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**A COMPUTATIONAL STUDY OF PHASE SEPARATION IN
POLYMER SOLUTIONS UNDER A CONCENTRATION GRADIENT**

by

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B.Eng., South China University of Technology, Guangzhou, P.R. China, June 1996

A Thesis

presented to Ryerson University

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Abstract

A Computational Study of Phase Separation in Polymer Solutions under a Concentration Gradient, Baitao Jiang, MASc., Chemical Engineering, Ryerson University 2007

Anisotropic porous polymeric materials fabricated from the phase separation method via spinodal decomposition are used in various practical engineering applications. Examples include anisotropic porous polymeric membranes for separation processes and holographic polymer dispersed liquid crystal films for electro-optical devices. We have studied numerically the formation of anisotropic porous polymeric materials by imposing an initial linear concentration gradient across a model polymer solution. The mathematical model is composed of the non-linear Cahn-Hilliard theory to describe spinodal decomposition dynamics, the Flory-Huggins theory for polymer solution thermodynamics, and the slow mode theory combined with the Rouse law for polymer diffusion. The computer simulations include uniform (no gradient) and non-uniform (with an initial concentration gradient) cases. For the non-uniform cases, the initial concentration gradient is placed at three different regions of polymer sample for the purpose of comparison. All the simulation results are in good agreement with published experimental observations which are reported from the applications of porous polymeric membranes. The structure development shows that an anisotropic porous morphology forms when an initial linear concentration gradient is applied to the model polymer solution.

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Nomenclature

Symbols	Description	Units
A	pre-exponential factor or collision frequency factor	
A_d^*	dimensionless area of a droplet	
c	solvent volume fraction	
c_c^*	dimensionless critical solvent concentration	
c_{eq}^*	upper equilibrium value at the binodal line	
c_o^*	dimensionless initial average solvent concentration	
c_H	high equilibrium value	
c_L	low equilibrium value	
d^*	dimensionless diameter of droplet	
$\langle d_{eq}^* \rangle$	dimensionless average equivalent diameter	
D	mutual diffusion coefficient	
D_R	self-diffusion coefficient (Rouse law)	
D_T	thermodynamic factor	
D_1	self-diffusion coefficient of solvent	
D_2	self-diffusion coefficient of solute	
E_a (J)	activation energy	
E	extent of phase separation	
f	monomer functionality	

$f(c)$	local free energy of mixing	(J)
$\mathbf{J}$	interdiffusional flux	
k_B	Boltzmann's constant	(J/K)
k_1	polymerization rate constant	(s ⁻¹)
M	polymer diffusion mobility	(m ⁵ J ⁻¹ s ⁻¹ × 10 ⁻²³)
n	order of reaction	
$\mathbf{n}$	the outward unit normal to a bounding surface	
N	number of nodes in the spatial discretization	
N_{seg}	number of polymer segments	
N_1	degree of polymerization of solvent	
N_2	degree of polarization of solute	
p	extent of reaction	
P^*	perimeter of a droplet	
R	gas constant	(JK ⁻¹ mol ⁻¹)
Q	thermodynamic factor	
$\langle S_f \rangle$	average shape factor	
t	time	(s × 10 ³)
T	temperature	(K)
T_c	critical temperature	(K)
T_f	final temperature	(K)
T_i	initial temperature	(K)

x^*, y^*	dimensionless distance of rectangular coordinates	
$\overline{X}_w$	weight average degree of polymerization	
$\overline{X}_n$	number average of degree of polymerization	
ΔG_M	change in Gibbs free energy of mixing	(J)
ΔH_M	change in enthalpy of mixing	(J)
ΔS_M	change in entropy of mixing	(J/K)

Greek Letters

α	branching coefficient	
χ	Flory's interaction parameter	
χ_c	critical value of Flory's interaction parameter	
ϕ_1	volume fractions of component 1	
ϕ_2	volume fractions of component 2	
κ	gradient energy coefficient	(Jm ⁻¹ × 10 ⁻⁷)
Λ	kinetic factor	
μ_1^{0*}	dimensionless standard chemical potential of pure solvent	
μ_1	chemical potential of solvent	(J)
μ_2	chemical potential of solute	(J)
θ	theta temperature	(K)
τ	total induction time	(s × 10 ³)
τ_{poly}	polymerization induction time	(s × 10 ³)

τ_{ps}	phase separation induction time	(s $\times 10^3$)
ν	volume of a cell or segment	(m ³ segment ⁻¹ $\times 10^{-27}$)
Ω	number of possible arrangement in the lattice space	
ξ_{seg}	frictional coefficient of a polymer segment	
ψ	dimensionless entropy of dilution parameter	
$\Delta\mu_1^*$	dimensionless change of the solvent chemical potential	

Superscripts

*	dimensionless variables
β, γ	phases of polymer solution

Chapter 1 General Introduction

1.1 Phase Separation in Polymer Solutions

Phase separation is a technique that is widely used to fabricate functional polymeric materials, such as microporous membranes and polymer dispersed liquid crystal (PDLC) films [1-44]. In recent years, substantial effort has been put into the research of improvement of anisotropic polymer materials.

When a binary polymer solution system is thrust into the spinodal region of its phase diagram, it tends to be unstable and initiates phase separation. During phase separation the original homogeneous one phase polymer solution will eventually separate into two phases, which includes a solvent-rich phase and a solute-rich phase. This phenomenon is called spinodal decomposition (SD). Figure 1.1 shows a schematic phase diagram of a binary polymer solution. Outside the solid curve (binodal line) a homogeneous single phase region exists. The dotted area which is isolated by the solid curve (binodal line) and the dashed curve (spinodal line) is the metastable region. The shaded area under the dashed curve (spinodal line) is the spinodal region. The intersection point of the binodal line and spinodal line is the critical point at which the corresponding temperature and concentration are the critical temperature T_c and critical concentration c_c , respectively. There are two main mechanisms to describe the phase separation process regarding the two regions. In the metastable, region phase separation is caused by the droplet nucleation and growth (NG) mechanism while within the spinodal region phase separation is caused by the spinodal decomposition (SD) mechanism. Two types of

methods are commonly applied to induce phase separation in the spinodal region. One is the thermally-induced phase separation (TIPS) method which rapidly changes the temperature of the polymer solution; the other is the polymerization-induced phase separation (PIPS) method which requires polymerization to induce phase separation.

Figure 1.1: Schematic of a binary phase diagram for a polymer solution.

1.2 Methods of Phase Separation

The two processes which initiate the phase separation within unstable region are called the thermal-induced phase separation (TIPS) and the polymerization-induced phase separation (PIPS) methods.

1.2.1 Thermal-Induced Phase Separation Method

The TIPS method requires quickly changing the temperature of a polymer solution system by cooling a polymer solution with an upper critical solution temperature (UCST) or heating a polymer solution with a lower critical solution temperature (LCST). In this thesis, only the first is studied. Figure 1.2 shows schematically the phase diagram of the TIPS process. The TIPS process is to quench a homogeneous binary mixture with an average concentration c_0 from an initial temperature T_i to a final temperature T_f into the spinodal decomposition region, which is the shaded area inside the long-dashed line in Figure 1.2. Two types of morphologies will form after phase separation; among them are the droplet-type and interconnected-type morphologies which are sketched in Figure 1.2. The black regions represent solvent-rich regions while the white regions represent the solute-rich regions. For an off-critical quench (routes A and C), when the average initial concentration is not at the critical concentration of the phase diagram will result in the droplet-type morphology. For a critical quench (route B), when the average initial concentration is at the critical concentration of the phase diagram will result in the interconnected-type morphology. The sketched phase separated structures are shown in three squares in line with three different routes. The density and size of the droplets can be controlled by the quench temperature and the initial average concentration. In this research all three routes will be investigated to study the separating mechanism and its resulting morphologies.

Figure 1.2: Schematic of the TIPS process showing cooling a binary mixture. The unfilled circles denote initial average concentration c_0 , and T_i and T_f are the initial and final temperature for quenching, respectively. A and C represent the off-critical quenches and result in a droplet-type structure; whereas B represents the critical quench and results in an interconnected structure. T_c and c_c are the critical temperature and concentration, respectively, at the critical point.

1.2.2 Polymerization-Induced Phase Separation Method

The PIPS process involves both polymer diffusion and polymerization occurring spontaneously [6]; therefore, it is more complex than the TIPS process. Figure 1.3 [8] shows a sketch of how a phase diagram shifts to the right side due to the increase of solute degree of polymerization during the phase separation. The morphology of the

PIPS process will result in a droplet-type since the phase diagram will continuously shift; therefore, the quench becomes an off-critical quench type.

Figure 1.3: Schematic of phase diagram of PIPS method. Note that as the number of polymerization of solute increases, the phase diagram shifts right side from symmetric to very asymmetric as described in reference [8].

1.3 Formation of Anisotropic Structure Materials from Phase Separation

Many studies have been conducted on the isotropic structure development from the phase separation process to fabricate polymeric materials with uniform distribution [10-16]. Recent years, researchers have become more interested in forming the materials with anisotropic structures which significantly improve the physical properties and functionalities of permeability, throughput, and cleanability [17-20]. The structural morphology can be induced by imposing to the system an external fluctuation, such as an

electric field [21,22], a concentration gradient [22], a shear flow [24], a temperature gradient [7-9,25-26] or a chemical reaction [27-30]. The external fluctuation of this study is to impose a linear initial concentration gradient to a polymer solution system prior to the phase separation by both the TIPS and PIPS methods.

1.4 Thesis Objectives

The overall goal of this thesis is to study the phase separation via a spinodal decomposition phenomenon in a polymer solution under an externally imposed spatial concentration gradient through computer simulations. Figure 1.4 shows the flowchart for this thesis study. The mechanisms of phase separation via spinodal decomposition and the effect of a the spatial concentration gradient are discussed, investigated and compared with similar classical experimental work. The objectives of this thesis are as follows:

1. To develop a mathematical model that describes the phase separation process via a spinodal decomposition phenomenon and its structural morphology development under a concentration gradient in a binary polymer solution system.
2. To implement, solve, and validate a one-dimensional model obtained in objective 1 for the TIPS method. The model will incorporate the Cahn-Hilliard theory [31] and Flory-Huggins theory [32] and show the understanding of the effect of the spatial concentration gradient on the conventional TIPS method.
3. To implement, solve, and validate a two-dimensional model obtained in objective 1 for the TIPS method. Four simulation cases are conducted to investigate and verify the effect of the spatial concentration gradient on the morphology development.

4. To implement, solve, and validate a one-dimensional model obtained in objective 1 for the PIPS method. The model will show an understanding of the effect of spatial concentration gradient on the classic PIPS method.

Figure 1.4: Computational modeling flowchart for the objectives in this thesis.

1.5 Methodology and Approach

This thesis utilizes mathematical modeling and computer simulation techniques to study the effect of a spatial concentration gradient on the phase separation phenomenon via

spinodal decomposition in a binary polymer solution system. The mathematical model is developed and implemented as part of the thesis objectives using two classical theories (Flory-Huggins and Cahn-Hilliard theory). The mathematical model is solved using a computerized program in a workstation system. The numerical data obtained from the simulations are finally analyzed and presented for comparison with existing published experimental results found in the literature.

In this thesis, the following steps are followed in the mathematical modeling and computer simulations of the formation of the structural anisotropic morphology:

1. Specify the independent and dependent variables of the model. The independent variables are time and spatial dimensions of polymer sample. The dependent variables include: (a) the solvent concentration in the TIPS method, and (b) the solvent concentration and the degree of polymerization in the PIPS method.
2. Derive the governing time-dependent partial differential equations to describe the phase separation process in a binary polymer solution under a spatial concentration gradient for both TIPS and PIPS methods.
3. Determine the initial and boundary conditions to solve the governing equations developed in step 2. The infinitesimal concentration fluctuation is initially presented across the polymer solution sample. The zero flux and natural boundary conditions are applied.
4. Nondimensionalize the governing equations, and the initial and boundary conditions obtained in steps 2 and 3.
5. Develop the Galerkin finite element formulations of the dimensionless governing equations and auxiliary equations obtained in step 4.

