhanced when the concentration of the crystallizable component increases in one phase that has domain large enough. The reason is that the degree of supercooling will
be enhanced because equilibrium melting temperature elevates with increasing the concentration of crystallizable component. Therefore, in one blends with a fixed concentration, the effect of the degree of phase separation on nucleation can be predominantly addressed by the concentration change during the phase separation.

On the other hand, with the idea that phase morphology might have an effect on the nucleation behavior, many researchers have tried to study the crystallization nucleation behavior in different phase morphologies. Study in nucleation behavior during crystallization has high criterion for experiments, because the size of the crystal nuclei is very small and it’s also temperature dependent. The nuclei are only able to be precisely in-situ measured by the synchrotron wide angle X-ray scattering. According to the two kinetic mechanisms of liquid-liquid phase separation, there are two types of crystalline-rich phases: the crystalline-rich matrix phase and the crystalline-rich dispersed phase. When crystallization takes place in the crystalline-rich dispersed droplet phase, and also if the phase domain size is smaller than 5μm, the fractionated crystallization which differentiates the homogeneous nucleation and heterogeneous nucleation could happen. The fractionated crystallization results in the confinement effect of the domain size. When the size of crystallizable domain is so small that the domain has none of heterogeneous nucleus inside, the homogeneous nucleation occurs within this small droplet phase, which requires large degree of supercooling to form homogeneous nuclei.

For crystallization in the crystallizable-component-rich matrix phase, some researchers are concerned with the migration of nuclei and the interfacial free energy
between both phases of melt blends. Nuclei close to a sharp interface were found to migrate fast and efficient,\textsuperscript{112} which is contrary to partially miscible blends in which no evidence could be found for a fast migration.\textsuperscript{112,113} Also, some researches proposed the effect of heterogeneous surface nucleation.\textsuperscript{114} However, not all interfaces can produce additional nucleating centers. For immiscible and highly incompatible polymer blends, since their interfacial tension is higher, and the interface is very sharp, such interfaces can rarely induce new nuclei.\textsuperscript{115}

This section addresses crystallization in the polymer blends. Although our project design focuses on the miscibility of polyethylene blends, we obtained the inspiration for this project from the crystallization behavior difference between miscible and immiscible crystalline-amorphous polymer blends. In addition, these factors are critical in analyzing the experimental method for determining the phase diagram of a crystalline-amorphous polymer blend. Therefore, a good understanding of the crystallization behavior as described above is necessary.
CHAPTER III
EXPERIMENT

3.1 Experimental Objective

The goal of this research is to figure out an effective way to separately monitor two phenomena (LLPS and crystallization) in the crystalline-amorphous PE blends via crystallization kinetics and phase morphology, suppressing the coupling at the maximum level.

3.2 Conceptual Experiment Design

We need to specifically design an experimental procedure to meet the requirement that the liquid-liquid phase separation must be carried out before the crystallization: a two-step isothermal process. The first step of this experiment is to isothermally anneal the blend at a temperature within the binodal curve boundary yet above the melting temperature of the crystalline phase; thus crystallization is not able to take place. In this way, the liquid-liquid phase separation can be carried out into the late stage at equilibrium, where both of the phases can be obtained. At the second step, the isothermal crystallization is then carried out by quenching the sample to a lower temperature below the melting point depression line, where crystallization takes place rapidly. Further, concentration changes in both phases of the polymer blend are virtually impossible to occur further due to this rapid crystallization. Then the phase
morphologies are preserved. (shown in Figure 3.2.1) Utilizing this two-step isothermal experiment, the measured crystallization kinetics and observed crystal morphology in these binary blends may also serve as indicators to determine binodal and spinodal curves.

Figure 3.2.1 Illustration of two-step annealing process and its affect on the final morphology above and below the crystallization temperature.

3.2.1 Design for Determination of the Binodal Curve of the Liquid-Liquid Phase Separation

We need to set up a series of different annealing temperatures for the first step isothermal experiment, and each step needs to have a long coarsening time. As soon as the binodal temperature is reached, the crystallization kinetics in the second step isothermal experiment will speed up due to the liquid-liquid phase separation. Since the crystallizable polyethylene-rich phase is formed and coarsened during the initial annealing step, less “poisoning” is present to slow down the crystallization kinetics.
caused by the non-crystallizable polyethylene (Section 2.4.2). Therefore, the annealing temperature where the crystallization kinetics shows a sudden increase is on the binodal curve for that specific concentration. Using blends with different concentrations, the binodal curve of the entire concentration range can be obtained.

Figure 3.2.2 illustrates the experimental process (a and b) and the changes in the crystallization (c) in terms of the first-step annealing temperatures. In Figures 3.2.2a and 3.2.2b show annealing of the samples at $T_{a1}$ and $T_{a2}$, respectively, for an appropriate time, in which both are in the miscible single-phase region. The sample is then quenched below the crystallization temperature beneath the USCT curve. As shown in Figure 3.2.2c crystallization takes place out of the homogeneous single phase because the blend is not allowed to phase separate during quenching. This scenario leads to a situation where the crystallization is strongly “poisoned” leading to relatively slow crystallization kinetics.
Figure 3.2.2 Illustrating the determination of binodal point at one concentration (1). The first-step annealing temperature \( T_a \) is above the binodal point. The first-step annealing temperature \( T_{a2} < T_{a1} \), and both of them are in the miscible region. \( T_c \) in Case \( a \) and Case \( b \) are same. Figure \( c \) illustrates the morphology change from the beginning stage of the first-step annealing \( (T_{a1}) \) to the ending stage of the first-step annealing \( (T_{a1}') \), then to the crystallization morphology.

Unlike Figure 3.2.2, Case \( a \) in Figure 3.2.3 shows that \( T_{a3} \) has touched the binodal point. As long as phase separation has reached the late stage (or equilibrium), the crystallization at the second-step will occur out of the phase-separated crystallizable-polymer-rich phase. In this phase, the concentration of crystalline polymer shifts to the higher value along the tie line during phase separation, as illustrated in Figure 3.2.3a. and Figure 3.2.3c, thus the crystallization is less
“poisoned”, and becomes faster. Annealing at $T_{a4}$ in Figure 3.2.3b has the same crystallization kinetics as Case a at $T_{a3}$. The only difference is in the development of the phase morphology, which will be discussed in detail later.

Figure 3.2.3 Illustrating the determination of binodal point at one concentration (2). The first-step annealing temperature is at and below the binodal point. The first-step annealing temperature is $T_{a4} < T_{a3}$, $T_{a3}$ touches the binodal line, and $T_{a4}$ is below binodal point. $T_c$ in Case a and Case b are same. Figure c illustrates the morphology change from the beginning stage of the first-step annealing ($T_{a1}$) to the ending stage of the first-step annealing ($T_{a1}'$), then to the crystallization morphology.

According to the mechanism of the crystallization selection process, annealing at $T_{a1}$ and $T_{a2}$ would not introduce any change into the crystallization rate at the second-step annealing. Only annealing at $T_{a3}$ allows for the selection process to begin
to effect and play an important role on the crystallization growth rate. Therefore, through the sudden change in crystallization kinetics, the binodal point can be determined.

