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Miscibility and Phase Separation Dynamics in Binary Polymer Mixtures and Diblock Copolymers

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Contents

Chapter 1. General Introduction

1-1. Background of This Study	1
1-2. Flory-Huggins Theory	3
1-3. Scattering Function of Polymer Mixtures and Diblock Copolymers in the Single-Phase State	7
1-4. Ginzburg Criterion	10
1-5. Limitation of the Flory-Huggins Theory	11
1-6. Phase Separation Dynamics of Binary Polymer Mixtures	12
1-7. Outline of This Thesis	16

Chapter 2. Effects of Microstructural Change on the Miscibility of Deuterated Polysulfone and Protonated Polysulfone Blends

2-1. Introduction	20
2-2. Experimental Section	21
2-2-1. Sample Characteristics and Sample Preparation	21
2-2-2. SANS	24
2-3. Scattering Function in a Single-Phase State of Polymer Blends	25
2-4. Results	26
2-5. Discussion	30
2-5-1. Miscibility and the χ parameters for Blends of d-PSU and Various m-PSUs	30
2-5-2. Mean-field Analysis on the Effective χ Parameter	40
2-6. Conclusion	45

Chapter 3. Microstructural Effects on the Ginzburg Number and the Crossover Behavior in Deuterated Polybutadiene and Polystyrene Blends

3-1. Introduction	49
3-2. Experimental Section	52
3-2-1. Sample Preparation and Characterization	52
3-2-2. SANS	52
3-3. Results and Discussion	52
3-4. Conclusion	58

Chapter 4. High Pressure Cell for Small-Angle Neutron and Light Scattering Studies of Phase Transitions in Polymer Systems

4-1. Introduction	61
4-2. Instrumentation	64
4-2-1. SANS and LS Cells	64
4-2-2. Temperature and Pressure Control Units	71
4-2-3. Correction for the Change of Sample Thickness	73
4-3. Experimental Section	73
4-3-1. SANS	74
4-3-2. Sample Preparation and Characterization	75
4-4. Results and Discussion	75
4-5. Conclusion	79

Chapter 5. Small-Angle Neutron Scattering Study of Anomalous Mixing Behaviors in Deuterated Polystyrene/Poly(vinyl methyl ether) Mixtures near the Glass Transition Temperature

5-1. Introduction	82
5-2. Experimental Section	83

5-2-1. Sample Preparation and Characterization	83
5-2-2. SANS	84
5-2-3. DSC	85
5-3. Results	86
5-3-1. DSC	86
5-3-2. SANS	86
5-4. Analysis and Discussion	92
5-4-1. Conventional Mean-Field Theory Based on RPA	92
5-4-2. SANS Profiles in the Low q Region	94
5-4-3. SANS Profile in the Whole q Region	104
5-4-4. Modified RPA Theory	108
5-4-5. Nonequilibrium Effect	111
5-5. Conclusion	113

Chapter 6. Crossover of Domain-Growth Behavior from Percolation to Cluster Regime in Phase Separation of Non-Isometric Polymer Mixtures

6-1. Introduction	116
6-2. Experimental Section	117
6-2-1. Sample Preparation and Characterization	117
6-2-2. Light Scattering	118
6-3. Results	119
6-3-1. Time Change in Scattering Profiles	119
6-3-2. Time Change in q_m and I_m	122
6-4. Discussion	127
6-4-1. Time-Evolution of Characteristic Length Scale	127
6-4-2. Scaled Structure Factor	128
6-4-3. Time Change in $\langle \eta(t)^2 \rangle$	138
6-4-4. Reduced Plot on q_m and I_m	140
6-5. Conclusion	145

Chapter 7. Heterogeneous Percolation-to-Cluster Transition in Phase Separation of a Non-Isometric Polymer Mixture

7-1. Introduction	149
7-2. Experimental Section	150
7-2-1. Sample Characterization and Preparation	150
7-2-2. Light Scattering	151
7-2-3. TEM and OM Observation	151
7-3. Results	152
7-3-1. Time-Evolution of Light Scattering Profiles	152
7-3-2. Time Change in q_m and I_m	155
7-3-3. Real Space Observation	159
7-4. Discussion	163
7-4-1. Time-Evolution of Phase-Separated Domains Involving Percolation-to-Cluster Transition	163
7-4-2. Observation of Morphology of the Phase-Separated Domains with Two Different Characteristic Lengths	167
7-4-3. Time Change in Scaled Structure Factor	169
7-5. Conclusion	174

Chapter 8. Intermittency of Droplet Growth in Phase Separation of Non-Isometric Polymer Mixtures

8-1. Introduction	177
8-2. Experimental Section	180
8-2-1. Sample Preparation and Characterization	180
8-2-2. Cloud Points	181
8-2-3. Time-Resolved Light Scattering	181
8-3. Results and Discussion	182
8-3-1. Calculation of Binodal and Spinodal Curves	182
8-3-2. Time-Evolution of Scattering Profiles	183
8-3-3. Time-Evolution of q_m and I_m	185
8-3-4. Scaled Structure Factor at Deep and Shallow Quenches	190

8-3-5. Scattering Maximum Arising from Form Factor of Single Droplets	194
8-3-6. Quench-Depth Dependence of Scaled Structure Factor	195
8-3-7. A Possible Model for Intermittent Growth	197
8-4. Conclusion	202

Summary	205
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List of Publications	208
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Acknowledgments	211
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Chapter 1

General Introduction

1-1. Background of This Study

In the past few decades, numerous studies have been conducted on phase transitions of binary polymer systems such as mixtures of two different polymer species and diblock copolymers from both academic and industrial points of view. From the former viewpoint, their studies have attracted our interests as one of important subjects in statistical physics, while, from the latter viewpoint, studies of relationships between phase separated structures and material properties have been carried out to develop industrial products with a high performance.

In this dissertation, I shall study static and dynamic properties of phase transitions for binary polymer systems. I focus on their miscibility as their static properties. The miscibility of binary polymer systems is characterized by the Flory-Huggins interaction parameter χ which is proportional to segregation power between different components. Though the χ parameter was originally defined as a parameter involving difference in the potential energies between the adjacent monomers of two species upon mixing, in this work I determined the χ parameter by using small-angle neutron scattering (SANS) and explored the miscibility of binary polymer systems through the χ parameter evaluated in this work. Original definition of the χ parameter and the method of its estimation from SANS will be introduced in the Secs. 1-2 and 1-3, respectively. The χ parameter determined from SANS, χ_{SANS} , is affected not only by difference in the potential energies between adjacent monomers of two species upon mixing but also by other various physical factors, e.g., the free volume change upon mixing. Generally, χ_{SANS} is functions of thermodynamic variables such as temperature, pressure and so on. At this stage, though temperature dependence

of χ_{SANS} has been explored by numerous researchers, pressure effects on χ_{SANS} have not well been investigated. Furthermore, physical factors which influence χ_{SANS} are not clear, either. With these points in my mind, I investigated pressure effects on χ_{SANS} and clarified some physical factors which influence χ_{SANS} as described below; effects of microstructural change of constituent polymers, effects of thermal concentration fluctuations near critical point, and effects of asymmetry in mobility of constituent polymers, which become increasingly important upon approaching the glass transition temperature of polymer mixtures, on χ_{SANS} .

In the dynamical properties, the phase separation process and kinetics of binary polymer systems have attracted my interests. These studies help us to understand an aspect of nonlinear and nonequilibrium statistical physics. Use of binary polymer systems in phase separation studies has the following advantage: Mutual diffusion of polymers is extremely slow compared with that of small molecules so that their phase separation processes occurs very slowly. Thus we can study the phase separation process for binary mixtures in detail by using the binary polymer mixtures as a model system.

The phase separation process and kinetics in binary polymer mixtures have so far been investigated mainly for mixtures which phase-separate into equal phase volumes (isometric mixture). On the other hand, the phase separation process and kinetics for non-isometric mixtures, have not been well investigated yet, though it is expected to find new aspects which cannot be observed for isometric mixtures. In non-isometric mixtures, two kinds of phase separation process can take place: spinodal decomposition (SD), and nucleation and growth (NG). NG process is inherent in non-isometric mixtures. Furthermore, phase-separated morphology for non-isometric mixtures depends upon their composition and quench depth, because the composition and quench depth affect volume fraction of each phase. The phase separation dynamics may

be significantly affected also by the composition and the quench depth, since phase separation dynamics strongly depends upon the phase-separating morphology as detailed in Sec. 1-6. Thus, in this dissertation, I investigated the phase separation dynamics as a function of the composition and the quench depth in the non-isometric polymer mixtures.

1-2. Flory-Huggins Theory

In this section, we shall introduce the theory developed by Flory and Huggins for explaining the miscibility of the binary polymer mixtures. Though the Flory-Huggins theory is oversimplified against real binary polymer mixtures, it captures the most important features of the miscibility in binary polymer mixtures such as its molecular-weight dependence, and the χ parameter defined in this theory is often used to estimate the miscibility of binary polymer mixtures.

Flory and Huggins calculated the change in the Gibbs free energy upon mixing, based upon the lattice model in the context of a mean-field approximation.¹⁻³ According to the Flory-Huggins representation, the change in the free energy ΔG_m per lattice is given by

$$\frac{\Delta G_m}{k_B T} = \frac{\phi_A \ln \phi_A}{N_A} + \frac{(1 - \phi_A) \ln(1 - \phi_A)}{N_B} + \chi \phi_A (1 - \phi_A) \quad (1-1)$$

with

$$\begin{aligned} \chi &= \frac{z}{k_B T} \left[\epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \right] \\ &= \frac{z}{k_B T} \Delta \epsilon \end{aligned} \quad (1-2)$$

where N_i is the degree of polymerization of i -th component ($i=A$ or B) with volume fraction ϕ_i . ϕ_i ($i=A$ or B) satisfies $\phi_A + \phi_B = 1$. ε_{ij} is the interaction energy between the components i and j , and z is an effective coordination number. χ is the Flory-Huggins interaction parameter. k_B and T are the Boltzmann constant and absolute temperature, respectively. ΔG_m is composed of two contributions; one is combinatorial entropy of mixing, the first two terms in the right-hand side of eq. (1-1), and the other is the enthalpic part characterized by the interaction parameter χ . The combinatorial entropy term favors mixing, since mixing necessarily leads to the increase in the combinatorial entropy and hence decreases ΔG_m . On the other hand, the enthalpic part can be divided into two criteria: (i) $\chi \leq 0$ and (ii) $\chi > 0$. In the case of $\chi \leq 0$, the enthalpic part favors mixing, because it decreases ΔG_m , and therefore polymer mixtures are necessarily miscible. In the case of $\chi > 0$, the enthalpic part does not favor mixing, as it increases ΔG_m , but rather favors phase separation. Thus, in the case of $\chi > 0$, the miscibility of polymer mixtures is essentially determined by a competition between the contribution of combinatorial entropy of mixing and the enthalpic contribution. In eq. (1-1), if N_A and N_B are identical and equal to N , the combinatorial entropy of mixing is inversely proportional to N , indicating that the effect of the χ parameter on the miscibility is enhanced by a factor of N (“ χN effect”), compared with the effect of the combinatorial entropy part. Although the Flory-Huggins model is very simple, it can give a qualitative account for the phase diagram of polymer mixtures. For example, many kinds of binary polymer mixtures with high-molecular weights are immiscible in the experimentally accessible temperature range, higher than the glass transition temperature and lower than the onset of the chemical degradation. This fact can be explained by the small combinatorial entropy of mixing.

Phase separation occurs only in the case when χ is larger than a threshold value, i.e., the χ value at critical point, χ_c . The value χ_c and the critical composition of component A, $\phi_{A,c}$, are presented in the following forms;

$$\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2 \quad (1-3)$$

and

$$\phi_{A,c} = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}}. \quad (1-4)$$

For a symmetrical mixture ($N_A = N_B = N$) χ_c and $\phi_{A,c}$ become

$$\chi_c = 2/N \quad \text{and} \quad \phi_{A,c} = 1/2, \quad (1-5)$$

respectively.

At $\chi > \chi_c$, the mixtures phase-separate into the two coexisting phases where the compositions of component A are ϕ_A' and ϕ_A'' . We can calculate the binodal curve (coexisting curve) from eq. (1-1), i.e., the relation between χ and ϕ_A' and ϕ_A'' , for $\chi \geq \chi_c$ using the relation that the chemical potential of each component in one coexisting phase equals that in the other coexisting phase. For a symmetrical mixture ($N_A = N_B = N$) we obtain the following equation at both composition ($\phi_A^* = \phi_A'$ or ϕ_A'') for the binodal curve;

$$\chi = \frac{1}{N(1 - 2\phi_A^*)} \ln \frac{1 - \phi_A^*}{\phi_A^*}. \quad (1-6)$$

In Fig. 1-1 the binodal curve calculated from eq. (1-6) is shown for a symmetrical mixture ($N_A=N_B=1000$). For $\chi \geq \chi_c$ when overall volume fraction of component A in a polymer mixture is in the range of

$$\phi_A' \leq \phi_A \leq \phi_A'', \quad (1-7)$$

the polymer mixture is in the two-phase state. When overall volume fraction of component A is in the range of

$$\phi_A < \phi_A', \phi_A > \phi_A'', \quad (1-8)$$

the polymer mixture is in the single-phase state. The region inside the binodal curve can be divided into two regions: metastable and unstable states.

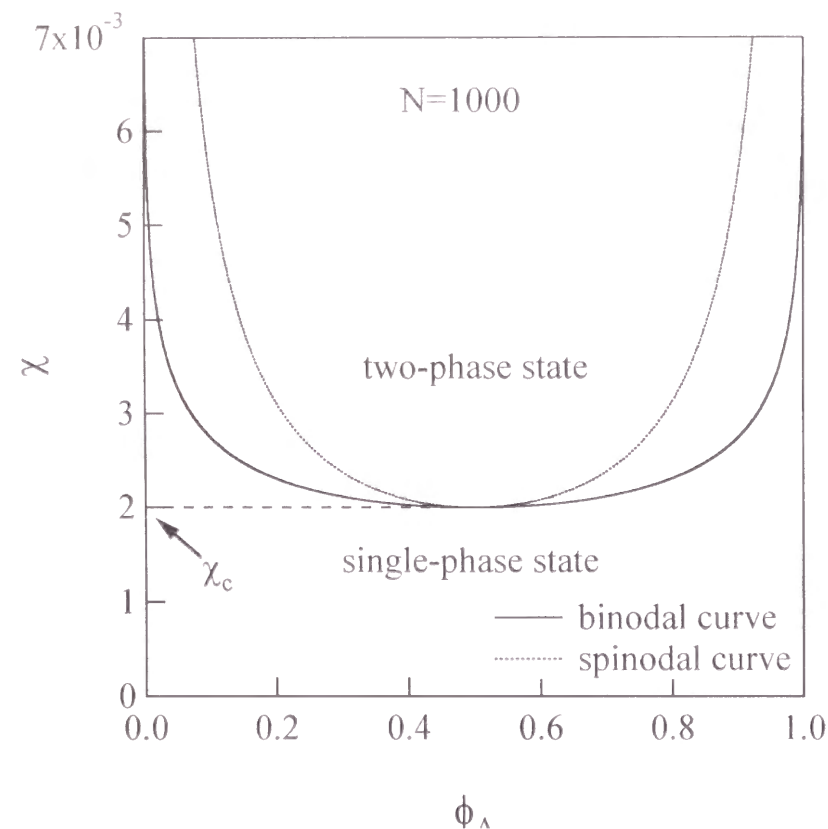


Figure 1-1 Phase diagram for a symmetric polymer blend ($N_A = N_B = 1000$).

The boundary between them is called spinodal curve, which is defined by the following equation using the relation $\frac{\partial^2}{\partial \phi_A^2} \left(\frac{\Delta G_m}{k_B T} \right) = 0$;

$$\chi_s = \frac{1}{2} \left(\frac{1}{N_A \phi_A} + \frac{1}{N_B (1 - \phi_A)} \right), \quad (1-9)$$

where χ_s is the χ parameter at spinodal point. The region inside the spinodal curve is the unstable region, while the region between binodal curve and spinodal curve is the metastable region. The spinodal curve for a symmetrical mixture ($N_A = N_B = 1000$) based upon eq. (1-9) is also shown in Fig. 1-1.

When a polymer mixture is quenched from a single-phase state into an unstable state, even concentration fluctuations with infinitesimally small amplitudes lead to the decrease of the free energy and grow with time. This type of phase separation is called spinodal decomposition. In the case when a polymer blend is quenched from a single-phase state into a metastable state, though concentration fluctuations with small amplitude cause the increase of the free energy, those with their amplitude larger than a critical one lead to the decrease of the free energy. Therefore, the concentration fluctuations with their amplitude smaller than the critical one decay with time, while those with their amplitude larger than the critical one grow. This type of phase separation is called nucleation and growth.

1-3. Scattering Function of Polymer Mixtures and Diblock Copolymers in the Single-Phase State

As described in the previous section, the χ parameter is a key parameter to estimate the miscibility of binary polymer systems. In this dissertation, I estimated the χ parameter from the scattering data in the single-phase state and

discussed the miscibility of them through it. In this section, I shall present the relation between the χ parameter and the scattering function. Although, in the Flory-Huggins theory, only the polymer mixtures are dealt with, the miscibility between the components in diblock copolymers can be similarly discussed through the χ parameter estimated from the scattering experiments. I will describe not only the scattering functions of polymer mixtures but also those of diblock copolymers below.

We shall consider the structure factor $S(q)$ as a function of wave number q in the single-phase state for binary polymer systems including polymer mixtures comprised of polymer A and polymer B and A - B diblock copolymers in which two constituent polymers A and B are covalently bonded at their ends. The structure factor is the Fourier transformation of correlation function for the spatial fluctuations of compositions of polymers A and B , e.g., ϕ_A and ϕ_B and is proportional to the scattering function $I(q)$. Hereafter we shall designate the fluctuations as composition fluctuations or concentration fluctuations.

According to the theory of de Gennes and Leibler based upon random phase approximation (RPA), the structure factor $S(q)$ is presented in the following form;^{4, 5}

$$I(q) = C_0 k_N S(q) \quad (1-10)$$

$$S(q)^{-1} = S_2(q)/W_2(q) - 2\chi, \quad (1-11)$$

where

$$S_2(q) = S_{AA}(q) + S_{BB}(q) + 2S_{AB}(q) \quad (1-12)$$

$$W_2(q) = S_{AA}(q)S_{BB}(q) - S_{AB}(q)^2. \quad (1-13)$$

The function $S_{ij}(q)$ [$i, j = A$ or B] are the Fourier transforms of the density-density correlation function of monomers i and j for the Gaussian chain. k_N is the contrast factor between A and B components for the scattering. C_0 is a constant which depends on the experimental condition.

As for polymer mixtures, since $S_{AB}(q)=0$ in eqs. (1-11) to (1-13), the $S(q)$ [defined hereafter by $S_{\text{mixture}}(q)$] is given by the following equation;⁴

$$\frac{1}{S_{\text{mixture}}(q)} = \frac{1}{S_{AA}(q)} + \frac{1}{S_{BB}(q)} - 2\chi \quad (1-14)$$

$$S_{ii}(q) = N_i \phi_i g_{D, \text{mixture}}(x_i) \quad (i = A \text{ or } B) \quad (1-15)$$

with

$$g_{D, \text{mixture}}(x_i) = \frac{2}{x_i^2} [x_i + \exp(-x_i) - 1] \quad (1-16)$$

and

$$x_i = q^2 R_{g,i}^2. \quad (1-17)$$

$g_{D, \text{mixture}}(x_i)$ and $R_{g,i}$ is the Debye function which represents the scattering from a single Gaussian chain and the radius of gyration of i -th component, respectively. It should be noted that $S_{\text{mixture}}(q)$ monotonously decreases with q .

On the other hand, in the case of A - B diblock copolymers $S_{AB}(q) \neq 0$. From eqs. (1-11) to (1-13), $S(q)$ in the diblock copolymer, defined hereafter by $S_{\text{block}}(q)$, is represented by the following form;⁵

$$\frac{1}{S_{\text{block}}(q)} = \frac{S_{AA}(q) + S_{BB}(q) + 2S_{AB}(q)}{S_{AA}(q)S_{BB}(q) - S_{AB}(q)^2} - 2\chi \quad (1-18)$$

$$S_{AA}(q) = N g_{D, \text{block}}(x_f) \quad (1-19)$$

$$S_{BB}(q) = N g_{D, \text{block}}(x, 1-f) \quad (1-20)$$

$$S_{AB}(q) = N [g_{D, \text{block}}(x, 1) - g_{D, \text{block}}(x, f) - g_{D, \text{block}}(x, 1-f)]/2 \quad (1-21)$$

with

$$g_{D, \text{block}}(x, f) = 2[fx + \exp(-fx) - 1]/x^2, \quad (1-22)$$

$$x = q^2 R_g^2, \quad (1-23)$$

and

$$f = \frac{N_A}{N_A + N_B}, \quad (1-24)$$

where N and R_g are, respectively, the polymerization index and the radius of gyration of the diblock copolymers.

From eqs. (1-18) - (1-24), $S_{\text{block}}(q)$ has a maximum at a finite wave number q^* . The reciprocal of q^* has about the size of radius of gyration of the diblock copolymer. Since we know N , ϕ , and f , we can estimate the χ parameter from the fitting of the scattering function expressed by eqs. (1-14) - (1-17) or (1-18) - (1-24) to the experimental scattering data in the single-phase state.

1-4. Ginzburg Criterion

In Secs. 1-2 and 1-3, we discussed the free energy of mixing for binary polymer mixtures and the scattering functions of binary polymer mixtures and diblock copolymers in the single-phase state in the context of the mean-field theory. However, it is well-known that the mean-field approximation is not valid near the critical point. So far, many studies have been made about the criterion on the validity of the mean-field approximation for polymer mixtures. In this section I shall give a review on theoretical prediction regarding the validity of the mean-field approximation for binary polymer mixtures.

de Gennes and other researchers argued the condition for validity of the mean-field approximation on symmetric mixtures of two polymer species with equal degree of polymerization and equal segment length in each component, i.e., Ginzburg criterion.⁶⁻⁸ According to their prediction, the condition where the mean-field approximation is valid is given by⁶⁻¹⁰

$$\frac{C}{N} \frac{216 \{(1-\phi)^3 + \phi^3\}^2}{\phi^2(1-\phi)^2} \ll \varepsilon, \quad (1-25)$$

where ε is a reduced temperature difference and is given by $\varepsilon = |1 - T / T_c|$ with T_c being a critical temperature. C is a universal constant. Eq. (1-25) predicts that the Ginzburg criterion depends only on the degree of polymerization and is proportional to N^{-1} for mixtures with a given ϕ , indicating the mean-field theory is generally valid in a very wide temperature range for the polymer mixtures with high-molecular weight. However, in chapter 3, contrary to the theory, it is clearly demonstrated that the constant C in the Ginzburg criterion is not necessarily universal and may be affected by the free volume change of polymer mixtures upon mixing.

1-5. Limitation of the Flory-Huggins Theory

As discussed in Sec. 1-4, the Flory-Huggins theory cannot well describe the phase behavior near the critical point of binary mixtures due to the effect of thermal composition (concentration) fluctuations. In addition to the breakdown of the theory near the critical point, it has been recently pointed out that the theory has the following significant problems.

First of all, the theory cannot explain the lower critical solution temperature (LCST) type phase diagram, since the theory does not include the free energy change due to free volume change upon mixing. This exclusion of

the free volume change upon mixing also leads to the fact that the theory cannot well describe pressure effects on the miscibility. Secondly, in the theory, monomer is dealt with as a object which occupies one site in the lattice. Therefore, the theory neglects the real monomer shape. Thirdly, the χ parameter defined in the Flory-Huggins theory is a parameter related to local interactions between adjacent monomers. The long-range interaction beyond the length scale of monomers is not taken consideration. If such a long-range interaction exists, the χ parameter determined by SANS may be a function of wave number. Actually, in some cases it was found that the χ parameter estimated from SANS measurements had a wave number dependence.^{11, 12} The corrections on the above problems for the Flory-Huggins theory have been proposed by many theorists in order to describe the miscibility of real polymer mixtures.^{8, 13-20} In this dissertation I estimated the χ parameter from SANS data by using RPA theory. In this case, the χ parameter obtained by the analysis is not the parameter as described by eq. (1-2) but a phenomenological parameter including various physical factors other than combinatorial entropy of mixing.

1-6. Phase Separation Dynamics of Binary Polymer Mixtures

In Secs. 1-2 - 1-5, I introduced some important studies regarding the static properties of the binary polymer systems. In this section, I will introduce earlier studies regarding the dynamical properties such as the phase separation dynamics via spinodal decomposition (SD), and nucleation and growth (NG).

The time-evolution of characteristic wave length of concentration fluctuations $\Lambda_m(t)$ in phase separation dynamics is often described by a power law:

$$\Lambda_m(t) \sim t^\alpha, \quad (1-26)$$

where α is the scaling exponent which characterizes the phase separation process of the system. $\Lambda_m(t)$ is usually related to the peak wave number $q_m(t)$ observed in the phase separation experiments using the scattering technique.

$$\Lambda_m(t) = 2\pi / q_m(t) \quad (1-27)$$

The value α in eq. (1-26) depends on the phase separation mechanism. The relationship between the value α and the phase separation mechanism was explored in earlier theoretical studies. Kawasaki and Ohta obtained $\alpha = 1$ for isometric fluid mixtures with percolating domains based on the theory which describes interface dynamics with hydrodynamics.²¹ The value $\alpha = 1$ for percolating domains has also been obtained from the phenomenological approach of Siggia.²² For the droplets structures their size is predicted to evolve with time with an exponent of $\alpha = 1/3$, when the droplets grow via either diffusion-coalescence with hydrodynamic interactions²³ or the evaporation-condensation (Lifshitz-Slyozov-Wagner law).^{24, 25}

Many studies of phase separation process in polymers have so far been focused for isometric mixtures and mixtures with their components having nearly equal molecular weight and viscosity. The mixtures satisfying the latter conditions are called symmetric mixtures. The phase separation for the isometric and symmetric mixtures occurs via SD. From earlier studies, the phase separation process via SD can be classified into three regimes: (i) early stage, (ii) intermediate stage and (iii) late stage.²⁶ In the early stage, the amplitudes of the concentration fluctuations with various Fourier modes grow with time according to the Cahn's linearized theory.²⁷ The wavelength of the dominant mode of the concentration fluctuations (characteristic wavelength of concentration fluctuations $\Lambda_m(t)$) is independent of time. In the intermediate stage, both the mean-squared amplitude of concentration fluctuations

$\langle \eta^2(t) \rangle$ and characteristic wavelength $\Lambda_m(t)$ increase with time. In the late stage, $\langle \eta^2(t) \rangle$ attains an equilibrium value independent of time, while $\Lambda_m(t)$ increases with time.

For a given isometric and symmetric mixture, the peak wave number $Q_m(t; \Delta T)$ at a given time of the phase separation process at a given quench depth ΔT reduced by a characteristic wave number $q_m(0; \Delta T)$ in the early stage at the given ΔT was found to become a universal curve independent of ΔT against the time τ reduced by the characteristic time t_c at the given ΔT . $Q_m(t; \Delta T)$ and τ are described as follows, respectively:

$$Q_m(t; \Delta T) = q_m(t; \Delta T) / q_m(0; \Delta T) \quad (1-28)$$

and

$$\tau = t / t_c \quad (1-29)$$

with

$$t_c = [q_m^2(0; \Delta T) D_{app}]^{-1}. \quad (1-30)$$

D_{app} is the mutual diffusion coefficient. This result demonstrates that difference in quench depth does not affect nature of the phase separation mechanism but only give changes in time scale and spatial scale of the phase separation. This is called dynamical scaling postulate, which was proposed by Langer-Bar-on-Miller²⁸ or Chou-Goldburg²⁹ in the isometric mixtures of small molecules.

For non-isometric mixtures, there exist two kinds of phase separation processes: SD and NG. In SD process, each phase is initially percolating, while the phase-separated structures induced by NG have droplets morphology.

In the case of SD process, the phase-separating morphology is expected to significantly depend upon volume fraction of each phase. Even though each phase is percolating at the beginning of SD, in some cases, as time proceeds, the

minority phase cannot keep percolation any longer. Consequently, the minority phase changes into droplets morphology, i.e., percolation-to-cluster transition (PCT) takes place. PCT may take place at the quite early stage, if volume fraction of minority phase is small at early times. Otherwise, PCT may occur at the late stage where interface of the phase-separated structures is well defined or may not occur even at the late stage. Thus, the phase separating morphology in the non-isometric polymer mixtures is expected to depend upon volume fraction of each phase and therefore upon composition and quench depth, because they strongly affect volume fraction of each phase. Furthermore, the phase separation kinetics in the non-isometric mixtures is also expected to strongly depend upon composition and quench depth, since it is significantly affected by the phase-separating morphology. Hence, in this dissertation, I investigated the phase separation kinetics and phase-separating morphology for non-isometric polymer mixtures in wide range of compositions and quench depth.

Only few studies have been carried out on the phase separation dynamics via NG for non-isometric polymer mixtures. Recently, Tokuyama and Enomoto theoretically studied dynamics of phase separation undergoing NG for binary systems for which the interfacial energy provides the only driving force in phase separation.^{30, 31} According to them, when volume fraction of minority phase is small (< 0.14), after nucleation stage, the phase separation dynamics can be divided into three stages: (i) growth stage, (ii) intermediate stage and (iii) coarsening stage. In the growth stage, the interactions among droplets are not important and therefore the droplets nucleated grow directly and independently from supersaturated solution. In the intermediate stage, long-range interactions among droplets become important and the growth of droplets from the solution is affected by the long-interactions among droplets. In the coarsening stage, the growth of the droplets from the solution does not occur and the phase separation dynamics is dominated by Lifshitz-Slyozov-Wagner law. They predict that the

time-evolution of the peak wave number in the growth stage, the intermediate stage, and the coarsening stage proceed with exponents of 0, 2/9 and 1/3, respectively. We shall study this problem experimentally by using polymer mixtures as a model system.

1-7. Outline of This Thesis

This thesis is composed of two parts: (i) the static properties of binary polymer systems such as binary polymer mixtures and diblock copolymers (chapters 2-5) and (ii) the phase separation process and kinetics of non-isometric polymer mixtures (chapters 6-8). The concrete contents in each chapter are as follows.

In chapter 2, I investigated the effects of microstructural change in polymer chains on the miscibility of polymer mixtures (A/B) comprised of two different polymer species A and B . I applied two kinds of modification to polymer chains of A in A/B mixtures: (i) the modification of the end group of polymer chains (A_E) and (ii) the modification of main chain with an incorporation of a small amount of comonomer (A_C). I, then, compared the miscibility in three kinds of polymer mixtures, A/B , A_E/B and A_C/B . Consequently, it was found that subtle microstructural change gave rise to a large change in the miscibility of the polymer mixtures.

In chapter 3, I studied the effects of microstructural changes in polymer chains on the Ginzburg criterion of polymer mixtures. I prepared three kinds of deuterated polybutadiene / polystyrene mixtures where the deuterated polybutadiene have the same degree of polymerization but different microstructure. Although the theories by de Gennes and others predicted that the Ginzburg criterion in polymer mixtures depends only upon degree of polymerization for mixtures with a given composition, I experimentally found

that the Ginzburg criterion is non-universal and depends on the microstructural change.

In chapter 4, I described the instrumentation of high pressure cells for SANS and light scattering (LS) studies. The specially designed and constructed high pressure cells enable us to study the pressure effect on the miscibility of polymer mixtures and block copolymers. A preliminary experiment using the SANS pressure cell showed that the miscibility of a diblock copolymer increases with pressure.

In chapter 5, I studied temperature dependence of the χ parameter for various polymer mixtures near the glass transition temperature T_g in the single-phase state. I experimentally found that, for polymer mixtures with a large difference in the T_g 's of each component, a negative contribution to the χ parameter arises near the T_g of the mixture, i.e., the mixture becomes more miscible near the T_g , driven by asymmetry in mobility of each component. Furthermore, it was shown that the χ parameter with the negative contribution has the anomalous interaction range over a few nanometer.

In chapter 6, I investigated the phase separation process involving a morphological change from percolated phase-separating structures to cluster of droplets, i.e., percolation-to-cluster transition (PCT). The process can be divided into three regimes: (i) percolation regime, (ii) PCT regime and (iii) cluster regime. The details of the phase separation kinetics in each regime will be described in chapter 6.

In chapter 7, I studied the phase separation dynamics and the phase separating morphology slightly below the threshold, below which PCT takes place. As a result, it was found that PCT takes place not homogeneously and isotropically, but it rather occurs *heterogeneously* and *anisotropically*.

In chapter 8, I studied the phase separation dynamics seemingly caused by nucleation and growth. It was found that after the two phases (droplets phase

and matrix phase) attain the equilibrium compositions, the phase separation dynamics was intermittent (or very slow) until the onset of diffusion-coalescence process of droplets in accordance with Lifshitz-Slyozov-Wagner law. The phase separation dynamics in the intermittent regime depends on quench depth. Hence, the phase separation dynamics does not obey the scaling postulate proposed by Chou and Goldberg and Langer-Bar-on-Miller which is confirmed to hold in the phase separation dynamics of many mixtures with isometric compositions.

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Chapter 2

Effects of Microstructural Change on the Miscibility of Deuterated Polysulfone and Protonated Polysulfone Blends

2-1. Introduction

This chapter focuses on the microstructural change effects on the miscibility of polymer blends. Here, it is shown that modification of the end-group of polymer chains or subtle modification in the backbone of the polymer chain such as small amount of random copolymerization gave rise to large change in the miscibility of the polymer blends.

Polysulfones (PSUs) are high-performance thermoplastics which have aromatic groups and sulfone groups (SO_2) in the backbone of the polymer chain. PSUs have characteristics of high temperature-resistance and excellent mechanical strength. On the other hand, to achieve better properties of polymer materials, blending a polymer with other polymers (polymer alloy) is generally a very useful technique, e.g., the mechanical properties may be improved. However, blending of PSU with other polymers is generally difficult because they are immiscible, which makes an application of it as polymer alloys difficult.

Reactive blending is a very useful technique for circumventing this difficulty and to compatibilize PSU with other polymers such as polyamides (PAs). The reactive blending of PSU and PA produces diblock or graft copolymers at the interfaces of two phases (e.g., PSU phase and PA phase) through a chemical reaction between end groups of PA and functional groups introduced into PSU. The block or graft copolymers thus produced behave as “surfactants”, lowering the interfacial tension of the two coexisting phases and hence decreasing the size of macrophase-separated domains. Thus, they act as a “compatibilizer”. For this reactive blending, it is necessary to attach a

functional group to PSU. This modification of PSU is expected to largely change the miscibility against unmodified PSU, because the change in combinatorial entropy on mixing of polymer blends is remarkably small relative to that of mixtures of small molecules^{1, 2} and therefore, even a subtle change in chemical structure of one component significantly affects the miscibility of polymer blends. In the reactive blending of PSU and PA, we blend the unmodified PSU with the modified PSU (m-PSU) and PA, i.e., we formulate a ternary mixture of unmodified PSU, m-PSU and PA. It is important to know the miscibility of unmodified PSU and m-PSU, because it is expected to strongly affect the reaction efficiency between the m-PSU and PA: the efficiency depends on whether unmodified PSU and m-PSU are phase-separated or not.

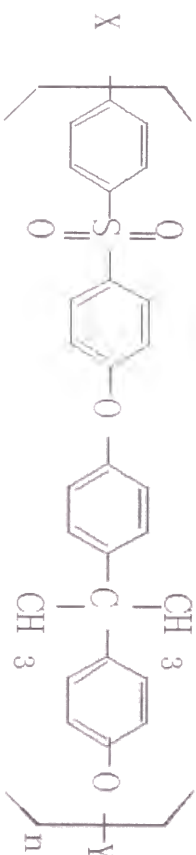
In this study, we prepared two-types of m-PSUs, e.g., a random copolymer of sulfone unit and diphenolic acid [IUPAC-name: 4,4-Bis-(4-hydroxyphenyl)-valeric acid] unit (DPA unit) with COOH group, designated as PSU-COOH, and PSU end-capped with phthalic anhydride (PhAh) group, designated as PSU-PhAh. Both modified PSUs can react with PAs to form the graft or block copolymers at the interfaces of the phase-separated domains which act as a compatibilizer, creating finely dispersed PSU-particles.³ We report on the miscibility between the blends of d-PSU and their m-PSUs.