-
6. Implement and solve the Galerkin finite element formulations obtained in step 5 by writing a computational source program (FORTRAN 77).
 7. Analyze the computational outputs obtained in step 6 and present the outputs using scientific visualization method. The computational outputs contain the primary and the secondary outputs, where the secondary outputs are derived from the primary ones. The primary outputs include: (a) solvent concentration for the TIPS method, and (b) solvent concentration and the degree of polymerization of the solute for the PIPS method. The secondary outputs are the results of the morphologies analyses.
 8. Validate the simulation results obtained in step 7 using published experimental and computational results found in the literature.

1.6 Thesis Organization

This thesis contains eight chapters. Chapters 1 – 3 provide the fundamental background knowledge. Chapter 4 presents the mathematical model development and numerical method techniques. Chapters 5 – 7 present the computer simulation results. Chapter 8 gives the conclusions and recommends for the future work in this field of research. The content of each chapter is given below.

Chapter 1 presents an overview and gives a general introduction to this thesis. This chapter covers the motivation, objectives, method of study and the organization of this thesis.

Chapter 2 gives a literature review of published work related to this thesis. The introduction and historical review of the formation of anisotropic morphology via the phase separation in polymer solutions are presented.

Chapter 3 presents necessary theoretical background to develop the mathematical model in this thesis. The theorems cover Flory-Huggins theory, Cahn-Hilliard theory, spinodal decomposition theory, and polymerization kinetics.

Chapter 4 presents the mathematical model development and lists all the governing and auxiliary equations. The numerical method and its solution techniques for solving the above equations are also presented.

Chapter 5 presents the numerical results and the analysis for a one-dimensional mathematical model for phase separation in polymer solutions using the TIPS method. The spatial concentration profiles are given in a one-dimension to reflect the influence of the spatial concentration gradient, compared with the case with no gradient.

Chapter 6 presents the numerical results and the analysis for a two-dimensional mathematical model for phase separation in polymer solutions using the TIPS method. The spatial concentration profiles are given in both three-dimensional plots and two-dimensional contour plots to characterize the formation of the structural anisotropy of the polymeric materials. Three quench cases, including two off-critical region quenches and one critical region quench, are simulated.

Chapter 7 presents the numerical data and the analysis for a one-dimensional mathematical model for phase separation in polymer solutions using the PIPS method. The spatial concentration profiles are given in a one-dimension to reflect the influence of the spatial concentration gradient on the conventional phase separation using the PIPS method.

Chapter 8 presents the conclusions and the recommendations for future work.

Chapter 2 Literature Review

This chapter provides a review of scientific and engineering applications of phase separation in binary polymer solutions. The methods discussed include both thermal-induced phase separation (TIPS) and polymerization-induced phase separation (PIPS) to make porous polymeric materials, and polymer dispersed liquid crystal (PDLC) films are introduced. Techniques used to obtain structural materials with anisotropic morphology by imposing an initial linear concentration gradient are reviewed.

2.1 Formation of Polymeric Membranes in Polymer Solutions

Porous polymeric membrane materials are conventionally produced by a phase separation process. Castro [33] reported in a *United States Patent* the methods for making microporous products. This study attracted many researchers to put efforts into the field of phase separation using the TIPS. Hiatt *et al.* [34] reported in their paper a range of membrane manufacturing processes, membrane structural characteristics and some typical engineering applications. As for the mechanism of phase separation they compared two different types of processes, nucleation and growth (NG) and spinodal decomposition (SD), which are determined by the composition change of components in the system and the cooling rate of the system. The dynamics indicated that the phase separation is induced by a thermal process if under SD and is much faster than NG since the one-phase-state is indeed stable in the metastable region. The cooling rate will also

affect the membrane structure development. Lloyd *et al.* [35] conducted a series of experiments to prepare microporous membranes via a TIPS method in polymer-diluent mixtures. The systems included two different phases: solid-liquid phase and liquid-liquid phase. The phase separation mechanism in terms of temperature and cooling rate was discussed. They found the relationship between phase separation mechanism and cooling rate where a faster cooling rate resulted in a spinodal decomposition mechanism while a slower cooling rate resulted in a nucleation and growth mechanism. The phase separation mechanism depended on the duration period of the phase-separated system passing through a metastable region. The droplet development was also discussed, in which a critical quench will result in a cross-linked structure while an off-critical quench will result in a droplet type structure. Lloyd *et al.* [17] investigated the effect of phase separation cooling rate and quench temperature on the formation of anisotropic and asymmetric membranes. A polymer-diluent solutions system was studied which included isotactic polypropylene and diphenyl ether. A concentration gradient, created by evaporating solution from one side, was imposed on the experimental sample before the cooling and quenching. The cooling and quenching were conducted in water and air separately to compare the effect of different cooling rates. They observed that the faster the cooling rate, the smaller the size of the droplets, which indicates the mechanism of phase separation via the TIPS method.

Graham *et al.* [36] studied the morphology development of a microporous poly(methyl methacrylate) membrane obtained by a TIPS method with small-angle light scattering and scanning electron microscopy (SEM). In this simulating work, the early phase separation process, the kinetics of domain growth and the cessation of domain growth by

solidification were investigated. Analysis according to the light scattering patterns and corresponding samples obtained during different periods indicated that mechanism of phase separation in both the initial phase separation and late-stage coarsening is SD, which was consistent with the prediction of Cahn-Hilliard theory. Barton *et al.* [37] simulated structure formation in polymer solutions under phase separation via spinodal decomposition by thermally quenching the system. As compared with their experimental work, the simulation results showed good qualitative and quantitative agreement. It was noted that a second spinodal decomposition process was occurred in a polymer-rich matrix. Matsuyama [38] investigated both the early stage and late stage of the TIPS process of polypropylene/methyl salicylate system by light scattering measurements. The data obtained in the early stage were consistent with the linear Cahn-Hilliard theory, and indicated that the phase separation mechanism in the early stage was SD. Understanding the kinetics throughout the whole phase separation process is essential to control and design the porosity.

2.2 Polymer Dispersed Liquid Crystal (PDLC) Films

West [39] described the formation and the morphology development of PDLC films obtained by the TIPS and PIPS methods. To investigate the mechanism of the PIPS method, West used a thermoset of epoxy by mixing Epon 828 with hexylamine. West also used thermoplastic epoxy formed by mixing one equivalent of Epon 828 with one equivalent of t-butylamine to study the TIPS process. The three phase-separated phases led to formation of droplets of liquid crystals dispersed in the polymer binder forming a scattering film. The droplet size and density for materials formed by the PIPS process are

largely dependent on the cure temperature, as the temperature increases, the size of the droplets decreases. In the TIPS method, the rate of cooling of the polymer melt affected the resulting droplet morphology. A faster cooling rate will result in smaller droplets and more remaining of the liquid crystals in the binder; while a slower cooling rate will result in larger droplets and less remaining of the liquid crystals in the binder. The conclusion West obtained was that the rate of cooling provided a good means of controlling device performance. Kim and Palffy-Muhoray [40] observed a droplet-type morphology formed via polymerization-induced phase separation of the liquid crystal and the polymer. Simulation results from the phase separation using both TIPS and PIPS methods were reported by Chan [6] when he performed computational simulation work on the formation of PDLC films. The simulation was conducted by applying the Galerkin finite element method to solve the fourth order Cahn-Hilliard partial differential equation. The analysis of data successfully showed that the diffusion coefficient and the temperature of the phase separation system have an effect on the droplet size and density of PDLC films. For a TIPS process, increasing the diffusion coefficient or a shallow quench will result in a decrease of droplet size and a denser droplet composition, while decreasing the diffusion coefficient or a deep quench will cause the opposite. For a PIPS method, the diffusion coefficient and the rate of polymerization will affect the droplet development. Increasing the diffusion coefficient or rate of polymerization will cause a smaller droplet size and higher droplet density.

2.3 Formation of Anisotropic Materials via Phase Separation

The formation of isotropic materials, such as polymeric membranes and PDLC films, has been extensively studied in recent decades. However, anisotropic materials with pore size variation are more desirable for some scientific and engineering applications or modifications. The phase separation in a binary mixture under a concentration gradient has been an interesting research field for decades. Jayalakshmi *et al.* [41] used a Helma quartz cell as a density-matched liquid mixture system to study the phase separation mechanism and morphology development under a weak concentration gradient. They were trying to find out the concentration dependence of the phase separation structures and the growth law. The concentration gradient was posed over the height of the sample and was symmetrical according to the critical point; therefore, the phase separation structures in the stable and unstable regions could be observed simultaneously. The two main phases under observation were the central zone and the off-critical zone. In the central zone, since it lies in the critical region, an interconnected structure was found, while in the off-critical zone the droplet morphology was found. Meanwhile, the rates of phase separation in the two different zones were compared, and it was found that the central zone had a faster rate of phase separation than that of the off-critical zone. This was due to the two different types of phase separation mechanism in two zones since the concentration gradient covered both stable and unstable regions. It confirmed that the SD was at the center and the NG was at other two sides. Lacasta *et al.* [42] also numerically simulated the phase separation dynamics with an initial concentration gradient in a binary

mixture. The model was developed from the Cahn-Hilliard equation and integrated using Euler discretization. At the critical region the convoluted structures were obtained while at the off-critical regions more droplet type structures were obtained. Different initial concentration values were compared and similar dynamics were observed in both the critical and the off-critical regions. A slight change of structure occurred when they decreased the initial concentration that droplet size formed at off-critical region also decreased; however, no specific reason was mentioned in the article. Lee *et al.* [7-9] simulated a phase separation phenomenon via spinodal decomposition under a linear spatial temperature gradient applied to the polymer solution system (off-critical quench) for both TIPS and PIPS processes. The computational results showed droplet-type morphology and successfully displayed an anisotropic structure for phase separated polymer solutions. It was observed that larger and denser droplets were found at the lower temperature side. This was due to the fact that the system at the lower temperature side will endure longer phase separating time comparing with that of the higher temperature side. Chan [5] investigated the effect of concentration gradient on the TIPS using computational simulation. The morphology showed that a graded droplet size was generally distributed along the length of polymer solution sample because the initial concentration gradient resulted in a difference of rate of phase separation.

Matsuyama *et al.* [17-18,23] conducted a series of experiments to investigate the formation and the structure control of anisotropic membranes via TIPS. To create an initial concentration gradient prior to the phase separation, they evaporated diluent from the top surface of an isotactic polypropylene-diphenyl ether melt-blend. After phase separation, pore size varied along the surface of the sample and resulted in the

asymmetrical and anisotropic microporous membrane materials. Mauri [35] simulated the phase segregation of a deeply quenched low-viscosity liquid binary mixture with an initial concentration gradient. The Peclet number, a ratio of the mass flux between the diffusion and the convection, was changed with different simulation cases. Among the simulation results, the critical region or the transition showed a change at different Peclet numbers. The reason for this was that the competition of diffusion and convection had an impact on the mass transfer between two phases and affected the formation of the phase transition. Chakrabarti [43] investigated asymmetric morphology development during spinodal decomposition in off-critical region of polymer mixtures. It was noted that the simulation results were in agreement with the experimental results. For off-critical quench, the rate of growth is strongly dependent on the bulk composition of the mixtures.

Chapter 3 Theoretical Background

This chapter presents the theoretical background on the phase separation, its model development, as well as the definitions of all the technical terms and scientific parameters. Phase separation is technically described as a de-mixing process of a homogeneous polymer-solvent mixture into an inhomogeneous phase separated system. The system involved in this study is restricted to a binary polymer solution. Polymer solution thermodynamics will be used in the model development in this research. The Flory-Huggins theory, to characterize the thermodynamics of a binary polymer solution, will be discussed. The spinodal decomposition (SD) is primarily considered as the mechanism for fabricating polymeric materials like membranes and PDLC films. The SD phenomenon, which can be described by the well-known Cahn-Hilliard (C-H) theory, is also discussed in this chapter to define the diffusion dynamic behaviour. For the PIPS part, the theory related to polymerization, including polymerization kinetics, will be presented as an important part of the theoretical background.