3.2.2 Design for Determination of the Spinodal Curve of the Liquid-Liquid Phase Separation

The spinodal curve is usually calculated based on theory or differentiated by the phase separation dynamics, which also can be identified where the liquid-liquid phase separated morphology changes from droplet growth to the bicontinuous phase morphology, as illustrated in Figure 2.3.3 and Figure 2.3.4. This specially designed experimental process enables the phase domains to evolve into the late stage of liquid-liquid phase separation, forming the relatively large scale of domain that is able to be decorated by the crystal. The crystal-decorated phase morphology reflects the consequence of the domination from the liquid-liquid phase separation, rather than from the competition of two mechanisms.

Therefore, continual lowering the annealing temperature at this chosen composition, as illustrated, lowering from $T_{a4}$ (in Figure 2.3.3.b) to $T_{a5}$ (in Figure 2.3.4), will lead crystalline phase domain showing the change in morphologies. This is becomes more apparent due to a decoration of the domain by the crystalline structure. If a change in the morphology occurs at $T_{a5}$ from the droplet domain to the bicontinuous domain, $T_{a5}$ is about at spinodal point. Therefore, if we carry out this type of experiment for different blend concentrations to detect the morphological change, reflecting the mechanism change from nucleation to spinodal decomposition,
the spinodal curves can be obtained experimentally by this morphology determination method. It should be noted that the crystallization kinetics are similar to the phase separated case as described previously.

![Spinodal Curves Diagram](image)

**Figure 3.2.4** Illustration of the determination of the spinodal point at the same concentration as Figures 3.2.2 and 3.2.3. The first-step annealing temperature is at the spinodal point for the given concentration. A change in the morphology and indicates a change in the phase separation mechanism.

### 3.3 Materials and Sample Preparation

In order to test this idea, a series of PE samples were used in this study. One of the components in the series of blends was a high-density polyethylene (HDPE) with a weight average molecular weight of 80k g/mol. The other component was a linear low-density polyethylene (LLDPE) with randomly distributed octane branches with a
weight average molecular weight of 70k g/mol and an octane branch concentration of 120 per 1000 carbon atoms. The components have polydispersities of ~ 2. The HDPE is the crystalline component of this series, and LLDPE is the amorphous component above 80 °C. In this dissertation, all the experiments were carried out above 80°C, which means LLDPE remained amorphous throughout, even it can crystallize at the room temperature. The detailed sample information is listed in the Table 3.3.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Branch Density</th>
<th>Tm</th>
<th>Tc</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>0.955g/cc</td>
<td>&lt;0.5ethyls/1000C</td>
<td>132.5</td>
<td>120.4</td>
<td>219.6J/g</td>
</tr>
<tr>
<td>LLDPE</td>
<td>0.870g/cc</td>
<td>12/per100C</td>
<td>56.1</td>
<td>43.2</td>
<td>47.5J/g</td>
</tr>
</tbody>
</table>

HDPE    linear homopolymer
LLDPE   ethylene-octane single-site metallocene copolymer

A series of PE blends were prepared by dissolving them in p-xylene at 120 °C for 24 hrs in order to intimately mix them. The solution was then quickly poured into a large excess amount of chilled methanol, and the blends rapidly precipitated. After filtration, the blend samples were washed with methanol and dried in a vacuum oven for 3 days. The samples were then ground into powder in liquid nitrogen.

A second method of freeze-dry was used in order to verify the integrity of the mixing in solution. Both components were dissolved in p-xylene at 120 °C for 24 hrs, then the whole solution was quickly put into a container with methanol-dry-ice slurry
(below 0 °C) to freeze both the solvent and polymer (p-xylene’s melting point is 13.26 °C). Afterwards, it was kept frozen, and then vacuum pumped for one week to dry the p-xylene solvent. This method is typical freeze-dry, which can preserve the blend’s intimate mixing in the state of solution.

3.4 Instrumentations

The major experimental instrumentations for this project are introduced in the following section, and the ways to prepare samples corresponding to each one are included as well.

3.4.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of blends and homopolymers were conducted using a TA TGA 2950. The temperature scale was carefully calibrated using the magnetic mull method. The weight was calibrated with the labeled standard materials and the error was less than 0.001 mg. Approximately 5 mg of the specimen was put in the sample pan and heated from 30°C to 600°C at a heating rate of 10°C/min under a nitrogen atmosphere. The 2% and 5% weight loss temperatures of the specimen were obtained and used as the estimation of the thermal and thermo-oxidative stability of the samples. Differential scanning calorimetry (DSC) experiments were performed after the TGA test, and the upper-limit of the scanning temperature in DSC was 30°C lower than the 2% weight loss temperature from the TGA.
3.4.2 Differential Scanning Calorimetry

The two-step isothermal method was conducted on a series of different blend compositions using a Perkin-Elmer PYRIS Diamond DSC with an Intracooler 2P apparatus. The temperatures and heat flows were calibrated using material standards at a cooling and heating rate of 10°C/min. The initial samples were prepared from solution participation. In order to ensure samples start from the same miscible state, all solution-participated blends were initially annealed at 190 °C for two hours to eliminate the thermal history, and then quenched to the prescribed annealing temperature which ranged between 190°C and 150°C at an interval of 5°C. At each temperature, the system was isothermally annealed for at least 6 hrs to allow any liquid-liquid phase separation to reach the late stage of coarsening and then quickly quenched to a lower preset temperature (such as at 120 °C) to crystallize the HDPE component. Heat flow versus crystallization time was record by the DSC. The crystallization kinetics was characterized by the crystallization half-time \((t_{1/2})\), as defined by the crystallization time where 50% of the final crystallinity has been achieved.

3.4.3 Phase Contrast and Polarized Light Microscopy

Phase morphologies after annealing and crystallization with the two-step isothermal method were observed via polarized light microscopy (PLM, Olympus BH-2) and phase contrast optical microscopy (PCOM, Olympus BH-2). Both of them were coupled with a calibrated Mettler heating stage (FP-90). The samples prepared for PLM and PCM had a typical thickness of 1 μm, and they were made into
the film by the freeze-dry method on a carbon-coated substrate surface. The thermal process for the films was identical to those in the DSC experiment.

3.4.4 Atomic Force Microscopy

An AFM (Digital Instrument Nanoscope IIIA) in tapping mode was utilized to obtain a modulus map and surface topology map of the blends. The modulus map is derived from AFM phase information and goes beyond providing simple topographical information to show variations in surface modulus which can be associated with compositional variations in the different phase domains. All AFM images were measured at a temperature of 80 °C, which is higher than the melting temperature of LLDPE but lower than the melting temperature of HDPE. This enabled the modulus map to differentiate between the HDPE-rich phase and the LLDPE-rich phase. The scanner was calibrated in both lateral and vertical directions using a standard grid. A typical measurement was a scan size of 20 μm, a scan rate of 0.5 Hz with operation and resonance frequencies of 300 kHz, and a resolution of 512 × 512.
CHAPTER IV

DETERMINATION OF THE BINODAL CURVE OF LIQUID-LIQUID PHASE SEPARATION WITH OVERALL CRYSTALLIZATION RATES OF THE BLENDS

4.1 Sample Degradation Test

The two-step isothermal annealing experiments require annealing samples at high temperature for relatively long time, so the degradation issue needs to be paid attention to. According to the TGA tests, the pure HDPE sample started to depredate 0.015% of weight percentage after annealing two hours at 200°C, and so did the pure LLDPE sample, as shown in Figure 4.1.1 and Figure 4.1.2. Therefore, the highest annealing temperature was chosen no higher than 190°C. The initial two-hour annealing to ensure the same starting state was set at 190°C.