2-2. Experimental Section

2-2-1. Sample Characteristics and Sample Preparation

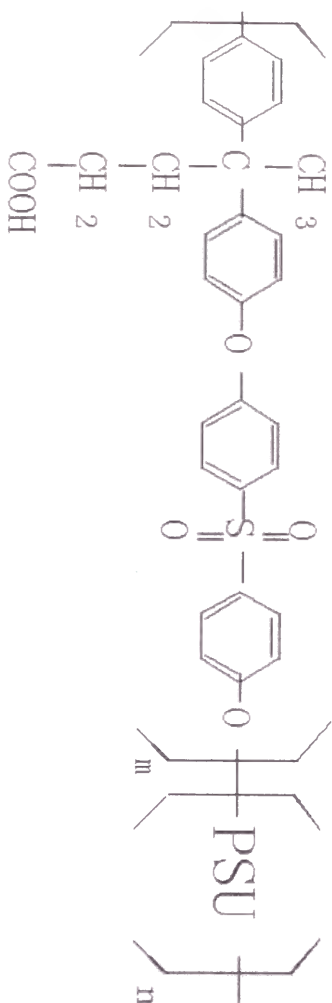
Figure 2-1 shows the chemical structures of PSU, PSU-COOH and PSU-PhAh. PSU has benzene rings and sulfone groups in the backbone with terminal Cl or OH groups. Three-kinds of PSUs were prepared; two of them have mostly Cl end-groups (PSU-Cl1 and PSU-Cl2), while one of them has mostly OH end-groups (PSU-OH). Their characteristics are shown in Table 2-1.

(a) PSU



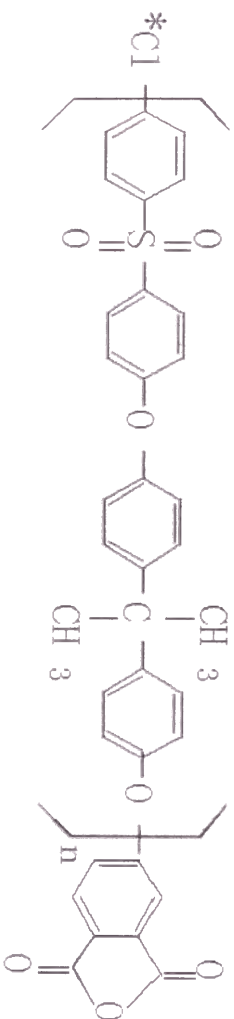
X, Y: Cl- or OH-group

(b) PSU-COOH (random copolymer of DPA unit and sulfone unit)



DPA unit

(c) PSU-PhAh



* or OH group

Figure 2-1 Chemical structures for (a) PSU, (b) PSU-COOH and (c) PSU-PhAh.

Table 2-1 Sample characteristics.

Specimen	T_g (°C)	N_w	N_w/N_n	DPA ^{a)} unit mol%	end group		
					PhAh %	OH %	Cl ^{b)} %
d-PSU	180	41	4.07	-	0	3	97
PSU-Cl1	177	24	2.49	-	0	5	95
PSU-Cl2	174	32	2.60	-	0	3	97
PSU-OH	169	34	3.17	-	0	87	13
PSU-COOH1.6	-	33	2.88	1.6	-	-	-
PSU-COOH4.5	180	40	3.89	4.5	-	-	-
PSU-COOH6.0	174	22	2.64	6.0	-	-	-
PSU-PhAh1	182	43	3.70	-	42	40	18
PSU-PhAh2	186	177	7.19	-	42	8	50

 T_g : Glass transition temperature obtained by DSC measurements. N_w and N_w/N_n : Weight-averaged degrees of polymerization N_w and heterogeneity indices for degree of polymerization N_w/N_n , respectively, which were obtained by means of light scattering and GPC measurements.a) Content of DPA unit was obtained by ¹H NMR.

b) The end-group was estimated by several methods such as titration, spectroscopy and elemental analysis.

PSU-COOH is a copolymer of DPA units and sulfone units. In this study, we prepared three-kinds of PSU-COOHs with different contents of DPA unit as shown in Table 2-1. PSU-PhAh is terminated with PhAh group. However, not all the end-groups are PhAh, there are still Cl groups or OH groups left over (incomplete conversion). Two-kinds of PSU-PhAhs were prepared as shown in Table 2-1. Both PSU-PhAh1 and PSU-PhAh2 have 42% PhAh end-groups on average. However, as PSU-PhAh1 has the lower molecular weight than PSU-PhAh2, the effect of end-group on the miscibility for the former is expected to be larger than that for the latter. Each of the above eight-kinds of PSUs or m-PSUs was blended with deuterated PSU (d-PSU) terminated mostly with Cl end-groups.

The blend samples were prepared by dissolving each polymer in dichloromethane. The solutions were mixed at room temperature and stirred for 30 minutes to prepare homogeneous solutions of the blends containing total amount of polymers by ca. 10 wt%. The polymer blend solutions were then precipitated in methanol at room temperature. The precipitate was isolated by filtration, dried at 50 °C in the vacuo for 12 hours, and then melt-pressed into films. The blend films obtained were sandwiched between copper plates for SANS (small-angle neutron scattering) measurements. All the blends prepared have a composition of 50/50 wt%/wt%.

2-2-2. SANS

SANS measurements were performed with the SANS instrument (SANS-J) at the Japan Atomic Energy Research Institute in Tokai. Neutron beam with wavelength $\lambda=6.5$ Å and $\Delta\lambda/\lambda=0.13$ monochromatized with a velocity selector was used for the measurements. Neutron scattered intensity was detected by a two-dimensional detector, and circularly averaged scattered intensity was obtained as a function of q , where q is a magnitude of the scattering vector given

by $q=(4\pi/\lambda) \sin (\theta/2)$. λ and θ are the wavelength and the scattering angle in the medium, respectively. The scattered intensity obtained was corrected for the detector sensitivity, transmission, and the scattering from empty cell. The corrected intensity was further reduced to the absolute units (cm^{-1}) using water (H_2O) as a standard sample for calibration.⁴

2-3. Scattering Function in a Single-Phase State of Polymer Blends

The structure factor $S(q)$ of polymer blends with molecular weight polydispersity in the single phase state is given by

$$\frac{k_N}{S(q)} = \frac{1}{\phi_1 N_{n,1} v_1 P_{w,1}(q)} + \frac{1}{\phi_2 N_{n,2} v_2 P_{w,2}(q)} - \frac{2\chi}{v_0} \quad (2-1)$$

with

$$k_N = N_0 \left(\frac{a_1}{v_1} - \frac{a_2}{v_2} \right)^2 \quad (2-2)$$

according to calculation based upon random phase approximation (RPA).^{5, 6} k_N and N_0 are contrast factor and Avogadro's number, respectively. a_i is the neutron scattering length for i th component ($i=1$ or 2) with volume fractions ϕ_i , number-averaged degree of polymerization $N_{n,i}$ and molar volume of the segment v_i . v_0 is reference volume defined by $v_0=(\phi_1/v_1 + \phi_2/v_2)^{-1}$. $P_{w,i}(q)$ is a weight-averaged form factor of the single polymer chain for i th component. χ is the Flory-Huggins segmental interaction parameter between the two polymers comprising blends. This is an *effective* interaction parameter per segment. In the small q range, $P_{w,i}(q)$ is presented in the following form;⁶

$$P_{w,i}(q) \approx \frac{N_{w,i}}{N_{n,i}} \left(1 - \frac{1}{3} \frac{N_{z,i}}{N_{n,i}} R_{g,n,i}^2 q^2 \right) \quad (2-3)$$

where $N_{w,i}$ and $N_{z,i}$ are the weight- and z-averaged degrees of polymerization for i th component, respectively. $R_{g,n,i}^2$ is square of the number-averaged radius of gyration for i th component. From eqs. (2-1) and (2-3), $S(q)$ in the small q range is given in the Ornstein-Zernike (O-Z) form;

$$S(q)^{-1} = S(0)^{-1} + Aq^2, \quad (2-4)$$

$$S(0)^{-1} = \frac{1}{k_N} \left(\frac{1}{\phi_1 N_{w,1} v_1} + \frac{1}{\phi_2 N_{w,2} v_2} - \frac{2\chi}{v_0} \right). \quad (2-5)$$

We can estimate the parameter χ from the value of $S(0)^{-1}$ by using eq. (2-5).

2-4. Results

Figure 2-2 shows the neutron scattering profiles for the blend of

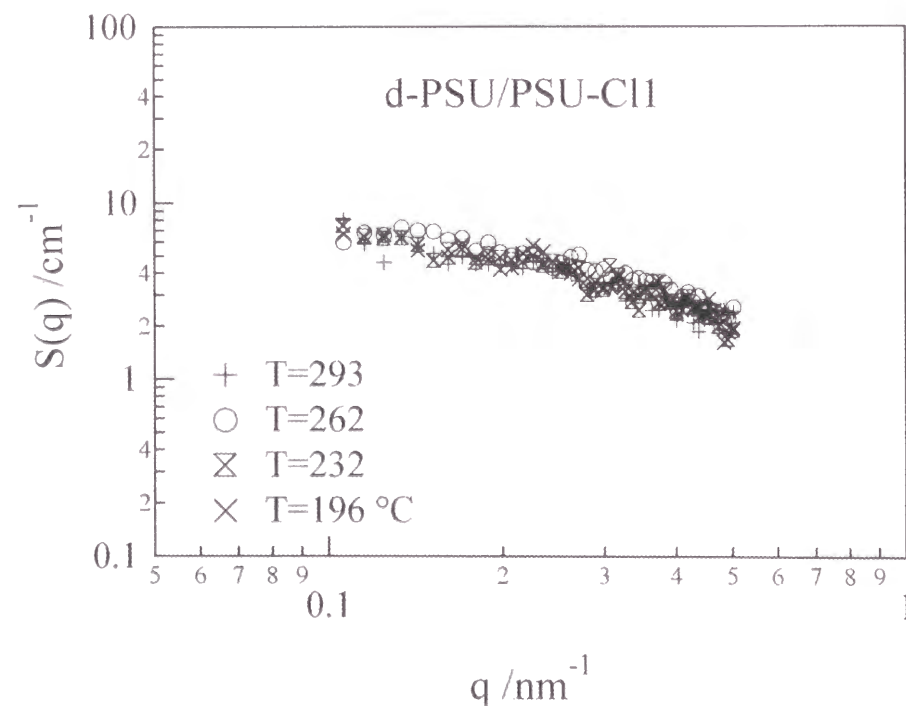


Figure 2-2 Temperature dependence of the scattering structure factor for d-PSU/PSU-C11.

d-PSU and PSU-C11 (d-PSU/PSU-C11; hereafter, we designate the blends of X and Y as X/Y) at various temperatures. The scattering profiles for d-PSU/PSU-C11 have almost no temperature dependence and a gradual q -dependence. Though we do not show the scattering profiles for d-PSU/PSU-C12 and d-PSU/PSU-OH here, they are very similar to that for d-PSU/PSU-C11, i.e., they are almost independent of temperature and they have a gradual q -dependence.

Figure 2-3 shows the scattering profiles for (a) d-PSU/ PSU-PhAh1 and (b) d-PSU/ PSU-PhAh2 at various temperatures. Similarly to the scattering profile for d-PSU/PSU-C11, both of the scattering profiles are almost independent of temperature. However, the scattering profiles for d-PSU/ PSU-PhAh1 in the temperature range from 283 to 201 °C have a slight upturn (an excess scattering) in the small q ($q < 0.14 \text{ nm}^{-1}$), while such upturn is not observed in the scattering profile of d-PSU/PSU-PhAh2. As the upturn of the scattering profile for d-PSU/PSU-PhAh1 is weak and therefore not very obvious, we measured the scattering profile in the q range smaller than 0.08 nm^{-1} , i.e., the q range which was not covered by the *in situ* measurements at temperatures from 283 to 201 °C, on the blend sample vitrified by rapidly quenching the blend from 201 °C to room temperature which is lower than the glass transition temperature of the blend (182 °C).⁷ The scattering profile in the smaller q ($q < 0.08 \text{ nm}^{-1}$) has more remarkable excess scattering than that in the larger q ($q > 0.08 \text{ nm}^{-1}$) {see the data represented by filled circles in Fig. 2-3(a)}. Figure 2-4 shows the scattering profiles for three blends of d-PSU with PSU-COOH having contents of (a) 1.6 mol% DPA unit (d-PSU/PSU-COOH1.6), (b) 4.5 mol% DPA unit (d-PSU/PSU-COOH4.5) and (c) 6.0 mol % DPA unit (d-PSU/PSU-COOH6.0). In Fig. 2-4(a), the scattering profiles for d-PSU/PSU-COOH1.6 hardly depend upon temperature. However, the scattering intensity for d-PSU/PSU-COOH4.5 increases with a decrease of temperature in the q range

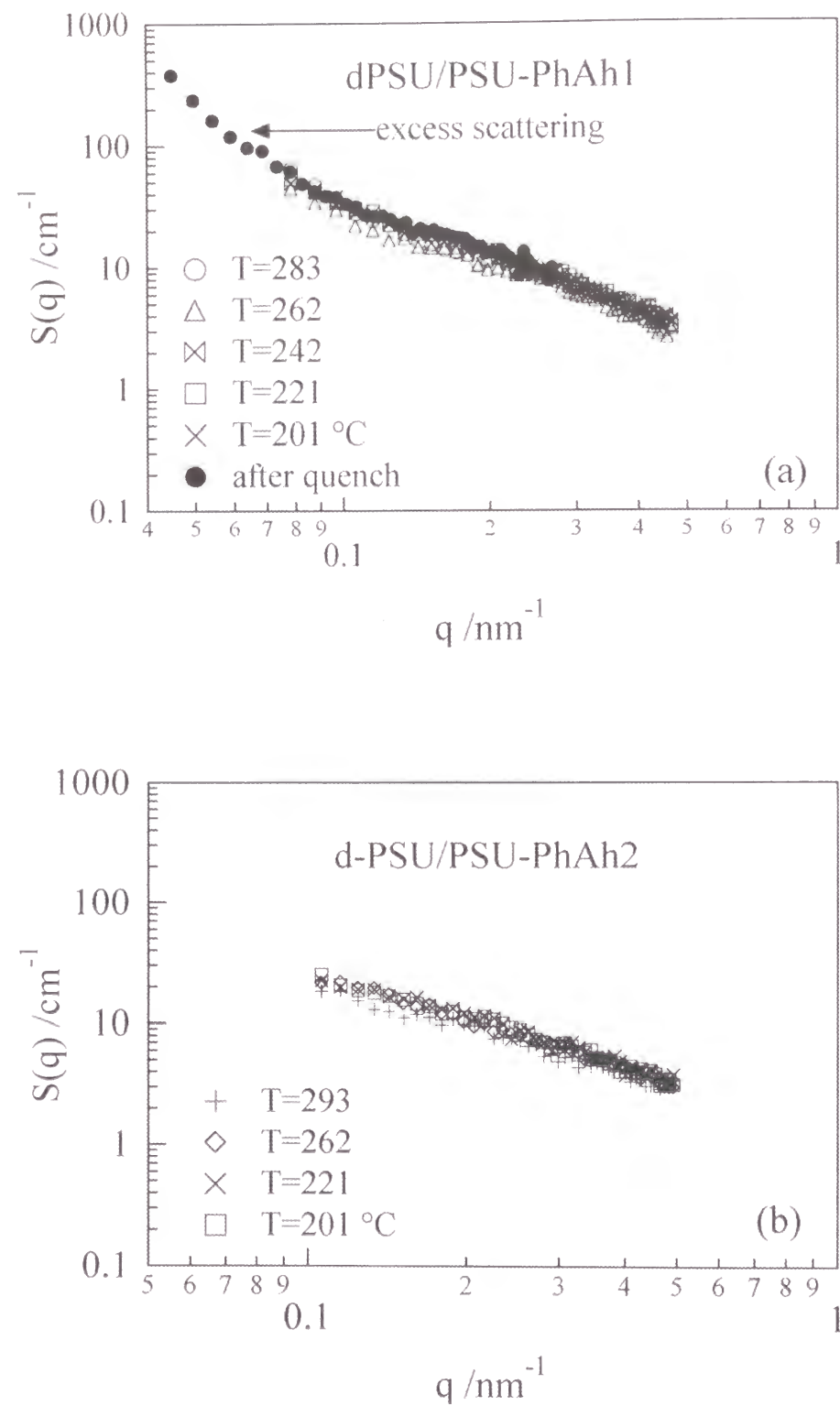


Figure 2-3 Temperature dependence of the structure factors for (a) d-PSU/PSU-PhAh1 and (b) d-PSU/PSU-PhAh2.

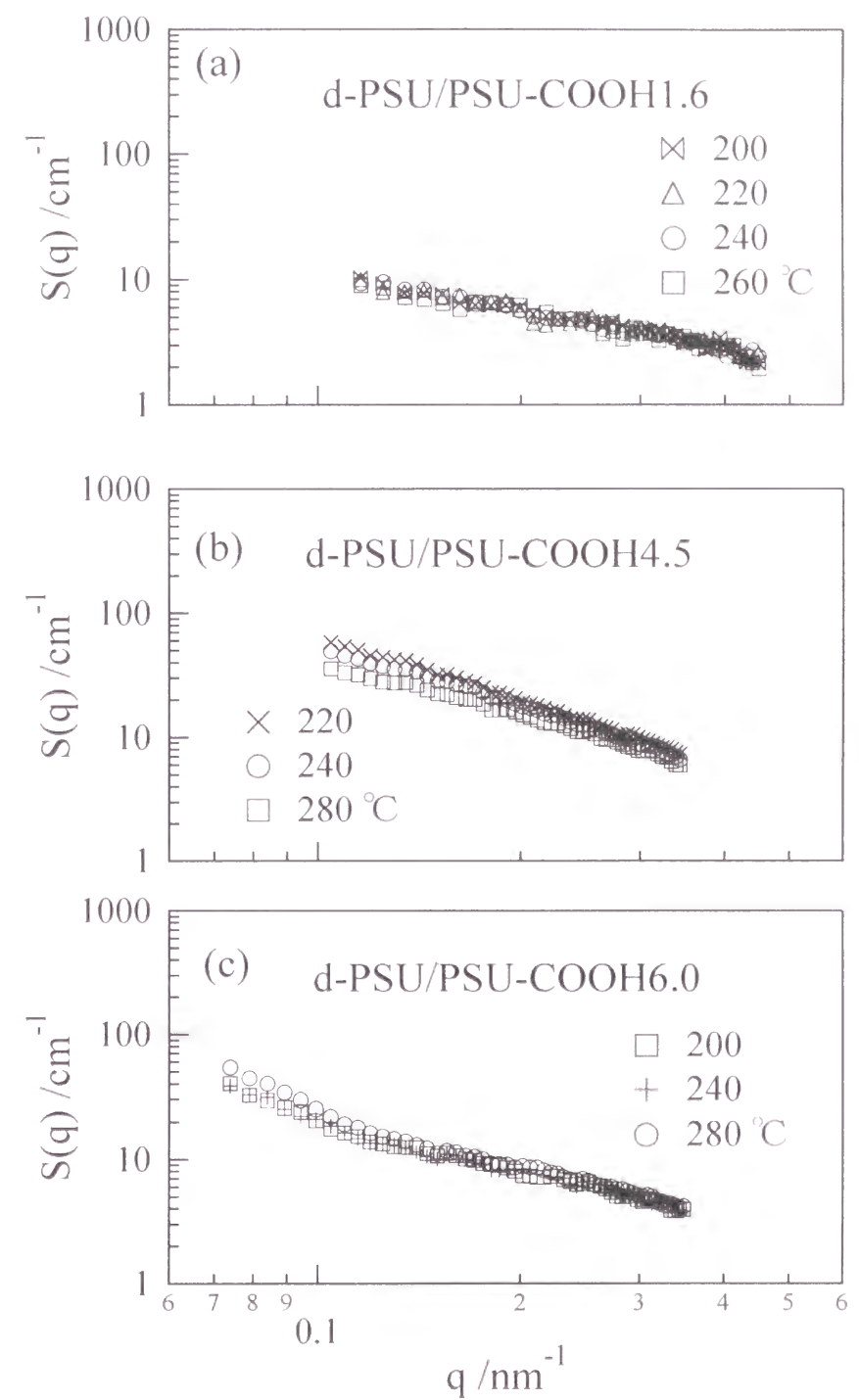


Figure 2-4 Temperature dependence of the structure factors for (a) d-PSU/PSU-COOH1.6, (b) d-PSU/PSU-COOH4.5 and (c) d-PSU/PSU-COOH6.0.

covered in this study {Fig. 2-4(b)}. On the other hand, the scattering profile for d-PSU/PSU-COOH6.0 exhibits an upturn in the small q ($q \leq 0.15 \text{ nm}^{-1}$) as shown in Fig. 2-4(c). In the high q ($q > 0.15 \text{ nm}^{-1}$), the scattering intensity is almost independent of temperature, while the scattering intensity in the small q ($q \leq 0.15 \text{ nm}^{-1}$) at 280°C is larger than those at 240 and 200°C .

2-5. Discussion

2-5-1. Miscibility and the χ parameters for Blends of d-PSU and Various m-PSUs

Figure 2-5 shows the Ornstein-Zernike plot [eq. (2-4): $S(q)^{-1}$ vs q^2] for d-PSU/PSU-C11. The $S(q)^{-1}$ has a linear relation against q^2 . This result indicates that d-PSU/PSU-C11 is in the single-phase state in the temperature range covered in this study. By using eq. (2-5), we can estimate the χ parameter from the $S(0)^{-1}$ obtained by an extrapolation of the linear relation

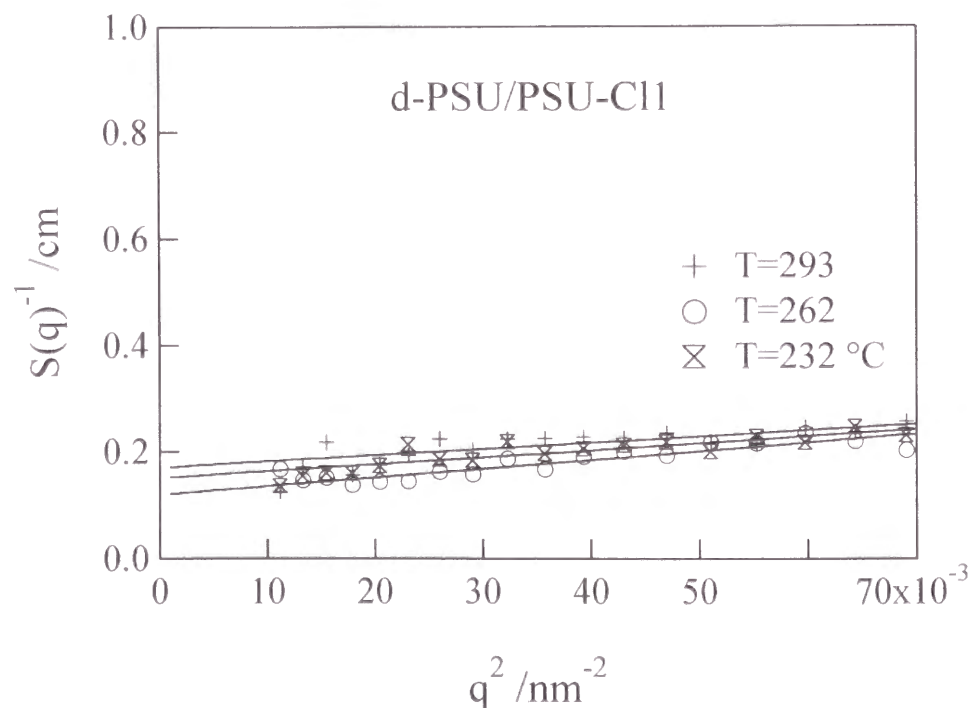


Figure 2-5 Ornstein-Zernike plot for d-PSU/PSU-C11 at various temperatures.

between $S(q)^{-1}$ and q^2 toward $q=0$. The result is presented later in Fig. 2-9. Similarly, we obtained the χ parameter for d-PSU/PSU-Cl2 and d-PSU/PSU-OH at various temperatures from the $S(0)^{-1}$. We will discuss their χ parameters in Fig. 2-9 later.

Figure 2-6 presents the Ornstein-Zernike plots for (a) d-PSU/PSU-PhAh1 and (b) d-PSU/PSU-PhAh2. In Fig. 2-6(a), $S(q)^{-1}$ for d-PSU/PSU-PhAh1 cannot be fitted well with the Ornstein-Zernike equation in the whole q range covered in this work. Though in the range of q^2 larger than $q^2 \approx 0.02 \text{ nm}^{-2}$, $S(q)^{-1}$ linearly increases with q^2 , $S(q)^{-1}$ deviates downward from the linear relation in the range of q^2 smaller than $q^2 \approx 0.02 \text{ nm}^{-2}$. The straight line in Fig. 2-6(a) represents a linear fitting to the data at $q^2 > 0.02 \text{ nm}^{-2}$ and its extrapolation toward $q^2 < 0.02 \text{ nm}^{-2}$. The value q^2 , where $S(q)^{-1}$ deviates downward from the linear relation, corresponds to that of q where the scattering profiles start to exhibit the upturn, as shown in Fig. 2-3(a). The excess scattering in the small q range is considered to be caused by phase separation. As discussed earlier, in the small q range, we probably observed the scattering due to the phase-separated domains, which causes a larger scattering intensity compared with that in the single-phase state. On the other hand, in the high q , we observed the scattering from thermal concentration fluctuations inside the phase-separated domains and therefore, the relation between $S(q)^{-1}$ and q^2 is linear. In Fig. 2-6(b), the $S(q)^{-1}$ for d-PSU/PSU-PhAh2 has a linear relation against q^2 and deviation from the linear relation is not observed, indicating that d-PSU/PSU-PhAh2 is in the single-phase state in the temperature range covered in this study. The χ parameter obtained from the Ornstein-Zernike plot is presented later in Fig. 2-9 and will be discussed later.

Though both of PSU-PhAh1 and PSU-PhAh2 have 42 % of their end groups replaced by PhAh on average, our results show that d-PSU/PSU-PhAh1 is in the two-phase state in the temperature range covered in this study,

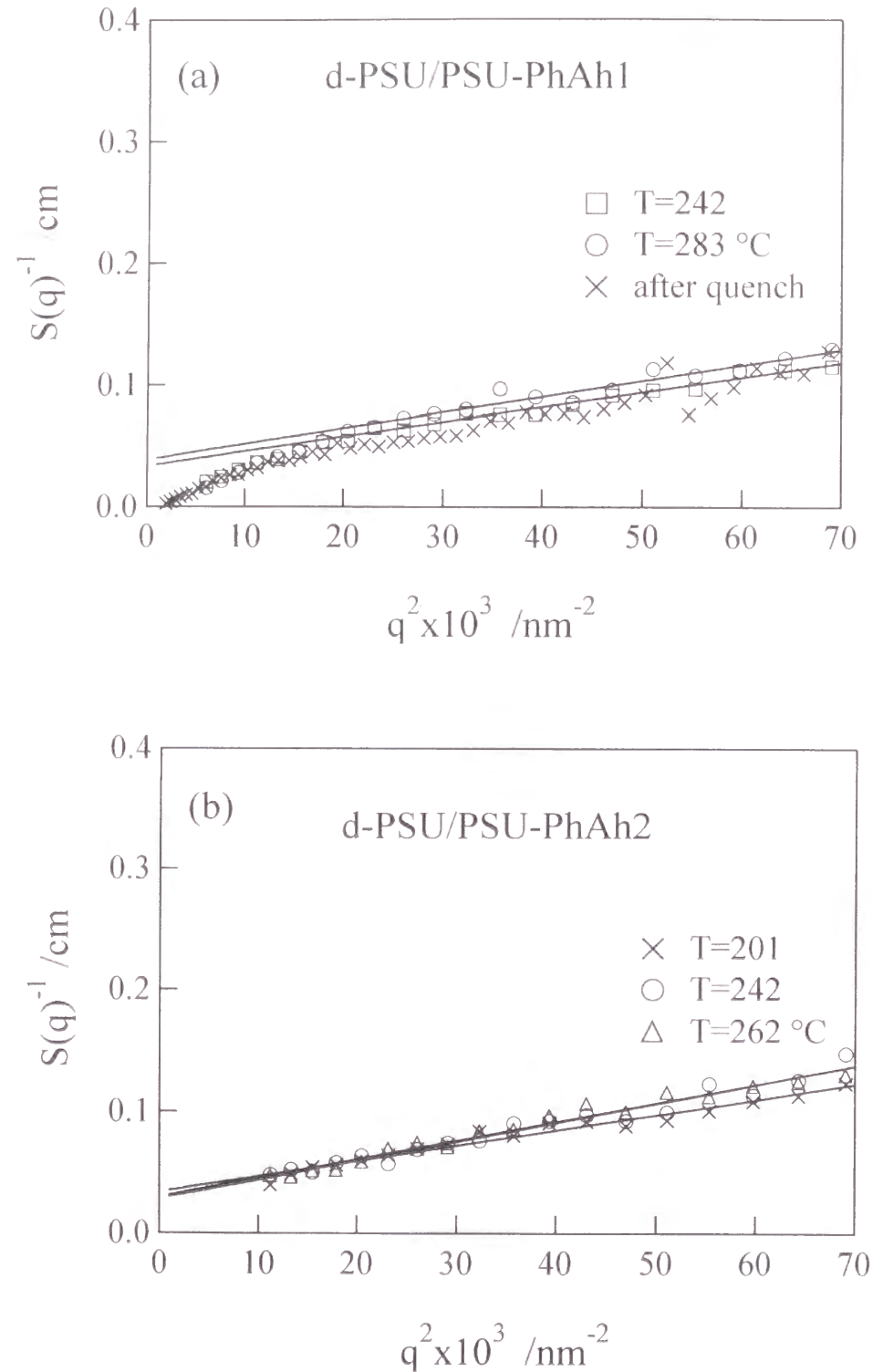


Figure 2-6 Ornstein-Zernike plots for (a) d-PSU/PSU-PhAh1 and (b) d-PSU/PSU-PhAh2 at various temperatures.

while d-PSU/PSU-PhAh2 is in the single-phase state. This result is considered to be due to the fact that molecular-weight of PSU-PhAh1 is smaller than that of PSU-PhAh2. Namely, the former effectively has a larger effect of PhAh end-groups on the miscibility of d-PSU/PSU-PhAh than the latter. Thus, the effect of PhAh end-groups on the miscibility of d-PSU/PSU-PhAh is significant, and the effect largely depends on the molecular weight of PSU-PhAh or volume fraction of the end group. The mean-field analysis on the interactions between the end groups and those between the end groups and the middle groups will be presented in the following section.

As shown in Fig. 2-4, the scattering profiles for d-PSU/PSU-COOH1.6 have almost no temperature dependence, while the scattering intensity for d-PSU/PSU-COOH4.5 increased with decreasing temperature, which means that the concentration fluctuations increase with a decrease of temperature. Namely, the latter result indicates that d-PSU/PSU-COOH4.5 has a phase diagram characteristic of an upper critical solution temperature (UCST). On the other hand, for d-PSU/PSU-COOH6.0, the upturn of the scattering intensity in the small q ($q < 0.15 \text{ nm}^{-1}$) was observed. This result is also considered to be caused by the fact that d-PSU/PSU-COOH6.0 is in the two-phase state as in the case of d-PSU/PSU-PhAh1. In order to confirm it, we present the Ornstein-Zernike plot in Fig. 2-7 for (a) d-PSU/PSU-COOH1.6, (b) d-PSU/PSU-COOH4.5 and (c) d-PSU/PSU-COOH6.0. As shown in Fig. 2-7(a), the relation between the $S(q)^{-1}$ and q^2 is linear and the $S(0)^{-1}$ obtained by extrapolation from the linear relation toward $q=0$ is almost independent of temperature, which means that the χ parameter is independent of temperature as will be shown in Fig. 2-9 later. Thus, d-PSU/PSU-COOH1.6 is in the single-phase state in the temperature range covered in this work.

In Fig. 2-7(b) the relation between $S(q)^{-1}$ and q^2 for d-PSU/PSU-COOH4.5 is linear, similarly to that for d-PSU/PSU-COOH1.6, indicating that

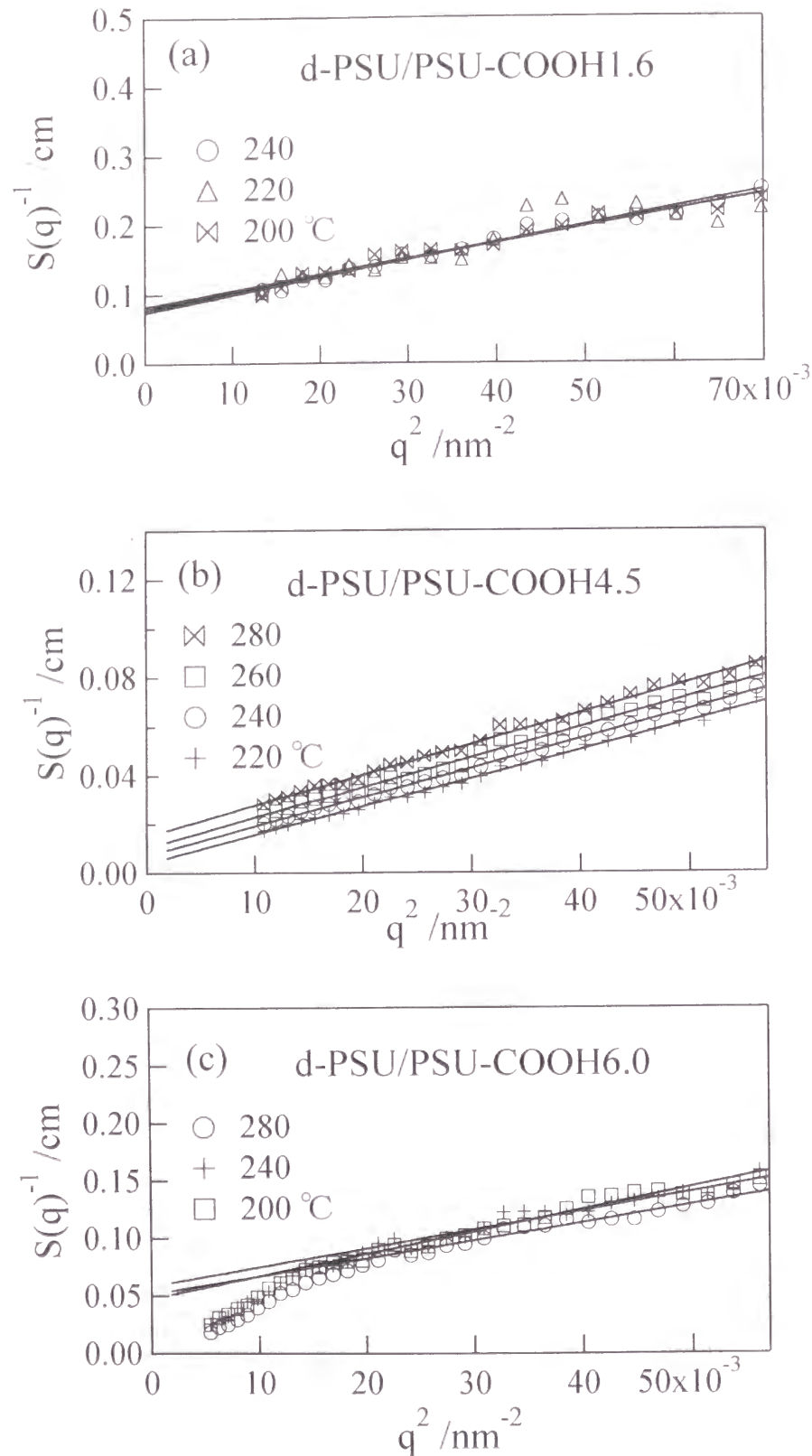


Figure 2-7 Ornstein-Zernike plots for (a) d-PSU/PSU-COOH1.6, (b) d-PSU/PSU-COOH4.5 and (c) d-PSU/PSU-COOH6.0 at various temperatures.

d-PSU/PSU-COOH4.5 is in the single-phase state. However, the temperature dependence of $S(q)^{-1}$ for d-PSU/PSU-COOH4.5 is different from that for d-PSU/PSU-COOH1.6. The $S(q)^{-1}$ decreases with decreasing temperature, reflecting the UCST behavior. We estimated the χ parameter from the $S(0)^{-1}$ obtained by extrapolating the linear relation toward $q=0$. In Fig. 2-8 we show the plot of the χ parameter against reciprocal absolute temperature T^{-1} . The χ parameter linearly increases with increase of T^{-1} , the temperature dependence of which is given by

$$\chi = 0.00708 + 20.3 / T. \quad (2-6)$$

At spinodal point, $S(0)$ diverges, i.e., $S(0)^{-1}$ becomes zero. Therefore, by substituting zero for left-hand side of the eq. (2-5), the value of χ at spinodal point, χ_s , is given in the following form in the context of the mean-field theory,

$$\chi_s = \frac{v_0}{2} \left(\frac{1}{\phi_1 N_{u,1} v_1} + \frac{1}{\phi_2 N_{u,2} v_2} \right). \quad (2-7)$$

Thus the value of χ_s can be calculated from the molecular parameters and compositions. By extrapolating the relation of eq. (2-6) toward χ_s , we estimated mean-field spinodal temperature T_s of d-PSU/PSU-COOH4.5 was 201 °C.