3.1 Thermodynamics of Polymer Solutions

Thermodynamics of mixtures plays a vital role in the phase separation process of polymer solutions. The Flory-Huggins (F-H) theory is capable to describe the phase equilibrium and phase stability of polymer solutions [32,44-45]. The phase diagram of a binary polymer solution system can be determined using the F-H theory.

3.1.1 The Flory-Huggins Theory and Phase Diagram

The fundamental thermodynamics function to describe the phase equilibrium and phase stability of a binary system is the Gibbs free energy equation:

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (3.1)$$

where ΔG_M is the change in the Gibbs free energy of mixing, ΔH_M is the enthalpy change of mixing, T is the absolute temperature and ΔS_M is the entropy change of mixing.

A homogenous solution can be obtained when the Gibbs free energy of mixing is negative, $\Delta G_M < 0$, which implies that the Gibbs free energy of the mixture, G_{12} , is lower than the Gibbs free energy of the individual components, the solvent G_1 and the polymer G_2 [45]:

$$\Delta G_M = G_{12} - (G_1 + G_2) \quad (3.2)$$

A homogeneous one-phase mixture is more stable than its two pure components alone. However, phase separation can still occur when $\Delta G_M < 0$ since a system with two phases may be more stable than a homogeneous system. An additional condition is required to determine if the system is thermodynamically stable. It is found that the sign of the second derivative of ΔG_M with respect to the composition, $\partial^2(\Delta G_M)/\partial c_i^2$, determines this stability. For a polymer-solvent system to be thermodynamically stable, a positive sign is required for this second derivative [46].

One of the most common expressions for describing the free-energy of a polymer-solvent system is the F-H theory [32,44-45], which is based on a statistical lattice model. This classical theory starts with the Gibbs free energy expression as shown in equation (3.1)

and assumes the existence of a two-dimensional lattice. Each of these lattice sites can accommodate a single solvent molecule or a polymer segment having the same volume as a solvent molecule. The solvent molecule and polymer segments can be assigned to any free lattice site. The only restriction, however, is the connectivity of polymer chain segments. It must be ensured that two segments connected to each other lie on the nearest neighbouring lattice sites.

The method for calculating the contribution of the entropy change of mixing of the polymer solution system is similar to the method for small molecules and assuming the polymer solution has no temperature change; i.e., $\Delta H_M = 0$. In this method, it is assumed that there is neither a change in volume nor a change in enthalpy on mixing of the polymer chains with the low-molecular weight solvent. The calculations of the free energy change of mixing simplifies to the change in the entropy on mixing at a constant temperature and pressure. The entropy of the mixing is expressed below:

$$\Delta S_M = k_B \ln \Omega \quad (3.3)$$

where k_B is the Boltzmann's constant, and Ω is the number of possible molecule arrangements in the lattice space.

The entropy change of mixing for a polymer solution can be written as follows [45]:

$$\Delta S_M = -k_B [N_1 \ln c + N_2 \ln(1 - c)] \quad (3.4)$$

where c is the volume fraction of the solvent in the polymer solution, N_1 and N_2 are the degree of polymerization of the solvent and polymer, respectively. For a low molecular weight solvent, $N_1 = 1$.

It is an uncommon situation that a polymer solution system exhibits no change of heat or energy on mixing. To account for the non-ideality of a polymer solution system, the

enthalpy change of mixing ΔH_M can be obtained through the Flory's interaction parameter χ [45]:

$$\Delta H_M = k_B T \chi (1 - c) \quad (3.5)$$

After the derivation of the entropy and enthalpy contributions to the mixing of a polymer solution, equation (3.4) and (3.5) are substituted into equation (3.1) to obtain the free energy expression of the mixing of the polymer solution. Consequently, the F-H free energy can be expressed as below [45]:

$$f(c) = \frac{k_B T}{\nu} \left[\frac{c}{N_1} \ln c + \frac{(1-c)}{N_2} \ln(1-c) + \chi c(1-c) \right] \quad (3.6)$$

where ν is the volume of a cell or segment of polymer solution system. The first two terms on the right-hand side of equation (3.6) represent the contribution of the entropy changes, and the last term denotes the contribution of the enthalpy changes.

The χ in equation (3.6), Flory's interaction parameter, is the measurement of solvent power. The expression in terms of temperature is:

$$\chi = \frac{1}{2} - \psi \left(1 - \frac{\theta}{T} \right) \quad (3.7)$$

where ψ is the dimensionless entropy of dilution and θ is the theta temperature at which the polymer solution is at ideal state. The value of ψ used in this study is 1 while most common values measured are from 0.5 – 1.0 [45].

For illustrative purposes, Figure 3.1 shows a schematic of a binary polymer solution phase diagram. Figure 3.1 shows a plot of the Gibbs free energy of mixing, ΔG_M , versus solvent concentration at different temperatures, $T_4 > T_3 > T_2 > T_1$, in the top portion, and temperature vs. concentration in bottom portion. In the bottom portion of Figure 3.1, the

solid line and dashed line present the binodal line and spinodal line, respectively. The binodal line (spinodal line) is obtained from the first derivative (second derivative) of the F-H free energy expression for loci at all the temperatures [44]. The shaded area represents the spinodal decomposition region, and the region isolated by both binodal and spinodal lines represents the metastable region. The intersection of binodal and spinodal lines is the critical point, which is obtained by setting the second derivative of the F-H free energy equation equal to the third derivative. At the critical point, the relevant values are defined as follows:

$$c_c = 1 - \frac{1}{1 + N_2^{0.5}} \quad (3.8)$$

$$\chi_c = \frac{1}{2} \left(1 + \frac{1}{N_2^{0.5}} \right)^2 \quad (3.9)$$

$$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\theta\psi} \left(\frac{1}{N_2^{0.5}} + \frac{1}{2N_2} \right) \quad (3.10)$$

Where T_c and c_c are the critical temperature and concentration, respectively.

Figure 3.1: Schematic diagram of free energy of a polymer solution versus dimensionless solvent concentration at a series of temperatures ($T_4 > T_3 > T_2 > T_1$) in the top portion, and the corresponding binary phase diagram in the bottom portion [44].

3.2 Spinodal Decomposition Theory

3.2.1 Introduction to Spinodal Decomposition Phenomenon

Spinodal decomposition (SD) is often described by a sinusoidal wave, which describes the one-dimensional spatial solvent concentration fluctuation in polymer solutions. The SD phenomenon consists of three main stages [32,47,48] according to the time evolution of this sinusoidal wave as shown in Figure 3.2:

- (a) Early stage
- (b) Intermediate stage
- (c) Late stage

In the early stage of SD, the wavelength of the one-dimensional spatial concentration fluctuations remains constant; however, the wave amplitude increases with time. During the intermediate stage, both the wavelength and amplitude of the one-dimensional spatial concentration fluctuations increase with time. Finally, in the late stage, the wave amplitude is at its equilibrium composition values and remains constant, whereas the wavelength increases with time due to the coarsening effect.

Figure 3.2: Schematic diagram of the spatial composition fluctuations in the (a) early, (b) intermediate, and (c) late stages of spinodal decomposition at different time ($t_2 > t_1$). The solid curve (dashed curve) represents t_2 (t_1). The horizontal lines represent the low (c_L) and high (c_H) equilibrium compositions on the binodal curve. c_0 is the average concentration of the polymer.

3.2.2 Cahn-Hilliard Theory

The Cahn-Hilliard (C-H) theory describes the dynamic behaviour of the phase separation phenomenon via SD phenomenon in binary systems. The C-H equation is derived from the continuity equation of mass. The diffusion equation for SD is:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} \quad (3.11)$$

where c is the solvent concentration, t is the time and $\mathbf{J}$ is the interdiffusional flux.

Cahn [31] indicated that the interdiffusional flux $\mathbf{J}$ can be related to the gradient of chemical potential difference through a proportionality factor, M , the mobility, a function of solvent concentration c . The interdiffusional flux $\mathbf{J}$ can therefore be expressed as:

$$\mathbf{J} = -M(c) \nabla \frac{\delta F}{\delta c} \quad (3.12)$$

The non-linear C-H theory is based on the following expression for the total free energy of an inhomogeneous binary solution:

$$F(c) = \int_V \left[f(c) + \kappa \|\nabla c\|^2 \right] dV \quad (3.13)$$

where $f(c)$ is the local free energy of mixing, and κ , the interfacial energy parameter, is a positive constant. The first term in equation (3.13) represents the homogeneous free energy, while the second term accounts for any increases in free energy caused by concentration gradients. The Flory-Huggins (F-H) free energy density expression can be used to measure the homogeneous free energy term of equation (3.13). The chemical potential difference can be expressed as:

$$\frac{\delta F(c)}{\delta c} = \frac{\partial f(c)}{\partial c} - 2\kappa \nabla^2 c \quad (3.14)$$

Substituting equation (3.14) into (3.12), then substitute it into equation (3.11) yields:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[M(c) \nabla \left(\frac{\partial f(c)}{\partial c} - 2\kappa \nabla^2 c \right) \right] \quad (3.15)$$

In the early phase separation periods, the concentration fluctuations are small and equation (3.15) can be linearized about the average concentration c_0 . The linearized C-H equation can be expressed as follows [31]:

$$\frac{\partial c}{\partial t} = M \left(\frac{\partial^2 f(c)}{\partial c^2} \Big|_{c_0} \nabla^2 c - 2\kappa \nabla^4 c \right) \quad (3.16)$$

where M and κ are considered as constants in numerical studies. For relatively large diffusion distances, equation (3.16) simplifies to the diffusion equation. This means that there is uphill diffusion in the unstable region since $\left(\partial^2 f(c) / \partial c^2 \right)_{c_0} < 0$ in this region.

Equation (3.16) can be solved by the Fourier series with the following general solutions:

$$c(\mathbf{r}, t) - c_0 = \sum_{\mathbf{k}} A(\mathbf{k}, t) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (3.17)$$

$$A(\mathbf{k}, t) = A(\mathbf{k}, 0) e^{R(k)t} \quad (3.18)$$

$$R(k) = -Mk \left(\frac{\partial^2 f(c)}{\partial c^2} \Big|_{c_0} + 2\kappa k^2 \right) \quad (3.19)$$

where the wavenumber $k_i = 2\pi / \lambda_i$ (λ_i is wavelength for concentration fluctuation i) and $R(k)$ is the amplification factor. The linearized C-H equation is appropriate only for the early stage of spinodal decomposition because at intermediate and late stages the various Fourier modes start to interfere with each other [6].

3.2.2.1 Mobility

The mobility M is considered concentration-dependent in general studies of numerical analysis. Literature shows concentration dependence of the mobility term in either the interdiffusion [49-51] or self-diffusion [51-54] coefficient. The general approach to

derive the mobility is to relate it with the mutual diffusion coefficient via the second derivative of the free energy in terms of concentration for polymer solutions. The expression can be derived by comparing equation (3.12) to the classical diffusion equation:

$$\mathbf{J} = -D\nabla c \quad (3.20)$$

Rewriting equation (3.12) as:

$$\mathbf{J} = -M(c) \frac{\partial^2 f(c)}{\partial c^2} \nabla c \quad (3.21)$$

The mobility is related to the mutual diffusion coefficient as:

$$M(c) = \frac{D(c)}{\partial^2 f(c) / \partial c^2} \quad (3.22)$$

3.2.2.2 Diffusion Coefficient

Generally, the free volume theory, the Rouse law or the Reptation model are used to find the self-diffusion coefficient. The mutual diffusion coefficient D can be expressed as the product of a thermodynamic factor and a kinetic factor:

$$D = Q\Lambda \quad (3.23)$$

where Q is the thermodynamic factor related to the static correlation function of composition fluctuations, and Λ is the kinetic factor that can be expressed in terms of the diffusion coefficients of the components in the mixture. The kinetic factor is defined as a nonlocal generalization of an Onsager coefficient [55] and reflects the connectivity of polymer chains. The thermodynamic factor Q is expressed as follows [56]:

$$Q = \frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} \quad (3.24)$$

where ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. Two different types of diffusion process mode theories are mentioned in the literature [56-57].