![TGA result of pure HDPE sample. It started to degrade 0.015% of weight percentage at 200°C](image)

Figure 4.1.1 TGA result of pure HDPE sample. It started to degrade 0.015% of weight percentage at 200°C
Figure 4.1.2 TGA result of pure LLDPE sample. It started to degrade 0.015% of weight percentage at 200°C

4.2 Relationship between the Change in Overall Crystallization Rates of the Blends and the Binodal Points of Liquid-Liquid Phase Separation

Before discussing the experimental results, let us first take a look at the way we choose to characterize the crystallization rate.

4.2.1 Characterization of Overall Crystallization Rate

Based on the classical knowledge of crystallization, overall crystallization includes primary nucleation and crystal growth. The common way to experimentally study crystal growth rates is by measuring spherulite growth rate by optical microscopy. Meanwhile, the rate of primary nucleation is difficult to be experimentally investigated through the same way, since primary nucleus is very small and non-visible by eyes. Only synchrotron wide angle X-ray scattering possibly investigates nucleation of crystallization. It was found that at a typical degree of supercooling (~50 °C), the nucleus is perhaps 10^3 nm, much less than the volume of a molecule (10^4-10^6 nm for 60
thousand to 6 million molecular weights). In most cases, one way to evaluate overall crystallization rates uses dilatometry and calorimetry, which are adapted to measure crystallinity as a function of time. It can not differentiate between nucleation and crystal growth.

A widely used model for describing overall crystallization is the Avrami equation, which is derived from the statistics of the Poission equation (raindrops falling randomly on the surface of the water and leading expanding wave).116

\[
F(t) = 1 - \exp\left[-Kt^n\right]
\]

\[
\ln\left\{-\ln[1 - F(t)]\right\} = \ln K + n \ln t
\]

Usually, the Avrami equation fits polymeric crystallization data fairly well, because the good fitting to overall crystallization behavior is strongly correlated between the starting time of crystallization and $K$ and $n$ of Equation 4.2.1. A special consequence of this inherent correlation of the parameters of the Avrami equation is the difficulty in estimating the induction time for nucleation. It is estimated that the induction time must be more than 0.3 times the crystallization half time before it can be safely detected through the fitting of the Avrami equation in experimental data.116

Considering the reality of our experimental system, for the HDPE/LLDPE blends, the Avrami equation was not the best model to analyze data. First, the induction time of nucleation can not be recorded by calorimetry in the two-step isothermal process due to the fast crystallization. The induction time is critical for good fitting of the Avrami model. In addition, the complex of crystallization in the
blends fails to adhere to most assumptions in the Avrami equation, for instance, the non-linear growth rate due to the presence of a non-crystallizable component is against linear crystal growth rate assumption in the Avrami model. The second deviation would be that the non-constant crystallization volume caused by the concentration change in the HDPE-rich phase violates the assumption of constant crystallization volume. Finally, the crystal morphology does not exactly form typical spherulites, and also a perfection of crystals after crystallization occurs. All these facts deviate form the ideal assumptions in the Avrami equation. Hence, we chose another way to represent data.

Therefore, in my project, a more appropriate way to handle the crystallization rate in a polymer blend is by measuring crystallization times in DSC. The half-crystallization time, \( t_{1/2} \), is the crystallization time when crystallization reaches 50% of crystallinity and is inversely proportional to the overall crystallization rate. Also crystallization peak time, \( t_p \), which is the time to reach the exothermal peak during crystallization, can also be used to characterize the crystallization rate. The former is the parameter that averages over the entire crystallization rate, whereas the latter is the onset between crystal growth and perfection.

4.2.2 Binodal Points of Liquid-Liquid Phase Separation Determined by Change in Overall Crystallization Rates of the Blends

Figure 4.2.1a shows a set of heat flow thermal diagrams isothermally crystallized at 120 °C recorded by DSC for a 25/75 HDPE/LLDPE blend. Each thermal diagram corresponds to a different first-step annealing temperature ranging
from 175 °C to 140 °C at a 5 °C interval. Since all of these annealing temperatures are above the melting temperatures of both PE components of the blend, no crystallization occurs during the annealing. When the first-step annealing temperature is below the binodal curve, liquid-liquid phase separation occurs. In a UCST system quenched below the binodal line, the composition of the two phases is fixed by the location of the tie-line intersection with the binodal curve at the annealing temperature, and the weight fraction of each phase is determined by the initial blend concentrations as well as the final phase concentrations at each temperature according to the lever rule. In the 25/75 HDPE/LLDPE blend, the phase separation leads to a dispersed HDPE-rich phase in a HDPE-poor matrix. By quenching the system further to crystallize the HDPE component, while the LLDPE component remains a liquid, the effect of the liquid-liquid phase separation on the HDPE crystallization kinetics can be identified. It is expected that there is a change in the crystallization rate after liquid-liquid phase separation occurs during the isothermal annealing. The increased crystallization rate is due to the fact that within the HDPE-rich domains the probability of HDPE absorbing or depositing onto the crystal growth front and crystallizing is higher than that in the miscible blend. This is the selection process as described in Section 2.4.2. A decrease in $t_{1/2}$ is, therefore, an indication of liquid-liquid phase separation, and the onset of this decrease indicates the onset of the liquid-liquid phase separation.

Figure 4.2.1b is a plot of the $t_{1/2}$ values of the overall crystallization at 120 °C versus the annealing temperature of the first step. As we can see in this figure, the
$t_{1/2}$ values remain constant when the annealing temperature is above 170 °C. Below this temperature, the $t_{1/2}$ values start to decrease. If the isothermal crystallization peak time ($t_p$) in Figure 4.2.1a is used to characterize the overall crystallization kinetics instead of $t_{1/2}$, identical results are observed. The independence of $t_{1/2}$ with respect to the annealing temperature above 170 °C in the first step indicates that HDPE and LLDPE are miscible. The decrease in the $t_{1/2}$ values with decreasing annealing temperature indicates that 170 °C is the threshold below which the HDPE/LLDPE blend is phase separated. In Figure 4.2.1b, at temperatures far below 170 °C, the HDPE-rich phase has an even higher HDPE concentration due to further quenching below the binodal line, and thus, the crystallization rate is increasingly faster. The $t_{1/2}$ values for overall crystallization decrease as the HDPE concentration in the dispersed phase increases.

As the phase weight fractions develop in the early stage of phase separation, the overall crystallization rate will be annealing time dependent. In the late stage of phase separation, when the equilibrium phase weight fraction is reached, the overall crystallization rate should be constant. Note that even a constant overall crystallization rate only indicates that the phase-separated blend reaches the equilibrium weight fractions, yet the phase morphology of the liquid-liquid phase separation of the blend is still in a metastable state. The true equilibrium for binary liquid-liquid phase separation is completely-separated layers, for instance, when mixing water and oil, eventually the mixture separates into two layers with oil in the upper layer and water in the bottom layer. Water and oil are small molecules,
Figure 4.2.1 A blend of 25/75 HDPE/LLDPE after annealing at different temperatures for 6 hrs in the first step of the two-step isothermal experiment. (a) Set of DSC isothermal crystallization thermal diagrams at 120 °C of the second step; (b) Relationship between the crystallization $t_{1/2}$ values at 120 °C from the DSC results versus annealing temperatures in the first step for a blend of 25/75 HDPE/LLDPE. The onset temperature where the overall crystallization rate increases (the $t_{1/2}$ value decreases) is at 170 °C.
having fast diffusion rates. In polymer blends, however, it hardly ever reaches the morphological equilibrium due to the high viscosity and slow diffusion rate.