In Fig. 2-7(c), $S(q)^{-1}$ for d-PSU/PSU-COOH6.0 cannot be fitted well by eq. (2-4) for the whole range of q covered in this work. While $S(q)^{-1}$ linearly increases with q^2 in the high q region ($q^2 \geq 0.021 \text{ nm}^{-2}$), $S(q)^{-1}$ at $q^2 < 0.021 \text{ nm}^{-2}$ deviates downward from the linear behavior due to the same reason as that given in conjunction with the discussion of Fig. 2-6(a). The straight line in Fig. 2-7(c) was obtained by a linear fitting to the data in $q^2 > 0.021 \text{ nm}^{-2}$ and its

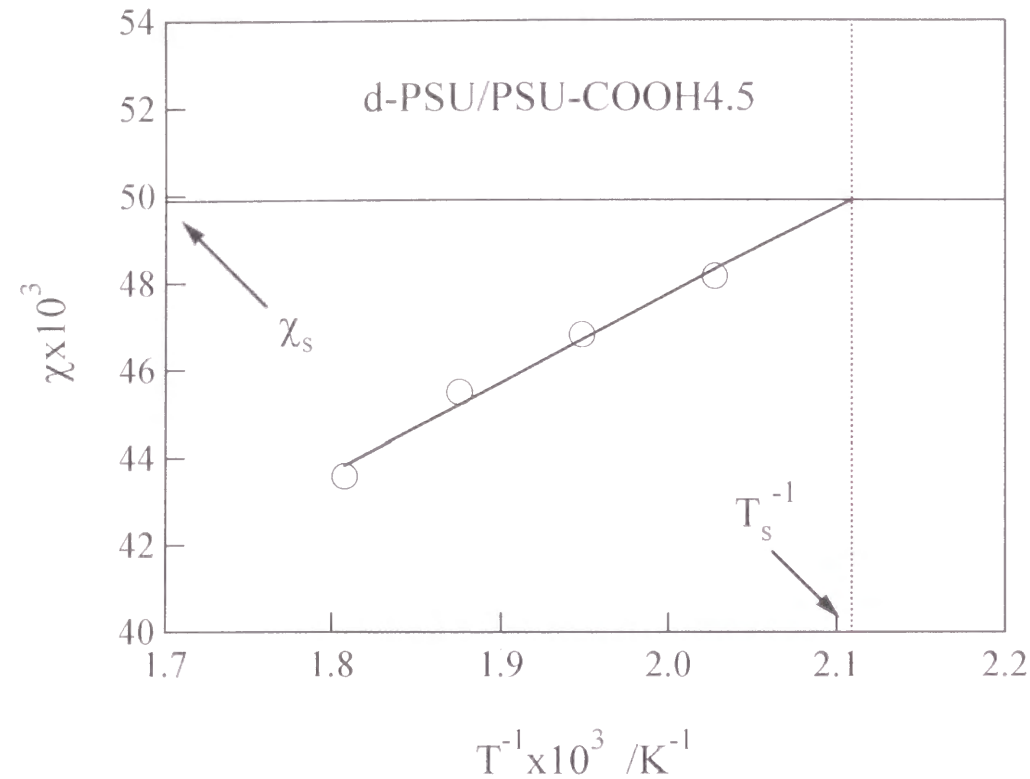


Figure 2-8 Plot of the Flory-Huggins segmental interaction parameter χ for d-PSU/PSU-COOH4.5 against reciprocal absolute temperature.

extrapolation toward $q^2 < 0.021 \text{ nm}^{-2}$. This behavior of $S(q)^{-1}$ is very similar to that for d-PSU/PSU-PhAh1. Namely, $S(q)^{-1}$ at $q^2 < 0.021 \text{ nm}^{-2}$ reflects the scattering due to the phase-separated domains, while $S(q)^{-1}$ at $q^2 \geq 0.021 \text{ nm}^{-2}$ is expected to originate from thermal concentration fluctuations inside the phase-separated domains. Thus, d-PSU/PSU-COOH6.0 is considered to be in the two-phase state.

Before discussing the interactions between d-PSU or PSU and the DPA units, let us first discuss the temperature dependence of the scattering profiles which show the upturn due to the phase-separated domains in the following two paragraphs.

As shown in Fig. 2-4(c) the scattering intensity at $q < 0.145 \text{ nm}^{-1}$ at $T=280^\circ\text{C}$ is larger than that at $q < 0.145 \text{ nm}^{-1}$ at $T=240$ and 200°C . This behavior is considered to be caused by the fact that these measurements were carried out in the cooling process and in the phase separation process. Namely, the sizes of the phase separating domains at $T=240$ and 200°C are larger than that at 280°C , because the phase-separating domains grow with time during the measurements from 280 to 200°C .

In the q scale covered by this SANS experiment, we often observe structures at the length scale smaller than that of the phase-separating domain, i.e., the q scale can be higher than the reciprocal of the phase-separating domain size. In such q scale, the scattering profile reflects a large-angle tail of the domain scattering. As the phase separated domains grow, the tail shifts toward smaller q , causing the scattered intensity at a given q (satisfying $q < 0.145 \text{ nm}^{-1}$) decreases.⁸ Consequently, the scattering intensity at 240 and 200°C is lower than that at 280°C . On the other hand, the scattering intensities at $q > 0.145 \text{ nm}^{-1}$ at $280, 240, 200^\circ\text{C}$ are almost the same. In this q scale, we observe the scattering due to thermal concentration fluctuations inside the phase-separated domains. In the time scale of our experiments the composition in each phase is predicted to already attain an equilibrium one and not to change with time. Moreover the composition in each phase seems to be almost independent of temperature over the temperature range covered in this experiment.

We now discuss the interactions between d-PSU or PSU and the DPA units. We note that while d-PSU/PSU-COOH1.6 and d-PSU/PSU-COOH4.5 were in the single-phase state in the temperature range covered in this study, d-PSU/PSU-COOH6.0 was in the two-phase state. From the point of view of molecular weight, d-PSU/PSU-COOH6.0 tends to be more miscible than d-PSU/PSU-COOH1.6 and d-PSU/PSU-COOH4.5, because the molecular weight of PSU-COOH6.0 is smaller than those of PSU-COOH1.6 and PSU-COOH4.5.

Therefore, the above result cannot be explained by effect of the molecular weight. Consequently, it should be primarily due to difference in content of DPA unit. Namely, because of a strong segregation effect of d-PSU or PSU against DPA unit, d-PSU/PSU-COOH6.0 with a larger content of DPA unit tends to segregate more than d-PSU/PSU-COOH1.6 and d-PSU/PSU-COOH4.5 having smaller contents of DPA unit. In the next section, we will discuss the interactions between d-PSU or PSU and DPA units in details.

In Fig. 2-9 we summarize the χ parameter for the blends investigated in this study. The χ parameters for d-PSU/PSU-CI1 and d-PSU/PSU-CI2 have almost no temperature dependence, reflecting that their scattering profiles do not change with temperature. The χ parameter for d-PSU/PSU-CI1 has almost the same as that for d-PSU/PSU-CI2 and is the smallest among the blends studied here. This result reveals that difference between molecular weight of PSU-CI1 and that of PSU-CI2 does not affect the χ parameter. The χ parameter for d-PSU/PSU-OH is slightly larger than those for d-PSU/PSU-CI1 and d-PSU/PSU-CI2. Thus, even the difference between Cl end-groups and OH end-groups affects the miscibility of d-PSU and PSU blends, if the degree of polymerization of PSU is small. This reveals again the significance of the interactions between the end groups as discussed earlier and as will be discussed later in the next section.

The χ parameter for d-PSU/PSU-PhAh2 hardly changes with temperature, similarly to the case of the blends of d-PSU/PSU-CI1, d-PSU/PSU-CI2 and d-PSU/PSU-OH. Furthermore, the χ parameter for d-PSU/PSU-PhAh2 is slightly larger than those for d-PSU/PSU-CI1, d-PSU/PSU-CI2 and d-PSU/PSU-OH. Note that N_w of PSU-PhAh2 is much larger than those of PSU-CI1, PSU-CI2 and PSU-OH and therefore from the points of view of molecular weight, the effect of end-groups of PSU-PhAh2 on the miscibility is expected to be much smaller than those of PSU-CI1, PSU-CI2 and PSU-OH. Nevertheless, as the χ

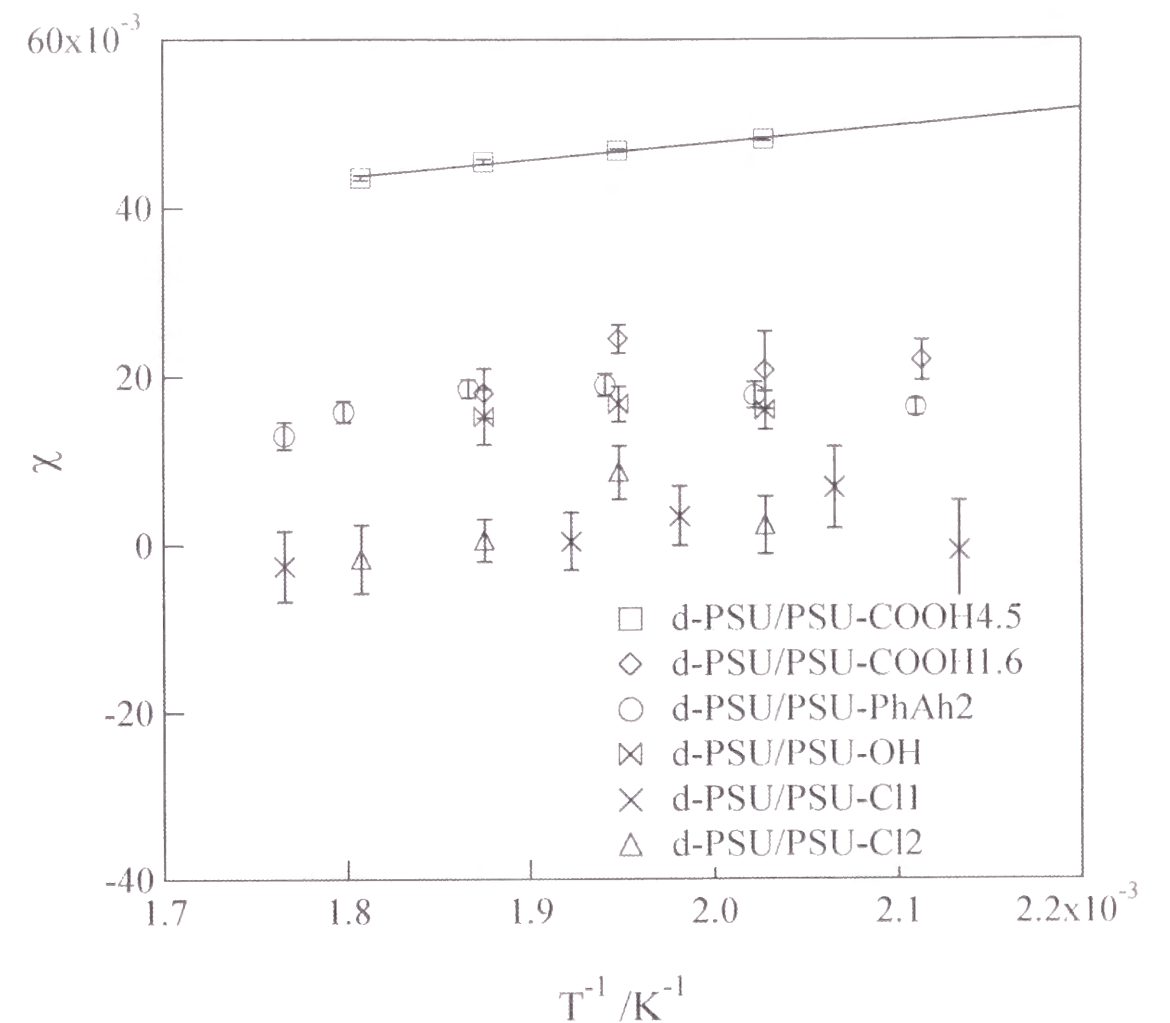


Figure 2-9 Plot of the Flory-Huggins segmental interaction parameter χ for d-PSU/PSU-CI1, d-PSU/PSU-CI2, d-PSU/PSU-OH, d-PSU/PSU-PhAh2, d-PSU/PSU-COOH1.6 and d-PSU/PSU-COOH4.5, against reciprocal absolute temperature.

parameter for d-PSU/PSU-PhAh2 is larger than those for d-PSU/PSU-CI1, d-PSU/PSU-CI2 and d-PSU/PSU-OH, the effect of end-groups of PhAh groups on the net χ parameter is expected to be very large compared with that of end-groups of Cl and OH. This point will be further discussed in the next section.

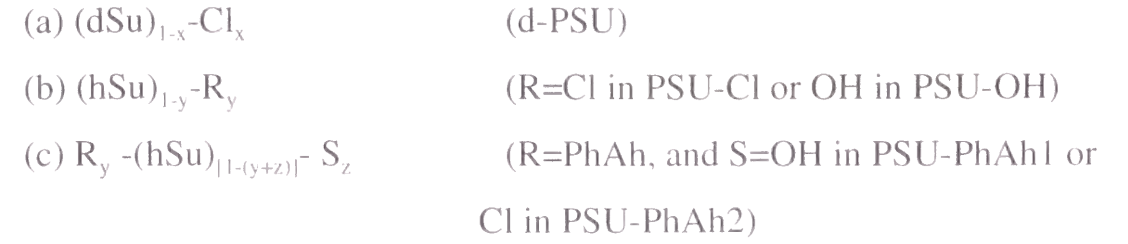
The χ parameter for d-PSU/PSU-PhAh1 is much larger than that for d-PSU/PSU-PhAh2, because the former blend phase-separated in the same

temperature range, as discussed earlier in conjunction with Fig. 2-3. The χ parameters for d-PSU/PSU-COOH1.6 and d-PSU/PSU-COOH4.5 are larger than those for d-PSU/PSU-Cl1, d-PSU/PSU-Cl2 and d-PSU/PSU-OH and d-PSU/PSU-PhAh2. Furthermore, the χ parameters for d-PSU/PSU-COOH4.5 is much larger than that for d-PSU/PSU-COOH1.6, which means that the miscibility of d-PSU/PSU-COOH is largely affected by slight change in the content of DPA unit included in PSU-COOH.

2-5-2. Mean-field Analysis on the Effective χ Parameter

In this section, we analyze the effective χ parameter for the blends of d-PSU with various m-PSUs on the basis of the mean-field approximation where the local composition is assumed to be spatially uniform (equal to the average composition). This assumption may not be rigorously true but may be good enough in the following qualitative discussion.

First, let us consider the end group effect on the effective χ parameters for d-PSU/PSU-Cl, d-PSU/PSU-OH and d-PSU/PSU-PhAh. For simplicity, we assume that both d-PSU and PSU-Cl have 100% Cl end groups, while PSU-OH has 100 % OH end group. Furthermore, as shown in Table 2-1, most of the end groups of PSU-PhAh1 are PhAh group or OH group, while PSU-PhAh2 has mostly PhAh end group or Cl end group. Therefore, each polymer is expressed as shown in Scheme 2-1. d-PSU is comprised of deuterated sulfone units (dSU) and Cl end group with the respective volume fractions being $(1-x)$ and x (part a). PSU-Cl or PSU-OH is composed of sulfone unit (hSU) and end group R where R is equal to Cl for PSU-Cl or OH for PSU-OH with the respective volume fractions being $(1-y)$ and y (part b). PSU-PhAh1 or PSU-PhAh2 is composed of end group R, end group S and the hSU unit with the respective volume fractions being y , z , and $[1-(y+z)]$ where R is PhAh, and S is OH in PSU-PhAh1 or Cl in PSU-PhAh2 (part c).



Scheme 2-1

In this case, the effective χ parameter for d-PSU/PSU-Cl, d-PSU/PSU-OH and d-PSU/PSU-PhAh is generally given by

$$\begin{aligned} \chi_{eff} = & xz\chi_{Cl-S} + x\{1 - (y + z)\}\chi_{Cl-hSu} + xy\chi_{Cl-R} \\ & + (1 - x)z\chi_{S-dSu} + (1 - x)\{1 - (y + z)\}\chi_{dSu-hSu} \\ & + (1 - x)y\chi_{R-dSu} - x(1 - x)\chi_{Cl-dSu} \\ & - z\{1 - (y + z)\}\chi_{S-hSu} \\ & - yz\chi_{S-R} - y\{1 - (y + z)\}\chi_{R-hSu}, \end{aligned} \quad (2-8)$$

where $z=0$ in the case of d-PSU/PSU-Cl or d-PSU/PSU-OH. Subscript M-N denotes the χ parameter between M group and N group in Scheme 2-1.

For d-PSU/PSU-Cl or d-PSU/PSU-OH, the effective χ parameter, χ_{eff} , is given as follows by substituting $z=0$ in eq. (2-8),

$$\begin{aligned} \chi_{eff} = & x(1 - y)\chi_{Cl-hSu} + xy\chi_{Cl-R} + (1 - x)(1 - y)\chi_{dSu-hSu} + (1 - x)y\chi_{R-dSu} \\ & - x(1 - x)\chi_{Cl-dSu} - y(1 - y)\chi_{R-hSu}, \end{aligned} \quad (2-9)$$

Eq. (2-9) is arranged as follows:

$$\begin{aligned} \chi_{eff} = & x\{(1 - y)\chi_{Cl-hSu} - (1 - x)\chi_{Cl-dSu}\} + y\{(1 - x)\chi_{R-dSu} \\ & - (1 - y)\chi_{R-hSu}\} + (1 - x)(1 - y)\chi_{dSu-hSu} + xy\chi_{Cl-R}. \end{aligned} \quad (2-10)$$

Since the χ parameter between deuterated sulfone unit and protonated one, $\chi_{\text{dSu-hSu}}$, is expected to be small,⁹⁻¹¹ the third term is considered to be small, i.e., $\chi_{\text{dSu-hSu}} \approx 0$.

In the case of d-PSU/PSU-Cl, since R=Cl, the fourth term is zero. Moreover, regardless of difference between degree of polymerization of PSU-Cl1 and that of PSU-Cl2, i.e., difference between $y=0.00853$ and $y=0.00667$, both of the effective χ parameters for d-PSU/PSU-Cl1 and d-PSU/PSU-Cl2 were unchanged and small. Therefore, the difference between $\chi_{\text{Cl-hSu}}$ and $\chi_{\text{Cl-dSu}}$ also should be small. Thus, eq. (2-10) leads to nearly zero for d-PSU/PSU-Cl.

In the case of d-PSU/PSU-OH, from the above consideration, since $\chi_{\text{dSu-hSu}} \approx 0$, $\chi_{\text{Cl-hSu}} \approx \chi_{\text{Cl-dSu}}$ and $(1-y) \equiv (1-x) \equiv 1$. Moreover $xy \chi_{\text{Cl-OH}} \equiv 8.11 \times 7.66 \times 7 \times 10^{-8} \equiv 4.35 \times 10^{-6}$, the value of which is much smaller than the measured effective χ value shown in Fig. 2-9 (of the order of 10^{-2}). Thus we have $\chi_{\text{Cl-OH}} \equiv 0$. Therefore eq. (2-10) is given as follows:

$$\chi_{\text{eff}} \equiv y \{ \chi_{\text{OH-dSu}} - \chi_{\text{OH-hSu}} \} \quad (2-11)$$

Thus, a small difference between $\chi_{\text{OH-dSu}}$ and $\chi_{\text{OH-hSu}}$ may cause the χ_{eff} for d-PSU/PSU-OH slightly larger than that for d-PSU/PSU-Cl.

We shall now consider the effective χ parameter for d-PSU/PSU-PhAh. Note in this case that y is larger than z , because of bulky PhAh group compared with Cl or OH group, although, in Table 2-1, mole percentage of PhAh group in the end group is almost the same as that of S group. The miscibility of d-PSU/PSU-PhAh was dramatically affected by the volume fraction of PhAh group as shown in the previous section, indicating that the χ parameter between PhAh group and other group is very large. In this case, the isotope effect on the χ parameter may be negligible compared with the χ parameters between

PhAh group and other group, i.e., $\chi_{\text{S-dSu}} \approx \chi_{\text{S-hSu}} \cdot \chi_{\text{dSu-PhAh}} \approx \chi_{\text{hSu-PhAh}}$, $\chi_{\text{Cl-hSu}} \approx \chi_{\text{Cl-dSu}}$.

Furthermore, as $\chi_{\text{dSu-hSu}} \approx xz \chi_{\text{Cl-S}} \approx 0$, eq. (2-8) is rewritten in the following form:

$$\begin{aligned} \chi_{\text{eff}} = & xy \chi_{\text{Cl-PhAh}} - x(y+z-x) \chi_{\text{Cl-hSu}} \\ & + z(y+z-x) \chi_{\text{S-hSu}} + y(y+z-x) \chi_{\text{hSu-PhAh}} \\ & - yz \chi_{\text{S-PhAh}}. \end{aligned} \quad (2-12)$$

As discussed in the previous section, since degree of polymerization of PSU-PhAh2 is larger than those of PSU-Cl1, PSU-Cl2 and PSU-OH, the end group effect on the effective χ parameter for the former with d-PSU is supposed to be smaller than that for the latter with d-PSU. Nevertheless, as shown in Fig. 2-9, the effective χ parameter for the former with d-PSU was larger than those for the latter with d-PSU. In the case of PSU-PhAh2, since S=Cl, eq. (2-12) leads to

$$\begin{aligned} \chi_{\text{eff}} = & (x-z)y \chi_{\text{Cl-PhAh}} - (x-z)(y+z-x) \chi_{\text{Cl-hSu}} \\ & + y(y+z-x) \chi_{\text{hSu-PhAh}}. \end{aligned} \quad (2-13)$$

y is larger than x in terms of volume fraction because of bulky PhAh group.¹³ Then, as $(x-z)$ and $(y+z-x)$ are positive,¹³ $\chi_{\text{Cl-PhAh}}$ or/and $\chi_{\text{hSu-PhAh}}$ should have very large values compared with the values of $\chi_{\text{Cl-hSu}}$ in order to cause the relatively large effective χ parameter for d-PSU/PSU-PhAh2. Especially, it seems to be reasonable that interactions between hSu and PhAh are largely repulsive because both of them are bulky. In the case when $\chi_{\text{Cl-PhAh}} \equiv \chi_{\text{hSu-PhAh}} \gg \chi_{\text{Cl-hSu}}$, we obtain

$$\chi_{\text{eff}} \equiv y^2 \chi_{\text{hSu-PhAh}} \quad (2-14)$$

Since y is very small quantity, $\chi_{\text{hSu-PhAh}}$ is expected to have a very large positive value.

On the other hand, in the case of d-PSU/PSU-PhAh1, eq. (2-12) leads to

$$\begin{aligned} \chi_{\text{eff}} = & x y \chi_{\text{Cl-PhAh}} - x(y+z-x) \chi_{\text{Cl-hSu}} \\ & + z(y+z-x) \chi_{\text{OH-hSu}} + y(y+z-x) \chi_{\text{hSu-PhAh}} \\ & - y z \chi_{\text{OH-PhAh}}. \end{aligned} \quad (2-15)$$

Since degree of polymerization of PSU-PhAh1 is smaller than that for PSU-PhAh2, y and z for the former are larger than those for the latter, respectively. As described above, if $\chi_{\text{Cl-PhAh}}$ or/and $\chi_{\text{hSu-PhAh}}$ have very large values, even the subtle change in y and z significantly affects the effective χ parameter for d-PSU/PSU-PhAh1 and consequently it may become much larger compared to that for d-PSU/PSU-PhAh2. This speculation seems to suitably explain our experimental results. Note that eq. (2-15) reduces to eq. (2-14) if $\chi_{\text{hSu-PhAh}} \cong \chi_{\text{Cl-PhAh}} \cong \chi_{\text{OH-PhAh}} \gg \chi_{\text{Cl-hSu}}$ and $\chi_{\text{OH-hSu}}$.

Finally, we shall consider the effective χ parameter for d-PSU/PSU-COOH. Since we do not have any information about the end group of PSU-COOH, we neglect the effects of end group on the effective χ parameter. Even if we neglect the end group effects, we can interpret a series of results for d-PSU/PSU-COOH. We consider the following scheme: d-PSU is comprised of only the dSu unit and PSU-COOH is composed of the hSu unit and the DPA unit with a volume fraction of $(1-y')$ and y' , respectively. In this case, the effective χ parameter for d-PSU/PSU-COOH is presented by

$$\chi_{\text{eff}} = y' \chi_{\text{DPA-dSu}} + (1-y') \chi_{\text{dSu-hSu}} - y'(1-y') \chi_{\text{DPA-hSu}}. \quad (2-16)$$

Under the approximation of $\chi_{\text{DPA-dSu}} \approx \chi_{\text{DPA-hSu}}$ and $\chi_{\text{dSu-hSu}} \approx 0$, the eq. (2-16) is described as follows:

$$\chi_{\text{eff}} = -y'^2 \chi_{\text{DPA-hSu}}. \quad (2-17)$$

As shown in the previous section, the effective χ parameter and miscibility for d-PSU/PSU-COOH was very sensitive to the content y' of DPA unit in PSU-COOH. Therefore, it can be concluded that $\chi_{\text{DPA-hSu}}$ has a very large positive value, i.e., interactions between DPA unit and sulfone unit are largely repulsive.

The large repulsive interactions between the PhAh group and the hSu or dSu units or between the DPA units and the hSu or dSu units may suggest that the PhAh groups or the DPA groups may form aggregates even in the case when no macrophase separation is observed. If the DPA and/or PhAh groups formed aggregates, it would certainly affect the reactive blending of the PSU and PA. Hence this point reserves future works.

2-6. Conclusion

We investigated the miscibility of blends of deuterated polysulfone (d-PSU) and modified polysulfones (m-PSUs) by means of small-angle neutron scattering. The d-PSU studied here has mostly Cl end-groups. The χ parameter for blends of d-PSU and PSU having mostly OH end-groups (PSU-OH) is slightly larger than that for blends of the d-PSU and PSU having mostly Cl end-groups (PSU-Cl). The miscibility of blends of d-PSU and the PSU end-capped with phthalic anhydride group (PSU-PhAh) largely depends on the degrees of the polymerization of PSU-PhAh. Moreover, the χ parameter for the blend of d-PSU and PSU-PhAh had almost no temperature dependence. As a repulsive interaction between PhAh groups and sulfone unit is so strong that d-PSU/PSU-PhAh1 studied in this work was phase-separated. The miscibility of

blends of d-PSU and a random copolymer of sulfone unit and DPA unit (PSU-COOH) strongly depends on the content of DPA unit. The larger the content of DPA unit, the larger the χ parameter for the blend of d-PSU and PSU-COOH. While the χ parameter for the blend of d-PSU and PSU-COOH with a content of 1.6 mol% DPA unit had almost no temperature dependence, the χ parameter for the blend of d-PSU and PSU-COOH with a content of 4.5 mol% DPA unit showed a UCST type behavior. Furthermore, the blend of d-PSU and PSU-COOH with a content of 6.0 mol% DPA unit was phase-separated in the temperature range covered in this work.

References and Notes

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- ⁶ S. Sakurai, H. Hasegawa, T. Hashimoto, I. G. Hargis, S. L. Aggarwal and C. C. Han, Macromolecules **23**, 451 (1990).
- ⁷ The blend under consideration is phase-separating and hence the SANS profiles are time-dependent, especially at the small q range ($q < 0.08 \text{ nm}^{-1}$) where the profiles are sensitive to the phase-separating domains. In contrast to the profile in the small q range, the profile at the large q range ($q > 0.08 \text{ nm}^{-1}$) is less sensitive to the domains and hence to the time spent for the phase separation, because it depends on concentration fluctuations within the phase-separated domains.⁸ Therefore, we measured the SANS profile (including the profile at $q < 0.08 \text{ nm}^{-1}$) on the vitrified blend.

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¹¹ F. S. Bates, S. B. Dierker and G. D. Wignall, Macromolecules **19**, 1938 (1986).

¹² Spherical volume of Cl group per mole calculated from Van der Waals radius (0.180 nm) is 14.7 cm^3 , the molar volume of PSU is 355.9 cm^3 . If we assume that molar volume of OH group is equal to that of Cl group, x and y is given as follows:

$$x = 14.7 \times 2 / \{ (41/4.07) \times 355.9 + 14.7 \times 2 \} = 0.00811$$

$$y = 14.7 \times 2 / \{ (34/3.17) \times 355.9 + 14.7 \times 2 \} = 0.00766.$$

In this calculation, we used the number averaged degree of polymerization N_n , because the volume fraction of the end group with the volume v_e , f , is calculated as follows in taking polydispersity for the degree of polymerization distribution into consideration:

$$\begin{aligned} f &= 2 \sum_i n_i v_e / \left[\sum_i n_i N_i v_m + 2 \sum_i n_i v_e \right] = 2 v_e / \left[\frac{v_m \sum_i n_i N_i}{\sum_i n_i} + 2 v_e \right] \\ &= 2 v_e / [v_m N_n + 2 v_e] \end{aligned}$$

where n_i is the number of the polymers with degree of polymerization N_i and with volume per segment v_m .

The enthalpic contribution of the χ parameter (χ_H) calculated from solubility parameters of Cl group and OH group is ca. 0.07 at 280 °C. The solubility parameters of Cl group and OH group were cited from "Polymer Hand

Book (third edition)". Hence, $xy \chi_{\text{Cl-OH}}$ is very small and negligible compared with the measured effective χ value shown in Fig. 2-9.

¹³ The molar volume of PhAh is 96.9 cm³. The volume fraction of PhAh y is given by $y=96.9/\{(177/7.19)\times 355.9+96.9+14.7\}=0.0109$, and $z=14.7/\{(177/7.19)\times 355.9+96.9+14.7\}=0.00166$. Since $x=0.00811$, $(x-z)$, $(y+z-x) > 0$.

Chapter 3

Microstructural Effects on the Ginzburg Number and the Crossover Behavior in Deuterated Polybutadiene and Polystyrene Blends

3-1. Introduction

In this chapter, validity of the mean-field approximation, i.e., the Ginzburg criterion for polymer blends is reconsidered. It is well known that the mean-field theory is valid for polymer blends with large molecular weight, apart from a very narrow region close to the critical point. Here, we discuss the microstructural effects on the Ginzburg criterion for polymer blends.

In scattering experiments composition fluctuations in binary blends are measured by the static structure factor $S(q)$ as a function of the scattering vector q . At $q=0$ the structure factor is equal to the susceptibility, e.g., $S(0) \propto (\partial^2 \Delta G / \partial \phi^2)^{-1}$. ΔG is the Gibbs free energy of mixing and ϕ is the volume fraction of one component. Composition fluctuations in homogeneous binary polymer blends are described by the mean-field approximation, e.g., $S^{-1}(0) \propto \tau$, and by the 3D Ising model, e.g., $S^{-1}(0) \propto \tau^{1.24}$, far from and close to the critical temperature T_c of phase separation, respectively.¹⁻⁷ τ is the reduced temperature $|T_c - T| / T$. The crossover temperature between these asymptotic forms is estimated by the Ginzburg criterium. For incompressible polymer blends it was introduced by de Gennes¹ and further discussed by Binder² using the mean-field formalism. Their essential conclusion was that the Ginzburg number Gi , which is proportional to the reduced crossover temperature, is universal and inversely proportional to the degree of polymerization N , e.g., $Gi \propto N^{-1}$. However, recent scattering experiments^{8, 9} and lattice cluster theory computations^{10, 11} have shown that Gi is not a universal function of N . It is speculated that the compressibility of the polymer blend appreciably influences Gi and thereby the crossover between the 3D Ising and the mean-field regime. In this chapter we present further and clearer experimental

evidence of the invalidity of the proposed universality. We have investigated three d-PB/PS (deuterated polybutadiene /polystyrene) blends by small-angle neutron scattering (SANS) near their critical compositions of $\phi_c \cong 0.5$. All blends were prepared with the same average degree of polymerization of $\bar{N} \cong 23$ with a different number of 1,2 (vinyl) units of the d-PB component. The change in the molecular structure of the PB molecule by three different amounts of the vinyl group will somewhat change the mutual enthalpic term Γ_h of the Flory-Huggins parameter $\Gamma(\Gamma = \Gamma_h/T - \Gamma_\sigma)$, but it will certainly influence the packing of the monomers, e.g., the isothermal compressibility or the free volume change upon mixing, which is in the free volume contribution to ΔG . This changes the segmental entropic term Γ_σ .¹²⁻¹⁵ In this way the Flory-Huggins interaction parameter was modified without being influenced by chemical alterations.

As demonstrated recently^{8,9} $S(0)$ can be very well described by the crossover function given in eq. (3-1) in homogeneous systems over the whole temperature range of the mean-field and the 3D Ising range. With $\hat{\tau} = \tau / Gi$ and $\hat{S}(0) = S(0)Gi / C_{MF}$ one gets¹⁶⁻¹⁸

$$\hat{\tau} = \left[1 + 2.333\hat{S}(0)^{\Delta/\gamma} \right]^{(\gamma-1)/\Delta} \times \left\{ \hat{S}^{-1}(0) \left[1 + 2.333\hat{S}(0)^{\Delta/\gamma} \right]^{r/\Delta} \right\} \quad (3-1)$$

Equation (3-1) is a universal function of $\hat{S}(0)$ and $\hat{\tau}$ with Gi and C_{MF} as the characteristic parameters of the system. The critical exponents are those for the 3D Ising case, namely the exponents of the susceptibility $\gamma \cong 1.24$ and the universal correction-to-scaling exponent $\Delta \cong 0.5$. The factor C_{MF} is the critical amplitude of the susceptibility of the mean-field approximation in the one-phase regime. Using the Flory-Huggins theory and thereby the Flory-Huggins parameter Γ one gets⁹

$$C_{MF} = 0.5/(\Gamma_\sigma + \Gamma_c) \quad (3-2)$$

Γ_c indicates the value for Γ at T_c with $\Gamma_c = 0.5[1/V_1\phi_c + 1/V_2(1-\phi_c)]$. Gi as defined in eq. (3-1) is equal to the reduced temperature where a deviation of about 10 % of the crossover function from the 3D Ising form is obtained.⁸ It can be expressed by the ratio of the Ising to the mean-field critical amplitudes of the susceptibility,⁹ namely

$$Gi = 0.069(C / C_{MF})^{1/(\gamma-1)} \quad (3-3)$$

Gi or, respectively, C_{MF} and C are obviously nonuniversal. With eq. (3-2) Gi depends on specific properties of the monomers described by Γ_σ . Only for $\Gamma_\sigma \ll \Gamma_c$ one gets a universal value $Gi \propto N^{-1}$, because $C \propto N^{(2-\gamma)}$ ^{19, 20} and $C_{MF} \propto \Gamma_c^{-1} \propto N$, following eqs. (3-2) and (3-3). This result is in agreement with the formerly discussed prediction by de Gennes and Binder for incompressible blends.^{1, 2} However, if $\Gamma_\sigma \geq \Gamma_c$ the parameters C_{MF} and Gi become nonuniversal. Consequently, no simple universal scaling can be predicted for Gi . Because of the large exponent $1/(\gamma-1) \cong 4.2$ in eq. (3-3), a large segmental entropic term Γ_σ might appreciably increase Gi and thereby widen the temperature range of the 3D Ising regime. Γ_σ is related to the free volume or to the compressibility as it was clearly demonstrated in Ref. 11 where the pressure dependence of Γ was studied for several blends. In the pressure range up to 1.2 kbar it was found that Γ_h is more or less constant, while the absolute value of Γ_σ strongly decreases with pressure. This finding is consistent with lattice cluster theory calculation.^{10, 11} It is generally known that the dilution of a binary polymer mixture with a solvent as a third component increases Gi ²¹ because of the increase of the free volume contribution as well as the decrease of the number of blobs per chain.²² In this respect, it seems reasonable to consider the free volume as a third component.^{10, 11}

3-2. Experimental Section

3-2-1. Sample Preparation and Characterization

The polymers were synthesized by standard anionic polymerization techniques²³ using sec.-butyllithium as initiator. Benzene was the polymerization solvent for polystyrene (PS) and for the polybutadiene with 93 % 1,4-microstructure [d-PB(1,4)]. The polybutadienes with an increased fraction of vinyl microstructure were prepared using tetrahydrofuran [d-PB(1,2)] and diethylether [d-PB(1,4/1,2)] as polar modifiers. Heterogeneity indices smaller than 1.1 were obtained as determined by size exclusion chromatography. Number average molecular weights M_n of the polymers were measured by vapor pressure osmometry. The microstructure of the polybutadienes was characterized by ¹³C NMR spectroscopy. In order to get homogeneous blends the polymer mixtures were dissolved in benzene and freeze dried under high vacuum until a constant weight was achieved. For protection from chemical degradation, 0.1 % of 2,6-di-tert-butyl-4-methylphenol was added and sample cells were filled and closed under an inert gas atmosphere. The characteristic sample parameters are summarized in Table 3-1.