The slow mode theory was derived from a random-phase approximation under the condition of microscopic incompressibility and its expression is shown below [56-57]:

$$\frac{1}{\Lambda_{slow}} = \frac{1}{N_1 D_1 \phi_1} + \frac{1}{N_2 D_2 \phi_2} \quad (3.25)$$

where D_1 and D_2 are the self-coefficients of polymer segments 1 and 2 in the blend.

The fast mode theory was derived by omitting the dynamic correlations between the velocities of different particles. It is expressed below [56-58]:

$$\Lambda_{fast} = \phi_1 \phi_2 (N_1 D_1 \phi + N_2 D_2 \phi) \quad (3.26)$$

The expressions of interdiffusion coefficient in terms of the self-diffusion coefficient are:

For the slow mode theory:

$$\frac{1}{D_{slow}} = \frac{\frac{1}{N_1 D_1 \phi_1} + \frac{1}{N_2 D_2 \phi_2}}{\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2}} \quad (3.27)$$

For the fast mode theory:

$$D_{fast} = \phi_1 \phi_2 [(N_1 D_1 \phi_2) + (N_2 D_2 \phi_1)] \left[\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} \right] \quad (3.28)$$

It was assumed that the slowly diffusing component controls the mutual diffusion process for the slow mode theory, while the fast diffusing component controls the interdiffusion process for the fast mode theory. By evaluating the theory formulas, e.g., $D_1 \ll D_2$, the slow mode theory predicts $\Lambda_{slow} \rightarrow D_1 N_1 \phi_1$, indicating that the slowly diffusing component will dominate the diffusion process. In contrast, under the same conditions,

the fast mode theory yields $\Lambda_{fast} \rightarrow D_2 N_2 \phi_1$. Thus the quickly diffusing component will control the diffusion process.

In addition to the free-volume theory, there are other models used to derive the coefficient, i.e., the spring-and-bead models, the Rouse law, the Kirkwood-Risemen theory and the Reptation theory [59].

The spring-and-bead model describes the dynamics of polymer chains. It assumes a polymer chain as a dumbbell, and its two beads are connected by elastic spring. The beads contain all the mass while the spring is massless according to this model. The modulus of elasticity is the ratio of tensile stress to the tensile strain described by the Hookean behavior of springs, and the polymeric dynamics is similar to that of the Brownian motion of a system of coupled harmonic oscillators.

The Rouse law is used for this study. It assumes that there is no entanglement effect between polymer segments which allow the solvent to flow through the polymer coil freely [60]. This theory is restricted to systems with short polymer chains and without entanglement effects. Its limitation is the absolute free movement of polymer chains and is affected by friction. The solvent self-diffusion coefficient from the Rouse law is expressed below [59]:

$$D_R = \frac{k_B T}{N_{seg} \zeta_{seg}} \quad (3.29)$$

where D_R is the self-diffusion coefficient derived from the Rouse law, k_B is the Boltzmann's constant, T is the temperature, N_{seg} is the number of polymer segments and ζ_{seg} is the frictional coefficient of a polymer segment. From equation (3.29), it is easy to

find that the diffusion coefficient is inversely proportional to the molar mass of the polymer (i.e, $D_R \propto \frac{1}{M}$).

3.3 Polymerization Kinetics

Polymerization kinetics is required for the PIPS process. There is a great number of studies of the polymerization kinetic rate equation [32,45,61]. The conventional kinetic rate equation for an n -th order reaction of a single reactant is expressed as follows [55]:

$$\frac{dp}{dt} = k_1 (1-p)^n \quad (3.30)$$

where p is the extent of reaction, k_1 is the rate constant, and t is time.

The weight-average $\overline{X_w}$ and number-average $\overline{X_n}$ degree of polymerization are expressed as follows [61]:

$$\overline{X_w} = \frac{1+\alpha}{1-\alpha(f-1)} \quad (3.31)$$

$$\overline{X_n} = \frac{1}{1-(\alpha f/2)} \quad (3.32)$$

where f is the monomer functionality, the number of reactive sites, and α is the branching coefficient. The branching coefficient α is defined as the probability that two branch units of a given functional group are connected together in a random fashion.

The critical branching coefficient is defined as:

$$\alpha_c = \frac{1}{f-1} \quad (3.33)$$

For a single reactant monomer, α_c is 0.5. In addition, when $\overline{X}_n$ is equal to 4 $\overline{X}_w$ is infinite. It is noted that $\overline{X}_w$ reflects the growth of polymer chains leading to an infinite network formation. The weight average degree of polymerization is used in this study to represent the molecular weight growth of the solute, i.e. $N_2 = \overline{X}_w$.

Chapter 4 Governing Equations and Method of Solution

This chapter presents the model development of the phase separation process. The governing equations, which are appropriate for both TIPS and PIPS methods, along with the auxiliary equations are presented. The method of solution is introduced at the end.

4.1 Governing Equations for Spinodal Decomposition

The total free energy of an inhomogeneous binary polymer solution can be expressed as follows [62]:

$$F(c) = \int_V \left[f(c) + \kappa \|\nabla c\|^2 \right] dV \quad (3.13)$$

The Flory-Huggins free energy can be used to describe the homogeneous free energy as in equation (3.13). It is expressed as [45,61]:

$$f(c) = \frac{k_B T}{v} \left[\frac{c}{N_1} \ln c + \frac{(1-c)}{N_2} \ln(1-c) + \chi c(1-c) \right] \quad (3.6)$$

Flory's interaction parameter χ is related to the temperature via the theta temperature θ and dimensionless entropy of the dilution parameter ψ [45,61]:

$$\chi = \frac{1}{2} - \psi \left(1 - \frac{\theta}{T} \right) \quad (3.7)$$

The C-H equation is derived using the continuity equation of mass and the total free energy. It is expressed as:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[M(c) \nabla \left(\frac{\partial f(c)}{\partial c} - 2\kappa \nabla^2 c \right) \right] \quad (3.15)$$

where M is the mobility.

The interfacial energy parameter κ is dependent on molecular weight and is expressed as [15]:

$$\kappa = \kappa_0 N_2 \quad (4.1)$$

where κ_0 is the interfacial energy parameter for a linear polymer. It is noted that the interaction between the polymer and solvent increases with the growth of the polymer chains.

The overall C-H equation governing the TIPS via spinodal decomposition is described as follows:

$$\frac{\partial c}{\partial t} = \nabla M \cdot \nabla \left(\frac{\partial f}{\partial c} \right) + M \nabla^2 \left(\frac{\partial f}{\partial c} \right) - 2\kappa \nabla M \cdot \nabla^3 c - 2\kappa M \nabla^4 c \quad (4.2)$$

4.2 Linear Initial Concentration Gradient

A linear initial concentration gradient is applied to the polymer solution sample prior to the phase separation commencing.

For the one-dimension simulation, the linear initial concentration gradient is applied to the length L before the phase separation. A concentration gradient is applied across the range of $0 \leq x^* \leq 1$ and its expression is as follows:

$$c_o^* = c_{o,l}^* + 0.1x^* \quad (4.3)$$

where c_o^* is the concentration at dimensionless location x^* . For the two-dimension simulation, the linear initial dimensionless concentration gradient applies along the x^* -axis only.

4.3 Mobility

The mobility M is composition dependent in this study, contrary to conventional studies which have assumed it to be constant. Two different theories are used to describe the mobility of polymer under phase separation. Chan [63] presented both slow mode and fast mode theories [58] and indicated that the fast mode theory predicts that the diffusion rate is restricted by the fast-diffusing component, whereas the slow mode theory predicts that the mutual diffusion of the binary polymer solution is restricted by the slow-diffusing component. The slow mode theory is used in this study. It shows the mobility M is related to the self-mobilities of the individual components M_1 for the solvent and M_2 for the polymer [58]:

$$\frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2} \quad (4.4)$$

where M_1 and M_2 are the self-mobility for solvent and polymer, respectively. The self-diffusion coefficient can be expressed via the self-mobility as:

$$D_i = M_i \frac{\partial^2 f(c)}{\partial c_i^2} \quad (4.5)$$

where $i = 1, 2$, c_1 is the solvent concentration and c_2 is the polymer concentration.

The Rouse law [60] is used to determine the self-diffusion coefficient of the degree of polymerization. It assumes there are no entanglement effects between polymer chains

and is appropriate for polymer with short chains. The expression for the self-diffusion coefficient is showed below:

$$D_i = \frac{k_B T}{\xi_i N} \quad (4.6)$$

where $i=1,2$, ξ_1 is the frictional coefficient per segment of solvent, and ξ_2 is the frictional coefficient per segment of polymer molecule.

The final expression of mobility M , which is derived by substituting equation (3.6), (4.5) and (4.6) into equation (4.4), assuming $\xi = \xi_1 = \xi_2$ and there are no entanglement effects between polymer chains, is presented as:

$$M = \frac{\nu c(1-c)}{\xi} \quad (4.7)$$

4.4 Governing Equation for TIPS

The equation governing the TIPS phenomenon via spinodal decomposition (SD) is obtained after substituting equation (4.7) into equation (4.2). For the TIPS process the solute degree of polymerization is kept constant.

4.4.1 One-Dimensional Governing Equation

For the one-dimensional case the governing equation is shown below:

$$\begin{aligned}
\frac{\partial c}{\partial t} = & \left(\frac{k_B T}{\xi} \right) \left[-\frac{1}{N_1} + \frac{1}{N_2} - 2\chi(1-2c) \right] \left(\frac{\partial c}{\partial x} \right) \left(\frac{\partial c}{\partial x} \right) \\
& + \left(\frac{k_B T}{\xi} \right) \left[\frac{1-c}{N_1} + \frac{c}{N_2} - 2\chi c(1-c) \right] \left(\frac{\partial^2 c}{\partial x^2} \right) \\
& - \left(\frac{2\kappa_0 \nu N_2}{\xi} \right) (1-2c) \left(\frac{\partial c}{\partial x} \right) \left(\frac{\partial^3 c}{\partial x^3} \right) \\
& - \left(\frac{2\kappa_0 \nu N_2}{\xi} \right) [c(1-c)] \left(\frac{\partial^4 c}{\partial x^4} \right)
\end{aligned} \tag{4.8}$$

After applying scaling (see Appendix A) to equation (4.8), the governing equation in dimensionless form for the one-dimensional case is:

$$\begin{aligned}
\frac{\partial c^*}{\partial t^*} = & D^* T^* \left[-\frac{1}{N_1} + \frac{1}{N_2} - 2\chi(1-2c^*) \right] \left(\frac{\partial c^*}{\partial x^*} \right) \left(\frac{\partial c^*}{\partial x^*} \right) \\
& + D^* T^* \left[\frac{1-c^*}{N_1} + \frac{c^*}{N_2} - 2\chi c^*(1-c^*) \right] \left(\frac{\partial^2 c^*}{\partial x^{*2}} \right) \\
& - N_2 (1-2c^*) \left(\frac{\partial c^*}{\partial x^*} \right) \left(\frac{\partial^3 c^*}{\partial x^{*3}} \right) \\
& - N_2 [c^*(1-c^*)] \left(\frac{\partial^4 c^*}{\partial x^{*4}} \right)
\end{aligned} \tag{4.9}$$