Furthermore, in these phase-separated morphologies, the HDPE-rich domains possess sizes which must be large enough (usually larger than the micrometer scale) to not affect the crystallization rates.\textsuperscript{108}

When increasing the concentration of HDPE, blends gradually close to the even volume fraction. Because the two components have a comparable magnitude of molecular weight (up to 100k g/mol), the 50/50 composition is around the critical composition. Figure 4.2.2a shows a set of DSC isothermal diagrams which record the crystallization process at 122 °C for a 45/55 HDPE/LLDPE blend after the samples were annealed at different temperatures for 6 hrs. It is evident that the onset annealing temperature of where the overall crystallization speeds up shifts to much higher temperature (185 °C). This can be clearly observed in Figure 4.2.2b in which the $t_{1/2}$ versus annealing temperatures is plotted.

Continuing increasing the volume fraction of HDPE, above the 50/50 composition, HDPE becomes the major component, such as in the case of 83/17 HDPE/LLDPE. The liquid-liquid phase separation consists of a dispersed LLDPE-rich phase and an HDPE-rich matrix phase. Figure 4.2.3a shows the experimentally-observed DSC thermal diagrams at 124 °C for the overall crystallization, and Figure 4.2.3b is a plot of $t_{1/2}$ versus annealing temperature. It is evident that the crystallization rate increases after liquid-liquid phase separation even when HDPE is the majority phase.
Figure 4.2.2 A blend of 45/55 HDPE/LLDPE after annealing at different temperatures for 6 hrs in the first step of the two-step isothermal experiment. (a) Set of DSC isothermal crystallization thermal diagrams at 122 °C of the second step; (b) Relationship between the crystallization $t_{1/2}$ values at 122 °C from the DSC results versus annealing temperatures for a blend of 45/55 HDPE/LLDPE. The onset temperature where the overall crystallization rate increases (the $t_{1/2}$ value decreases) is at 187 °C.
Comparing Figure 4.2.1a with Figure 4.2.3a, the isothermal crystallization at 123 °C in the DSC thermal diagrams of the 83/17 HDPE/LLDPE blend exhibits a different behavior after phase separation. For the 25/75 HDPE/LLDPE blend, the most apparent change is that the $t_p$ of crystallization is shifted as shown in Figure 4.2.1a, yet the shape of the curve and the heat of crystallization do not alter. However, in the 83/17 HDPE/LLDPE blend, the overall crystallization $t_p$ values are less shifted, but the shape of the diagrams before and after $t_p$ have noticeably changed as shown in Figure 4.2.3a. These curves are shallower at the higher annealing temperatures when the crystallization takes place in the miscible blend and steeper at the lower annealing temperatures after the phase separation has occurred. As a result, the crystallization $t_{1/2}$ values change drastically as shown in Figure 4.2.3b. In this case, the $t_p$ and $t_{1/2}$ values do not closely corresponding to each other. This shape change as shown in Figure 4.2.3a is due to the fact that when the crystallization takes place in the miscible blend, the HDPE crystallizes out of the miscible liquid and leaves an increasing amount of LLDPE at the crystal growth front. Therefore, the concentration of the HDPE is continuously decreasing, leading to a prolonged crystallization process. These results may also occur due to the relatively lower crystallinity (the crystallinity issue is discussed in Section 4.2.4)
Figure 4.2.3 A blend of 83/17 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of the two-step isothermal experiment. (a) Set of DSC isothermal crystallization thermal diagrams at 123 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 123 °C and annealing temperature for a blend of 83/17 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 160 °C.
These three blends with different volume fractions of HDPE are the typical examples from the crystalline minority phase to the majority phase. In order to probe the whole shape of the binodal curve for this set of HDPE-LLDPE polyethylene blends, the same investigations were carried out at other volume fractions. The following are the isothermal diagrams and plots of $t_{1/2}$ versus annealing temperatures for each of those compositions.

For all blends with HDPE concentrations between 15% and 83%, trends similar to those shown in Figures 4.2.1 and 4.2.3 are observed. Using blends with different compositions, the binodal curve across the entire composition range can be constructed.
Figure 4.2.4 a blend of 15/85 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 119 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 119 °C and annealing temperatures for a blend of 15/85 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 165 °C.
Figure 4.2.5 A blend of 31/69 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 120 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 120 °C and annealing temperatures for a blend of 31/69 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 175 °C.
Figure 4.2.6 A blend of 40/60 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 122 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 122 °C and annealing temperatures for a blend of 40/60 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 185 °C.
Figure 4.2.7 A blend of 52/48 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 122 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 122 °C and annealing temperatures for a blend of 52/48 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 185 °C.
Figure 4.2.8 A blend of 59/41 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 122 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 122 °C and annealing temperatures for a blend of 59/41 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 180 °C.
Figure 4.2.9 A blend of 63/37 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 124 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 124 °C and annealing temperatures for a blend of 63/37 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 175 °C.
Figure 4.2.10 A blend of 75/25 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 123 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 123 °C and annealing temperatures for a blend of 75/25 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 165 °C.
Figure 4.2.11 A blend of 80/20 HDPE/LLDPE after isothermally annealed at different temperatures for 6 hrs in the first step of annealing. (a) Set of DSC isothermal crystallization thermal diagrams at 123 °C of the second step; (b) Relationship between the $t_{1/2}$ values of overall crystallization at 123 °C and annealing temperatures for a blend of 80/20 HDPE/LLDPE. The overall crystallization rate increases (the $t_{1/2}$ value decreases) at 160 °C.
Figure 4.2.12 shows the onset temperatures of the $t_{1/2}$ values with changes in the HDPE concentration for this series of HDPE/LLDPE blends. The solid line was drawn as the guiding-eye curve. It is a binodal-like curve for liquid-liquid phase separation in terms of phase stability, if approached through our experimental design, which should be close to the thermodynamic binodal curve. It shows that this binodal curve is more or less symmetric with the critical point at a HDPE concentration of 48%. The critical temperature is 187 °C. The symmetric shape is evidence of the comparable molecular weights used in this series of blends.