3-2-2. SANS

The neutron experiments were performed at the SANS-U diffractometer at the JRR-3M reactor in JAERI, Japan. The scattering data were corrected for background and then evaluated in absolute units by calibration with a Lupolen standard. The wavelength of the neutrons was $\lambda=8.1 \text{ \AA}$ with $\Delta\lambda/\lambda \cong 0.1$; the sample to detector distance was 4 m.

3-3. Results and Discussion

All experiments were performed for sufficient small q values such that the

Table 3-1 Polymer characteristics: d-PB: deuterated polybutadiene; PS: polystyrene. The heterogeneity indices are smaller than 1.1 as determined by size exclusion chromatography.

System	M_n^a (g/mol)	V_n (cm ³ /mol)	N_n	Microstructure ^b (%)		
				1,2	cis-1,4	trans-1,4
d-PB (1,4)	2100	2100	35	7	40	53
d-PB (1,2/1,4)	1900	1900	32	54		46
d-PB (1,2)	2000	2000	33	91		9
PS	1900	1750	18			

^a By vapor pressure osmometry in toluene.

^b By ¹³C NMR spectroscopy in deuteriochloroform.

data could be analyzed by the Ornstein-Zernike approximation

$$S^{-1}(q) = S^{-1}(0) + Lq^2 \tag{3-4}$$

$S(0)$ is the susceptibility and $L=\xi^2/ S(0)$, where ξ is the correlation length of the composition fluctuations. In Fig. 3-1 scattering data of sample *B* are plotted for various temperatures in a Zimm representation. All scattering data follow a straight line according to eq. (3-4). In Fig. 3-2 the normalized susceptibilities $\hat{S}(0)$ of the samples *A* and *B* are plotted versus the normalized reduced temperature $\hat{\tau}$ in a double logarithmic scale together with the fitted crossover function of eq. (3-1) depicted as a solid line. The experimental data are very well described by the crossover function. The data of sample *B* are completely within the 3D Ising range with $\tau < Gi$, while the data of sample *A* are entirely within the crossover range with

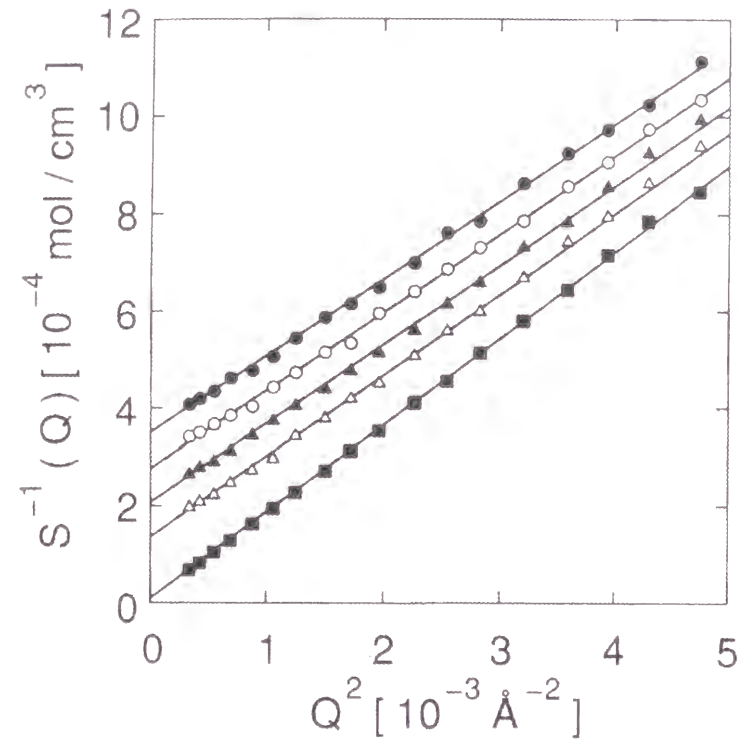


Figure 3-1 SANS data from sample B in Zimm representation at $T=(\bullet)$ 122.6, $(\circ)$ 114.2, $(\blacktriangle)$ 104.9, $(\triangle)$ 96.3, and $(\blacksquare)$ 78.8 °C. The spinodal temperature is at $T=77.4$ °C. The straight lines represent the Ornstein-Zernike approximation of eq. (3-4) from which the susceptibility $S(0)$ is extrapolated.

$\tau > Gi$. The dotted line in Fig. 3-2 represents the correction to scaling form for the mean-field approximation as obtained from the crossover function eq. (3-1) in the limit of $\hat{\tau} \gg 1$:¹⁶⁻¹⁸

$$\hat{S}^{-1}(0) = (\hat{\tau} - 1) \left[-1.098(\hat{\tau} - 1)^{-0.411} \right]. \quad (3-5)$$

Clearly, the experimental data do not coincide with the mean-field approximation. To apply the (mean-field) Flory-Huggins theory directly to the experimental data

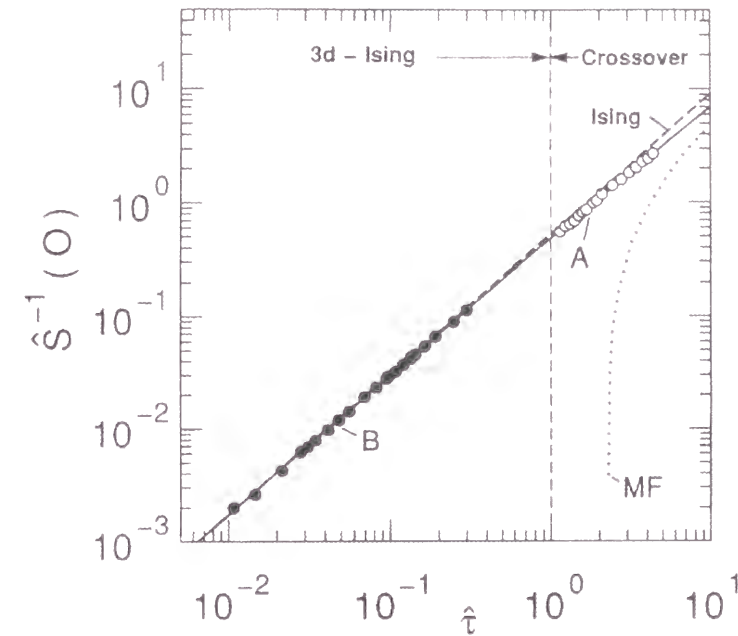


Figure 3-2 The susceptibilities of samples A and B versus the reduced temperature normalized to the universal form of the crossover function in eq. (3-1). The data of sample B are well within the 3D Ising regime (dashed line). The data of sample A are in the crossover range where a description either with the 3D Ising or with the mean-field approximation (dotted line) is rather poor. According to the Ginzburg criterium for incompressible blends the data from both samples should be in the same range.

one has to measure at considerable higher temperatures. The resulting fit parameters Gi and C_{MF} of eq. (3-1), together with T_c , Γ_σ and Γ_h , are summarized in Table 3-2. Γ_σ is evaluated from C_{MF} with eq. (3-2) and Γ_h from $\Gamma_h = T_c^{MF}(\Gamma_c + \Gamma_\sigma)$. The value of T_c^{MF} is calculated from $T_c^{MF} = T_c/(1 - Gi)$ as obtained from the condition $\hat{S}(0) = 0$ in eq. (3-5). The Ginzburg number for system B is about 25 times larger than for A while the Flory-Huggins parameter for sample B is roughly twice as large as for A (Table 3-2). The value of Γ_σ for the samples A and B is 2 and 3 times larger than Γ_c , respectively. These results quite clearly demonstrate the nonuniversality of Gi and supports our observation in Ref. 8 where chemically different blends were studied as a function of $\bar{N}$. Figure 3-3 shows the inverse susceptibility $S^{-1}(0)$ versus the reduced temperature τ of all samples. The two solid lines describing the data of samples A and B represent the crossover function already shown in Fig. 3-2. Surprisingly, this crossover function *could not* be fitted to the data of sample C with the highest vinyl content. In this sample supposedly the value of Γ_σ and, therefore, of the free volume change upon mixing is largest. Instead, in a temperature range from about $T_c + 22$ K to T_c a crossover from 3D Ising to another critical behavior is observed with a critical exponent $\gamma^* \cong 1.39$. Below T_c phase separation occurs. The corresponding data below T_c are not shown in Fig. 3-3.

We speculate that the observation of the critical exponent $\gamma^* \cong 1.39$ in sample C with the highest vinyl content can be interpreted as the occurrence of the “Fisher renormalized” critical behavior. Generally, very close to T_c the dilution of a polymer blend with a solvent may lead to the crossover from 3D Ising to the so called Fisher renormalized (FR) critical behavior, e.g., $S(0) \propto \tau^{\gamma^*}$ with $\gamma^* = \gamma/(1-\alpha) \cong 1.39$, where $\alpha \cong 0.11$ is the 3D Ising critical exponent of the specific heat. This crossover is caused by fluctuations of the total polymer density.^{21, 24, 25} So far, the observation of the FR critical behavior was reported for the ternary liquid ethanol-water-chloroform system.²⁶ The FR crossover was discussed but not observed

Table 3-2 Results for the blends from the crossover function. Systems: A [d-PB(1,4)/PS], B [d-PB(1,2/1,4)/PS], and C [d-PB(1,2)/PS]. The average degree of polymerization of the blend has been calculated from $\bar{N}^{-1} = \phi_A / N_A + \phi_B / N_B$.⁵ T_c^{MF} was evaluated from $T_c^{MF} = T_c/(1-Gi)$ as obtained from eq. (3-5).

System	A	B	C
$\phi(\text{d-PB})$	0.5	0.525	0.521
Γ_c (10^{-3}mol/cm^3)	1	1.04	1.04
$\bar{N}$	23.7	22.5	22.8
$10^2 Gi$	1.53	38.3	-
C_{MF} (cm^3/mol)	169	124	-
C (cm^3/mol)	118	187	-
$1/T_c$ (10^{-3}K^{-1})	3.027 (57.4 °C)	2.854 (77.4 °C)	2.689 (98.8 °C) ^a
$1/T_c^{MF}$ (10^{-3}K^{-1})	2.98 (62.6 °C)	1.76 (295 °C)	-
Γ_σ (10^{-3}mol/cm^3)	1.97	3.01	-
Γ_h (mol K/cm^3)	1	2.3	-

^a T_c critical temperature of Fisher renormalized critical range.

in the polymer blend polystyrene/poly(methylmethacrylate) in a solvent.²⁷ There is evidence of a FR critical behavior from dynamical light scattering experiments for the binary blend PB/d-PS with a low molecular weight²⁸ and for the high molecular ternary blend PB/d-PS in a solvent.²⁹ Two diffusive relaxation modes were observed in both cases. The slower one was interpreted in terms of density fluctuations. Their correlation length has critical exponent in agreement with the FR prediction. Therefore, in binary blends density fluctuations are visible by dynamical light scattering which might give rise to the Fisher renormalized critical behavior as for sample C in Fig. 3-3.

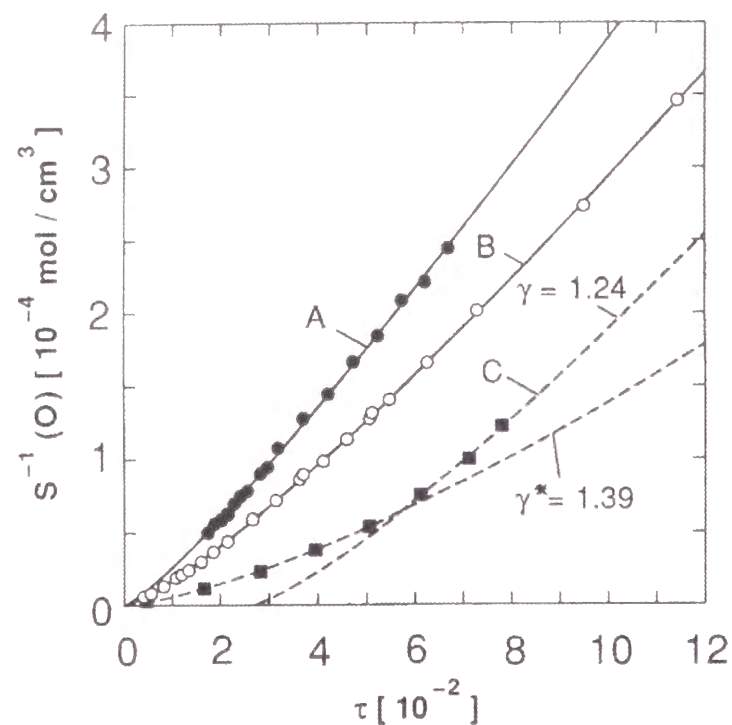


Figure 3-3 Inverse susceptibility versus the reduced temperature. The data of systems A and B are the same as in Fig. 3-2. The solid lines are fits of the crossover function in eq. (3-1). $S(0)$ of system C shows a crossover from 3D Ising ($\gamma \cong 1.24$) to the Fisher renormalized (FR) critical behavior ($\gamma^* \cong 1.39$). The increase of G_i together with the observation of the FR critical behavior with the vinyl content of the d-PB component is an indication of the increase of free volume change upon mixing or compressibility.⁶

3-4. Conclusion

In summary, the susceptibility $S(0)$ in three d-PB/PS polymer blends was measured by SANS. The blends were chosen with the same degree of polymerization ($\bar{N} \cong 23$) near their critical composition $\phi_c \cong 0.5$, and with a d-PB statistical copolymer of different vinyl contents. It was found that the Ginzburg number strongly increases with the degree of the vinyl content. For the sample with the highest vinyl content, unexpectedly, a crossover to a critical behavior

similar to the Fisher renormalized one was found. This crossover is predicted in ternary systems such as for binary polymer blends in a solvent very near T_c . A larger amount of vacancies or free volume change upon mixing in our sample C could be like a third and chemically inert component which leads to density fluctuations near the critical temperature.

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Chapter 4

High Pressure Cell for Small-Angle Neutron and Light Scattering Studies of Phase Transitions in Polymer Systems

4-1. Introduction

In chapters 2 and 3, the miscibility and critical phenomena of polymer blends were investigated by using temperatures as thermodynamic variables. In this chapter we study pressure effects on the miscibility of a diblock copolymer by using the high-pressure cells for small-angle neutron scattering.

Recently, numerous studies have been made on phase transitions of polymer systems such as polymer mixtures, polymer solutions and block copolymers.^{1, 2} Small-angle neutron scattering (SANS) and light scattering (LS) have made a great contribution to phase transition studies of critical phenomena, miscibility and phase separation processes, etc. Temperature has so far been used as the thermodynamic variable in most of the phase transition studies. However, it has been pointed out that pressure is also an important thermodynamic parameter in phase transitions of polymer systems.³⁻⁹ Pressure affects the free volumes of polymer systems and hence their phase transitions. In polymer systems, the combinatorial entropy term in Flory-Huggins expression of free energy of mixing is inversely proportional to the degree of polymerization N .¹⁰ It means that the contribution of the other factors to the free energy of mixing becomes N times larger than that in a small molecular system, and therefore, it is expected that the free volume effects also become N times larger.

With these points in mind, we have designed and constructed two high pressure cells, one for SANS and the other for LS measurements. By using the cells, we can investigate the effect of pressure on the miscibility and the critical phenomena of polymer systems. In addition, we can study the kinetics and the phase transition process induced by a pressure jump. So far, many experimental

attempts have been made to study the dynamics of phase transitions of polymer systems by temperature jumps. However, a temperature jump cannot be completed instantaneously and it takes some time for the target temperature to be attained by thermal conduction. Unless the time is sufficiently short relative to the rate of the phase transition, it is extremely difficult to investigate the dynamics. The response of pressure in a pressure jump is much faster and enables us to follow the dynamics of a rapid phase transition. As an example of dynamic measurements by a pressure jump, we show a time-resolved neutron scattering measurement of the microphase separation process of a diblock copolymer.

Several high pressure cells for the scattering studies of polymer systems have been reported to date. High-pressure cells for SANS were reported by the groups in Jülich^{5, 6} and at National Institute of Standards and Technology (NIST)⁷, for small-angle X-ray scattering (SAXS) by the group in Princeton University⁸ and for LS from supercritical polymer liquids and solutions by Kojima et al.⁹ Comparisons of the maximum applicable pressure P_{max} , the stability of pressure ΔP , the measurable temperature range T_{range} and the stability of temperature ΔT for their cells are summarized in Table 4-1. The maximum applicable pressure is 200 [MPa] for Jülich, 100 [MPa] for NIST, 300 [MPa] for Princeton, 34.3 [MPa] for Kojima et al. and 200 [MPa] for our cell. ΔP are of the order of 0.5% of the applied pressure for Princeton, 0.01 [MPa] for Kojima et al. and 0.5 [MPa] for the duration of several hours for our cell. Temperature can be varied from 253 to 473 K with accuracy of ± 0.1 K for Jülich, from 273 to 458 K with accuracy of ± 0.05 K for Princeton, to 573 K with accuracy of ± 0.1 K for Kojima et al. and from 273 to 523 K with accuracy of ± 0.005 K during the 30 minutes measurement for our cell. Thus, our cell has equal or higher performance compared with other high pressure cells.

Among many features of these high-pressure cells, we are most interested in the methods employed to separate the sample and the pressurizing liquid.

Table 4-1. Comparison between performance of our high pressure cell and those of others' cells.

	Jülich	NIST	Princeton	Kojima et al.	This work
P_{max} /MPa	200	100	300	34.3	200
ΔP /MPa	-	-	0.5 % ^a	0.01	0.5
T_{range} /K	253-473	-	273-458	-573	273-523
ΔT /K	± 0.1	-	± 0.05	± 0.1	± 0.005

^a The accuracy and resolution of the sensor are of the order of 0.5 % of the applied pressure.

The sample is separated from the pressurizing liquid by an O-ring in the two cells for SANS in Jülich and at NIST. The pressurizing liquid comes into direct contact with sample in the cell of the Princeton group. Kojima et al. used the sample itself (supercritical polymer solutions) as the pressurizing liquid.

On the other hand, we employ a free piston and an O-ring, and use either of them to separate the liquid sample from the pressurizing liquid depending on the viscosity of the sample. It seems that these methods are most reliable for the separation. The free piston is used for low viscosity liquids such as dilute polymer solutions or small-molecular liquids and the O-ring is used for high viscosity liquids such as polymer blends or block copolymers (These details are discussed in Sec. 4-2). It is difficult to keep low viscosity liquids inside the O-ring. By using both methods properly, not only high viscosity liquids but also low viscosity liquids can be measured in our cells.

Moreover, we have designed the body of our cells with two screw holes besides that for applying pressure through a pressurizing liquid, so that we can make various modifications, e.g., (i) temperature and pressure of the sample can be

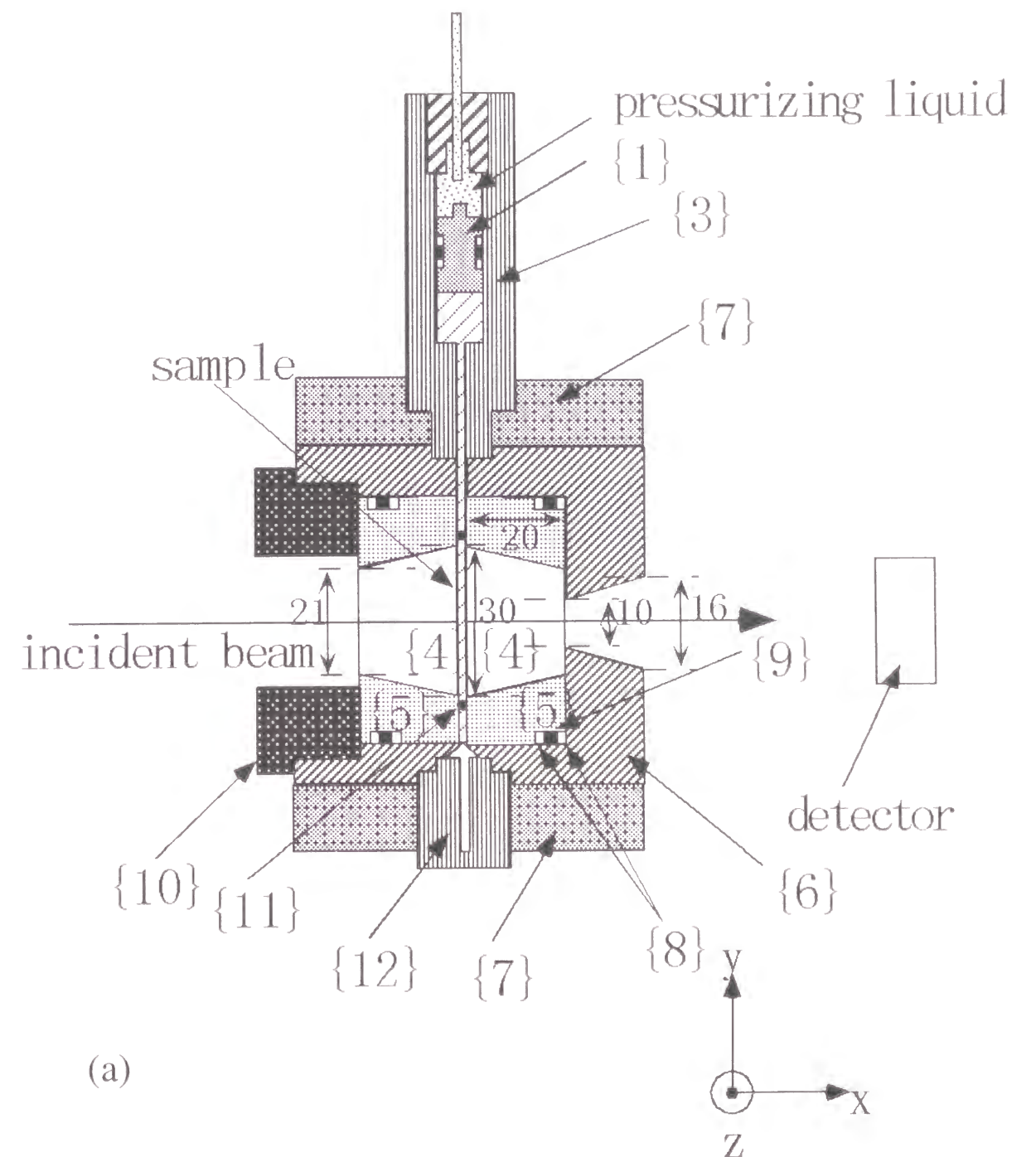
directly measured by inserting a pressure gauge and a thermometer into these holes, (ii) an apparatus for pressure drop to an arbitrary pressure can be fixed on the cells by using these holes, (iii) an apparatus for pressure release can be fixed on the cells to avoid the drift of pressure with an increase of temperature as pointed out by NIST group ⁷, etc. The additional advantage of our cells is that time-resolved measurements after pressure jumps can be performed. In addition, by using both cells for SANS and LS, we can investigate structures (fluctuations) of a very wide spatial scale.

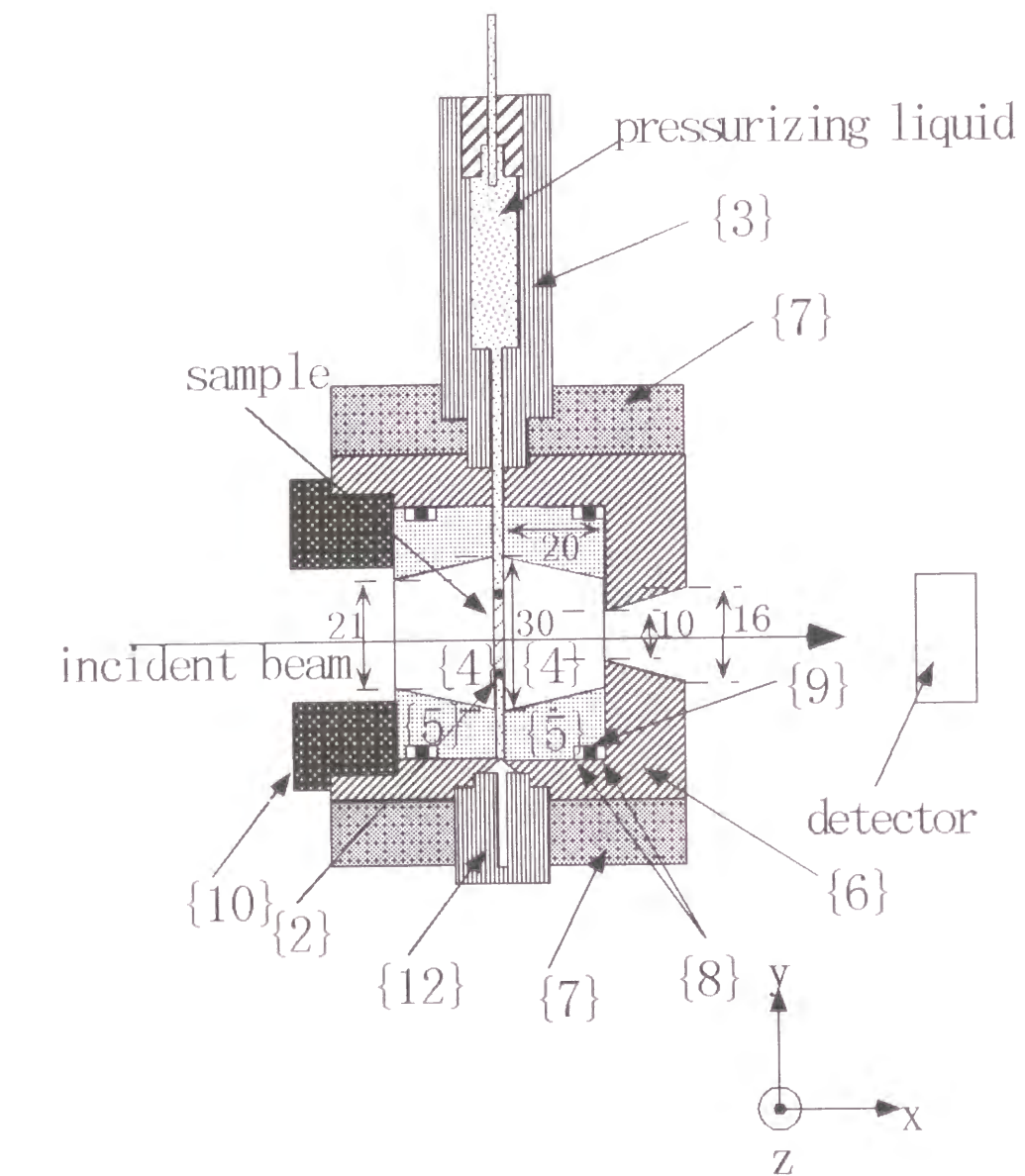
In this chapter, we report on the design and the construction of the high-pressure cells for SANS and LS studies of polymer systems and also on a preliminary SANS experiment with the cell: pressure effects on the miscibility and the order-disorder transition temperature (T_{ODT}) of a deuterated polybutadiene-*block*-polyisoprene diblock copolymer (DPB-HPI) and its microphase separation process by a pressure jump. We show that pressure strongly affects the SANS profiles of this system.

4-2. Instrumentation

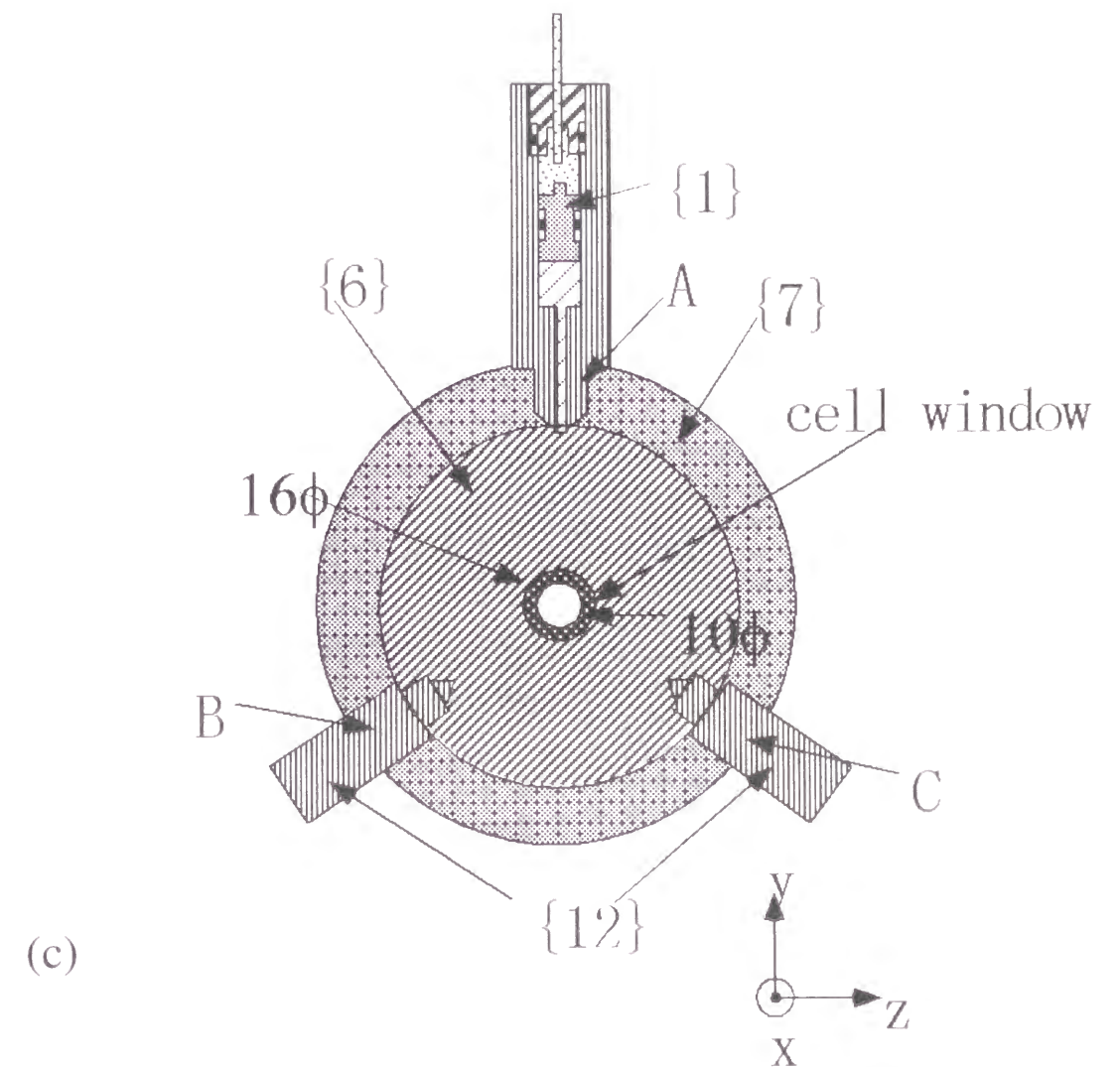
4-2-1. SANS and LS Cells

The sample is separated from the pressurizing liquid in two ways: by a free piston {1} (Fig. 4-1a) and by an O-ring made of silicon {2} (Fig. 4-1b). These figures show the cross-sectional views of the high pressure cell for SANS studies of polymer systems (hereafter shortened to “the SANS cell”) in a plane parallel to the incident beam, while Fig. 4-1c shows that perpendicular to the incident beam viewed from the detector side. Figures 4-2a and 4-2b show cross-sectional views of the high pressure cell for LS studies (“the LS cell”) in a plane parallel to and perpendicular to the incident beam viewed from the detector side, respectively. The only difference between the SANS and LS cells is the aperture angles of the cell windows both on the incident and scattered sides.





(b)



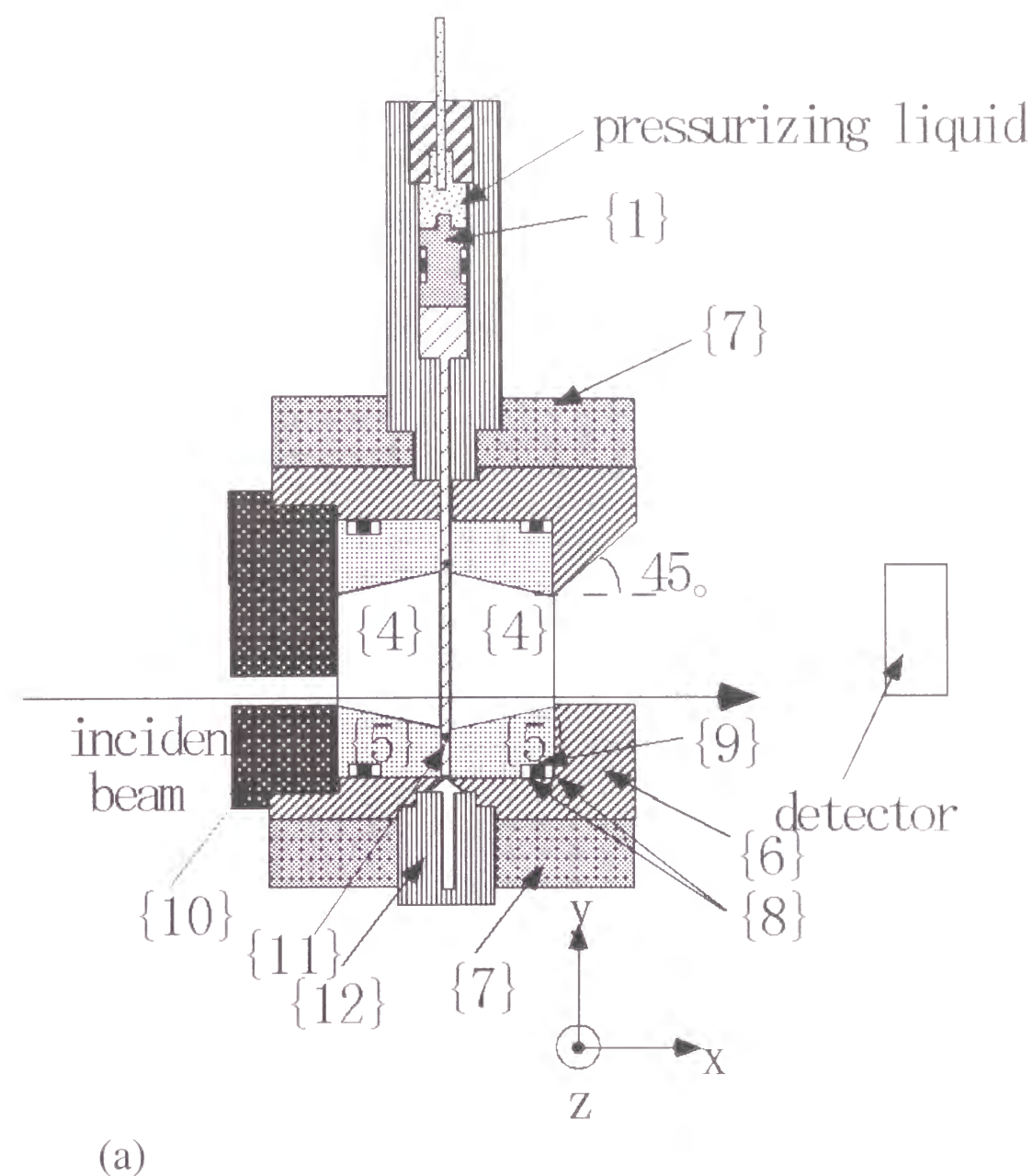
(c)

Figure 4-1. Cross-sectional views of the high pressure cell for SANS parallel to incident beam: free piston method (a) and O-ring method (b).