4.4.2 Two-Dimensional Governing Equation

For the two-dimensional case the governing equation is shown below:

$$\begin{aligned}
\frac{\partial c}{\partial t} = & \left(\frac{k_B T}{\xi} \right) \left[-\frac{1}{N_1} + \frac{1}{N_2} - 2\chi(1-2c) \right] \left[\frac{\partial c}{\partial x} \frac{\partial c}{\partial x} + \frac{\partial c}{\partial y} \frac{\partial c}{\partial y} \right] \\
& + \left(\frac{k_B T}{\xi} \right) \left[\frac{1-c}{N_1} + \frac{c}{N_2} - 2\chi c(1-c) \right] \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right] \\
& - \left(\frac{2\kappa_0 \nu N_2}{\xi} \right) (1-2c) \left[\frac{\partial c}{\partial x} \frac{\partial^3 c}{\partial x^3} + \frac{\partial c}{\partial y} \frac{\partial^3 c}{\partial x \partial y^2} \right] + \left[\frac{\partial c}{\partial y} \frac{\partial^3 c}{\partial x^2 \partial y} + \frac{\partial c}{\partial y} \frac{\partial^3 c}{\partial y^3} \right] \\
& - \left(\frac{2\kappa_0 \nu N_2}{\xi} \right) [c(1-c)] \left[\frac{\partial^4 c}{\partial x^4} + 2 \frac{\partial^4 c}{\partial x^2 \partial y^2} + \frac{\partial^4 c}{\partial y^4} \right]
\end{aligned} \tag{4.10}$$

Applying scaling (see Appendix A) to equation (4.10), the governing equation in dimensionless form for the two-dimensional case is:

$$\begin{aligned}
 \frac{\partial c}{\partial t} = & D^* T^* \left[-\frac{1}{N_1} + \frac{1}{N_2} - 2\chi(1-2c^*) \right] \left[\frac{\partial c^*}{\partial x^*} \frac{\partial c^*}{\partial y^*} + \frac{\partial c^*}{\partial y^*} \frac{\partial c^*}{\partial x^*} \right] \\
 & + D^* T^* \left[\frac{1-c^*}{N_1} + \frac{c^*}{N_2} - 2\chi c(1-c^*) \right] \left[\frac{\partial^2 c^*}{\partial x^{*2}} + \frac{\partial^2 c^*}{\partial y^{*2}} \right] \\
 & - N_2 (1-2c^*) \left(\left[\frac{\partial c^*}{\partial x^*} \frac{\partial^3 c^*}{\partial x^{*3}} + \frac{\partial c^*}{\partial y^*} \frac{\partial^3 c^*}{\partial x^* \partial y^{*2}} \right] + \left[\frac{\partial c^*}{\partial y^*} \frac{\partial^3 c^*}{\partial x^{*2} \partial y^*} + \frac{\partial c^*}{\partial y^*} \frac{\partial^3 c^*}{\partial y^{*3}} \right] \right) \\
 & - N_2 \left[c^* (1-c^*) \right] \left[\frac{\partial^4 c^*}{\partial x^{*4}} + 2 \frac{\partial^4 c^*}{\partial x^{*2} \partial y^{*2}} + \frac{\partial^4 c^*}{\partial y^{*4}} \right]
 \end{aligned} \tag{4.11}$$

where the superscripted asterisks indicate dimensionless variables.

4.5 Governing Equation for PIPS

For the PIPS process, the degree of polymerization of polymer increases continuously with time. The expression for the growth rate of N_2 is obtained from the kinetic rate equation for self-condensation reaction [55]:

$$\frac{dp}{dt} = k_1 (1-p)^n \tag{3.30}$$

where p is the reaction extent, k_1 is the rate constant, t is the time and n is the order of reaction. The polymeric network can be formed as polymerization proceeds; therefore, a tri-functional monomer is considered in this study. The order of reaction $n = 2$ is used in equation (3.30) based on a bimolecular condensation reaction. Consequently, the reaction extent is derived as below:

$$p = \frac{k_1 t}{1 + k_1 t} \tag{4.12}$$

The molecular weight of the polymerization can be obtained from the molecular size distribution functions [61], and the weight average degree of polymerization X_w and the number average weight degree of polymerization X_n can be expressed as follows:

$$\overline{X_w} = \frac{1+\alpha}{1-\alpha(f-1)} \quad (3.31)$$

$$\overline{X_n} = \frac{1}{1-(\alpha f/2)} \quad (3.32)$$

where α is the branching coefficient and f is the monomer functionality. Expressions for obtaining α are normally functions of the proportion of reactants and reaction extent. For a single tri-functional monomer, α is equal to p . The weight average degree of polymerization X_w better reflects the molecular weight growth leading to an infinite network formation. So it is used in this study to represent the solute degree of polymerization ($N_2 = X_w$). N_2 can be obtained as:

$$N_2 = \frac{1+p}{1-p(f-1)} \quad (4.13)$$

Substituting equation (4.12) into equation (4.13) yields:

$$N_2 = \frac{1+2k_1t}{1+2k_1t-fk_1t} \quad (4.14)$$

where k_1 , the rate constant, is temperature-dependent from the Arrhenius equation [59]:

$$k_1 = A \exp\left(-\frac{E_a}{RT}\right) \quad (4.15)$$

where A is the pre-exponential factor or collision frequency factor, E_a is the activation energy, R is the ideal gas constant and T is the absolute temperature of the polymer solution system.

Substituting equation (4.15) into equation (4.14) yields N_2 in terms of time and temperature as:

$$N_2 = \frac{1 + 2At \exp(-E_a / RT)}{1 + 2At \exp(-E_a / RT) - fAt \exp(-E_a / RT)} \quad (4.16)$$

The equation governing the PIPS process via spinodal decomposition (SD) can therefore be derived by substituting equation (4.7) and (4.16) into (4.2) and will be presented in the following sections.

4.5.1 One-Dimensional Governing Equation

The following dimensionless one-dimensional fourth-order partial differential equation governing the PIPS phenomenon via SD is the following:

$$\begin{aligned} \frac{\partial c^*}{\partial t^*} = & D^* T^* \left[-\frac{1}{N_1} + \frac{1}{N_2} - 2\chi(1-2c^*) \right] \left(\frac{\partial c^*}{\partial x^*} \right) \left(\frac{\partial c^*}{\partial x^*} \right) \\ & + D^* T^* \left[\frac{1-c^*}{N_1} + \frac{c^*}{N_2} - 2\chi c^*(1-c^*) \right] \left(\frac{\partial^2 c^*}{\partial x^{*2}} \right) \\ & - N_2(1-2c^*) \left(\frac{\partial c^*}{\partial x^*} \right) \left(\frac{\partial^3 c^*}{\partial x^{*3}} \right) \\ & - N_2 [c^*(1-c^*)] \left(\frac{\partial^4 c^*}{\partial c^{*4}} \right) \end{aligned} \quad (4.17)$$

With

$$N_2 = \frac{1 + 2At \exp(-E_a / RT)}{1 + 2At \exp(-E_a / RT) - fAt \exp(-E_a / RT)} \quad (4.16)$$

4.6 Auxiliary Equations

4.6.1 Initial Condition

Phase separation under SD can be initiated by infinitesimal concentration fluctuations within the system. When the polymer solution system is at its original one phase state, concentration fluctuations could occur. The dimensionless expression for the initial condition is expressed as follows:

$$\begin{cases} c^*(x^*, t^* = 0) = c_0^* + \delta c^*(x^*, t^* = 0) \\ c^*(x^*, y^*, t^* = 0) = c_0^* + \delta c^*(x^*, y^*, t^* = 0) \end{cases} \quad (4.18)$$

where c_0^* is the dimensionless (initial) average concentration, $\delta c^*(x^*, t^* = 0)$ and $\delta c^*(x^*, y^*, t^* = 0)$ represent the initial concentration fluctuations at thermal equilibrium.

4.6.2 Boundary Conditions

Two sets of boundary conditions are considered in this study. One is the zero mass flux boundary conditions and the other is the natural boundary conditions.

The zero mass flux boundary conditions are obtained by setting the mass flux $\mathbf{J}$ to zero, which physically predicts a system with no mass being exchanged within its surroundings [64-65].

The zero mass flux boundary condition for the one-dimensional case is expressed as follows in dimensionless form [13]:

$$\frac{\partial^3 c^*}{\partial x^{*3}} = 0 \text{ at } t^* > 0, \text{ and } x^* = 0 \text{ and } x^* = 1 \quad (4.19)$$

The zero mass flux boundary conditions for the two-dimensional case are expressed as follows in dimensionless form:

$$\frac{\partial^3 c^*}{\partial x^{*3}} + \frac{\partial^3 c^*}{\partial x^* \partial y^{*2}} = 0 \text{ at } t^* > 0, \text{ and } x^* = 0 \text{ and } x^* = 1 \quad (4.20)$$

$$\frac{\partial^3 c^*}{\partial y^{*3}} + \frac{\partial^3 c^*}{\partial x^{*2} \partial y^*} = 0 \text{ at } t^* > 0, \text{ and } y^* = 0 \text{ and } y^* = 1 \quad (4.21)$$

The natural boundary condition was obtained from a variation analysis, and its formula is expressed below [64]:

$$(\nabla c) \cdot \mathbf{n} = 0 \quad (4.22)$$

where $\mathbf{n}$ is the outward unit normal to a bounding surface.

The natural boundary condition in the one-dimensional case is expressed as follows in dimensionless form [13]:

$$\frac{\partial c^*}{\partial x^*} = 0 \text{ at } t^* > 0, \text{ and } x^* = 0 \text{ and } x^* = 1 \quad , \quad (4.23)$$

The natural boundary conditions in the two-dimensional case are expressed as follows in dimensionless form:

$$\frac{\partial c^*}{\partial x^*} = 0 \text{ at } t^* > 0, \text{ and } x^* = 0 \text{ and } x^* = 1 \quad (4.24)$$

$$\frac{\partial c^*}{\partial y^*} = 0 \text{ at } t^* > 0, \text{ and } y^* = 0 \text{ and } y^* = 1 \quad (4.25)$$

4.7 Method of Solution

As presented in the previous sections, the governing equations obtained are non-linear fourth-order partial differential equations. To solve those equations, the Galerkin Finite Element Method (GFEM) is used in this study to discretize space. This section will

briefly describe the application of this method. Detailed analysis on GFEM can be found in references [38,66-69].

The general approach to solving a partial differential equation with GFEM is first to establish a general form of equation with initial and boundary conditions:

$$L(u) = 0 \text{ for } a \leq x \leq b \text{ and } a \leq y \leq b \quad (4.26)$$

Its solution is a summation of products of linearly independent functions $\phi_j(x, y)$ and unknown coefficients $u_j(t)$, and below is the solution expression:

$$u_a(x, y, t) = \sum_{j=1}^N u_j(t) \phi_j(x, y) \quad (4.27)$$

where N is the number of nodes in the spatial discretization of the computer domain.

The nonzero residual R can be obtained by substituting equation (4.27) into equation (4.26) and is expressed as follows:

$$R = L(u_a) \neq 0 \quad (4.28)$$

The residual R is then forced to zero; therefore, the approximate solution u_a will approach the real solution. By setting the integration of the inner product of the residual R and a set of independent weighted functions w_i equal to zero the weighted residual vector F_i is obtained as:

$$F_i = \iint R w_i dx dy = \iint L(u_a) w_i dx dy = 0 \quad (4.29)$$

In the Galerkin method the weighted functions are equal to the basis functions; therefore:

$$F_i = \iint R \phi_i dx dy = 0, i, j = 1, 2, \dots, N \quad (4.30)$$

Equation (4.30) will spawn a set of nonlinear ordinary differential equations which can be solved by Newton-Raphson iteration method and a first-order implicit predictor-corrector

time integration method. Convergence is satisfied until the difference of the length of the solution vector between two successive computed solution vectors is less than 10^{-6} .

Hermitian bicubic basis functions are chosen as the appropriate basis functions for the solution of the fourth-order partial differential equation [68-69]. The approximate solution in two dimensions can be expressed as:

$$u_a = \sum_{j=1}^N \left(u_j \phi_{j,0} + \frac{\partial u_j}{\partial x} \phi_{j,1} + \frac{\partial u_j}{\partial y} \phi_{j,2} + \frac{\partial^2 u_j}{\partial x \partial y} \phi_{j,3} \right) \quad (4.31)$$

The basis functions interpolate both solutions and the derivatives at the spatial nodal points. For the one-dimensional case there are four basis functions, while for the two-dimensional case there are sixteen basis functions constructed by a product of one-dimensional counterparts for both the x - and y - directions (see Appendix B).