![Figure 4.2.12](image)

Figure 4.2.12 The square dots are experimental data, and the solid-line curve was drawn to guide eye. Binodal curve for the HDPE/LLDPE blend deduced from the onset temperatures where of the $t_{1/2}$ begins to decrease with annealing temperature (the overall crystallization rate starts to increase).
In this case, the phase boundary of LLPS ranging from 150 °C to 190 °C is above the melting temperature curve of the crystalline component HDPE, as shown in the 4.2.13. The lozenge shape dots are the melting temperature depression curve which is calculated from the thermodynamic equilibrium hypothesis in the assumed miscible phase. In miscible blends, at the melting point \( T_m \) of the crystalline component, the chemical potential of crystalline component in the liquid phases should be equal to its chemical potential in the crystallization, shown as following:

Crystalline component’s chemical potential in the liquid mixture (using Florry-Huggins approximation):

\[
\mu_2^* - \mu_2^0 = \frac{RTV}{V_1} \left[ \ln \frac{x_2}{m_2} + (1-x_2) \left( \frac{1}{m_2} - \frac{1}{m_1} \right) + \chi_{12} (1-x_2)^2 \right]
\]

Equation 4.2.3

Crystalline component’s chemical potential in the crystallization:

\[
\mu_2^C - \mu_2^0 = -(\Delta H_2 - T \Delta S_2) = -\Delta H_2 (1 - \frac{T}{T_m^0})
\]

Equation 4.2.4

then, at \( T=T_m \)

\[
\mu_2^* - \mu_2^0 = \mu_2^C - \mu_2^0
\]

Equation 4.2.5

The subscript 1 means amorphous polymer and 2 means crystalline polymer; \( x \) is volume fraction, \( V_1 \) or \( V_2 \) means the molar volume of the repeating unit; \( m \) is degree of polymerization; \( \Delta H_2 \) is heat of fusion of crystalline component; and \( \Delta S_2 \) is entropy of the crystalline component. \( T_m^0 \) is the equilibrium melting temperature.

However, these calculated melting points are based on the assumption of miscible phase, which deviates from the real melting temperatures in immiscible phases. In fact, the region within the miscibility gap should reveal the invariant
melting temperatures, hypothesized as the dot line in Figure 4.2.13, because the initial concentrations of HDPE eventually change and reach the same equilibrium points after phase separation.

![Figure 4.2.13 The Binodal curve for the HDPE/LLDPE blend intercepts with melting temperature depression curve. The square dots are experimental data. The lozenge dots are the calculated melting temperature points. The dot line is the hypothesized melting temperature curve.](image)

Figure 4.2.13 The Binodal curve for the HDPE/LLDPE blend intercepts with melting temperature depression curve. The square dots are experimental data. The lozenge dots are the calculated melting temperature points. The dot line is the hypothesized melting temperature curve.

4.3 Time to Reach Composition Equilibrium in Liquid-Liquid Phase Separation

According to the content of Section 4.2, the binodal-like curve for liquid-liquid phase separation can be plotted out by connecting the crystallization rate changes at various concentrations. Obviously, this binodal-like curve is phase stability dependent. In order to represent the actual thermodynamic binodal curve to the maximum extent, the first-step annealing should meet the requirement of reaching the
sufficient phase stability at the compositional equilibrium. Therefore, the length of
time that it takes the blends to reach the compositional equilibrium is another
important factor which guarantees the least effect of further liquid-liquid phase
separation on the crystallization during the second-step annealing

Figure 4.3.1 demonstrate this principle for a blend with a 45/55
HDPE/LLDPE composition, which is close to the critical composition (see the phase
diagram in Figure 4.2.12). The isothermal annealing temperature in the first step
was set at 150 °C, and the blend samples were maintained at that temperature for
different annealing times. The samples were then quenched to a crystallization
temperature of 122 °C for crystallization. With an increase in the first-step annealing
time, the crystallization rate eventually reached a constant value. The reason for the
plateau of crystallization rate is that the weight fraction of HDPE in the HDPE-rich
phase is unchangeable at this point, in other words, it reached the phase weight
fraction equilibrium for the phase (the weight fraction at the intersection of the tie line
of 150 °C with the binodal curve). From a comprehensive point of view, apart from
the weight fraction, the plateau also means the separated phase domain has been large
enough to eliminate any confinement during crystallization. From the data in Figure
4.3.1, it is evident that the annealing time at 150 °C must be longer than 300 minutes
in order to reach a constant overall crystallization rate. The length of time needed
reflects the slow liquid-liquid phase separation kinetics to reach the equilibrium phase
weight fractions with sufficiently large domain sizes. For the rest of the experiments,
including blends at other concentrations, the annealing time was longer than 300
minutes to ensure a constant overall crystallization rate. Therefore, it can be deduced that changes in the $t_{1/2}$ value in these experiments are sole indications of reaching the binodal curve.

Figure 4.3.1 The $t_{1/2}$ values of the overall crystallization in the second step at 122 °C versus annealing times in the first step at 150 °C for a blend of 45/55 HDPE/LLDPE.

The kinetics of liquid-liquid phase separation is strongly associated with the viscosity of the blends. Data in Figure 4.3.1 comes from a blend of 45/55 HDPE/LLDPE. When the volume fraction of HDPE in blends is less than 45%, the liquid-liquid phase separation takes place at a faster rate due to the lower viscosity, and vice versa. However, based on the lever rule on the tie-line of the phase diagram, the HDPE-rich phase can still reach equilibrium relatively fast even though blends with higher concentrations of HDPE have higher viscosity. Therefore, we chose 360 minutes as the first-step annealing time for the rest of the concentrations based on the data in Figure 4.3.1
4.4 Crystallinity Dependence on the Liquid-Liquid Phase Separation

The crystallinity is dependant on the annealing temperature in the first step. It was found that when the crystallization rate starts increasing there is also a change in crystallinity. Figure 4.4.1 shows the crystallinities for the two blends with HDPE concentrations of 25% and 55%. The crystallinities in this figure have been normalized by taking the weight fraction of HDPE into account. At the onset temperature of phase separation, the crystallinities discontinuously increase when the annealing temperature enters into the liquid-liquid phase separation region. This observation indicates that liquid-liquid phase separation not only enhances the overall crystallization kinetics, but also increases the quality and/or quantity of the crystals in the blend.
Figure 4.4.1  HDPE crystallinity changes as a function of annealing temperature in the first step for two blends of (a) 55/45 and (b) 25/75 HDPE/LLDP.
CHAPTER V

DETERMINATION OF THE SPINODAL CURVE FOR LIQUID-LIQUID PHASE SEPARATION WITH CRYSTAL-DECORATED PHASE MORPHOLOGIES OF THE BLENDS

5.1 Relationship between Metastable Phase Morphology and the Spinodal Curve of Liquid-Liquid Phase Separation

The spinodal curve in liquid-liquid phase separation is difficult to determine experimentally for crystalline-amorphous blends with isorefractive indices, so their phase diagrams are based on theoretical calculations in most of cases. In this study, we try to utilize both crystallization and liquid-liquid phase separation to construct a spinodal curve via morphological observations.

When the annealing temperature is in the metastable region between the binodal and spinodal curves, in the other word, phase separation occurs through a nucleation-and-growth mechanism resulting in droplet-like domains by overcoming a nucleation barrier. When the annealing temperature is in the unstable region (below the spinodal curve), liquid-liquid phase separation follows a spinodal decomposition mechanism where the phases form bicontinuous domains without any energy barrier. As long as the phase morphology is metastable, rather reaching the two-layer equilibrium phase morphology of a blend, one can use the phase morphology to
distinguish between these two mechanisms.\textsuperscript{58, 117, 118} Usually, only small molecules can reach the two-layer morphological equilibrium, such as the mixture of water and oil.

Through the first-step annealing process, the separated phase morphology would be developed to the late stage over large scale. In this situation, crystals formed in the large HDPE-rich phase with a stable weight fraction have fewer defects than ones formed in the LLDPE-rich phase; therefore, with neat crystals filling in, the HDPE-rich phase can be decorated. Based on the structure self-similarity during coarsening, described in Section 2.2.2.3.2, the shape of this domain structure does not change. The HDPE-rich phase with the crystal-decorated morphology has enhanced the contrast in phase morphology, and has preserved the late stage morphology of liquid-liquid phase separation. Because of this the two phase separation mechanisms can be distinguished.