Cross-sectional views for SANS (c) perpendicular to incident beam. The incident beam is in the x direction from left to right in (a) and (b), and out of the paper in (c). {1}: free piston, {2}: Silicon O-ring, {3}: stainless pipe screwed into the body of the cell, {4}: sapphire windows, {5}: stainless-steel frames on the sapphire windows, {6}: body of the cell made of stainless-steel, {7}: cast aluminum heater, {8}: copper O-rings, {9}: Teflon O-ring containing copper powder, {10}: stainless-steel screw which has an opening for the neutron beam in the center, {11}: metal spacer, {12}: stoppers or a thermometer or a pressure gauge. {A, B and C}: screw holes.

As shown in Figs. 4-1a and 4-1b, the free piston {1} is placed inside the stainless pipe {3} which is screwed into the body of the cell {6} and the O-ring {2} is placed between the sapphire windows {4}. 20 mm thick sapphire windows of a truncated-cone shape {4} are attached to a frame made of stainless-steel (SUS630) {5} and the sample is sandwiched between the bottom sides of the windows. The sapphire windows are lapped to fit the stainless-steel frame. As tapered windows are used, they are tightly fixed on the frame as pressure is applied and can hold pressure up to 200 [MPa]. The top and bottom diameters of the truncated-cone windows are 21 mm and 30 mm, respectively. The body of the cell {6} is made of stainless-steel which is surrounded by a cast aluminum heater {7}. Besides the silicon O-ring {2}, three O-rings, two made of copper {8} and one made of Teflon containing copper powder {9}, are the pressure seals between the body of the cell {6} and the stainless-steel frames {5} fixed on the sapphire windows. The O-ring made of Teflon containing copper powder {9} is placed between the two copper O-rings {8}. A stainless-steel screw {10} which has an opening for the neutron beam path in the center is tightened on the body of the cell in order to fix the windows. The opening of the screw of the LS cell is much smaller than that of the SANS cell as shown in Figs. 4-1a and 4-2a. As shown in Fig. 4-1, the SANS cell has a tapered opening on the detector side. Maximum and minimum diameters of the opening are 16 and 10 mm, respectively. A q -range less than $2.0 \times 10^{-3} [\text{\AA}^{-1}]$ for $\lambda = 7 [\text{\AA}]$ can be covered in the SANS cell, where q is a scattering vector and defined as $q = (4\pi/\lambda) \sin(\theta/2)$ with λ and θ being the wavelength in the medium and the scattering angle, respectively.

The LS cell has a slit opening on the detector side (Fig. 4-2). The opening is tapered at an angle of 45° in one direction in order to cover a wide q range. The range of scattering angles in the sample is within 28° , which means that the q range is within $7.23 \times 10^{-4} [\text{\AA}^{-1}]$ for $\lambda = 6328 [\text{\AA}]$.



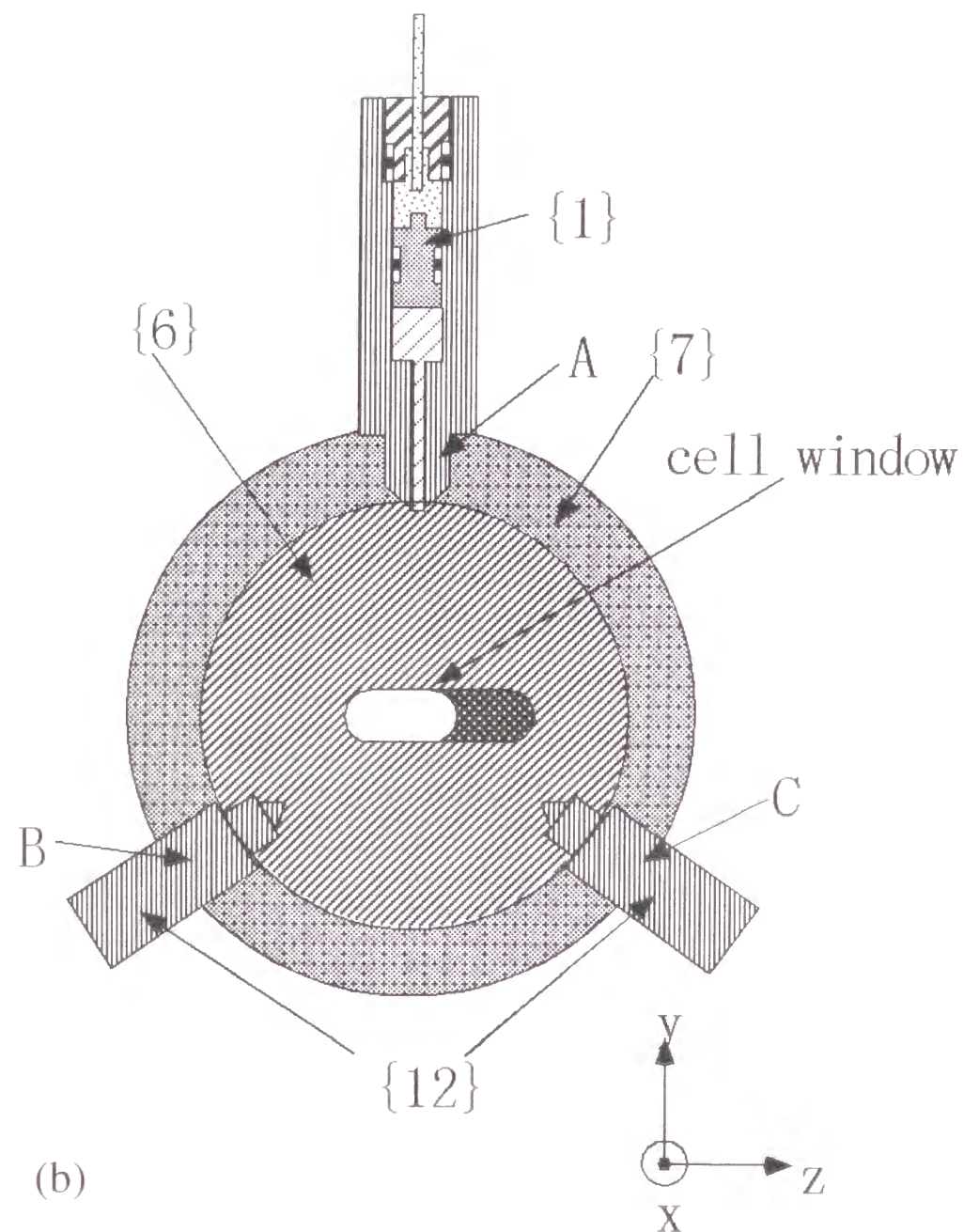


Figure 4-2. Cross-sectional views of the high pressure cell for LS parallel (a) and perpendicular (b) to incident beam. The numbers designating the parts of the cell and the direction of incident beam are the same as those in Fig. 4-1.

Sample thickness can be adjusted by a metal spacer {11} between 0.2 and 3mm.

The body of the cell has three screw holes A, B and C (Figs. 4-1c and 4-2b). One of them (A) is for applying pressure through a pressurizing liquid. By inserting a thermometer {12} or a pressure gauge {12} into the other holes (B and C), we can directly measure the temperature and the pressure of the sample. When they are not used, the screw holes {12} are plugged with stoppers.

4-2-2. Temperature and Pressure Control Units

A schematic diagram of the high pressure apparatus including the pressure gauge and the temperature controller is shown in Fig. 4-3. The body of the cell is connected by a flexible stainless-steel capillary tube {1} to a manually operated pump {2} filled with a pressurizing liquid such as diethylene glycol or paraffin oil (Fig. 4-3). Pressures up to 200 [MPa] can be generated by the pump which is equipped with a valve for pressure release {3} (Fig. 4-3). By opening the valve and releasing the pressure, we can perform dynamic measurements of phenomena induced by the pressure drop. (The current apparatus allows only a pressure drop to 0.1 [MPa]. However, a small modification will allow a pressure drop to an arbitrary pressure) Pressure is measured with a 6 inch Heise gauge {4} (Fig. 4-3) which can read up to 250 [MPa]. The pressure is stable within ± 0.5 [MPa] during an experiment of several hours. The cell can be heated up by a cast aluminum heater {7} which encloses the body of the cell. Moreover, the cell is covered with a thermal shield {5} (Fig. 4-3), with quartz windows. Temperature is monitored with a platinum resistance {6} attached to the body of the cell and controlled by a computer, and another platinum resistance {7} is attached to the cast aluminum heater for temperature control. The attainable temperature range is between 273 and 523 K. The accuracy of temperature control is within ± 0.005 K during a measurement time of 30 minutes.

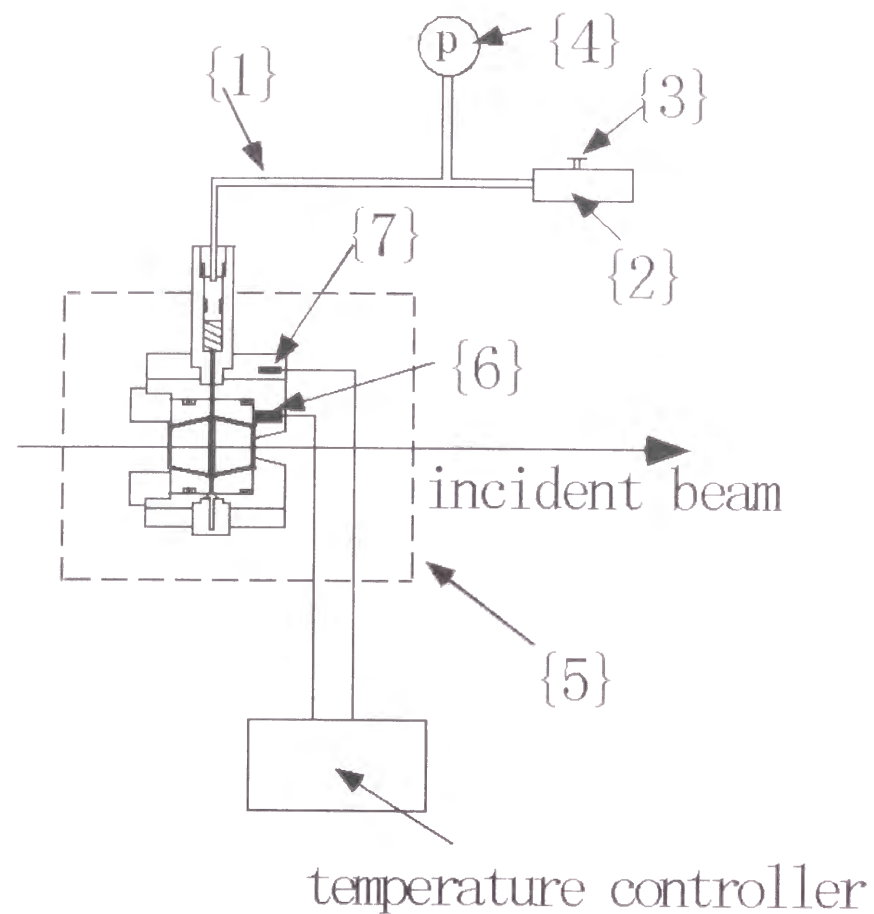


Figure 4-3. Schematic diagram of the high pressure apparatus. {1}: capillary tube, {2}: manually-operated pump, {3}: valve attached to the pump, {4}: Heise pressure gauge, {5}: thermal shield, {6}: platinum resistor attached to the stainless of the body, {7}: platinum resistor attached to cast aluminum heater.

4-2-3. Correction for the Change of Sample Thickness

There is a structural problem with the cell. As the cells do not have the mechanism to hold the two pieces of the windows ({4} in Figs. 4-1 and 4-2) in position, they tend to be pushed away from each other as the pressure increases, resulting in an increase in the sample thickness. Therefore, a correction for the change of sample thickness with pressure is necessary. The change of sample thickness is estimated by measuring the transmission of polyisoprene (HPI) homopolymer as a function of pressure.

According to Lambert's law, transmission $T_r (=I/I_0)$ of a sample is described by the following expression

$$T_r = \exp(-\tau d), \quad (4-1)$$

where I and I_0 are the transmitted intensity with and without the sample, respectively, d is the sample thickness, and τ is the turbidity which is a function of pressure. The value of τ at $P=0.1$ [MPa] is obtained by measuring the transmission of HPI homopolymer sample whose thickness is known. The pressure change of the density of HPI homopolymer is estimated from the pressure-volume-temperature (PVT) data in the literature.¹¹ Assuming the linear relation between the pressure change of τ and that of the density, the change of the sample thickness is evaluated by using eq (4-1). Figure 4-4 shows the pressure dependence of the sample thickness normalized to the thickness at $P=0.1$ [MPa], which is used for the absolute intensity correction.

4-3. Experimental Section

In this section, we report on a preliminary SANS experiment for deuterated polybutadiene-*block*-polyisoprene diblock copolymer (DPB-HPI). The experiment was carried out using the SANS cell with the O-ring method (Fig. 4-1b).

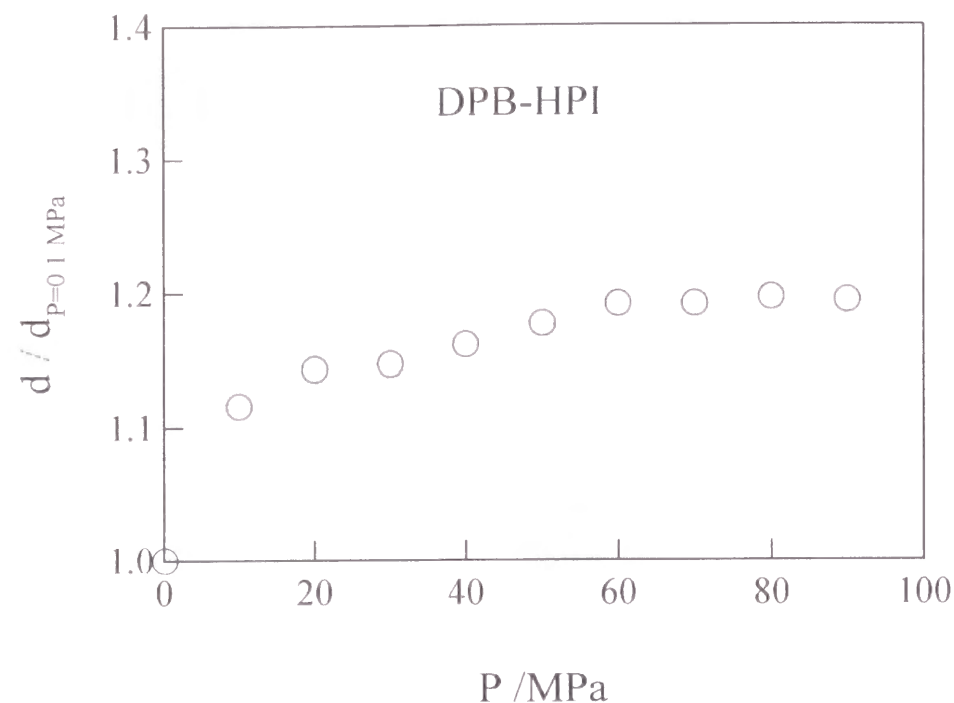


Figure 4-4. Sample thickness d normalized to that at $P=0.1$ MPa plotted as a function of pressure.

4-3-1. SANS

Small-angle neutron scattering (SANS) measurements were performed by using the SANS instrument (SANS-U) of the Institute for Solid State Physics of the University of Tokyo at the JRR-3M reactor at the Japan Atomic Energy Research Institute in Tokai. A neutron beam with the wavelength $\lambda=7\text{\AA}$ and $\Delta\lambda/\lambda \cong 0.1$ monochromatized by a velocity selector was used. The scattering intensity data were collected by a two dimensional detector and then circularly averaged in order to obtain the scattering profiles as a function of q . The scattering profiles were corrected for the empty cell, electrical background and transmission. The sample-

to-detector distance was 8 m. The obtained profiles were normalized to the absolute unit (cm^{-1}) by using Lupolen[®] as a standard sample.

4-3-2. Sample Preparation and Characterization

Deuterated polybutadiene-*block*-polyisoprene diblock copolymer (DPB-HPI) was used in this work. The DPB-HPI was synthesized by sequential living anionic polymerization. The number-averaged molecular weight M_n and polydispersity index (M_w/M_n) of the DPB-HPI are 4.90×10^5 (GPC, equivalent to standard polystyrene) and 1.11, respectively. Volume fraction of DPB is 0.53. The microstructure of the DPB and the HPI was estimated from ^2H -NMR and ^1H -NMR measurements, respectively. The microstructure of the DPB is 94.8 % 1,4 and 5.2 % 1,2 linkage. The microstructure of the HPI is 94.8 % 1,4 and 5.2 % 3,4 linkage.

4-4. Results and Discussion

In this section, we show the pressure dependencies of the order-disorder transition temperature (T_{ODT}) and the microphase separation process induced by a pressure jump for the DPB-HPI block copolymer. A diblock copolymer has two different component polymer chains connected by a covalent bond. Therefore, even when there is strong net repulsion between the two components, only microphase separation occurs instead of macrophase separation as observed in the liquid mixtures of small-molecules and polymer blends.^{12, 13} The microphase separation occurs at a temperature below T_{ODT} for the block copolymers of an upper critical order-disorder transition (ODT) temperature (UCODTT) type and above T_{ODT} for the block copolymers of a lower critical ODT temperature (LCODTT) type: the spatial scale of the microphase is on the order of ten nanometers (i.e., the order of the radius of gyration of the polymer chain). DPB-HPI used in this work possesses an LCODTT-type microphase transition at least at atmospheric pressure

($P=0.1$ [MPa]). Recently, it has been pointed out that thermal noise effect strongly affects T_{ODT} , giving a thermal fluctuation-induced first-order phase transition at T_{ODT} .¹⁴⁻¹⁹ It is an intriguing physical problem to study how pressure affects the thermal noise and therefore T_{ODT} and miscibility of block copolymers.

Pressure dependence of the scattering profiles for DPB-HPI at 341.4 K is shown in Fig. 4-5. Figure 4-6 shows the magnified view of the scattering profiles around the second-order scattering peak in Fig. 4-5 (at $q \approx 0.014$ [$\text{\AA}^{-1}$]). All the scattering profiles have the primary scattering maximum at $q_m \approx 0.007$ [$\text{\AA}^{-1}$]. Scattering profiles in diblock copolymers exhibit a broad scattering maximum even in the disordered state due to the correlation hole effect.^{14, 20} On the other hand, the higher order peaks caused by a periodicity with long-range order are a strong indication of the ordered state. It is found from Figs. 4-5 and 4-6 that the scattering profiles are significantly affected by magnitude of pressure applied. The maximum scattering intensity decreases with increasing pressure, indicating an increase in the miscibility. The second-order peak is observed at a pressure below 26 [MPa], indicating that DPB-HPI is in the ordered state, while the disappearance of the second-order peak at a pressure above 38 [MPa] suggests that it is in the disordered state. This behavior suggests that DPB-HPI has a phase diagram (pressure-composition diagram) of an upper critical order-disorder transition pressure (UCODTP) type. Namely, DPB-HPI is in the disordered state under high pressure, and in the ordered state under low pressure. The pressure suppresses microphase separation and promotes miscibility of the block chains. It is predicted from the result in Figs. 4-5 and 4-6 that the pressure at which the order-disorder transition occurs (P_{ODT}) is between 26 and 38 [MPa] at $T=341.4$ K. Meanwhile, the first- and second-order peaks are located at the scattering vectors in the ratio of 1:2, indicating that the alternating lamella structure is formed in the ordered state, which is consistent with the nearly symmetric composition of DPB-HPI.

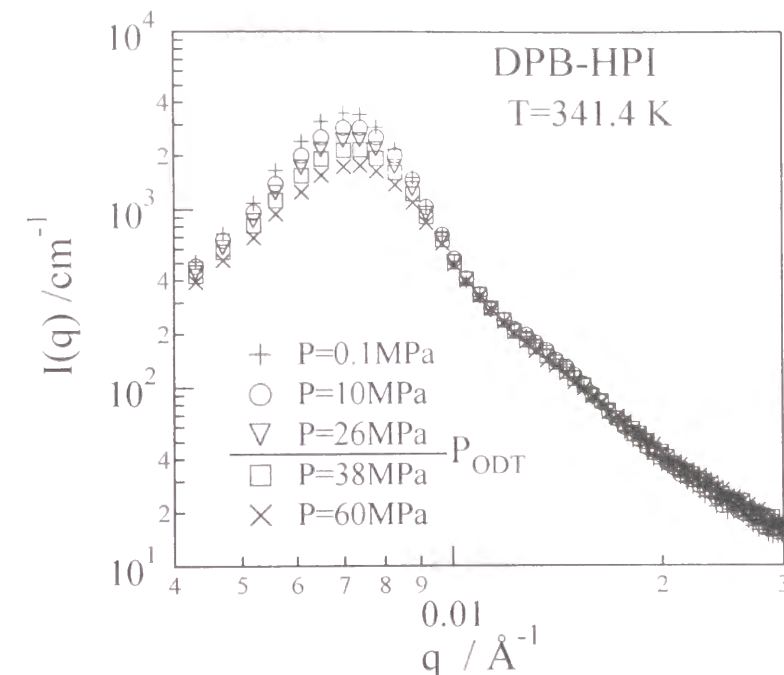


Figure 4-5. Scattering profiles for the DPB-HPI at various pressures at $T=341.4$ K.

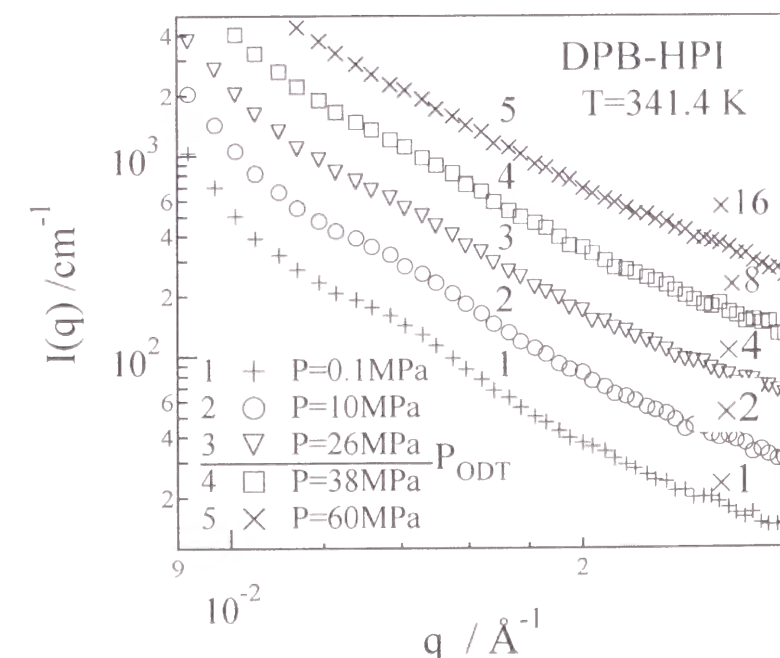


Figure 4-6. Magnification of Fig. 4-5 around the second-order peak at $q \approx 0.014$ $\text{\AA}^{-1}$.

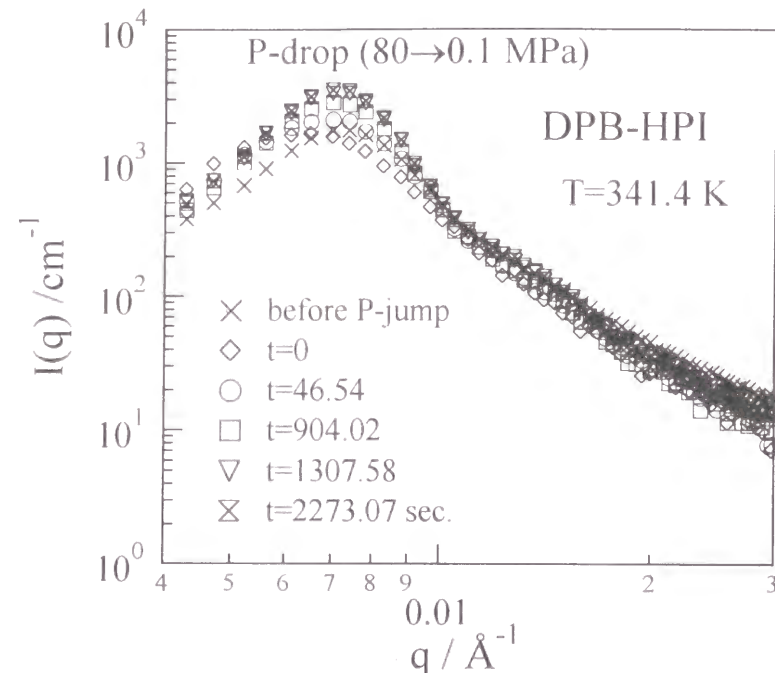


Figure 4-7. Time change in scattering profiles after the pressure drop (from 80 [MPa] to 0.1 [MPa]) at $T=341.4$ K.

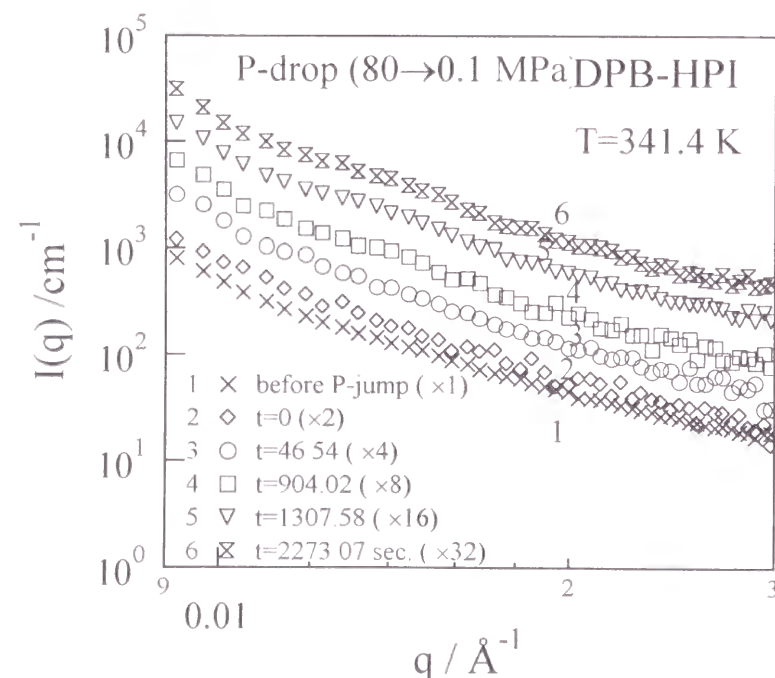


Figure 4-8. Magnification of Fig. 4-7 around the second-order peak at $q \approx 0.014 \text{ \AA}^{-1}$.

Time-resolved neutron scattering measurements during the phase transition induced by a pressure jump were performed in order to investigate microphase separation process of DPB-HPI. Figure 4-7 shows the change in the scattering profiles with time (in seconds) after DPB-HPI was quenched from a disordered state to an ordered state by a pressure drop. Pressure was dropped from 80 (single-phase) to 0.1 [MPa] (microphase-separated) at 341.4 K. Figure 4-8 shows a magnification of the scattering profiles around the second-order peak. Fluctuation of temperature was within ± 0.1 K during the measurements. The scattering profile in the equilibrium state before the pressure jump is also shown in Figs. 4-7 and 4-8. To our surprise, at the moment of the pressure jump ($t=0$), q_m (the value of q at the scattering maximum) shifts toward lower q as shown in Fig. 4-7. At later time q_m shifts back to its higher value. The scattered intensity also increases with time.

Moreover, as shown in Fig. 4-8, the profiles at $t \geq 904.02$ s start to exhibit a second-order peak. The appearance of the second-order peak implies that ordering into lamella microdomains started to occur with time. It was recently reported for a polystyrene-*block*-polyisoprene diblock copolymer that the microphase separation into lamella microdomains induced by temperature jump progresses via a nucleation and growth (NG) process with an incubation period of about 400 s at the quench depth ΔT of 2.7 K ($\Delta T = T_{ODT} - T$, where T_{ODT} and T are order-disorder transition temperature and measuring temperature, respectively).²¹ The effect of pressure on the incubation time or the NG process will be reserved for future work.

4-5. Conclusion

In summary, we have designed and constructed high pressure cells for both small-angle neutron scattering (SANS) and light scattering (LS) studies in order to investigate pressure effects on phase transitions of polymer systems. We can investigate structures of a wide spatial scale by using the cells. The cells can be used for both high and low viscosity liquids. Moreover, dynamics of phase

transitions induced by a pressure drop can be measured by using the cells. The maximum pressure that can be applied to the cells is ca. 200 [MPa], and the stability of pressure control is within ± 0.5 [MPa] during the measurement time of several hours. A Preliminary experiment on phase transitions of a diblock copolymer which are high viscosity liquids, have been carried out using the cell for SANS studies. The diblock copolymer has a phase diagram of UCODTP type phase diagram. The phase transition is significantly affected by the applied pressure.

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Chapter 5

Small-Angle Neutron Scattering Study of Anomalous Mixing Behaviors in Deuterated Polystyrene/Poly(vinyl methyl ether) Mixtures near the Glass Transition Temperature

5-1. Introduction

Mobility of polymers becomes extremely slow, as temperature is lowered or approaches the glass transition temperature (T_g). In this chapter, we discuss the influence of vitrification of polymers on the mixing behaviors of miscible polymer mixtures. This problem will be interesting especially for the miscible polymer mixtures having a large difference in T_g 's of pure components, because mobility of one constituent polymer is largely different from that of the other near the T_g of the mixture. Such asymmetry in mobility of each component may affect the miscibility of polymer mixtures. In fact, this work demonstrates that the asymmetry in mobility of each component does.

The thermal concentration fluctuations (TCF) of polymer mixtures in the single-phase state have been extensively studied from both experimental and theoretical points of view. SANS made great contributions to the studies of the TCF. There are many indications that the TCF of polymer mixtures in the single-phase state far above their glass transition are described well in the context of incompressible random phase approximation (RPA).¹ The Flory-Huggins' interaction parameter χ experimentally determined from the scattering profiles usually has the form as follows.²⁻⁵

$$\chi = \sigma + h / T \quad (5-1)$$

In this work we studied the TCF of polymer mixtures by means of the SANS method down to the temperature range in which the vitrification of the

mixtures becomes important. We prepared two types of mixtures, i.e. (i) deuterated polystyrene (DPS)/poly(vinyl methyl ether) (PVME) which has a large difference in the T_g 's of the pure components (the T_g 's of DPS and PVME are 378 and 251K, respectively) and (ii) deuterated polybutadiene (DPB)/protonated polybutadiene (HPB) and DPB/protonated polyisoprene (HPI) which have almost equal T_g 's for pure components (the T_g 's of DPB, HPB, and HPI are 186, 182 and 215K, respectively). Numerous studies on SANS behaviors in the single-phase state for the DPS/PVME mixture have been made so far.^{2-4, 6} However, most of these measurements were carried out at high temperatures at which the systems were free from vitrification. To our knowledge, the anomalous mixing behaviors in the DPS/PVME mixture have not been reported, except for the report by Schwahn et al.⁶ on the unusual behavior of the structure factor at scattering vector $q=0$. For the mixture of DPS/PVME 37/63 vol/vol they carried out SANS measurements down to a temperature of ca. 90 °C, which corresponds to a temperature of ca. 100 K above the T_g of the mixture. Even if measurements are performed near the T_g for particular blends with characteristics which we show in this chapter, we have to care about the annealing time: the annealing time should be sufficiently long. We emphasize that it is difficult to find the anomalous behaviors, unless we pay attention to the annealing time.

5-2. Experimental Section

5-2-1. Sample Preparation and Characterization

The characterization of the polymer samples used in the experiment is summarized in Table 5-1. DPS, DPB, HPB, and HPI were synthesized by living anionic polymerization. DPB and HPB have almost the same microstructures, i.e., DPB has 38% cis-1,4, 46% trans-1,4, and 16% 1,2 linkages, while HPB has 28% cis-1,4, 56% trans-1,4, and 16% 1,2 linkages. HPB and HPI were kindly

supplied by Japan Synthetic Rubber Co. Ltd. PVME was synthesized in toluene by cationic polymerization using boron trifluoride diethyl ether as the initiator. We prepared the binary mixtures of DPS/PVME with the compositions of 50/50 and 70.6/29.4 wt %/wt %. Hereafter we shall designate the composition X/Y wt %/wt % as X/Y for simplicity. We also prepared the other binary mixtures of DPB/HPB with the composition of 49.8/50.2 and DPB/HPI with the composition of 59.7/40.3. All the mixtures were dissolved in toluene, and the solvent was evaporated slowly in a Petri dish at room temperature. In order to remove the solvent perfectly, the DPS/PVME films were further dried in a vacuum oven at ca. 80 °C for 2 days. The DPB/HPB and DPB/HPI films were dried at room temperature for 2 days.

Table 5-1 Sample Characterization

sample	$M_n \times 10^{-3}$ ^a	M_w/M_n ^a	microstructure, % ^c		
			1,2	3,4	cis-1,4 trans-1,4
DPS	102	1.10			
PVME	27 ^b	1.40			
DPB	59	1.03	16		38 46
HPB	48	1.20	16		28 56
HPI	78	1.30		7.5	70.4 22.1

^a Measured by size exclusion chromatography equipped with light scattering.

^b Measured by membrane osmometry. ^c The microstructure for DPB was measured by ¹³C-NMR, while those for HPB and HPI were measured by IR spectroscopy.

5-2-2. SANS

The small-angle neutron scattering (SANS) experiments were carried out using a 20 m SANS instrument (SANS-J) at the JRR-3M research reactor of the Japan Atomic Energy Research Institute (JAERI) in Tokai. The cold neutrons

were monochromatized with a velocity selector to have the wavelength of $\lambda = 6.25$ or 3.57 Å with a distribution of $\Delta\lambda/\lambda = 0.13$, where $\Delta\lambda$ is the full width at half maximum (fwhm). The scattered neutrons were detected by a two dimensional $\text{Ri}\phi$ -type detector and corrected for empty cell scattering, detector sensitivity, and sample thickness and transmission. The electrical background of this instrument is small enough to be neglected against the observed scattering intensity. The two-dimensional data were circularly averaged to obtain scattering profiles as a function of magnitude of the scattering vector q [$= (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle] and then reduced to absolute units (cm^{-1}) using H_2O as the calibration standard.⁷ The coherent scattering intensity was obtained by subtracting the incoherent scattering. For this purpose the incoherent scattering of the blends was estimated from the scattering measurements of the component homopolymers, such as neat PVME for the DPS/PVME and neat HPI for the DPB/HPB and DPB/HPI, because the incoherent scattering of the blend specimens was originated mainly from the hydrogen atoms of the samples. In order to obtain the scattering profiles in a wide q region, the measurements were carried out at the detector position D and with λ as given: ($D = 6$ or 1.5m , $\lambda = 6.25\text{\AA}$) or ($D = 1.5\text{m}$, $\lambda = 3.57\text{\AA}$) for the DPS/PVME 50/50; ($D = 6$ or 1.5 m , $\lambda = 6.25\text{\AA}$) for the DPS/PVME 70.6/29.4; ($D = 10$ or 1.5 m , $\lambda = 6.38\text{\AA}$) for the DPB/HPB; ($D = 10\text{m}$, $\lambda = 6.85\text{\AA}$) for the DPB/HPI.

5-2-3. DSC

T_g 's of the homopolymers and the polymer mixtures were measured using Perkin-Elmer DSC apparatuses (DSC-7 and DSC-2C). The DSC measurements were performed in the heating cycle with the heating rate of 20 K/min in the temperature range 228-398 K for the DPS/PVME mixtures, 228-448 K for neat DPS, 180-286 K for neat PVME, and 145-271 K for DPB/HPB and DPB/HPI

mixtures as well as for neat DPB, HPB, and HPI. The calibration of the DSC-7 was performed according to the heat of fusion of indium and *n*-octadecane standards and that of the DSC-2C was performed by the heat of fusion of *n*-octane and *n*-dodecane standards. T_g was determined as the midpoint of the endothermic DSC curve observed.