Applying the divergence theorem:

$$\int_V \alpha \nabla \cdot \beta dV = \int_S \alpha n \cdot \beta dS - \int_V (\nabla \alpha) \cdot \beta dV \quad (4.32)$$

where α is a scalar, β is a vector, and S is the boundary of the domain V . The divergence theorem is used twice to reduce the order to a second-order partial differential equation. The finite difference method is used for time discretization. A first-order implicit Euler predictor-corrector method is used for time integration [70]. An adaptive time-step controller is used to minimize the computational time [70]. The main idea for this user-defined time-step controller is to increase the time step when the local truncation error of the solution is small or decrease the time step when the local truncation error is large. A mesh of 21×21 nodes is used in this study for the two-dimensional case. The Jacobian matrix of size is then expanded to 1764×1764 since four variables at each nodal point will be defined. An approach of mesh size of 33×33

nodes was conducted; however, the computation time took extremely long. Since the simulation results well predict the diffusion process, it is safe to choose the mesh size 21×21 nodes for this study.

The computer program was adapted from the code written by Chan [6] to solve the phase separation process in polymer solutions under isothermal condition. The computational results were generated by running the program on a Dell Precision PWS670 workstation with dual processor (3.20GHz and 3.19GHz) and 3.00 GB of RAM. For a fixed mesh setting, 21×21 nodes, the computational time for this program was about 24 ~ 36 hours per program, and a maximum of three programs can be run simultaneously.

Chapter 5 Results and Discussion:

1-D TIPS

This chapter presents the computational results of a one-dimensional thermal-induced phase separation (TIPS) phenomenon via spinodal decomposition (SD) in a polymer solution under an initial linear concentration gradient. This one-dimensional model is developed according to the Cahn-Hilliard theory for SD in terms of Flory-Huggins free energy equation, and the mobility was derived by the slow mode theory and Rouse law for the polymer diffusion process. The simulation results were obtained by solving the dimensionless governing equation (4.9) together with the dimensionless auxiliary equations (4.18), (4.19) and (4.23) using the Galerkin Finite Element Method. Two types of off-critical quenches are investigated and compared in this chapter: the uniform quench (with no concentration gradient) and the non-uniform quench (with concentration gradient). The uniform quench had an initial concentration of $c_0^* = 0.71$, which represents a conventional TIPS process. In the non-uniform quench, the concentration in the polymer solution ranged from $c_0^* = 0.71$ at one end of the sample (i.e., $x^* = 0$) to $c_0^* = 0.81$ at the other end of the sample (i.e., $x^* = 1.0$). This created a linear concentration profile with gradient of magnitude 0.1 as shown in Figure 5.1. The values for the parameters used in this simulation are listed in Table 5.1.

Figure 5.1: A linear initial concentration profile for one-dimension simulation.

Table 5.1: Dimensionless material parameter values used in one-dimensional TIPS process simulation.

Parameter	Value
$c_{o,1}^*$	0.71
$c_{o,2}^*$	0.71 (uniform quench); 0.81 (non-uniform quench)
N_2	10
D^*	2.0×10^4
T^*	0.60

5.1 Binary Phase Diagram of TIPS Process

Figure 5.2 is a plot of dimensionless temperature T^* versus dimensionless concentration c^* for a polymer solution [5,7,9,14]. This phase diagram is obtained by equating the first and second derivatives of the Flory-Huggins free energy equation curve to zero [14]. The solid line is the binodal line and the dashed line is the spinodal line. Dot A and B represent the lower ($c_{0,1}^* = 0.71$) and the upper ($c_{0,2}^* = 0.81$) limits of the linear concentration profile at the dimensionless temperature $T^* = 0.6$. This concentration profile creates a gradient of magnitude 0.1 in a sample with dimensionless unit length. The uniform quench ($c_{0,1}^* = 0.71$), dot A, is an off-critical quench, while the non-uniform quench ($c_0^* = 0.71 \sim 0.81$), interval AB, is a quench across the critical region.

Figure 5.2: Phase diagram of a binary polymer solution system of TIPS process.

5.2 Concentration Profiles

Figure 5.3 shows the time evolution of the dimensionless spatial concentration profiles of a TIPS process, an off-critical quench case (uniform quench) in a polymer solution at the following dimensionless times: (a) $t^* = 1.64$, (b) $t^* = 14.28$, (c) $t^* = 43.01$ and (d) $t^* = 627.24$. The dashed line is the dimensionless critical concentration $c_c^* = 0.7597$. The numbers in Figure 5.3(b) are reference numbers referring to the peak numbers at the dimensionless time $t^* = 14.28$. Droplet-type morphology will develop because of an off-critical quench [7]. Regions where $c^* > c_c^*$ ($c^* < c_c^*$) in Figure 5.3 represent the solvent-rich (solute-rich) regions. The four different times captured represent the three stages of spinodal decomposition are the early stage (Figure 5.3(a)), the intermediate stage (Figure 5.3(b)) and the late stage (Figure 5.3(c) and (d)), as defined by Hashimoto et al [47].

Figure 5.4 shows the time evolution of the dimensionless spatial concentration profiles of a TIPS process consisting of a non-uniform quench in a polymer solution with an initial linear concentration gradient at the following dimensionless times: (a) $t^* = 1.46$, (b) $t^* = 5.94$, (c) $t^* = 9.36$ and (d) $t^* = 131.08$. The initial concentration spatial profile was obtained to create a linear dimensionless concentration gradient of 0.1 across the interval $0 \leq x^* \leq 1$ [5]:

$$c_o^* = 0.71 + 0.1x^* \quad (5.1)$$

The concentration profiles show the different morphology patterns. Figure 5.4b and 5.4c show a linear initial concentration gradient creating a graded droplet-type morphology during the phase separation. The droplet size gradually increases along the x-axis from the lower initial concentration area to the higher area. Compared with Figure 5.4b and

5.4c, Figure 5.4d shows a decrease of number of droplets. This is due to the coarsening effect in the late stage, showing that the wave length increases with time [47]. The concentration profiles of the uniform quench obtained in this study are in good agreement with the previous published experiments [23].

Figure 5.3: Time evolution of the dimensionless concentration spatial profile for the uniform case where $c_0^* = 0.71$ at the following dimensionless times: (a) $t^* = 1.64$, (b) $t^* = 14.28$, (c) $t^* = 43.01$, and (d) $t^* = 627.24$. The dashed line in each graph represents the critical concentration c_c^* .

Figure 5.4: Time evolution of the dimensionless concentration spatial profile for the non-uniform case where there is a linear gradient in the initial concentration profile ($c_0^* = 0.71-0.81$) at the following dimensionless times: (a) $t^* = 1.46$, (b) $t^* = 5.94$, (c) $t^* = 9.36$, and (d) $t^* = 131.08$. The dashed line in each graph represents the critical concentration c_c^* .

5.3 Structural Anisotropy

Figure 5.5 shows the characteristic dimensionless droplet size d^* versus the peak number along the x^* -axis at dimensionless times $t^* = 14.28$ (uniform quench) and $t^* = 5.94$ (non-uniform quench). The characteristic length is defined as half of the wavelength of a one-dimensional spatial concentration profile. The unfilled circles represent the uniform quench, while the unfilled squares represent the non-uniform quench. The dimensionless times reflect the intermediate stages of the phase separations. For the uniform quench, the characteristic length d^* remains averagely unchanged and indicates the uniform distribution of the droplet size along the x -direction. For the non-uniform quench; however, it shows a continuous increase along the x -direction from peak number 1 to 7. This increase of droplet size indicates that the phase separating time decreases as the initial concentration increases, which creates a graded droplet size morphology with the presence of a linear initial concentration gradient. Similar computation results showed a graded droplet size when the polymer solutions undergo a TIPS process with a temperature gradient [7,9]. The droplet size distribution from the lower initial concentration to higher initial concentration is in agreement with the previous experiments [17].

Figure 5.5: Characteristic dimensionless droplet size, d^* , versus peak number.

5.4 Summary

In this chapter the effects of a linear concentration gradient on the morphology development and the evolution during the one-dimensional TIPS phenomenon via spinodal decomposition (SD) in a polymer solution (non-uniform case) through a modeling and computational simulation and the comparison with the conventional TIPS process (uniform case) were discussed. The one-dimensional TIPS process model was developed and implemented with the non-linear Cahn-Hilliard theory for SD, the Flory-Huggins free energy equation, and the slow mode theory together with the Rouse law for diffusion process.

The computational results were able to simulate the formation of an anisotropic polymer membrane by a TIPS method and were in good agreement with previous published results. The presence of a linear initial concentration gradient affected the rate of phase separation at different positions.

Chapter 6 Results and Discussion:

2-D TIPS

This chapter presents the numerical results of a two-dimensional study of the TIPS phenomenon in polymer solutions with initial linear concentration gradients. This two-dimensional model consists of the Cahn-Hilliard theory for SD, the Flory-Huggins free energy equation, and the slow mode theory and Rouse law for polymer diffusion. The simulation results are obtained by solving the dimensionless governing equation (4.11) with initial condition equation (4.18) and the dimensional auxiliary equations (4.20), (4.21), (4.24) and (4.25) using the Galerkin Finite Element Method. The simulation cases consist of two different types of quenches: the uniform quench and non-uniform quench. Four simulation cases are conducted and described in this chapter. Case 1 is the conventional TIPS quench with no concentration gradient applied in the system for the purpose of comparison. Cases 2, 3 and 4 are TIPS processes with linear initial concentration gradients applied in the system prior to phase separation. Case 2 and 3 are two off-critical quenches, while case 4 is a quench across the critical region. The parameter values used in this chapter are listed in Table 6.1.

Table 6.1: Dimensionless material parameter values used in the two-dimensional TIPS simulation studies.

Parameter	Values			
	no gradient	with linear concentration gradient along polymer solution sample		
Quench Type	off-critical	off-critical		across critical region
Case	Case 1	Case 2	Case 3	Case 4
c_o^*	0.60	0.60-0.68	0.80-0.85	0.52-0.88
D^*	3×10^3	4×10^3	3×10^3	8×10^3
N_2	10			
T^*	0.6			

6.1 Binary Phase Diagram

Figure 6.1 is a plot of dimensionless temperature T^* versus dimensionless concentration c^* , which is similar to that of the one-dimensional Figure 5.2. The solid (dashed) line represents the binodal (spinodal) curve. The first case represents a quench where the concentration is uniform (i.e., $c_o^* = 0.60$) across the whole polymer solution sample. The second and third cases represent quenches into the unstable off-critical region for polymer solution samples containing an initial linear concentration profiles along one direction (i.e., x^* -axis). The fourth case represents a quench into the unstable region for a polymer solution sample that has a linear concentration profile that spans across the critical and off-critical regions.

Figure 6.1: Phase diagram of a binary polymer solution system. The degrees of polymerization of solvent and polymer are $N_1 = 1$ and $N_2 = 10$, respectively. The solid line is the binodal line and the dashed line is the spinodal line. The dimensionless temperature T^* is kept at 0.6.

6.2 Concentration Profiles and Morphologies

Figure 6.2 shows the time evolution of the dimensionless concentration profiles $c^*(x^*, y^*)$ (first column) and the morphology (second column) formed during the TIPS via the spinodal decomposition for case 1 (uniform quench) [6,71]. The dimensionless times are (a) $t^* = 37.69$, (b) $t^* = 38.72$ and (c) $t^* = 39.97$. The black regions (white regions) in the pattern represent the solvent-rich regions (solute-rich regions) with $c^* > c_c^*$ ($c^* < c_c^*$) where $c_c^* = 0.7597$. The second column shows that droplet-type morphology develops and evolves during phase separation process. As respected for a quench with a uniform initial concentration, the droplets formed are approximately similar in size and distributed uniformly across the polymer solution sample.

Figure 6.2: Dimensionless concentration profiles c^* and morphologies for Case 1.

The next three cases represent polymer solutions containing linear concentration gradients across the polymer solution sample along the x^* -axis prior to phase separation as shown in Figure 6.3, 6.4 and 6.5.