5.2 Crystal-Decorated Metastable Phase Morphologies

Figure 5.2.1a is an AFM phase image of an HDPE/LLDPE 40/60 blend crystallized at 123°C after the sample was annealed at 175 °C for 24 hrs. As shown in Figure 4.1.21, this annealing temperature is below the binodal curve as determined by the crystallization kinetics study.
Figure 5.2.1 Images of a blend of 40/60 HDPE/LLDPE crystallized at 123 °C after annealing at 175 °C for 24 hrs: (a) AFM image and (b) PCOM image. (a) The nucleation-limited mechanism with spherical phase morphology, indicates that the phase separation occurs in between the binodal and spinodal curves; and (b) bright HDPE spherulites grow within the spherical phase domains.
Droplet domains with diameters ranging from 2 - 3 μm can be clearly observed. Figure 5.2.1b is a PCOM image of the identical blend. The bright spots in PCOM are crystals within the droplets. Based on this phase morphology observation, it can be concluded that the phase separation that takes place while annealing at 175 °C is between the binodal and spinodal curves corresponding to the nucleation-and-growth mechanism. This type of droplet morphology can be observed up to an annealing temperature of 180 °C, which coincides with the experimentally determined binodal curve.

Figure 5.2.2a shows a PCOM image of the same sample after it was annealed at 170 °C for 24 hrs in the first step and then quenched to 123 °C to crystallize the HDPE. This figure shows spherulitic crystals impinging each other, decorating a bicontinuous phase morphology on a large length scale. Figure 5.2.2 b is a PLM image of Figure 5.2.2a at the same location. It is evident from the spherulitic crystal decoration in the HDPE-rich domains that the phase morphology is bicontinuous. This indicates that the phase separation mechanism was spinodal decomposition meaning that the annealing temperature was below the spinodal line.

The AFM image in Figure 5.2.3a was taken for an identical blend after annealing at 145 °C for 24 hrs and crystallizing at 123 °C. As in Figure 5.2.2, this figure also shows a bicontinuous phase morphology with a number of crystals in the HDPE-rich domains. Figure 5.2.3b is the corresponding PLM image.
Figure 5.2.2 Images of a blend of 40/60 HDPE/LLDPE crystallized at 123 °C after isothermally annealing at 170 °C for 24 hrs. (a) Phase contrast microscopy (PCOM) image and (b) PLM image. (a) The spinodal decomposition mechanism bicontinuous phase morphology, indicating that the phase separation occurs below the spinodal curve; and (b) The HDPE spherulites grow within the bicontinuous phase domains.
Compared with Figure 5.2.2b, the bicontinuous domains are smaller in Figure 5.2.3b, indicating that the increased viscosity at the lower annealing temperature had increased the coarsening time of the phase morphology, thus the morphology in Figure 5.2.3b is preserved from the early stage of coarsening, only at the small scale of phase domain, while the one in Figure 5.2.3a is recorded from the later stage of coarsening, being able to reach the large scale. However, despite the difference in size, these phase separation morphologies are both self-similar.

A continual decrease in the volume fraction of HDPE leads the crystallizable-HDPE-rich phase more dispersed as a minus component, thus causing more difficulty to experimentally characterize their phase morphology. Therefore, so far few studies have focused on the HDPE-rich dispersed phase morphology in PE blends. Figure 5.2.4a shows an AFM image for a 27/73 HDPE/LLDPE blend crystallized at 120 °C after annealing at 160 °C for 24 hrs in the first step. In order to observe HDPE-rich phase clearly, the LLDPE component in the matrix has been carefully washed away slightly at room temperature. In this way, crystals in HDPE-rich phase can still be preserved. It enables to obtain images shown in Figure 5.2.4. From Figure 5.2.4a, it is evident that the crystallized droplet-like-dispersed minority phase indicates that the liquid-liquid phase separation occurs through the nucleation-and-growth mechanism.

Compared with Figure 5.2.1a, crystal-filled droplets in Figure 5.2.4a are smaller than ones in Figure 5.2.1a, that is because of less HDPE volume fraction and
Figure 5.2.3 Images of a blend of 40/60 HDPE/LLDPE crystallized at 123 °C after isothermally annealing at 145 °C for 24 hrs, (a) AFM image and (b) PLM image.
lower first-step annealing temperature. In Figure 5.2.4a, the coarsening of small droplets was still ongoing.

Figure 5.2.4b shows an AFM image for a same 27/73 HDPE/LLDPE blend crystallized at 120 °C after annealing at 150 °C for 24 hrs. The sample was prepared through the same way as described for Case 5.2.4a. In Figure5.2.4b, crystal-decorated phase becomes bicontinuous. Furthermore, the crystals filled in the HDPE-rich phase show the characteristics of a dendrites or flat-grown lamella with large amount of screw dislocation. This explains the wondering of that why some HDPE-dispersed phases are difficult to be characterized by optical microscopy. Because these two crystal structures do not show birefringence under PLM, as there is no rotation of crystal stem along chain direction. Therefore, our two-step annealing process at large extent fully develops the phase morphology and crystal morphology. Even not with optical microscopy, the morphology of PE blends with extremely low volume fraction of crystallizable-component can be studied through our experimental design.

For blends with HDPE as the major component, the crystallization will occur in the matrix. Figure 5.2.5a shows an AFM image for a 70/30 HDPE/LLDPE blend crystallized at 90°C after annealing at 160 °C for 24 hrs in the first step. It is evident that the non-crystallizable LLDPE-rich droplets at 90 °C are the minority phase and the HDPE-rich phase is now the crystallized matrix. Figure 5.2.5b is the corresponding PLM image. In this case, droplet domain is LLDPE-rich domain, within which few crystals formed at 90 °C. Figure 5.2.5c is the corresponding PCOM
Figure 5.2.4 AFM images of a blend of 27/73 HDPE/LLDPE (a) crystallized at 120 °C after annealing at 160 °C for 24 hrs. It indicates the nucleation-limited mechanism with dot-like-baby crystal phase morphology, indicating that the phase separation occurs in between the binodal and spinodal curves (b) crystallized at 120 °C after annealing at 150 °C for 24 hrs. Dendrites or flat-grown crystals are within the bicontinuous phase domains, indicating that the phase separation occurring under spinodal curves.
image, the contrast of droplet LLDPE-rich domain is enhanced due to the crystallization of the matrix. This phase morphology indicates that the liquid-liquid phase separation occurs through the nucleation-and-growth mechanism. The only difference between Figures 5.2.1 and 5.2.5 is that the minority and majority phase compositions in Figures 5.2.5a, 5.2.5b and 5.2.5c are inversed.