5-3. Results

5-3-1. DSC

The T_g 's of the binary mixtures and the neat component polymers determined by DSC are summarized in Table 5-2. A single T_g was observed for all the mixtures, suggesting that they are in the single-phase states. According to the results, it should be stressed that the mixtures of DPB/HPB and DPB/HPI have a small difference in the T_g 's which are 4 and 29 K, respectively. On the other hand, the mixture of DPS/PVME has a large difference in the T_g 's which is 127 K.

5-3-2. SANS

As is well-known, the mobility of polymers becomes very small near their T_g . Therefore, it is important to specify the thermal programs in our SANS measurements near T_g . We carried out the SANS measurements for all the mixtures in cooling cycles from far above the T_g down to near the T_g of the

mixtures. All the measurements were started after the system was equilibrated at the specified temperatures for ca. 25-30 min.

Figure 5-1 shows the double logarithmic plots of the SANS profiles for the mixtures of DPS/PVME (50/50) (a) and (70.6/29.4) (b) at various temperatures. The temperature range of the measurement was 243-423 K for DPS/PVME 50/50 and 303-423 K for DPS/PVME 70.6/29.4. The T_g 's for the two mixtures were determined to be 276 and 311 K from the DSC measurements, respectively. Thus the temperature range for SANS measurements extends from far above the T_g 's of the mixtures to below them. The q range of SANS measurements is 0.139-2.72 nm⁻¹ for the DPS/PVME 50/50 mixture and 0.087-1.66 or 0.418 nm⁻¹ for the DPS/PVME 70.6/29.4 mixture. At each temperature, the scattering profiles for both mixtures show the monotonous decreases of the scattering intensity as a function of q , showing the asymptotic behavior of q^{-2} in the high- q region. As the temperature increases, the scattering intensity for both mixtures increases in the low- q region, which indicates that DPS/PVME has a phase diagram with the LCST behavior. In other words, the TCF becomes larger as the temperature is raised close to the phase boundary. In the temperature region below 273 K, which is expected to be the T_g of the mixture, the scattering profiles for the DPS/PVME 50/50 mixture shows no change with temperature in the entire q region observed. TCF is frozen, because the mobility of polymers is extremely low below the T_g . Therefore, it is expected that the relaxation time of TCF becomes longer than the time scale of the measurements.

Figure 5-2 shows the double logarithmic plot of the SANS profiles obtained for the DPB/HPB mixture in the temperature range of 183-343 K. It should be mentioned that the T_g of the mixture obtained by DSC was 184 K, which is close to the lowest limit of our SANS measurements. The q range of the measurement was 0.04-1.29 nm⁻¹.

Table 5-2. DSC Results on T_g 's for Homopolymer and Blend Samples

neat sample	T_g /K	blend sample	component, wt %/wt%	T_g /K
DPS	378	DPS/PVME	50/50	276
PVME	251	DPS/PVME	70.6/29.4	311
DPB	186	DPB/HPB	49.8/50.2	184
HPB	182	DPB/HPI	59.7/40.3	196
HPI	215			

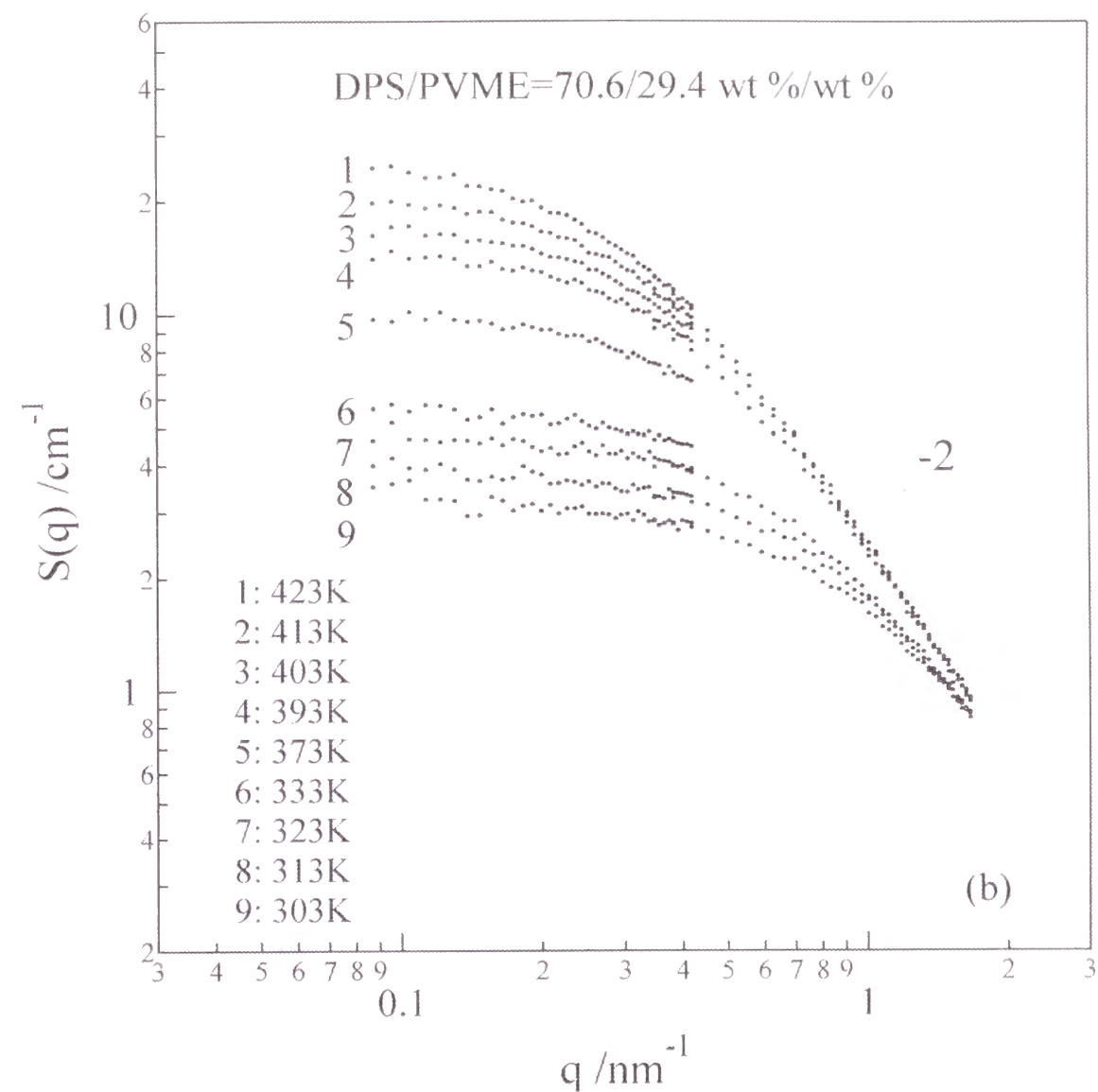
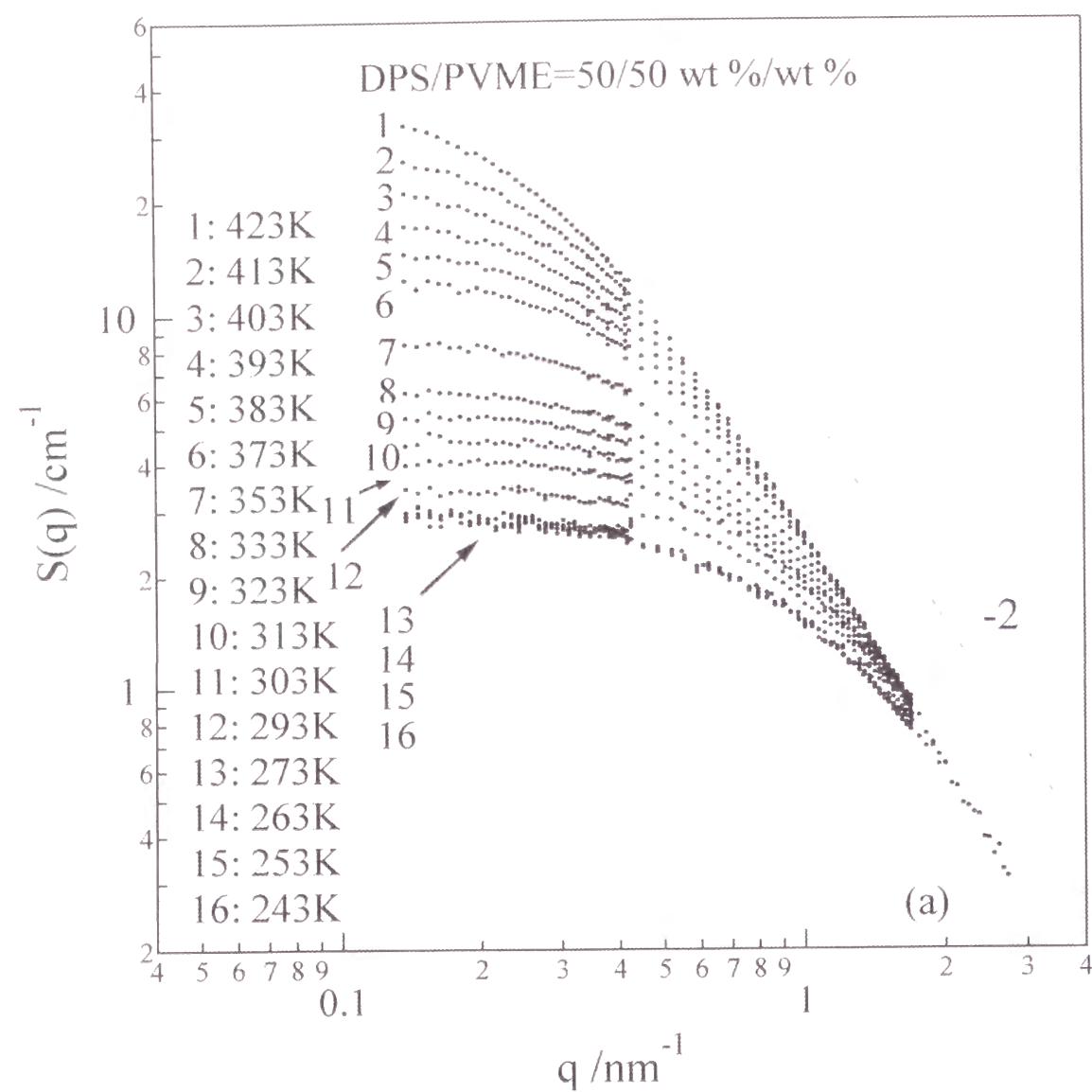


Figure 5-1. SANS profiles for the DPS/PVME (a) 50/50 and (b) 70.6/29.4 mixtures at various temperatures.

At each temperature, the scattering profiles show the monotonous decreases in the scattering intensity as a function of q , showing the asymptotic behavior of q^{-2} in the high- q region. In the low- q region, the scattering intensity increases with decreasing temperature, indicating that the DPB/HPB mixture has a phase diagram with an upper critical solution temperature (UCST) behavior. In the temperature region below 193 K, the scattering profiles become independent of temperature in the entire q range observed, probably due to vitrification of the mixture. This temperature (193 K) is slightly higher than the T_g (184 K) determined by DSC measurement.

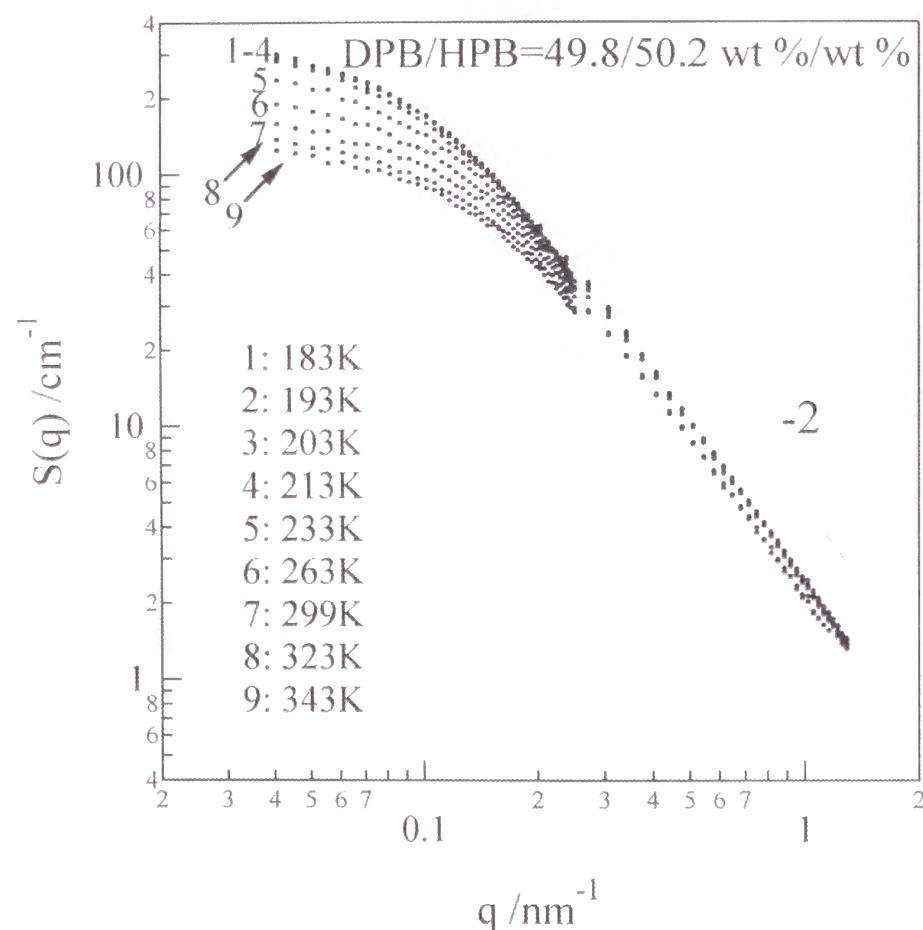


Figure 5-2. SANS profiles for the DPB/HPB mixture at various temperatures.

Figure 5-3 shows the double logarithmic plot of the SANS profiles for the DPB/HPI mixture in the temperature range 193-333 K. It should be stressed that the T_g for this mixture obtained by DSC was 196 K, which is the lowest bound of the temperature range in our SANS measurements. The q range for SANS is 0.0477 - 0.200 nm^{-1} . The scattering profiles for DPB/HPI show the monotonous decreases of the scattering intensity as a function of q . In this case the q range of the SANS data was not enough to observe the asymptotic behavior of q^{-2} in the high- q region. In the low- q region the scattering intensity increases with increasing temperature, which means that the DPB/HPI mixture⁵ has an LCST-type phase diagram, as is the case of the DPS/PVME mixtures.²⁻⁴

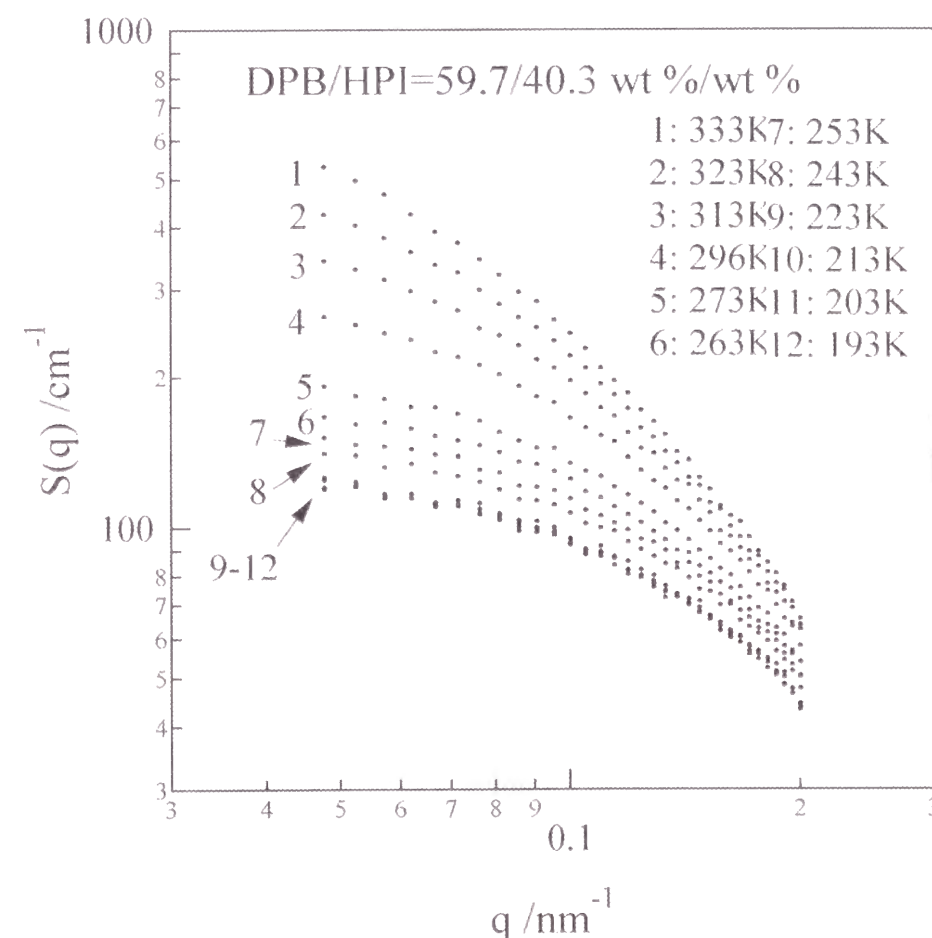


Figure 5-3. SANS profiles for the DPB/HPI mixture at various temperatures.

5-4. Analysis and Discussion

5-4-1. Conventional Mean-Field Theory Based on RPA

de Gennes presented the static structure factor $S(q)$ for a binary mixture in the single-phase state on the basis of RPA.¹ So far the structure factor $S(q)$ for the polymer mixtures, in which the condition of incompressibility is ensured, is well described by the de Gennes theory. For the mixtures of component polymers 1 and 2 having asymmetric segmental volume and the polydispersity in the molecular weight given by the Schultz-Zimm distribution, $S(q)$ is modified as follows:⁸

$$\frac{k_N}{S(q)} = \frac{1}{\phi_1 N_{n,1} v_1 g_D(x_1)} + \frac{1}{\phi_2 N_{n,2} v_2 g_D(x_2)} - \frac{2\chi}{v_0} \quad (5-2)$$

with

$$k_N = N_0 \left(\frac{a_1}{v_1} - \frac{a_2}{v_2} \right)^2 \quad (5-3)$$

and

$$g_D(x_i) = \left[x_i - 1 + \left(\frac{h_i}{h_i + x_i} \right)^{h_i} \right] \quad (5-4)$$

where

$$x_i = q^2 R_{g,i}^2 = \frac{q^2 N_{n,i}^2 b_i^2}{6} \quad (5-5)$$

and

$$h_i = \left\{ \left(\frac{N_w}{N_n} \right)_i - 1 \right\}^{-1} \quad (i = 1 \text{ or } 2) \quad (5-6)$$

Here $N_{n,i}$ and $N_{w,i}$ denote the number- and weight-average degree of polymerization for the i th component ($i = 1$ or 2). ϕ_i is the volume fraction for component i with the volume of the monomeric unit v_i , the mean square radius of gyration of molecule $R_{g,i}$, and statistical segment length b_i . a_i is the neutron scattering length of the monomeric unit for component i . N_0 is Avogadro's number and v_0 is the molar volume of the reference cell calculated by $v_0 = (\phi_1/v_1 + \phi_2/v_2)^{-1}$. $g_D(x_i)$ is the well-known Debye function for an isolated Gaussian chain of component i . χ denotes the Flory segmental interaction parameter.

For small q values, the expansion of eq. (5-2) in powers of q up to q^2 leads to an expression in Ornstein-Zernike (O-Z) form, as follows:

$$S^{-1}(q) = S^{-1}(0) [1 + q^2 \xi^2] = S^{-1}(0) + A q^2 \quad (5-7)$$

$S^{-1}(0)$ is related to the free energy of mixing per unit volume Δg_m .

$$\begin{aligned} S^{-1}(0) &= \frac{1}{k_N} \partial^2 \left(\frac{\Delta g_m}{RT} \right) / \partial \phi^2 \\ &= \frac{1}{k_N} \left(\frac{1}{\phi_1 N_{w,1} v_1} + \frac{1}{\phi_2 N_{w,2} v_2} - \frac{2\chi}{v_0} \right) \end{aligned} \quad (5-8)$$

and

$$A = \frac{1}{3k_N} \left[\frac{J_1 R_{g,1}^2}{\phi_1 N_{w,1} v_1} + \frac{J_2 R_{g,2}^2}{\phi_2 N_{w,2} v_2} \right] \quad (5-9)$$

with

$$J_i = \left\{ 2 \left(\frac{N_{w,i}}{N_{n,i}} \right) - 1 \right\} \quad (5-10)$$

Furthermore, the correlation length ξ for the TCF is given by

$$\xi^2 = AS(0) \quad (5-11)$$

5-4-2. SANS Profiles in the Low q Region

In this section, we will discuss the temperature dependence of SANS profiles in the low- q region. Figure 5-4 shows the O-Z plots [$S(q)^{-1}$ vs. q^2 plot] for the DPS/PVME mixtures with the compositions of (a) 50/50 and (b) 70.6/29.4 at various temperatures. Figures 5-5 and 5-6 also show the O-Z plots for DPB/HPB and DPB/HPI, respectively. As shown in Figs. 5-4 ~ 5-6, the reciprocal values of $S(q)$ in low- q regions are well fitted with a linear function of q^2 . The slope of the O-Z plot for the DPS/PVME 50/50 mixture gradually decreases as the temperature gets close to the T_g (276 K). However, at a temperature (283 K) just above the T_g , the slope suddenly increases. On the other hand, the slopes of the O-Z plots for the other blends show almost no change with the temperatures. These behaviors will be more clearly shown in Figs. 5-10 and 5-11, and discussed in detail later. The value of $S(0)^{-1}$, which is obtained from the linear extrapolation of the O-Z plot to $q=0$, is related to the thermodynamic stability of a given mixture, e.g. $S(0)^{-1}$ becomes zero at the spinodal point of the mixture.

Figure 5-7 shows the temperature dependence of $S(0)^{-1}$ thus obtained as a function of reciprocal absolute temperature T^{-1} for the DPS/PVME (a) 50/50 and (b) 70.6/29.4 mixtures. The error bars are smaller than the size of data symbols in this figure, so that the error bars are not attached especially to the data points.

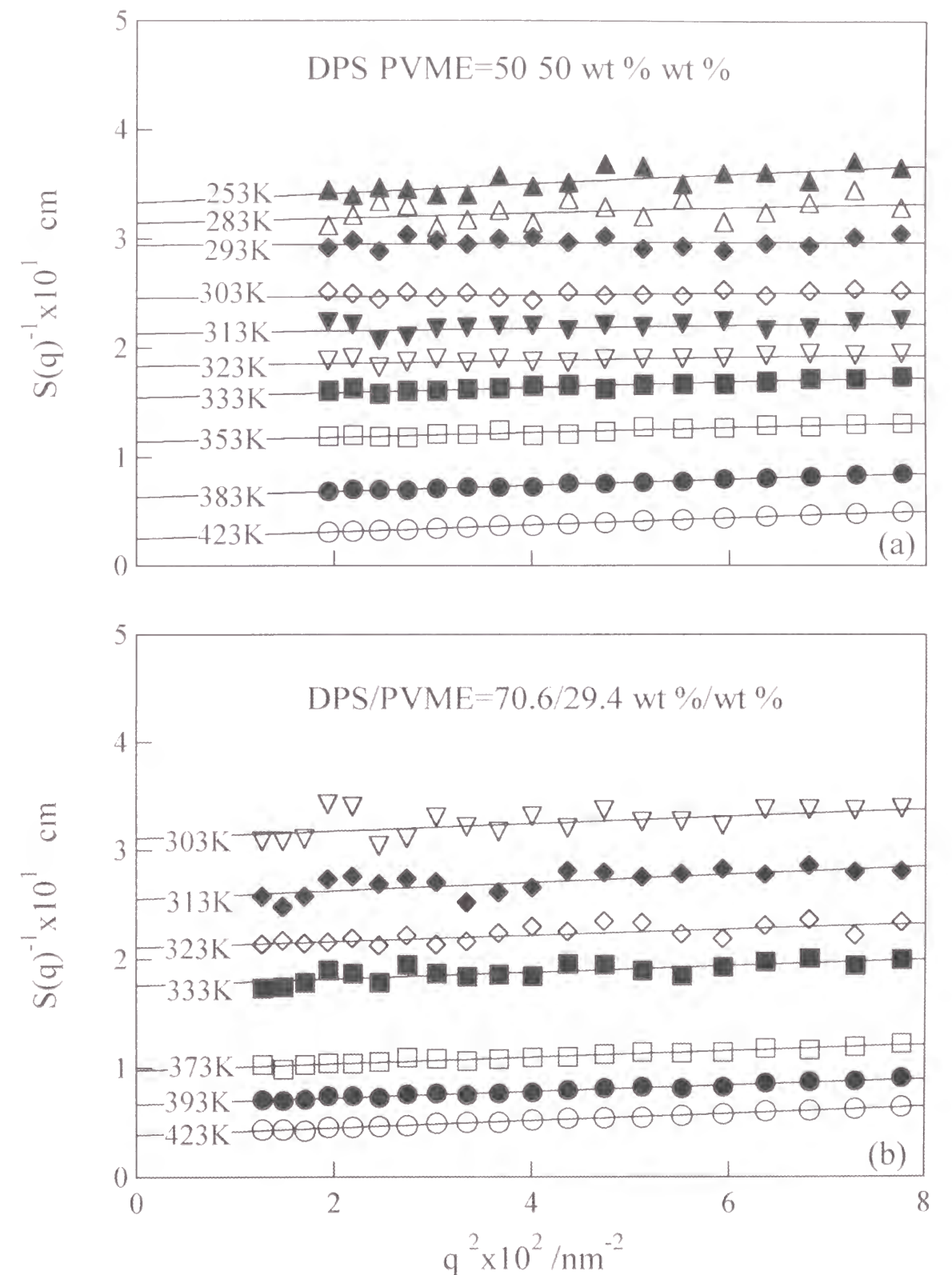


Figure 5-4. Plots of $S(q)^{-1}$ against the square of the scattering vector q for the DPS/PVME (a) 50/50 and (b) 70.6/29.4 mixtures at various temperatures.

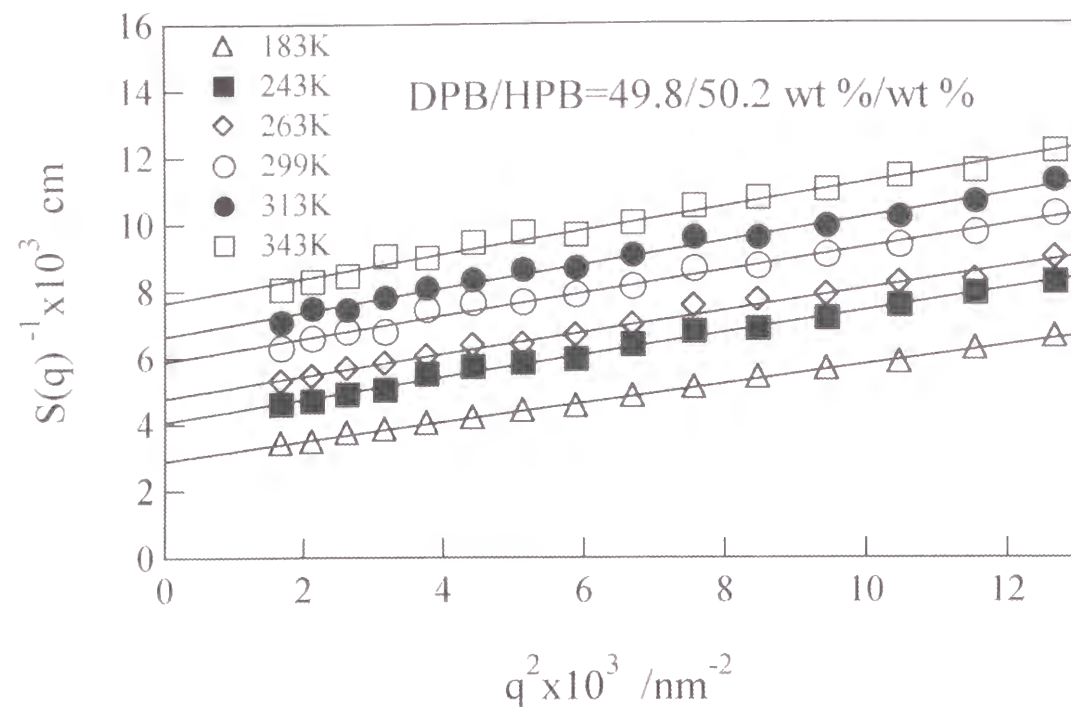


Figure 5-5. Plots of $S(q)^{-1}$ against the square of the scattering vector q for the DPB/HPB mixture at various temperatures.

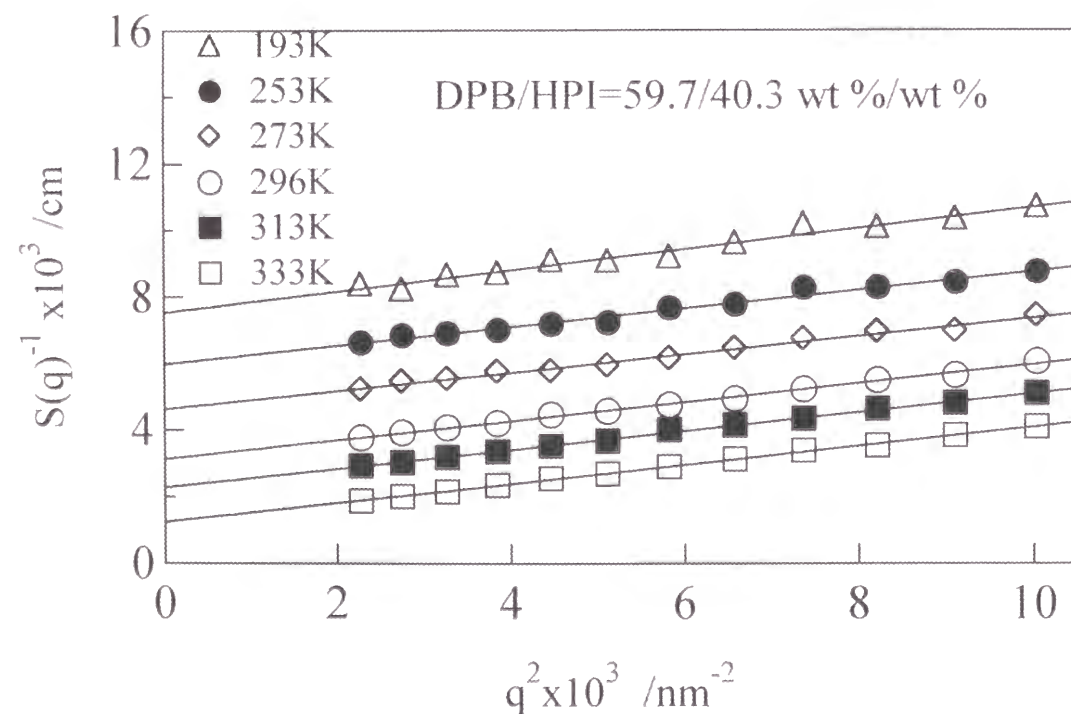


Figure 5-6. Plots of $S(q)^{-1}$ against the square of the scattering vector q for the DPB/HPI mixture at various temperatures.

Similarly, in the following figures we omit error bars in the case of error smaller than size of data symbols. In Fig. 5-7, we can find three regimes (I-III) for the DPS/PVME 50/50 mixture and two regimes (I and II) for the DPS/PVME 70.6/29.4 mixture as a function of T^{-1} . Regime III for the latter should be observed if the experiments were conducted to much lower temperatures. Regime I is in the temperature region much higher than the T_g of the mixture. So far most of the SANS studies on TCF in polymer mixtures have been carried out in this regime which is free from vitrification. In this regime, $S(0)^{-1}$ increases linearly with T^{-1} so that we find

$$S(0)^{-1} = -0.339 + 154/T \quad (5-12)$$

and

$$S(0)^{-1} = -0.331 + 156/T \quad (5-13)$$

for the DPS/PVME 50/50 and 70.6/29.4 mixtures, respectively. Here the mean-field spinodal temperatures T_s , at which $S(0)^{-1} = 0$, can be determined, are 454 and 471 K for the 50/50 and 70.6/29.4 mixtures, respectively.

The temperature ranges of 383-273 and 393-303 K for the DPS/PVME 50/50 and 70.6/29.4 mixtures, respectively, correspond to regime II. In this regime, $S(0)^{-1}$ deviates from the temperature dependence obtained in regime I: $S(0)^{-1}$ increases more rapidly with T^{-1} in regime II than in regime I. Deviation of $S(0)^{-1}$ from the linear dependencies on T^{-1} takes place at 383 and 393 K for the 50/50 and 70.6/29.4 mixtures, respectively. This deviation becomes larger as the temperature becomes closer to T_g . This phenomena have been reported by Schwahn et al. for a DPS/PVME mixture.⁶ We should note that the DPS/PVME mixtures have a large difference in the T_g 's of the pure components. This unexpected increase in $S(0)^{-1}$, or the unexpected suppression of $S(0)$ suggests that osmotic compressibility of the mixture tends to be suppressed

more strongly than the suppression predicted by the incompressible RPA theory, with decreasing temperature closer to the T_g of the mixture.

Regime III corresponds to the temperature range 273-243 K for the DPS/PVME 50/50 mixture. In this regime, $S(0)^{-1}$ does not change with T^{-1} . This implies that the TCF in the mixtures was frozen due to the vitrification. Thus we can determine the freezing temperature of the TCF which is very close to the T_g determined by DSC. However, it should be noted that the freezing temperature may be strongly influenced by the experimental conditions such as the cooling rate, because of the nonequilibrium effect remaining in the mixtures.

We emphasize that the unexpected phenomenon observed in regime II for the DPS/PVME mixture is not due to the nonequilibrium effect. The SANS measurements were carried out by the cooling process as mentioned in Sec. 5-3-2. If the system had been trapped in the non-equilibrium state at a given temperature near T_g , $S(0)^{-1}$ should have been smaller than that expected from RPA, i.e., $S(0)^{-1}$ vs. T^{-1} plots should have deviated downward from the straight line. However, in regime II, $S(0)^{-1}$ vs. T^{-1} plots for both DPS/PVME mixtures deviated upward.