Case 2 represents the case where initially the spatial concentration profile varies linearly from $c_o^* = 0.60$ at $x^* = 0$ to $c_o^* = 0.68$ at $x^* = 1.0$. Figure 6.3 shows the time evolution of the dimensionless concentration profiles $c^*(x^*, y^*)$ (first column) and the corresponding morphology (second column) formed during the TIPS phenomenon via spinodal decomposition for Case 2. The dimensionless times are as follow: (a) $t^* = 6.79$, (b) $t^* = 7.54$, and (c) $t^* = 8.47$. The black (white) regions are solvent-rich (solute-rich) regions where $c^* > c_c^*$ ($c^* < c_c^*$). The droplets are solvent-rich, and the matrix is polymer-rich because the initial average concentration range is relatively low. The results in this figure indicates that a droplet-type morphology developed and evolves at different rates along the x^* -axis. Droplets develop first at the right side edge ($x^* = 1$), and, over time, this front of droplet formation moves across the polymer solution towards the left side edge ($x^* = 0$). The earlier the droplet forms, the earlier it goes through the three stages of SD, as observed in Figure 6.3. The results for Case 2 are in agreement with the experimental results reported by Lloyd et al [23]. They applied TIPS method at a polymer/diluent system to make porous membrane. By partially evaporating diluent from one side of the system they create a concentration gradient along the nascent membrane prior to the phase separation. With smaller pores at the top surface and larger pores at the bottom surface, anisotropic structures were successfully obtained by the TIPS method.

Figure 6.3: Dimensionless concentration profiles c^* and morphologies for Case 2.

Case 3 represents the case of a polymer solution with a linear concentration profile initially, which spans from $c_o^* = 0.60$ at $x^* = 0$ to $c_o^* = 0.68$ at $x^* = 1.0$. Figure 6.4 shows the time evolution of the dimensionless concentration profiles $c^*(x^*, y^*)$ (first column) and corresponding morphology (second column) formed during the TIPS phenomenon via spinodal decomposition for Case 3. The dimensionless times are as follow: (a) $t^* = 15.77$, (b) $t^* = 19.21$, and (c) $t^* = 24.56$. The black (white) regions are solvent-rich (solute-rich) regions where $c^* > c_c^*$ ($c^* < c_c^*$). The droplets are solute-rich, and the matrix is solvent-rich because the initial average concentration range is relatively high. In this case, the droplets also develop and evolve through the three stages of SD progressively along the x^* -axis starting at the right side edge ($x^* = 0$). It is interesting to note that the results from Case 2 and 3 show similar but opposite trends. This is due to the fact that these two cases represent regions within the unstable region that is to the left (Case 2) and to the right (Case 3) of the critical concentration at $T^* = 0.60$, respectively. Regions to the left (right) of the critical concentration are relatively high in solute (solvent) concentration. The component with the lower concentration normally forms the dispersed droplet phase. Moreover, the reason why the droplets start to form initially at $x^* = 1.0$ for Case 2 and at $x^* = 0$ for Case 3 is that concentrations at these points are closer to the values of the critical concentration $c_c = 0.7597$. Chan and Rey [13] have shown theoretically, using the linearized Cahn-Hilliard equation, that the time for phase separation by SD increases gradually as the concentration increases or decreases from that of the critical concentration till it diverges at the two spinodal decomposition.

Figure 6.4: Dimensionless concentration profiles c^* and morphologies for Case 3.

Case 4 represents the case where a polymer solution sample has initially a linear concentration profile that ranges from $c_o^* = 0.52$ at $x^* = 0$ to $c_o^* = 0.88$ at $x^* = 1.0$. This initial concentration range spans both the critical and off-critical regions of the phase diagram at $T^* = 0.60$, and includes the concentration ranges of both Case 2 and 3. Figure 6.5 shows the time evolution of the dimensionless concentration profiles $c^*(x^*, y^*)$ (first column) and corresponding morphology (second column) formed during the TIPS phenomenon via spinodal decomposition for Case 4 at the following dimensionless times of: (a) $t^* = 2.62$, (b) $t^* = 3.28$, and (c) $t^* = 4.37$. The black (white) regions represent solvent-rich (solute-rich) regions where $c^* > c_c^*$ ($c^* < c_c^*$). The results for Case 4 are consistent with those from Case 2 and 3 discussed above; phase separation starts in the vicinity of the critical concentration ($c_c = 0.7597$) first, and the dispersed droplet phase are formed by the less-concentrated component.

Figure 6.5 also shows both the droplet-type morphology and interconnected structure formed during phase separation, as expected since the initial concentration range includes both the critical and off-critical regions. Lastly, the results for Case 4 is in agreement with the numerical results reported by Vladimirova et al. [35]; they simulated the phase separation of a low-viscosity liquid mixture with concentration range crossing the critical region for zero bulk flow in which diffusion is the only mass transfer mechanism. Lacasta et al. [42] also studied the phase separation dynamics in a concentration gradient applied across the critical region; however, the morphology at the critical region was not reported.

Figure 6.5 Dimensionless concentration profiles c^* and morphologies for Case 4.

6.3 Droplet Analysis and Count

Droplet analysis includes the characteristic analysis for the droplet size and the shape factor. The method of exclusion [72] is adapted for the analysis in this study. Figure 6.6 shows the domain is divided into five even observation fields. The dimension of each observation field has a dimensionless width of 0.2 along the x^* -direction and a dimensionless height of 1 along the y^* -direction. The droplets are then counted: when they fall into each individual observation region, each droplet is counted only once; when a droplet falls in more than one observation region, it will be counted into the most left observation field. Figure 6.7 shows the spatial droplet counts of Case 3 at the dimensionless time $t^* = 24.556$. The region numbers on the abscissa represent the observation fields at the following range of the x^* -direction:

(I) $0 \leq x^* < 0.2$, (II) $0.2 < x^* < 0.4$, (III) $0.4 < x^* < 0.6$, (IV) $0.6 < x^* < 0.8$ and (V) $0.8 < x^* \leq 1.0$.

Figure 6.6: Domain observation fields.

Figure 6.7: Spatial droplet counts for Case 1 ($t^* = 39.97$).

6.4 Droplet Equivalent Diameters

Figure 6.8 to Figure 6.11 show the dimensionless average equivalent diameter $\langle d_{eq}^* \rangle$ of the dispersed phase droplet at different observation field for the four cases listed in Table 6.1, the brackets $\langle \rangle$ denote an average value taken over one observation field. The average dimensionless equivalent diameter is defined as:

$$d_{eq}^* = \sqrt{4A_d^*/\pi} \quad (6.1)$$

where A_d^* is the dimensionless area of the droplet, and the values of A_d^* are measured using ScionImage™ software.

Figure 6.8 to Figure 6.11 show an overall growth of droplet size during phase separation. This is expected since droplet size increases with time during spinodal decomposition.

Figure 6.8 shows the droplet growth across a polymer solution sample for a uniform quench. In the late stage of phase separation, the size distribution is uniform in the sample as expected for a sample with no initial concentration variation. Figure 6.9 and Figure 6.10 show the droplet growth across a polymer solution sample for two non-uniform quenches, i.e., Case 2 and 3, respectively. These two figures indicate that droplets develop across the polymer solution sample during the phase separation, and that the droplets vary in size from large to small along the x^* -axis of the polymer solution sample. Figure 6.11 corresponds to Case 4, and it shows that droplets close to the critical concentration (Regions II and IV) develop droplets first, followed by the other regions.

Figure 6.8: Dimensionless average equivalent diameters of the dispersed phase droplets in different observation fields for Case 1 at the following dimensionless times: (a) $t^* = 37.69$, (b) $t^* = 38.72$, and (c) $t^* = 39.97$.

Figure 6.9: Dimensionless average equivalent diameters of the dispersed phase droplets in different observation fields for Case 2 at the following dimensionless times: (a) $t^* = 6.79$, (b) $t^* = 7.54$, and (c) $t^* = 8.47$.

Figure 6.10: Dimensionless average equivalent diameters of the dispersed phase droplets in different observation fields for Case 3 at the following dimensionless times: (a) $t^* = 15.77$, (b) $t^* = 19.21$, and (c) $t^* = 24.56$.

Figure 6.11: Dimensionless average equivalent diameters of the dispersed phase droplets in different observation fields for Case 4 at the following dimensionless times: (a) $t^* = 2.62$, (b) $t^* = 3.28$, and (c) $t^* = 4.37$.

6.5 Droplet Shape Factors

Figure 6.12 to Figure 6.15 show the average shape factor $\langle S_f \rangle$ of the dispersed phase droplets at different observation fields for all the four cases listed in Table 6.1, and the brackets $\langle \rangle$ denote an average shape factor, representing the average value within the observation field. The average shape factor is defined as:

$$S_f = P^* / d_{eq}^* \quad (6.2)$$

where P^* is the dimensionless perimeter of the droplet. The values of P^* are measured using ScionImage™ software. The shape factor is a measure of circularity. The shape factor of a perfect circular droplet is equal to π . The value of π is marked as a dashed line in Figure 6.12 to Figure 6.15 as a reference line. Since in Case 4 the concentration gradient passes across the critical region, the shape factor at observation field III ($0.4 < x^*, 0.6$) was not recorded. Figure 6.12 to Figure 6.15 show that the droplets formed are generally circular, since the $\langle S_f \rangle$ values are close to π . This is expected during the early stage and intermediate stages of phase separation by SD.

Figure 6.12: Average shape factor of the dispersed phase droplets in different observation fields for Case 1 at the following dimensionless times: (a) $t^* = 37.69$, (b) $t^* = 38.72$, and (c) $t^* = 39.97$. The horizontal dashed lines show the value of π .

Figure 6.13: Average shape factor of the dispersed phase droplets in different observation fields for Case 2 at the following dimensionless times: (a) $t^* = 6.79$, (b) $t^* = 7.54$, and (c) $t^* = 8.47$. The horizontal dashed lines show the value of π .

Figure 6.14: Average shape factor of the dispersed phase droplets in different observation fields for Case 3 at the following dimensionless times: (a) $t^* = 15.77$, (b) $t^* = 19.21$, and (c) $t^* = 24.56$. The horizontal dashed lines show the value of π .

Figure 6.15: Average shape factor of the dispersed phase droplets in different observation fields for Case 4 at the following dimensionless times: (a) $t^* = 2.62$, (b) $t^* = 3.28$, and (c) $t^* = 4.37$. The horizontal dashed lines show the value of π .

6.6 Summary

This chapter presented the numerical results of a mathematical model that describes the two-dimensional TIPS phenomenon via SD in polymer solutions with a linear initial concentration gradient (non-uniform quenches) and the comparison with the conventional TIPS process (uniform quench). This model was developed under the non-linear Cahn-Hilliard theory to describe the dynamic behaviour of TIPS via SD, the Flory-Huggins free energy equation for the polymer solution thermodynamics, the slow mode mobility theory and the Rouse law for the polymer diffusion process and a linear initial concentration gradient applied prior to the phase separation. As a result, the linear initial concentration gradient had an effect on the droplet distribution, the droplet size and the shape factor. The computational results are in good agreement with the published results found in the literature. A linear initial concentration gradient applied prior to the phase separation formed anisotropic structural polymer materials.

Simulation of an initial concentration gradient applied across the critical region was also conducted. Although an accurate calculation to determine the length of the transition region was not performed, it was able to obtain two types of structure morphology during the phase separation.