On the other hand, Figures 5.2.6a, 5.2.6b, and 5.2.6c are the PLM, PCOM and AFM images for the same blend crystallized at 90 °C after annealing at 150 °C for 24 hrs. In Figure 5.2.6a, two types crystal morphologies exhibit. One is large and fully-developed crystal spherulites with complete maltese cross, and another is partly-developed crystal only with fractioned birefringence. To eliminate the birefringence effect, Figure 5.2.6b shows the corresponding image from PCOM, which clearly shows a bicontinuous phase with enhanced contrast by large amount of crystallization. Figure 5.2.6c shows the microscopic texture of the bicontinuous phase. The bicontinuous phase morphology indicates that the spinodal decomposition mechanism was dominant. Again, the crystallization takes place in the majority phase, which is the opposite of what is seen in Figure 5.2.3.
Figure 5.2.5 Images of a blend of 70/30 HDPE/LLDPE crystallized at 90 °C after isothermally annealing at 160 °C for 24 hrs, (a) AFM image and (b) PLM image.
(a) The nucleation-limited mechanism with spherical phase morphology, indicating that the phase separation occurs in between the binodal and spinodal curves;
(b) The HDPE spherulits grow outside of the spherical phase domains.
Figure 5.2.5 (continued) Images of a blend of 70/30 HDPE/LLDPE crystallized at 90 °C after isothermally annealing at 160 °C for 24 hrs, PCOM (c).
(c) The contrast of LLDPE droplet domain is enhanced due to the crystallization of the matrix.

Figure 5.2.6 Images of a blend of 70/30 HDPE/LLDPE crystallized at 90 °C after isothermally annealed at 150 °C for 24 hrs, PLM (a).
(a) The HDPE spherulits grow within one of the bicontinuous phase domains.
Figure 5.2.6 (continued) Images of a blend of 70/30 HDPE/LLDPE crystallized at 90 °C after isothermally annealed at 150 °C for 24 hrs, PCOM (b) and AFM (c).
(b) The bicontinuous phase domain exhibits due to the enhanced contrast from the crystallization.
(c) The spinodal decomposition mechanism with a bicontinuous phase morphology, indicating that the phase separation occurs below the spinodal curve.
It is evident that even after a prolonged annealing time of 24 hrs, the coarsening of the bicontinuous phase as observed in Figures 5.2.2, 5.2.3 and 5.2.6 does not lead to a change of phase morphology. Liquid-liquid phase separation morphology changes can thus be used to experimentally identify the mechanism of the spinodal decomposition.

Using this approach at different compositions, the phase stability diagram spinodal line can be added to the UCST binodal line. A complete phase diagram with the experimentally determined binodal and spinodal curves is shown in Figure 5.2.6. The open circles in Figure 5.2.6 represent the observation of the bicontinuous phase morphology being decorated by the spherulitic crystal morphology.

One issue that remains is whether during the quench to the crystallization temperature, a further phase separation occurs, and whether this could obscure the observations? One necessity we have to adhere to is fast crystallization. The crystallization at second-step annealing all completed within 20 minutes at specifically chosen crystallization temperature corresponding to each blend with different volume fraction, especially at low HDPE volume fraction. Meanwhile, based on the experiment data from Section 3.3, after samples quenched from the miscible state to immiscible state, single phase has to spend at least 300 minutes to completely separate, reaching weight-fraction equilibrium within each phase. Therefore, we have estimated that the overall crystallization rate at the crystallization temperature in our experiment is about twenty times faster than the liquid-liquid phase separation rate. Furthermore, through the first step annealing, separate phase morphology has been
coarsening to the relatively large scale. Therefore, further phase separation to obscure the already coarsened phase morphology is limited and hindered by the crystallization.

Figure 5.2.7 Complete phase diagram for this series of HDPE/LLDPE blends. The binodal curve is determined by the onset of a decrease in $t_{1/2}$ values (increase of the overall crystallization rates) as shown in Figure 4.1.23, while the spinodal curve is determined by the phase morphology change.

Finally, caution still needs to be taken when using this approach. As shown in Figure 5.2.7, both the binodal and spinodal lines are in the phase diagram. The spinodal line only exists in a perfect “mean-field” blend. In reality, this line can rather be described as a temperature region. Therefore, we speculate that we should see this region in which the phase morphological change is gradual. Further detailed experiments need to be conducted to explore this aspect.
5.3 Theoretical Calculation of Spinodal Curve

Based on the experimentally observed binodal curve, the spinodal line can be theoretically calculated with Flory-Huggins theory. Based on the experimental data of that the critical HDPE composition is 0.48, and the critical temperature is 187 °C, combined with molecular weights, according to the criterion of the critical point, the critical value of the interaction parameter can be determined as $3.49 \times 10^{-4}$, which matches the value estimated for this type of blend.$^{119,120,121}$ By neglecting composition and molecular weight effects, we can simply adopt the interaction parameter form: $\chi = A/T + B$. Here, the interaction parameter is only a function of temperature. Experimental data fitting indicates that $\chi = 0.2735/T - 2.4454 \times 10^{-4}$. For the real PE blends system, in the melt, the interaction parameter is largely dependent on the branch density, as well as associated with molecular weight and branch distribution. By varying the $\chi$ value in terms of this linear relation with temperatures, the spinodal curve is calculated, which is shown as the dotted line in the Figure 5.2.7. It is a close approximation to the experimentally observed one. Therefore, the determination of the spinodal curve by the crystal-decorated phase morphology through this two-step annealing process is reasonable.
Figure 5.3.1 Complete phase diagram for this series of HDPE/LLDPE blends. The binodal curve is determined by the onset of a decrease in $t_{1/2}$ values (increase of the overall crystallization rates) as shown in Figure 4.1.23, while the spinodal curve is determined by the phase morphology change. The dotted line is a Flory-Huggins prediction of the spinodal line.
CHAPTER VI
SHORTAGE OF THE NON-ISOTHERMAL CRYSTALLIZATION
APPROACHING LIQUID-LIQUID PHASE SEPARATION

In the last two chapters, all experiments were carried out through our specially
designed two-step-isothermal process. It is clear that the experimental results shown
in Figure 5.2.6 are well fitted by the Flory-Huggins theory of mixing. The diagram of
this HDPE/LLDPE blend system shows the UCST with the critical points located at
the temperature of 187 °C and the volume fraction of HDPE at 0.48.

Since most industrial researches about the crystallization kinetics utilize the
$T_c$ (crystallization temperature) in DSC temperature scanning experiments as a
characteristic of crystallization rate. They assumed that when $T_c$ shifts to higher
values, it indicated the acceleration of crystallization. Consequently, they deduced
whether phase separation occurs or not from the shift in $T_c$. Having constructed phase
diagram through our two-step isothermal experiments, we would like to compare the
non-isothermal method of thermal analysis with ours. Two types of thermal treatments
were performed here.

1. Thermal Treatment A: In this set of experiments, the DSC temperature scanning
process had three steps: first, the miscible sample was heated up to 190 °C at a heating
rate of 10 °C/min and isothermally annealed at 190 °C for half an hour under
protection of nitrogen atmosphere to erase the thermal history as well as further enhance homogeneity; Second, it was cooled to 0 °C at a rate of 10 °C/min to record the crystallization from the homogeneous state; and third, it was heated to 190 °C again at a rate of 10 °C/min to record the melting of the crystals. The miscible sample blends at various volume fractions were prepared in the same way by precipitating the blends of xylene solution at 120 °C into the methanol, then washed three times with methanol, and vacuum dried for three days.

2. Thermal Treatment B: Another set of samples at various volume fractions were annealed at 150 °C for 6 hours to make phase separation, then quickly quenched to 0 °C, followed by the temperature scanning. The DSC samples were heated to 190 °C at a rate of 10 °C/min to record the melting peak; and then cooled to 0 °C at 10 °C/min to record crystallization. These set of samples are surely phase-separated due to 6 hours annealing at 150 °C, according to the phase diagram obtained in Figure 4.2.23.