On the other hand, completely different temperature dependencies of $S(0)^{-1}$ were observed for the DPB/HPB and DPB/HPI, as shown in Figs. 5-8 and 5-9. The temperature dependencies of $S(0)^{-1}$ for both mixtures are classified into two regimes corresponding to regimes I and III defined for the DPS/PVME mixtures. In regime I above T_g (223-343 and 243-333 K for the DPB/HPB and DPB/HPI mixtures, respectively), $S(0)^{-1}$ changes linearly with T^{-1} . Upon decreasing temperature, the temperature dependence of $S(0)^{-1}$ changes from regime I to III without going through regime II. In the temperature ranges of 193-223 and 213-243 K, respectively, for the mixtures of DPB/HPB and DPB/HPI, which are believed to be just above their T_g 's, $S(0)^{-1}$ shows only the

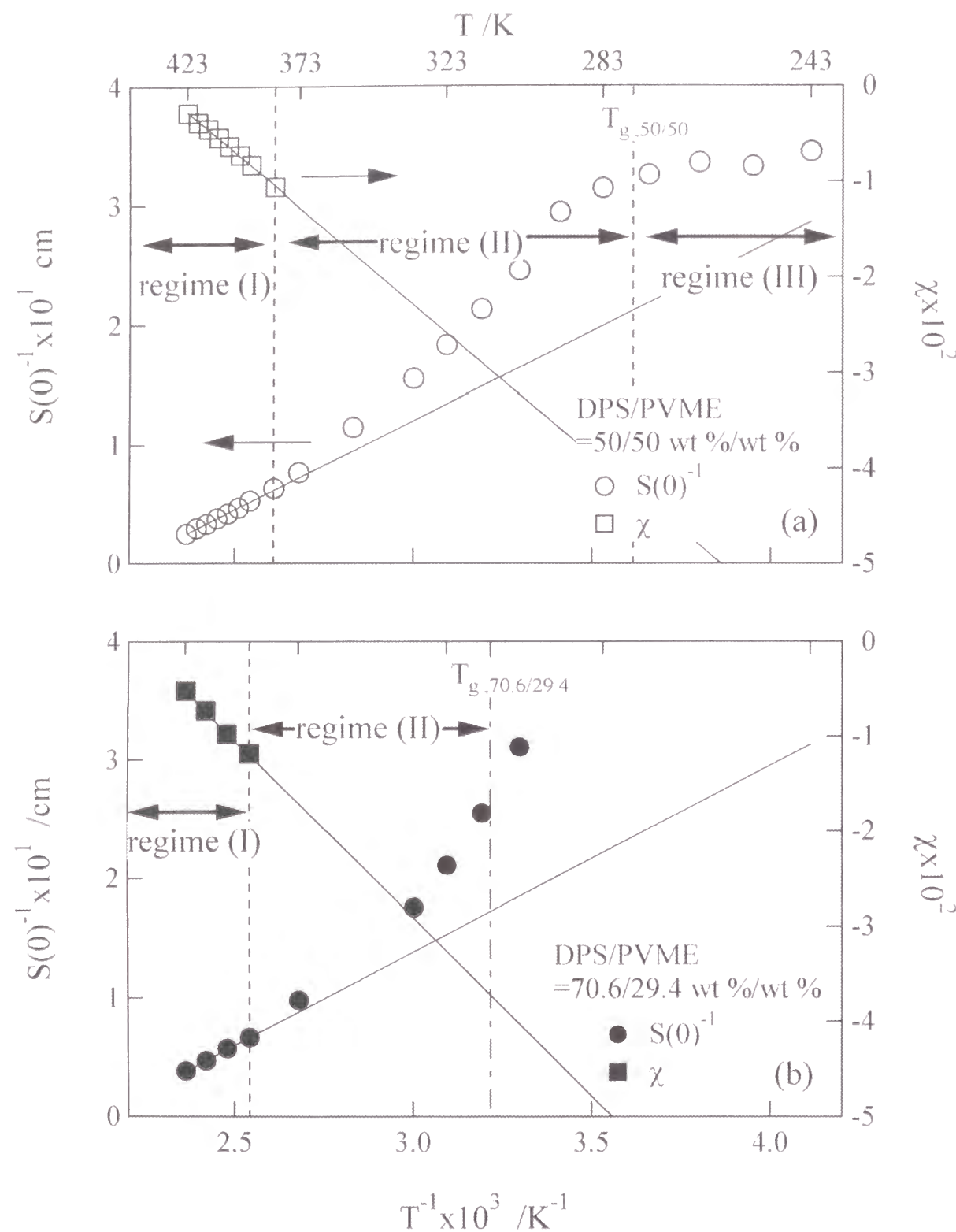


Figure 5-7. Plots of reciprocal zero wavenumber structure factor $S(0)^{-1}$ and Flory-Huggins parameter χ vs inverse temperature for the DPS/PVME (a) 50/50 and (b) 70.6/29.4 mixtures.

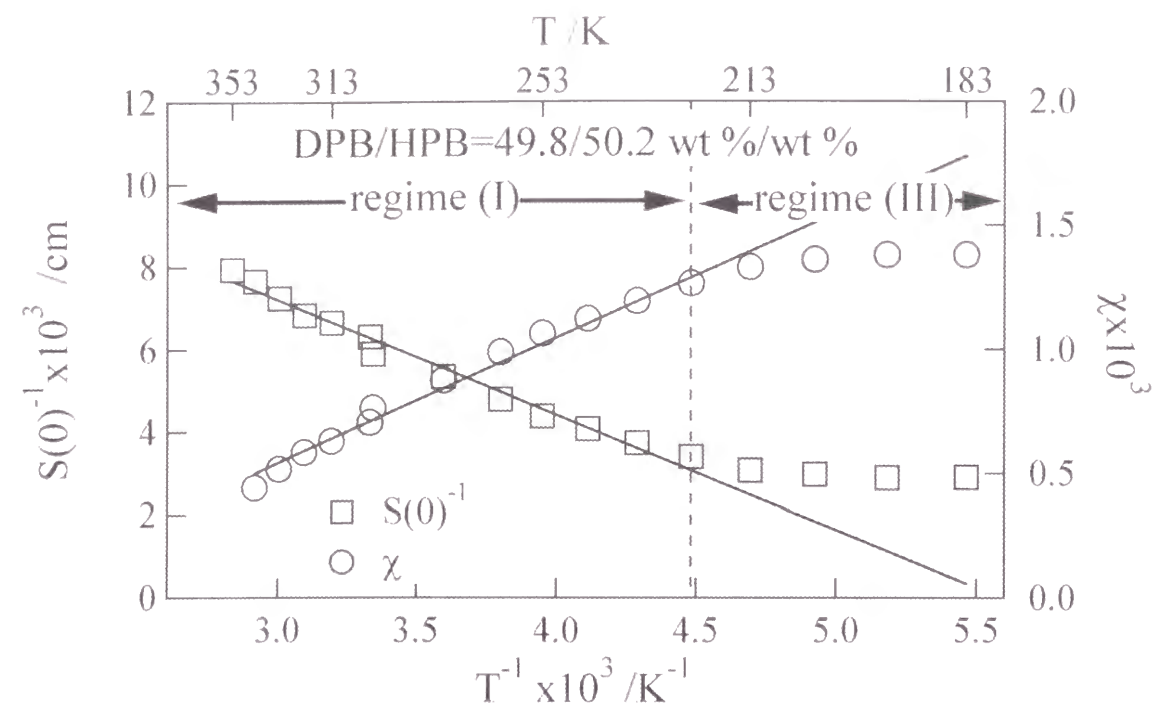


Figure 5-8. Plots of reciprocal zero wavenumber structure factor $S(0)^{-1}$ and Flory-Huggins parameter χ vs inverse temperature for the DPB/HPB mixture.

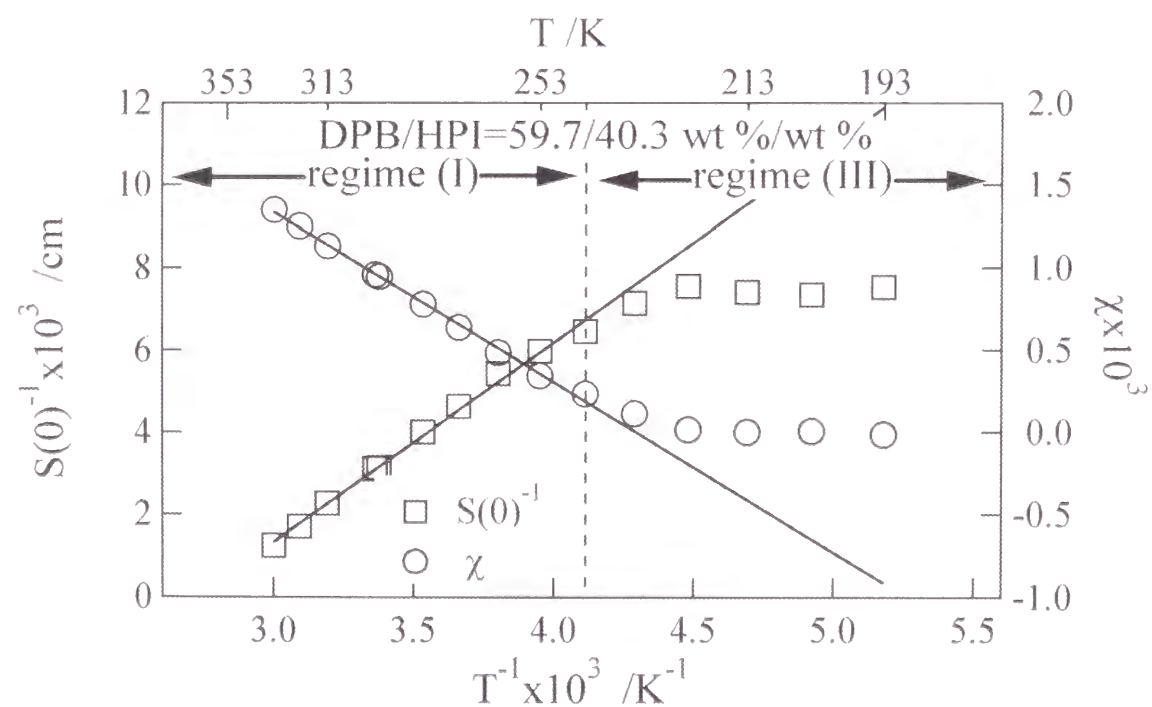


Figure 5-9. Plots of reciprocal zero wavenumber structure factor $S(0)^{-1}$ and Flory-Huggins parameter χ vs inverse temperature for the DPB/HPI mixture.

gradual change with T^{-1} . This behavior implies that as the temperature approaches the T_g of the mixture, the dynamics toward the equilibrium state becomes slower and the mixtures are trapped in a nonequilibrium state. At temperatures below 193 and 213 K for the mixtures of DPB/HPB and DPB/HPI, respectively, $S(0)^{-1}$ becomes constant, due to the vitrification. Here it should be denoted that the T_g thus evaluated by SANS is slightly higher than that determined by the DSC measurements. This discrepancy again reflects the difference in the temperature programs used in these two experiments. The program for the SANS experiment took a much longer time than that for the DSC experiment.

Thus the scattering behavior of regime II is unique to the DPS/PVME mixtures which have a large difference in the T_g 's of the pure components, while this regime was not observed for the mixtures of DPB/HPB or DPB/HPI, which has the small difference in the T_g 's of the pure components.

It is noteworthy to estimate the temperature dependence of the slope A in the O-Z plot. If the parameters R_g and v_i in eq. (5-9) do not have any temperature dependence, A should be independent of T from the prediction of conventional RPA equation [see eq. (5-9)]. Figure 5-10 shows the plots of A as a function of T^{-1} for the DPS/PVME (a) 50/50 and (b) 70.6/29.4 mixtures. In the temperature range corresponding to regime I, A shows only a little change for both mixtures. However, in regime II, A decreases markedly for the DPS/PVME 50/50 mixture. It should be stressed that the degree of this decrease is much larger than that expected from the thermal expansions of R_g and v_i ; e.g. the thermal expansivity of the unperturbed chain dimension for PS is given by $[d \ln(R_g^2)/dT = -1.1 \times 10^{-3} \text{ K}^{-1}]^9$ and the thermal expansion coefficient $1/V(\partial V/\partial T)$ for PS is $[5.1-6.0 \times 10^{-4} \text{ K}^{-1}]^{10}$. The unexpected change of A will be shown to be explained by taking into account the q dependence of the χ parameter, in the context of the incompressible RPA (see Sec. 5-4-4 for the details).

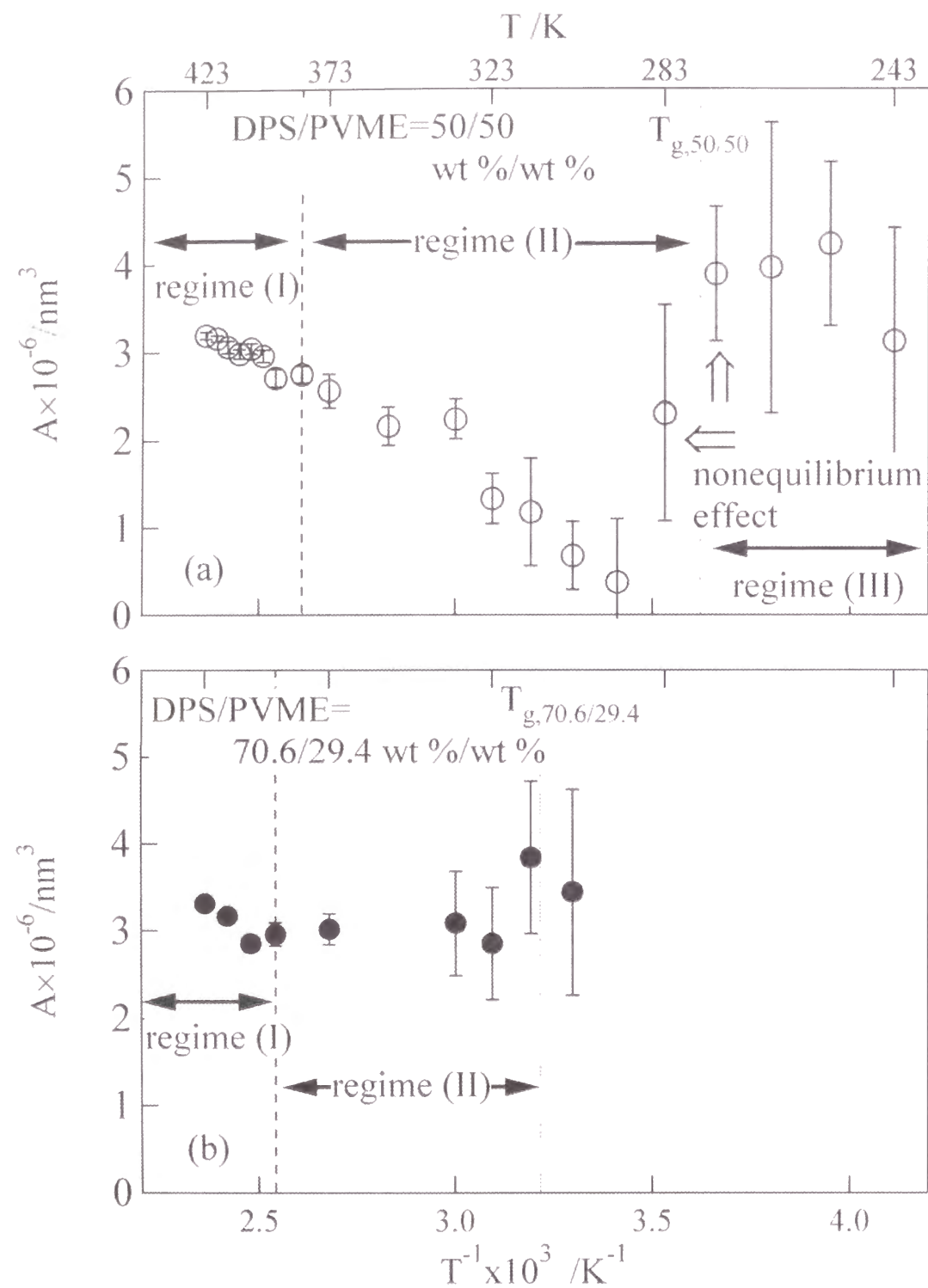


Figure 5-10. Slope of Ornstein-Zernike plot as a function of reciprocal temperature for the DPS/PVME (a) 50/50 and (b) 70.6/29.4 mixtures.

At a temperature between 283 and 293 K, the value of A for the 50/50 mixture jumps up as shown in Fig. 5-10a. This phenomenon will be discussed in Sec. 5-4-5. At temperatures below 273 K, A becomes constant due to the vitrification of the mixture. On the other hand, for the 70.6/29.4 mixture the decrease of A was not as significant as that for the 50/50 mixture. We speculate that this result for the 70.6/29.4 mixture was due to insufficient annealing time. As is mentioned in Sec. 5-1, we stress that the anomalous behavior near the T_g is strongly affected by annealing time. Hence, in order to perfectly understand the behavior, we must have enough information concerning dynamics of the systems under consideration, e.g. the relaxation time of TCF. The study of composition dependence of the relaxation process of TCF will be the subject of future work.

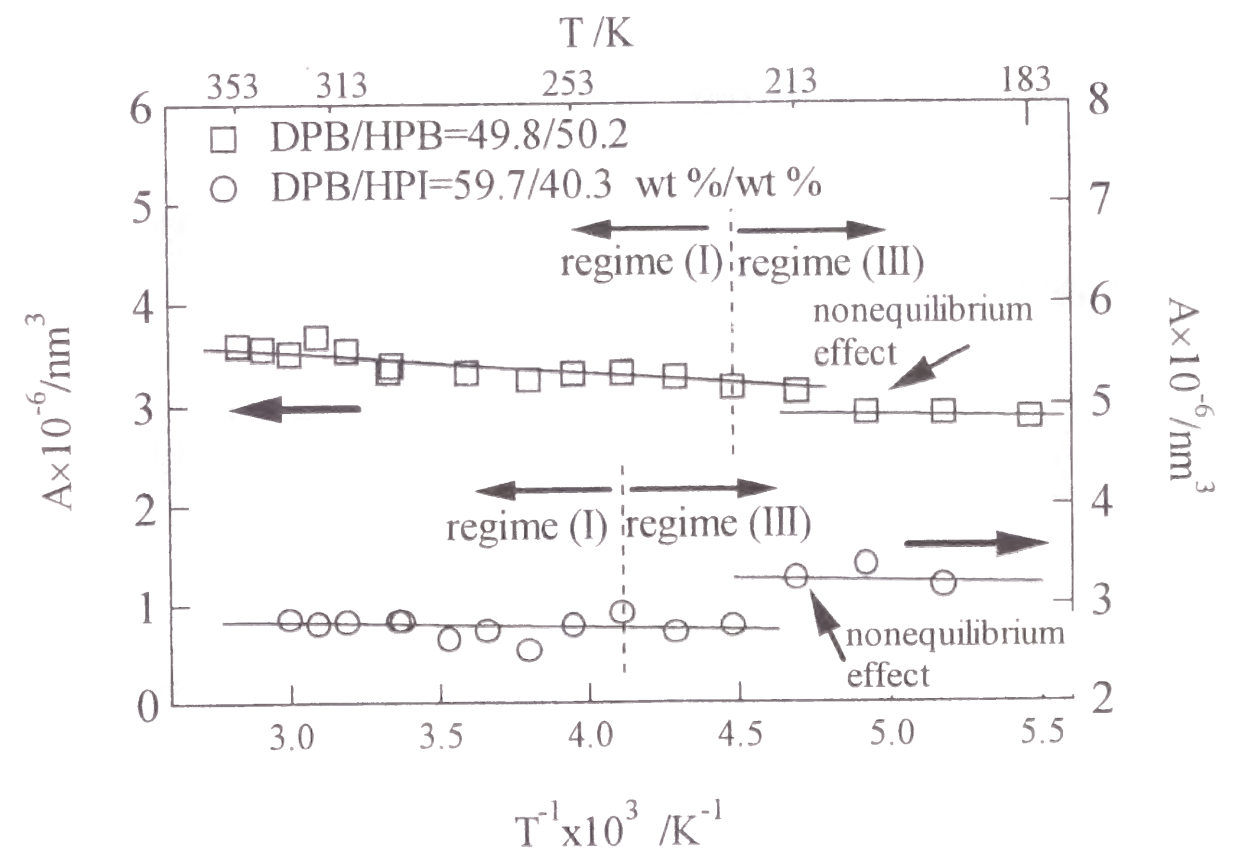


Figure 5-11. Slope of Ornstein-Zernike plot as a function of reciprocal temperature for the DPB/HPB (square) and DPB/HPI (circle) mixtures.

Fig. 5-11 shows the changes in A as a function of T for the mixtures of DPB/HPB and DPB/HPI. In contrast with the DPS/PVME mixtures, A is independent of T in both regimes I and III, as described by eq. (5-9). Thus the unexpected behaviors for the DPS/PVME mixture in regime II seem to be related to the large difference in the T_g 's of the pure components. Studies for other blends with very different T_g 's will be carried out in future work.

5-4-3. SANS Profile in the Whole q Region

In this section, we discuss the SANS profiles in the whole q region covered in this experiment. Flory's interaction parameter χ was estimated by curve-fitting of eq. (5-2) to the SANS profiles in regime I, in which the vitrification is not important. Parts a and b of Fig. 5-7 show the estimated χ for the DPS/PVME 50/50 and 70.6/29.4 mixtures, respectively, as a function of T . The temperature dependencies of χ for both mixtures show a good linearity with T^{-1} in regime I and are described by

$$\chi = 0.0702 - 30.9/T \quad (\text{for DPS/PVME 50/50}) \quad (5-14a)$$

$$\chi = 0.0817 - 36.8/T \quad (\text{for DPS/PVME 70.6/29.4}) \quad (5-14b)$$

We calculated the scattering functions at the temperatures corresponding to regimes I and II by using eq. (5-2) and eq. (5-14a) for the temperature dependence of χ . Figure 5-12 shows the scattering functions thus estimated and the SANS profiles for the DPS/PVME 50/50 mixture. At the temperatures corresponding to regime I, e.g. 383, 403, and 423 K, the calculated scattering function (solid lines) shows a good agreement with the experimental profiles (symbols), whereas at the temperatures in regime II, e.g. 303 and 353 K, the

calculated function (solid lines) deviates upward from the experimental one especially in the low- q region. Nevertheless, even in regime II, there is a nice agreement between the experimental profiles and the calculated scattering functions in the higher q region.

Figure 5-13 shows the differences between the theoretical $[S(q)_{\text{theory}}]$ and experimental structure factors $[S(q)]$ normalized by $S(q)$, for the DPS/PVME 50/50 mixture at various temperatures. The degree of deviations in the low- q

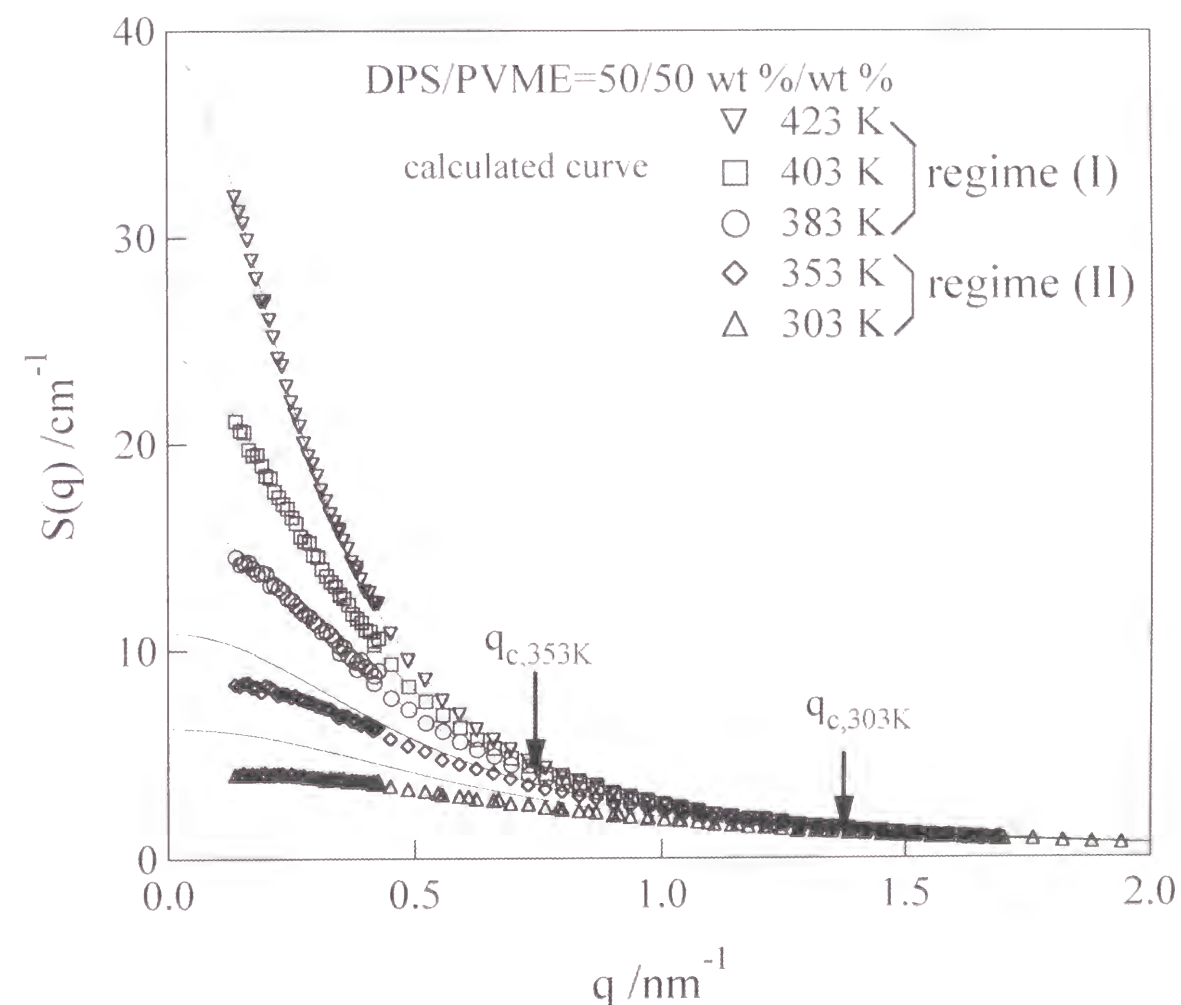


Figure 5-12. Comparison of experimental SANS profiles with the theoretical curves (solid line) calculated by using eqs. (5-2) and (5-14a) for the DPS/PVME 50/50 mixture.

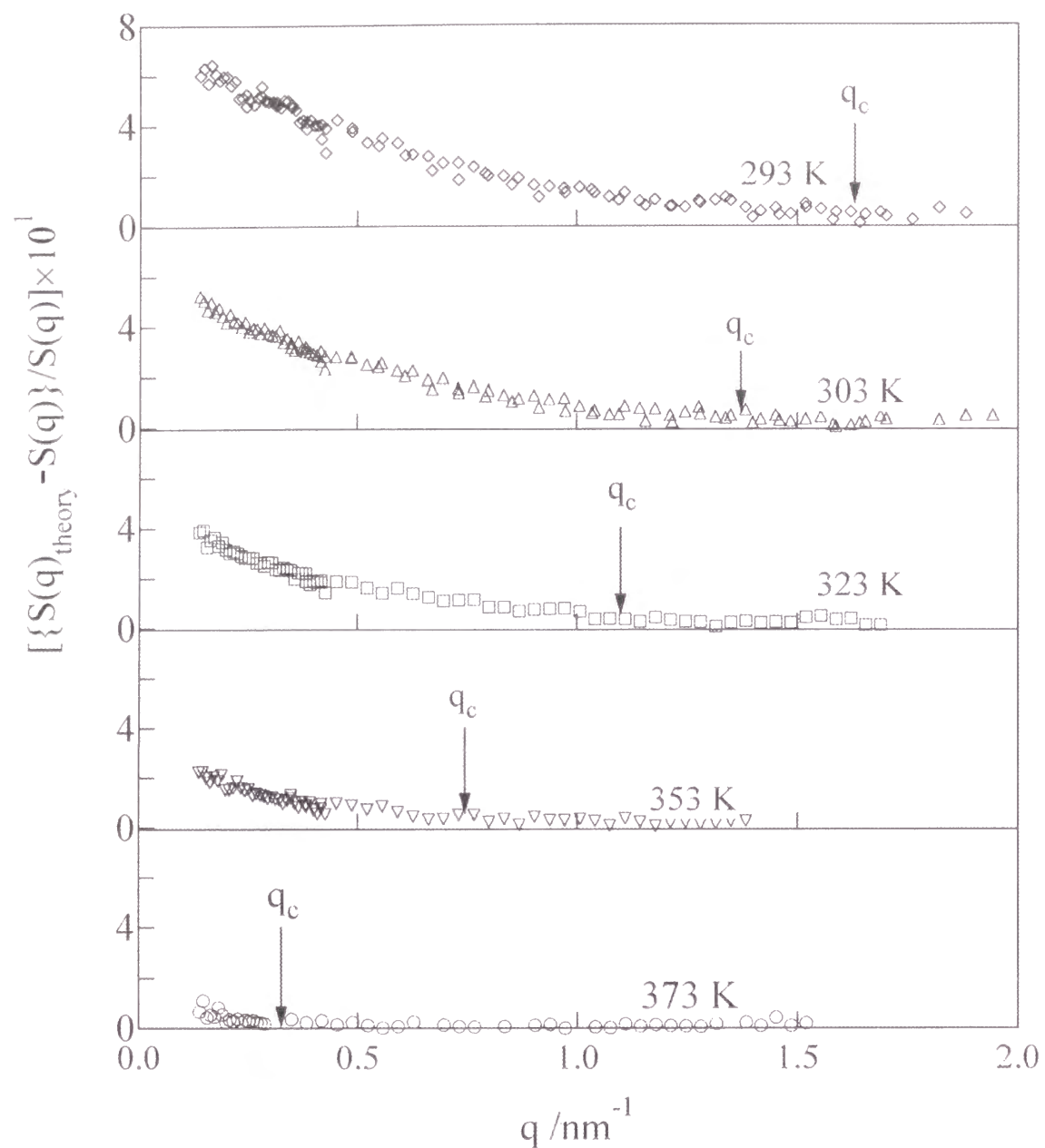


Figure 5-13. Plots of the differences between the theoretical curves, $S(q)_{\text{theory}}$, and the experimental structure factors, $S(q)$, which are normalized by $S(q)$, as a function of q at various temperatures. The arrow shows the position of q_c at each temperature.

region becomes larger as the temperature becomes closer to the T_g of the mixture (276 K). The result indicates that near the T_g the intensities of the long wavelength modes of TCF tend to be suppressed compared with those expected by the incompressible RPA theory. In addition, the critical wavenumber q_c , below which the deviation becomes significant, can be determined at each temperature. It shifts toward a higher q as the temperature approaches the T_g as shown in Fig. 5-14. The q region in which TCF is suppressed becomes wider as the temperature approaches the T_g .

By using eq. (5-2), χ was also estimated for the mixtures of DPB/HPB and DPB/HPI in regime I and regime III (see Figs. 5-8 and 5-9). The obtained χ values also show the good linearity with T^{-1} in regime I. On the other hand,

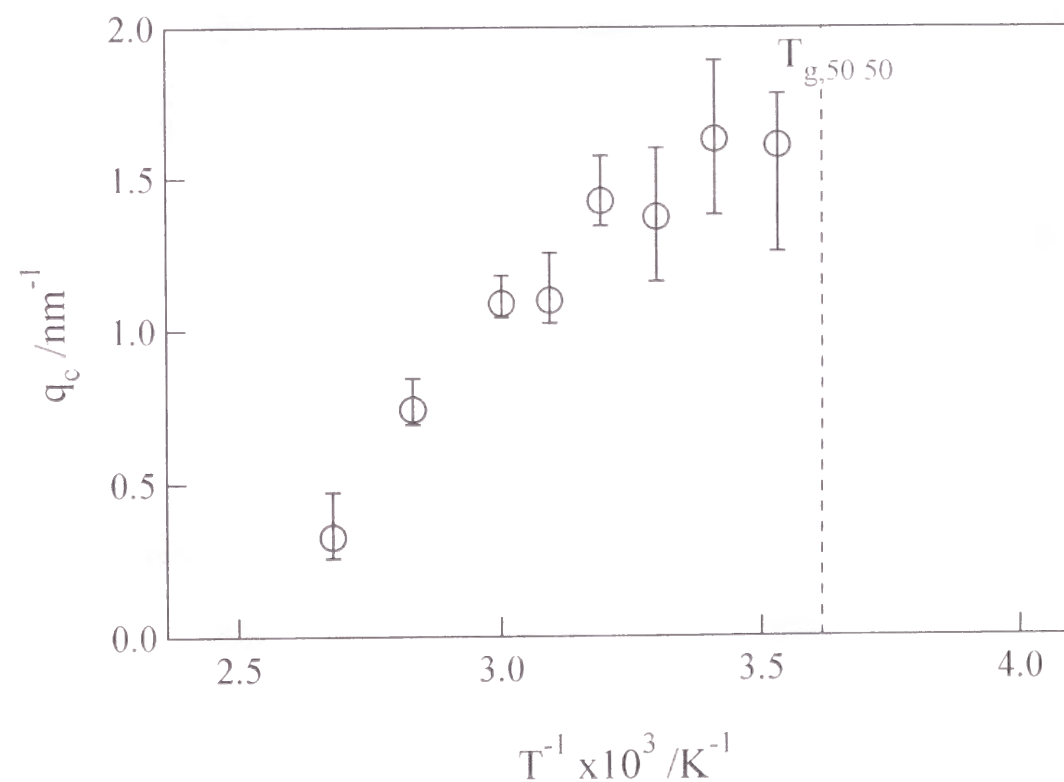


Figure 5-14. Plots of q_c as a function of reciprocal temperature.

χ remains constant in regime III where the TCF is frozen due to vitrification.

5-4-4. Modified RPA Theory

As we mentioned in Secs. 5-4-2 and 5-4-3, the SANS behavior for the DPS/PVME 50/50 mixture in regime II, i.e., the suppression of $S(q)$ at $q < q_c$, and the remarkable decrease of A near the T_g , cannot be explained by the conventional RPA theory. Recently, several theoretical attempts which take into account the compressibility effects on scattering function have been made.¹¹⁻¹⁵ Therefore, it may be expected that our anomalous behaviors of $S(q)$ at $q < q_c$, and A in regime II have been caused by such compressible effects. However, it has been recently shown by Bidkar and Sanchez that the apparent radius of gyration, or statistical segment length, is overestimated, if we analyze the scattering data predicted from the compressible polymer blends by using the conventional RPA theory.¹¹ If our scattering data in the low q region are analyzed by using the conventional RPA, then the value of the statistical segment length obtained becomes 2.3 Å at $T = 293$ K. It is too small. Moreover, according to Bidkar and Sanchez, this value should be *overestimated* rather than underestimated. Hence, we tentatively interpret that the anomalous behaviors we found may not be due to the compressible effects.

Here, we analyze the anomalous SANS behavior in regime II, in the context of the incompressible RPA, by taking the q dependence of χ into account.^{16, 17}

$$\chi(q) = \chi_{loc} + \chi_{nonloc} \left(1 - \frac{r_0^2 q^2}{6} \right) + O(q^4) \quad (5-15)$$

χ_{loc} denotes local contributions of the effective χ parameter which originate from the local interaction of the segments. χ_{nonloc} denotes nonlocal

contributions of the effective χ parameter which affect the q dependence of χ . r_0 is the interaction range parameter. Using eq. (5-15), $S(0)^{-1}$ and A are modified as follows.

$$\frac{1}{S(0)} = \frac{1}{k_N} \left(\frac{1}{\phi_1 N_{w,1} v_1} + \frac{1}{\phi_2 N_{w,2} v_2} - \frac{2}{v_0} (\chi_{loc} + \chi_{nonloc}) \right) \quad (5-16)$$

and

$$A = \frac{1}{3k_N} \left[\frac{J_1 R_{g,1}^2}{\phi_1 N_{w,1} v_1} + \frac{J_2 R_{g,2}^2}{\phi_2 N_{w,2} v_2} + \frac{\chi_{nonloc} r_0^2}{v_0} \right] \quad (5-17)$$

Here, we assume that the contribution of χ_{nonloc} is significant only in regime II and small enough to be neglected in regime I. Therefore, χ_{loc} is expressed by eq. (5-14a)

$$\chi = 0.0702 - 30.9 / T \quad (5-18)$$

for the DPS/PVME 50/50 mixture. Using eq. (5-18), we can estimate χ_{nonloc} from the values of $S(0)^{-1}$ in regime II. In addition, r_0 can be estimated from the values of slope A and χ_{nonloc} by using eq. (5-17). The results obtained are shown in Fig. 5-15. As shown in Fig. 5-15, χ_{nonloc} is negative and the absolute value becomes larger, as the temperature becomes closer to the T_g . The result indicates that the nonlocal term of the attractive interactions (χ_{nonloc}) and the well-known local attractive interaction term (χ_{loc}) increase upon approaching T_g . This nonlocal term is responsible for suppressing the amplitude of TCF with long wavelengths. On the other hand, the value of r_0 obtained is ca. 3-4 nm independent of the temperature.