Chapter 7 Results and Discussion:

1-D PIPS

This chapter presents the computational results of a one-dimensional polymerization-induced phase separation (PIPS) phenomenon via the spinodal decomposition (SD) in a polymer solution under an initial linear concentration gradient. This one-dimensional model is developed according to the Cahn-Hilliard theory for SD in terms of the Flory-Huggins free energy equation, and the mobility is derived by the slow mode theory and the Rouse law for a polymer diffusion process. The simulation results are obtained by solving the dimensionless governing equations (4.16) and (4.17) together with the dimensionless auxiliary equations (4.18), (4.19) and (4.23) using the Galerkin Finite Element Method. There are two types of off-critical quenches to be investigated and compared in this chapter: the uniform quench (with no concentration gradient) and the non-uniform quench (with concentration gradient). The uniform quench has an initial concentration value of $c_0^* = 0.50$ which represents a conventional PIPS process. The non-uniform quench has an initial linear concentration gradient of $c_0^* = 0.48 - 0.50$ so that the magnitude of the concentration gradient is 0.02. The degree of polymerization N_2 will increase with time. It is evaluated by equation (4.16) and displayed by Figure 7.2. The values for the parameters used in this chapter are listed in Table 7.1

Table 7.1: Dimensionless material parameter values used in the one-dimensional PIPS simulation

Parameter	Value
$c_{o,1}^*$	0.50 (uniform quench); 0.48 (non-uniform quench)
$c_{o,2}^*$	0.50
D^*	1.0×10^6
f	3
E^*	10
A^*	1.0×10^{13}
T^*	0.5

7.1 Phase Diagram

Figure 7.1 is a plot of dimensionless T^* versus dimensionless solvent concentration c^* . The solid lines represent the binodal lines and the long-dashed lines represent the spinodal lines. The three phase equilibrium curves represent the solute degree of polymerization $N_2 = 1$, $N_2 = 5$ and $N_2 = 10$, showing the phase curves shifting to the right side with higher temperature and solvent concentration. After rearranging equation (4.14), the degree of polymerization of solute can be expressed as:

$$N_2 = \begin{cases} \frac{1}{1 - f/(1/k_1 t + 2)}, & t > 0 \\ N_2 = 1, & t = 0 \end{cases} \quad (7.1)$$

It is noted that the value of N_2 increases with time t as shown in Figure 7.2.

Recall the expression for critical concentration:

$$c_c = 1 - \frac{1}{1 + N_2^{0.5}} \quad (3.8)$$

It is noted that when time N_2 increases, the value of c_c increases, reflecting the shift to right as shown in Figure 7.1 [6].

Figure 7.1: Binary phase diagram of polymer solution used in this study with solute degree of polymerization $N_2 = 1, 5$ and 10 . The solvent degree of polymerization is 1 . The solid lines represent the binodal lines and the dashed lines represent the spinodal lines. The filled and unfilled circles represent the lower ($c_{0,1}^* = 0.48$) and upper ($c_{0,2}^* = 0.50$) limits of the linear initial concentration gradient. The uniform case is represented by unfilled circle at coordinate $(c_0^* = 0.50, T^* = 0.50)$ [6].

Figure 7.2: Schematic of solute degree of polymerization N_2 versus dimensionless time t^* . N_2 increases with dimensionless time t^* .

7.2 Concentration Profiles

Figure 7.3 shows the time evolution of the dimensionless spatial concentration profiles for the PIPS phenomenon (uniform quench) in a polymer solution at the following dimensionless times: (a) $t^* = 3.741$, (b) $t^* = 3.743$, (c) $t^* = 3.745$ and (d) $t^* = 3.747$. The dashed line is the initial average concentration, $c_0^* = 0.50$. It is evident that a droplet-type of morphology develops since the average concentration c_0^* remains at the off-critical point at any time during the phase separation [6]. The four different times captured show that the three stages of spinodal decomposition are early stage (Figure 7.3(a)), intermediate stage (Figure 7.3(b)) and late stage (Figure 7.3(c) and (d)). Figure

7.4 shows the time evolution of the dimensionless spatial concentration profiles of the PIPS phenomenon (non-uniform quench) in a polymer solution with an initial linear concentration gradient at the following dimensionless times: (a) $t^* = 4.483$, (b) $t^* = 4.489$, (c) $t^* = 4.491$ and (d) $t^* = 4.492$. The initial concentration spatial profile c_0^* is obtained by creating a linear dimensionless concentration gradient of 0.02 across the interval $0 \leq x^* \leq 1$:

$$c_0^* = 0.48 + 0.02x^* \quad (7.2)$$

The concentration profiles from Figure 7.3 and Figure 7.4 show different morphology patterns. Figure 7.4 shows a graded droplet-type morphology during the phase separation with a linear initial concentration gradient. The droplet size gradually increases along the x -axis. Lee *et al.* [8] simulated the PIPS process under a temperature gradient and obtained a graded droplet size distribution in the sample. Figure 7.4 shows good agreement with their results.

Figure 7.3: Time evolution of the dimensionless spatial concentration profiles for the uniform case, $c_o^* = 0.50$, at the following times: (a) $t^* = 3.741$, (b) $t^* = 3.743$, (c) $t^* = 3.745$ and (d) $t^* = 3.747$. The horizontal dashed lines represent the initial average concentration $c_o^* = 0.50$.

Figure 7.4: Time evolution of the dimensionless spatial concentration profiles for the non-uniform case, $c_o^* = 0.48 - 0.50$, at the following times: (a) $t^* = 4.483$, (b) $t^* = 4.489$, (c) $t^* = 4.491$ and (d) $t^* = 4.492$. The horizontal dashed lines represent the initial average concentration $c_o^* = 0.49$.

7.3 Summary

In this chapter the effect of a linear concentration gradient on the morphology development and evolution during the one-dimensional PIPS phenomenon via spinodal decomposition (SD) in a polymer solution (non-uniform case) through the modeling and computational simulation and the comparison with the conventional PIPS process (uniform case) were discussed. The one-dimensional PIPS process model was developed and solved with the non-linear Cahn-Hilliard theory for SD, the Flory-Huggins free energy equation, and the slow mode theory together with the Rouse law for a diffusion process.

The computational results simulated the formation of the anisotropic polymer membranes induced by the PIPS method. The presence of a linear initial concentration gradient affected the rate of phase separation at different positions. A linear initial concentration gradient resulted in an anisotropic morphology.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

This thesis presented a mathematical modeling and simulation of the phase separation phenomenon via spinodal decomposition in polymer solutions with a linear initial concentration gradient. Two types of methods applied in the phase separation which included the thermally-induced phase separation (TIPS) process and the polymerization-induced phase separation (PIPS) process were discussed in this thesis. The mathematical model was composed of the non-linear Cahn-Hilliard theory to describe the dynamic behavior of phase separation via spinodal decomposition, the Flory-Huggins free energy equation to describe the polymer solution thermodynamics, the slow mode mobility theory and the Rouse law to describe the diffusion process, and a linear initial concentration gradient applied prior to the phase separation.

This thesis successfully developed, implemented, solved and partially validated the mathematical model for the TIPS process in both one-dimension and two-dimensions and in one-dimension for the PIPS process. Both uniform quenches and non-uniform quenches were conducted and compared with differently applied linear initial concentration gradients. For TIPS in two dimensions, a linear initial concentration gradient was placed at three different regions, two off-critical and critical regions, in the study domain. When the concentration gradient was applied across the critical region,

two types of phase separation morphologies occurred, and proved the relationship between the rate of phase separation and position. The morphology development of the uniform quench, which was the conventional phase separation process via spinodal decomposition, showed a uniform distribution of the droplet size. For non-uniform quench (with the presence of a linear initial concentration gradient), the morphology resulted in a graded size distribution and predicted structural anisotropic polymer materials. Larger droplets were found at the side with a higher initial concentration, while smaller droplets were found at the side with a lower initial concentration. A linear initial concentration gradient applied prior to the phase separation successfully predicted an anisotropic structural morphology.

8.2 Recommendations

The two-dimensional computation simulation of the PIPS process was initiated without completion due to the extremely long computational time. Future work on a two-dimensional numerical study of a PIPS process is suggested.

For the quench when the concentration gradient is applied across the critical region, more nodal points should be defined in the transition region where the maximum rate of phase separation occurs to determine transition length.

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Appendix A Scaling Relationships

The following scaling relationships used in this thesis are to obtain the dimensionless governing and auxiliary equations, initial and boundary conditions.

(a) Dimensionless concentration:

$$c^* = c \quad (\text{A.1})$$

(b) Dimensionless space:

$$x^* = \frac{x}{L} \quad (\text{A.2})$$

(c) Dimensionless temperature:

$$T^* = \frac{T}{\theta} \quad (\text{A.3})$$

(d) Dimensionless time:

$$t^* = \frac{2\nu\kappa_0}{\xi L^4} \quad (\text{A.4})$$

(e) Dimensionless Diffusion Coefficient:

$$D^* = \frac{k_B \theta L^2}{2\nu\kappa_0} \quad (\text{A.5})$$

(f) Dimensionless Pre-exponential Factor:

$$A^* = \frac{AL\xi}{2\nu\kappa_0} \quad (\text{A.6})$$

(g) Dimensionless Activation Energy:

$$E_a^* = \frac{E_a}{R\theta} \quad (\text{A.7})$$

Appendix B Hermitian Basis Functions for Galerkin Finite Element Method

The Hermitian bi-cubic basis functions for the Galerkin finite element method are expressed below.

The four basis functions for a one-dimensional element with two nodes are:

$$\phi_1 = 1 - 3\xi^2 + 2\xi^3 \quad (\text{B.1a})$$

$$\phi_2 = \xi - 2\xi^2 + \xi^3 \quad (\text{B.1b})$$

$$\phi_3 = 3\xi^2 - 2\xi^3 \quad (\text{B.1c})$$

$$\phi_4 = \xi^3 - \xi^2 \quad (\text{B.1d})$$

where $\xi = \frac{x}{h_x}$, and h_x is the length of the element in the x-coordinate.

For a two-dimensional element with four nodes, there are four interpolating functions at each element in both x- and y-coordinates based on the one-dimensional element:

$$F_1(\xi) = 1 - 3\xi^2 + 2\xi^3 \quad (\text{B.2a})$$

$$F_2(\xi) = \xi - 2\xi^2 + \xi^3 \quad (\text{B.2b})$$

$$F_3(\xi) = 3\xi^2 - 2\xi^3 \quad (\text{B.2c})$$

$$F_4(\xi) = \xi^3 - \xi^2 \quad (\text{B.2d})$$

$$F_1(\eta) = 1 - 3\eta^2 + 2\eta^3 \quad (\text{B.2e})$$

$$F_2(\eta) = \eta - 2\eta^2 + \eta^3 \quad (\text{B.2f})$$

$$F_3(\eta) = 3\eta^2 - 2\eta^3 \quad (\text{B.2g})$$

$$F_4(\eta) = \eta^3 - \eta^2 \quad (\text{B.2h})$$

where $\eta = \frac{y}{h_y}$, and h_y is the length of the element in the y-coordinate.

The sixteen basis functions for each two-dimensional element are:

$$\phi_1 = F_1(\xi)F_1(\eta) \quad (\text{B.3a})$$

$$\phi_2 = F_2(\xi)F_1(\eta) \quad (\text{B.3b})$$

$$\phi_3 = F_1(\xi)F_2(\eta) \quad (\text{B.3c})$$

$$\phi_4 = F_2(\xi)F_2(\eta) \quad (\text{B.3d})$$

$$\phi_5 = F_1(\xi)F_3(\eta) \quad (\text{B.3e})$$

$$\phi_6 = F_2(\xi)F_3(\eta) \quad (\text{B.3f})$$

$$\phi_7 = F_1(\xi)F_4(\eta) \quad (\text{B.3g})$$

$$\phi_8 = F_2(\xi)F_4(\eta) \quad (\text{B.3h})$$

$$\phi_9 = F_3(\xi)F_1(\eta) \quad (\text{B.3i})$$

$$\phi_{10} = F_4(\xi)F_1(\eta) \quad (\text{B.3j})$$

$$\phi_{11} = F_3(\xi)F_2(\eta) \quad (\text{B.3k})$$

$$\phi_{12} = F_4(\xi)F_2(\eta) \quad (\text{B.3l})$$

$$\phi_{13} = F_3(\xi)F_3(\eta) \tag{B.3m}$$

$$\phi_{14} = F_4(\xi)F_3(\eta) \tag{B.3n}$$

$$\phi_{15} = F_3(\xi)F_4(\eta) \tag{B.3o}$$

$$\phi_{16} = F_4(\xi)F_4(\eta) \tag{B.3p}$$

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