Figure 6.1.1a is the cooling behavior of HDPE homopolymer and seven blends at different volume fractions during the Treatment A. The crystallization temperatures shifted towards the lower temperature with an increase in the composition of LLDPE in the blend. This indicates that the crystallization barrier became larger when diluting the HDPE concentration in blends. In order to overcome the increasing crystallization barrier, a large degree of supercooling was required; therefore, at lower contents of HDPE, the crystallization temperatures of the blends were lower.
Figure 6.1.1 Temperature scanning curves of HDPE homopolymer and seven blends with various volume fractions: (a) exothermic cooling curve at a cooling rate of 10 °C/min, crystallization peak temperature chosen as $T_c$; (b) endothermic melting curve at heating rate of 10°C/min, also peak temperature of melting curve chosen as $T_m$. 

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Figure 6.1.1b is the melting behavior of homopolymer and seven blends at the same volume fractions as the ones in Figure 6.1.1a, also after Treatment A. This data was extracted from the scanning step three. The melting temperatures followed the decreasing trend as well when reducing the content of crystalline HDPE in the blends. But, it can be seen clearly that the decreasing trend became discontinuous where blends with 40%, 29%, and 15% of HDPE were higher than the one with 50% of HDPE. Even though, this does not violate the thermodynamic melting point depression theory, (because the melting temperatures here are not at the equilibrium melting temperature) Under kinetic considerations, the $T_m$ can shift to higher values due to crystal annealing during slow heating rate. Specifically, blends at the low contents of HDPE formed poor crystals during cooling. Poorer crystals are easier to anneal at a faster rate. Therefore, blends with the HDPE contents lower than 50% are able to anneal and result in an increase in the melting temperatures at a heating rate of 10 °C/min. Additional evidence of this is the splitting endothermic peaks shown in these blends, which were caused either by crystal annealing, or by liquid-liquid phase separation during the second step cooling, or by both.

For the non-isothermal DSC temperature scanning at a certain rate, the major debate is whether the liquid-liquid phase separation could happen simultaneously during cooling. This controversy goes back to the original inspiration of our experimental design, the desire to avoid the competition between crystallization and liquid-liquid phase separation. In this non-isothermal temperature scanning, although the samples started from the homogeneous miscible state, liquid-liquid phase
separation could occur during the cooling of both thermal treatments A and B, thus we lost control in determining whether crystallization took place in the miscible phase or immiscible phases.

In order to compare the non-isothermal $T_c$ from Thermal treatments A and B. Figure 6.1.2 shows the crystallization temperatures ($T_c$) versus volume fractions of HDPE. Black dots are the $T_c$ from Treatment A, and the red ones are from Treatment B. Combined with the phase diagram, as shown in Figure 6.1.3, it is found out that $T_c$ between two thermal treatments only can be distinguished within the spinodal curve. Crossing the tie line at $150^\circ$C, the range of HDPE volume fraction from 25% to 75% is within the spinodal curve, $T_c$’s from Treatment B measured in the immiscible late stage are $\sim2^\circ$C higher than the $T_c$’s form Treatment A.

Figure 6.1.2 plotted the crystallization temperatures ($T_c$) verses volume fractions of HDPE. Black dots are the $T_c$ from the treatment A, and red from the treatment B.
Figure 6.1.3 Combination of the phase diagram approached by two-step annealing process and $T_c$ curves verses HDPE volume fraction through non-isothermal analysis. Black solid squares in the bottom of the figure are $T_c$ from the treatment A and red solid squares from the treatment B.

Although Treatment A and B both involving the competition between liquid-liquid phase separation and crystallization, a 2 °C shifting of $T_c$ in Treatment B still indicates that at the late stage of phase separation crystallization can still be accelerated in the crystallizable HDPE-rich phase. However, when volume fractions are out of the range of 25% to 75% of HDPE, the non-isothermal method of thermal
analysis is not able to detect the crystallization rate alteration between treatments A and B. This may be either because of the fierce competition of the two mechanisms in Treatment A or the uncontrollable rough crystallization conditions during the non-isothermal process.

In Figure 6.1.2, the $T_c$ values within the spinodal curve, regardless of treatment A or B, are all relatively invariant and independent of volume fractions. This is further evidence of that liquid-liquid phase separation occurred during the cooling process at the cooling rate of $10^\circ C/min$, thus affecting the results of the $T_c$ by altering the initial concentration of HDPE. Therefore, the determination of $T_c$ depression in blends by non-isothermal methods is not a valid characteristic of the influence of phase separation on crystallization rate.

Above all, our specially designed two-step isothermal experiment is more accurate than the non-isothermal DSC scanning method to approach the liquid-liquid phase separation. It is more sensitive to the crystallization rate changes caused by the consequence of phase separation behaviors, even phase separation in the metastable region of the phase diagram. The two-step isothermal process truly suppresses the competition between liquid-liquid phase separation and crystallization during cooling, which successfully monitors the liquid-liquid phase separation and the thermal behaviors of the blend.
CHAPTER VII

SUMMARY

Our interest is in monitoring the liquid-liquid phase separation in a crystalline-amorphous blend via crystallization kinetics and phase morphology. An experimental procedure was specifically designed such that liquid-liquid phase separation occurs before crystallization. This experimental procedure is a two-step isothermal process. The first step is to isothermally anneal the blend to reach concentration equilibrium at temperatures below the binodal curve boundary yet above the melting temperature of the crystalline phase to prevent crystallization. This leaves the phase morphology in a metastable state. In the second step, the sample is isothermally crystallized by quenching it to a lower temperature where crystallization occurs rapidly. Further concentration changes in the phase domains in the polymer are minimal because of the fast rate of crystallization. Additionally, the phase morphology of the domains is also preserved by crystal decoration.

In order to test this experimental approach, a series of PE blends were made to study. This binary blend consisted of a crystallizable component HDPE and an amorphous component LLDPE that possessed randomly distributed octane branches at a concentration of 120 branches per 1000 carbon atoms, both of which are with isorefractive indices. Therefore, conventional techniques lying on the refractive index difference have difficulty in measurement of their miscibility. Our experimental
procedure was designed exactly for the blends with isorefractive indices. Though this experimental approach, it proves that the designed two-step isothermal experiment provides an effective way to experimentally monitor liquid-liquid phase separation of PE blends. Based on the selection process of crystallization, crystallization occurring from HDPE-rich phase in the immiscible state is less “poisoned” than it doing from the single phase in the miscible state. Therefore, the binodal curve was estimated from the enhancement of crystallization rates in the HDPE-rich phase. This estimation is close to the thermodynamic binodal curve, because liquid-liquid phase separation has been into the late stage at the first-step isothermal process, thus the concentration of HDPE in the HDPE-rich phase has already reached the equilibrium. In addition, fast crystallization preserved the morphology developing from the late stage of liquid-liquid phase separation. Therefore, according to the self-similarity of phase structure at the late stage, the spinodal curve was determined from the crystal-decorated phase morphology. The theoretical calculations support the spinodal curve deduced from the morphological changes.

This two-step isothermal experimental approach overcomes the difficulty in determining the miscibility of isorefractive index crystalline-amorphous blends, and also provides a way to experimentally determine the spinodal curve for liquid-liquid phase separation in those polymer blends. It demonstrates the possibility to monitor the liquid-liquid phase separation in a crystalline-amorphous blend via crystallization kinetics and phase morphology.
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