Recently, Khokhlov et al. theoretically predicted that for the polymer blends with a large difference in the T_g 's of the pure components, the effective

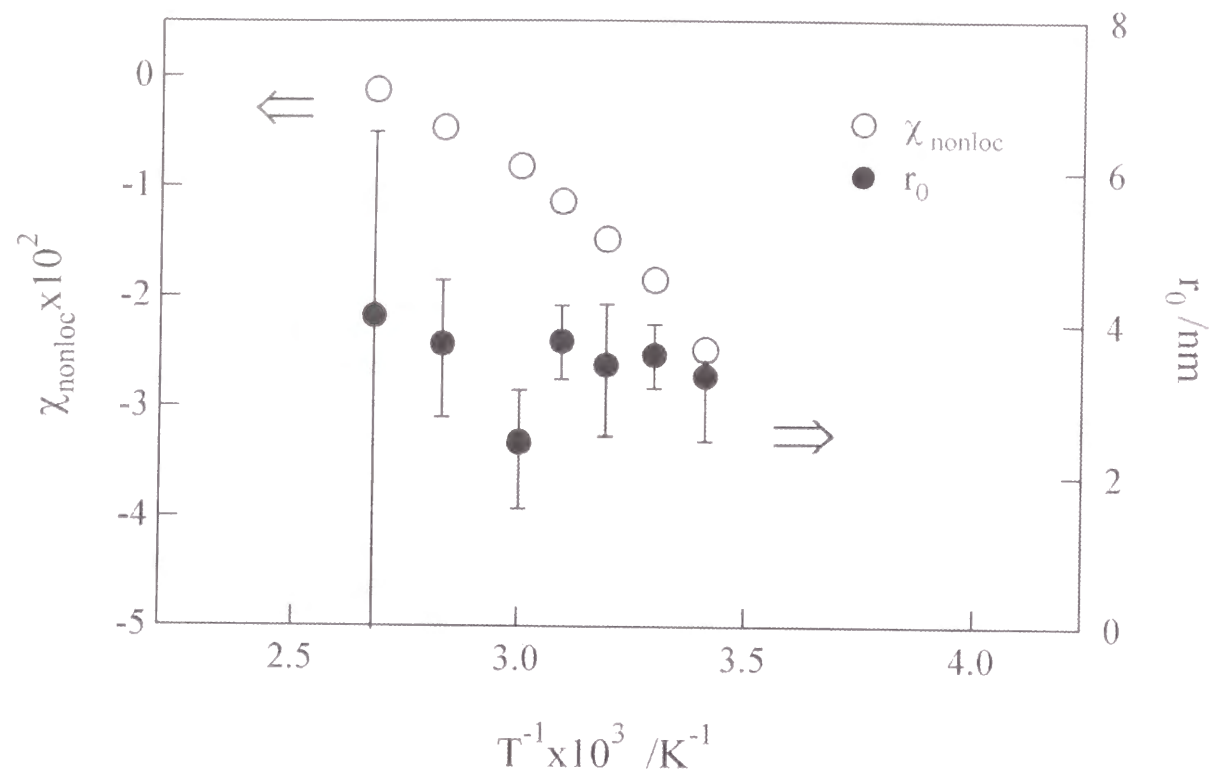


Figure 5-15. Plots of χ_{nonloc} and r_0 against reciprocal temperature.

χ parameter has the q dependence and that the scattering function at small q is suppressed relative to that predicted by the conventional RPA theory near the T_g of the mixture.¹⁷ According to them, it is expected that such suppression of scattering intensity in low q will be observed for polymer blends which have the following characteristics:¹⁷ (i) two components have very different T_g 's and (ii) at least one component has a bulky side group, so that their rotations are increasingly intercorrelated in space upon lowering the temperature toward the T_g of the blend in the single phase state. In such blends the rotational entropy makes a negative contribution to the χ parameter and the nonlocality of the rotational entropy is expected to become increasingly significant upon lowering the temperature toward the T_g . The entropy causes a decrease in the free energy of low- q modes of the system. That is, the entropy leads to the suppression of

TCF with long wavelengths. In addition, they suggest that under a given condition "microphase separation" for the mixture may take place near the T_g , which strongly suppresses the scattering intensity near $q \rightarrow 0$ as in the case of block copolymers, resulting in the scattering profile with a maximum.

In this work, though "microphase separation" or a maximum in the scattering profile was not observed, the anomalous SANS behavior in regime II, namely the suppression of the scattering intensity in the low- q region, shows a good qualitative agreement with their theory.

5-4-5. Nonequilibrium Effect

For our SANS experiments, we annealed sample specimens for ca. 25-30 min. at each temperature. As the temperature becomes closer to the T_g , the mobility of polymer chains becomes very low so that the time required for equilibration becomes longer. If the annealing time is not long enough, the mixture cannot attain the equilibrium state. For the DPS/PVME 50/50 mixture, the slope A for the O-Z plot suddenly increased at the temperature close to the T_g (see Fig. 5-10a). We believe that this phenomenon is due to a nonequilibrium effect, i.e. the q dependence in the relaxation time of the TCF. In general, the relaxation time of the TCF is faster for the Fourier modes having a higher wavenumber q . As shown in Fig. 5-16a, if measurement is carried out by changing the temperature from T_1 to T_2 ($T_1 > T_2$), then the TCF decreases for the system which has an LCST-type phase behavior, i.e. $S(q)^{-1}$ increases. Taking into consideration the q dependence of the relaxation time of the TCF, in the nonequilibrium state, the value of $S(q)^{-1}$ in the high- q range increases with time at a larger rate. Therefore, the slope A becomes bigger than that of the equilibrium state. On the other hand, the nonequilibrium effect for the system with a UCST-type phase behavior is opposite. The TCF increases by changing the temperature from T_1 to T_2 ($T_1 > T_2$), i.e. $S(q)^{-1}$ decreases. As the values

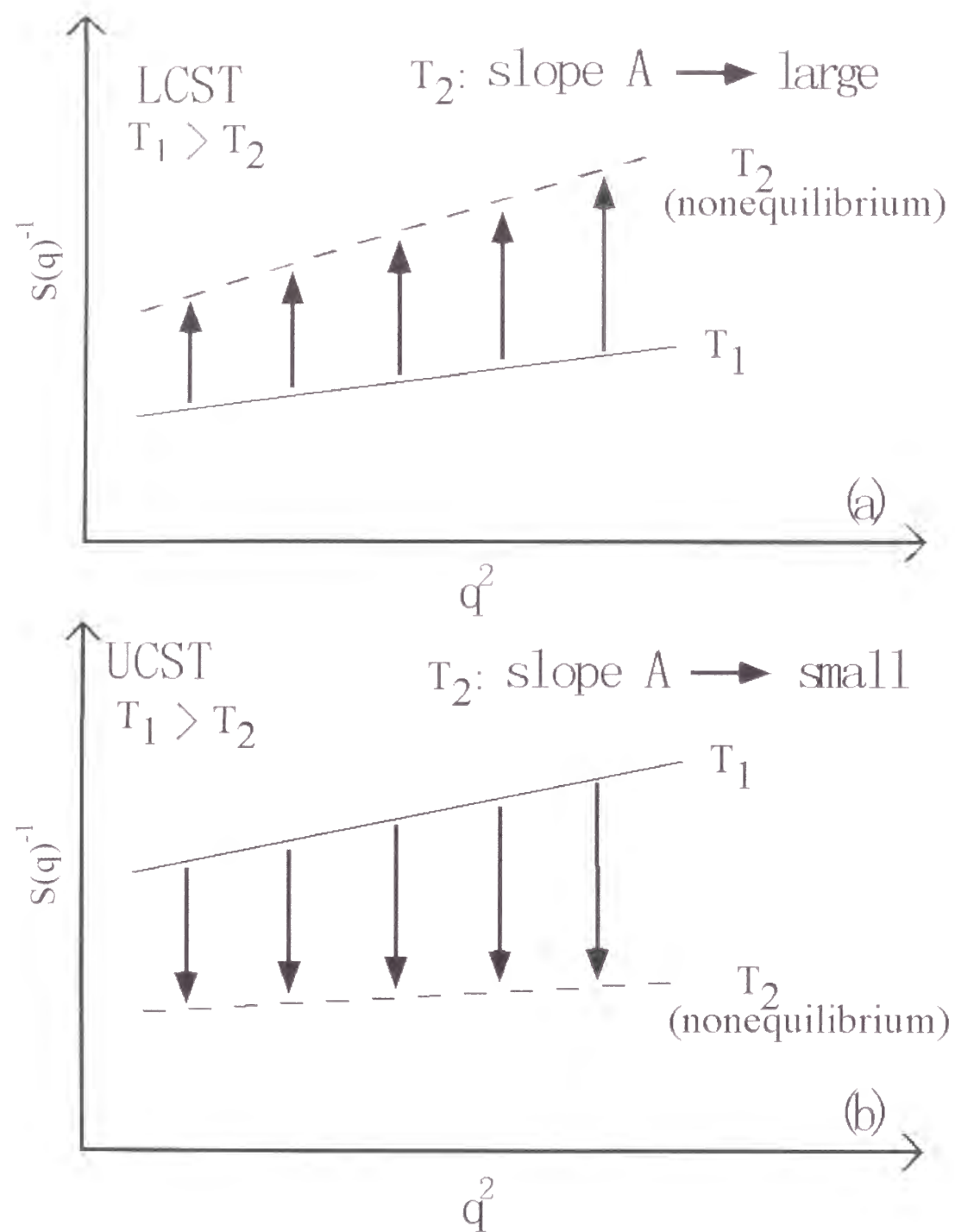


Figure 5-16. Schematic representation of the nonequilibrium effect on the Ornstein-Zernike plot for system with (a) LCST and (b) UCST type of phase behavior.

$S(q)^{-1}$ in the high- q range decrease at a larger rate, the slope A becomes smaller than that of the equilibrium state (Fig. 5-16b).

The nonequilibrium effect is also observed for the DPB/HPB and DPB/HPI mixtures if we observe Fig. 5-11 carefully. The A value for the DPB/HPI mixture suddenly increased at 213 K, while that for the DPB/HPB mixture decreased slightly at 203 K.

5-5. Conclusion

By using SANS techniques, we studied the thermal concentration fluctuations for two types of polymer mixtures, i.e. (i) DPS/PVME mixtures having a large difference in the T_g 's of the pure components and (ii) mixtures of DPB/HPB and DPB/HPI having a small difference in T_g 's of pure components. The range of temperature covered is very wide, from far above T_g to below the T_g of the mixture. We found that as the temperature comes closer to T_g , the scattering profiles $S(q)$ for the mixtures of DPS/PVME showed a significant deviation from the scattering function obtained in the context of incompressible RPA. In other words, the scattering intensity in the low- q region is suppressed relative to that predicted by the conventional RPA theory; the degree of suppression tends to increase with decreasing q . The suppression is more significant as the temperature approaches the T_g . To our surprise, the deviation took place from the temperature ca. 107 K above the T_g for the DPS/PVME 50/50 mixture. Furthermore, our SANS data suggest that in this temperature regime the effective interaction parameter shows the q dependence of the type given by eq. (5-15). On the other hand, the SANS behavior for both blends of DPB/HPB and DPB/HPI was well described by the conventional de Gennes scattering formula at all the temperatures.

It is expected from our SANS results that the deviation from de Gennes scattering formula near the T_g was caused by characteristics of the DPS/PVME

mixture:¹⁷ (i) the DPS/PVME mixture has very different T_g 's in pure components and (ii) DPS has a bulky side group; i.e., bulky benzene ring, while PVME does not have any bulky side groups. Hence, it is predicted that the rotational entropy made a significant contribution to attractive interaction term and the nonlocality of the rotational entropy became increasingly important upon approaching the T_g of the mixture.

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Crossover of Domain-Growth Behavior from Percolation to Cluster Regime in Phase Separation of Non-Isometric Polymer Mixtures

6-1. Introduction

In chapters 2-5, miscibility of binary polymer systems was discussed. Hereafter (in chapters 6-8), we discuss the phase separation dynamics and phase separating morphology for non-isometric polymer mixtures. In this chapter we investigate the phase separating dynamics involving the morphological change from percolation to cluster of droplets in the course of phase separation by means of time-resolved light scattering.

In recent years, there has been an increasing interest to investigate the dynamics of phase separation in non-isometric polymer mixtures.¹⁻¹³ So far, it was experimentally found by Hashimoto et al.² that the time evolution of the phase-separated structure for the non-isometric mixtures of poly(styrene-*ran*-butadiene) (SBR) and polybutadiene (PB) or SBR and polyisoprene (PI) having the large molecular weight was stopped in the course of phase separation ("spontaneous pinning" of domain growth). They explained that the behavior was due to "percolation-to-cluster transition (PCT)". According to them, a barrier based upon enthalpy of mixing ΔH_{mix} exists for transport of polymer chains across the interface of phase separated structure. This barrier is proportional to the Flory-Huggins interaction parameter χ and degree of polymerization N ($\Delta H_{mix} \sim \chi N k_B T$). The transport of polymer chains across the interface is necessarily needed for the growth of the cluster of the droplets, while it is not needed for that of the percolated phase-separating domains. Therefore, the domain growth for non-isometric polymer mixtures with a large

N is effectively pinned after PCT, because the barrier is very high for such polymer mixtures. Luger et al.⁶ showed that the domain growth after PCT appeared to be pinned from the observation of light scattering (LS) for a non-isometric mixture of PB and PI. However, their observation with optical microscopy on the same sample showed that the domain grows even during the pinning stage as observed by LS. In addition, Okada et al.¹⁰ reported that the pinning associated with PCT was not observed for non-isometric mixtures of polystyrene and poly(2-chlorostyrene). Thus, our understanding of the dynamics of phase separation for non-isometric polymer mixtures seems to be insufficient at present.

In this work, we focused on the phase separation dynamics, especially the dynamics after the onset of PCT for non-isometric mixtures of an PB and PI. For this purpose, we observed the phase separation process over a much longer time period than that reported in other experiments for non-isometric polymer mixtures by using LS. In this chapter, we aim to report our finding as follows: Before the onset of PCT domains grow rapidly according to the power law of percolation (percolation regime). The domain growth becomes very slow or may appear to stop at first sight after the onset of PCT if the time scale of observation is not enough (PCT regime). However, for observation in a sufficiently long time scale, the domain gradually grows, and then, in a much longer time scale, the time-evolution of phase separation obeys the growth law of cluster of droplets (cluster regime). Thus, on being triggered by PCT, the domain-growth behavior can be classified into those of three regimes, i.e., percolation regime, PCT regime and cluster regime.

6-2. Experimental Section

6-2-1. Sample Preparation and Characterization

The characteristics of PB and PI used in this study are summarized in Table 6-1. The PB and PI were synthesized by living anionic polymerization.

The mixtures (denoted PB/PI) with compositions of 50/50, 65/35 and 70/30 were prepared where x and y in x/y denotes the composition of PB and PI in weight percent, respectively. The PB/PI mixture having composition x/y is denoted hereafter PB/PI= x/y or the mixture x/y for simplicity. The mixtures were dissolved in toluene solution containing ca. 2-3 wt.% total amount of polymers. The solution was filtered by using a milipore film with a pore size $0.45\ \mu\text{m}$ to remove impurities in it and then casted in a petri dish by slowly evaporating the solvent for ca. 5 days at $20\ ^\circ\text{C}$. The mixture obtained was dried in a vacuum oven for ca. two days until the solvent was perfectly removed. Film specimen thus prepared was put on a glass plate and then degassed under

Table 6-1 Sample Characterization

Sample	$M_w \times 10^{-4}$ ^a	M_w/M_n ^a	Microstructure, % ^b			
			1,2	3,4	cis-1,4	trans-1,4
PB	5.8	1.20	16	-	28	56
PI	10.1	1.30	-	7.5	70.4	22.1

^a Measured by size exclusion and chromatography with light scattering.

^b Measured by IR spectroscopy.

vacuum for ca. 12 hours in order to avoid the scattering due to bubbling. The film was sandwiched between two glass plates in a sample holder.

6-2-2. Light Scattering

We measured cloud points for the PB/PI mixtures by using light scattering. The method of the cloud point measurement will be described in details in chapter 8.¹³ For the studies of phase separation dynamics, we measured the time change in light scattering profiles after the mixture was quenched from a single-phase state to a two-phase state. Such measurements

were carried out at various temperatures and for compositions with 50/50, 65/35 and 70/30.

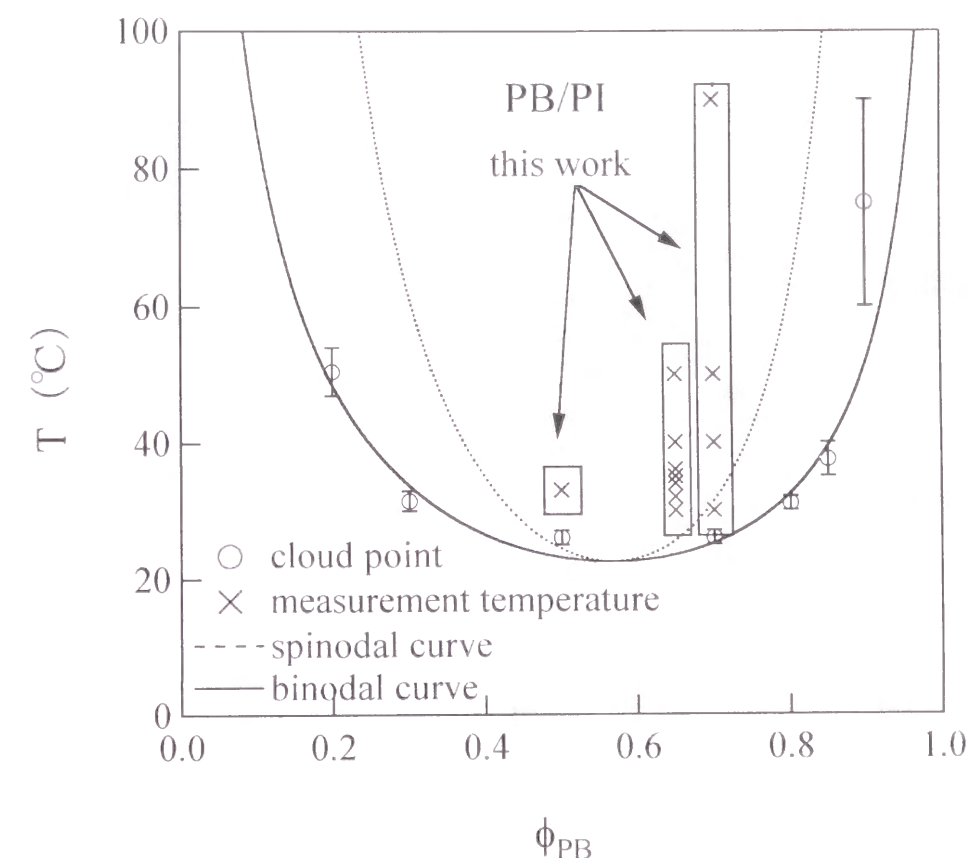


Figure 6-1 Cloud point curve (data points marked by open circles), binodal and spinodal curves (the solid and dotted lines, respectively) which are calculated using Flory-Huggins theory (see chapter 8 for details).

6-3. Results

6-3-1. Time Change in Scattering Profiles

Figure 6-1 shows the cloud points measured for the PB/PI mixture (data points marked by open circles) and the binodal curve (the solid line) which was determined by a fit to the cloud points using the Flory-Huggins theory,^{14, 15} as detailed in chapter 8.¹³ In addition, the spinodal curve (the dotted line) which

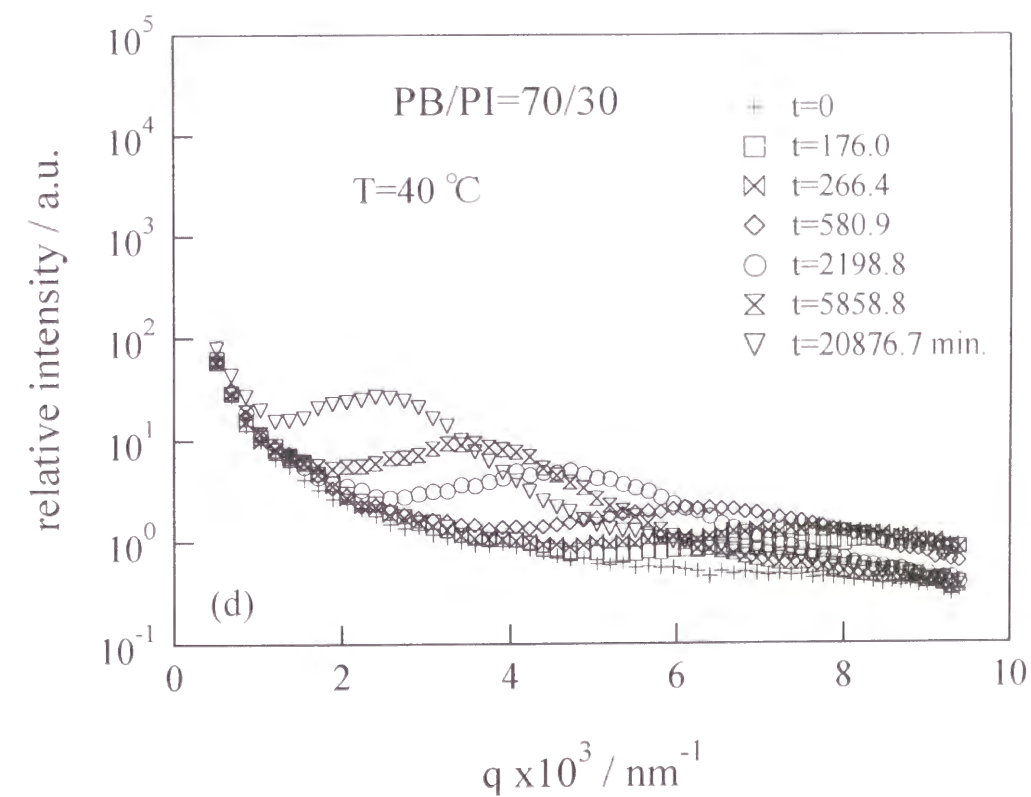
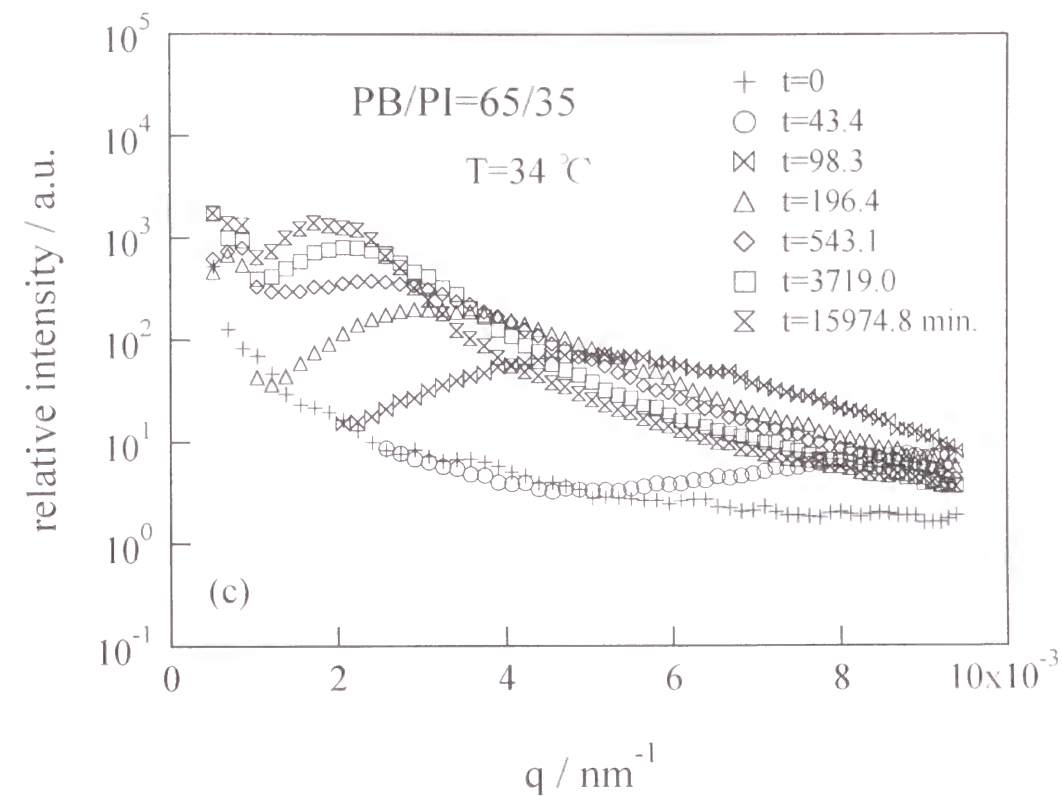
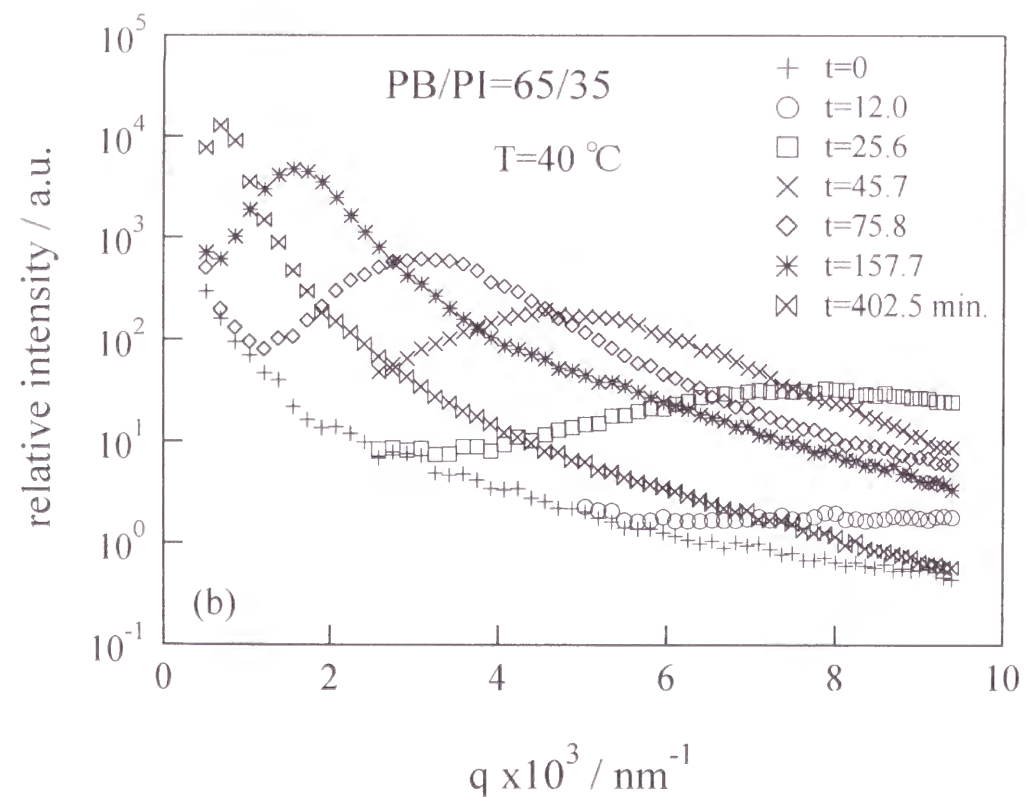
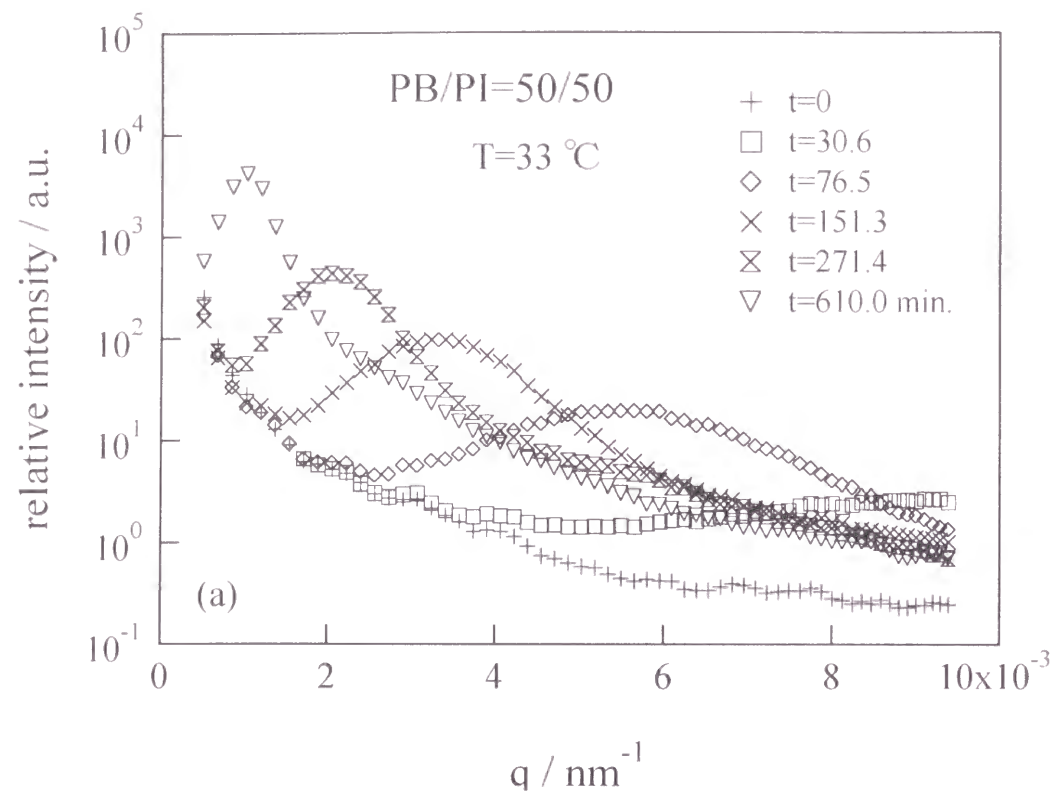


Figure 6-2 Time change in scattering profiles (a) at $T=33$ °C for the 50/50 mixture, (b) at $T=40$ °C for the 65/35 mixture, (c) at $T=34$ °C for the 65/35 mixture and (d) at $T=40$ °C for the 70/30 mixture.

was obtained by using the χ parameter estimated in the fit, is included in Fig. 6-1. In estimating the binodal and spinodal lines, χ was assumed to be independent of composition, $\chi=0.00628-1.38/T$. The PB/PI possesses a lower critical solution temperature (LCST).

Figure 6-2 presents time change in the scattering profiles for (a) the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$, (b) the 65/35 mixture at $T=40\text{ }^{\circ}\text{C}$, (c) the 65/35 mixture at $T=34\text{ }^{\circ}\text{C}$ and (d) the 70/30 mixture at $T=40\text{ }^{\circ}\text{C}$. The scattering profile is presented as a function of magnitude of the scattering vector $q\ [=4\pi\sin(\theta/2)/\lambda]$ where θ is the scattering angle and λ is the wavelength in the medium. With an elapse of time, each mixture shows scattering profiles with a scattering peak. The scattering peak shifts toward low q and the maximum scattering intensity increases with time, which means that the phase-separated structures grow with time. The kinetics of phase separation for each compositions or quenches is very different. The peak shift toward low q for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$ (part a) and that for the 65/35 mixture at $T=40\text{ }^{\circ}\text{C}$ (part b) are much faster than that for the 70/30 mixture at $T=40\text{ }^{\circ}\text{C}$ (part d). The peak shift for the 65/35 mixture at $T=34\text{ }^{\circ}\text{C}$ (part c) is as fast as that for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$ and that for the 65/35 mixture at $T=40\text{ }^{\circ}\text{C}$ until a certain time of the phase separation process. However, afterwards, the peak shifts suddenly gets slower. The peak for the 70/30 mixture at $T=40\text{ }^{\circ}\text{C}$ is broader than that for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$ and that for the 65/35 mixture at $T=40\text{ }^{\circ}\text{C}$. While the peak for the 65/35 mixture at $T=34\text{ }^{\circ}\text{C}$ is as sharp as that for the 50/50 mixture until a certain time of phase separation, afterwards it gets broader than that for the 50/50 mixture.

6-3-2. Time Change in q_m and I_m

In the analysis of the phase separation process, time-evolution of the magnitude of the scattering vector q_m at which scattering intensity has a

maximum value of I_m and the maximum intensity I_m are often described by power laws,

$$q_m \propto t^{-\alpha}, \quad (6-1)$$

$$I_m \propto t^{\beta}. \quad (6-2)$$

The scaling exponents α and β characterize the time evolution of phase-separated structures.

Figure 6-3 show the double logarithmic plot of (a) q_m versus time t and (b) I_m versus t for the 70/30 mixture at various temperatures and for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$. It is shown in Fig. 6-3 that the time changes in q_m and I_m for these measurements obey the power law. For the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$ which is a near-critical-mixture, α and β become 0.9 and 2.7, respectively, in the long time limit of the present experiment. On the other hand, the values of α and β for the 70/30 mixture in the long time limit are larger than 0.25 and less than 0.33, and larger than 0.75 and less than 1, respectively, at all temperatures covered in this experiment.

Figure 6-4 shows the double logarithmic plot of q_m (part a) and I_m (part b), respectively, as a function of t for the 65/35 mixture at various temperatures. The phase separation kinetics shows a remarkable temperature or quench-depth dependence for this mixture. At both temperatures of 40 and 50 $^{\circ}\text{C}$, α and β become 0.9 and 2.7, respectively, in the late time, behavior of which is similar to that for the near-critical-mixture (50/50 mixture). At 36 $^{\circ}\text{C}$, the time change in I_m shows the same behavior as those at 40 and 50 $^{\circ}\text{C}$ until ca. $t=110\text{ min}$. (cf. Fig. 6-8 later) (see the arrow marked on the I_m vs. t for the sake of convenience), afterwards it gradually becomes slow in the late time of this experiment, which may be highlighted by comparing the straight line drawn based on the data

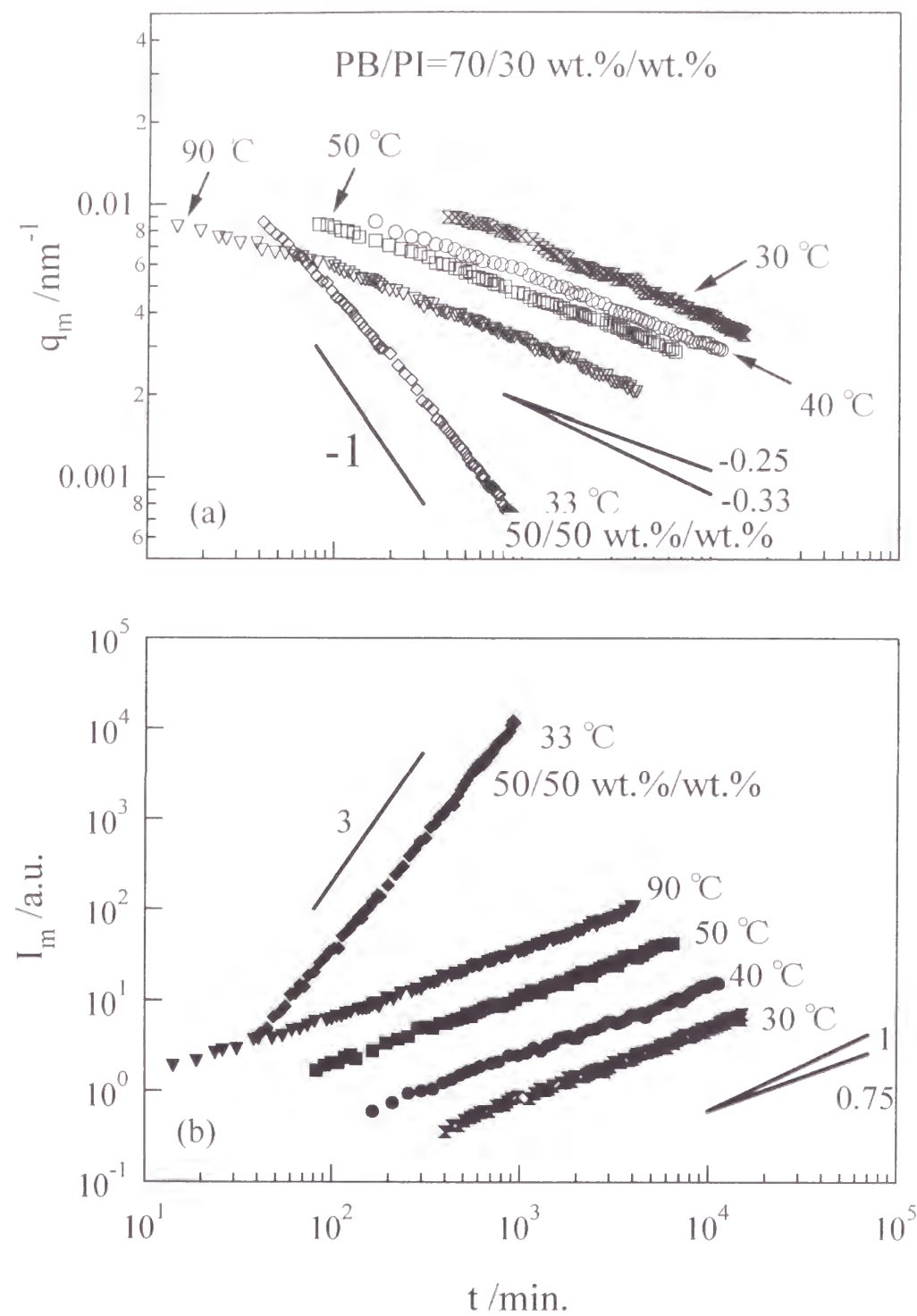


Figure 6-3 Plots of (a) $\log q_m$ and (b) $\log I_m$ versus $\log t$ at various temperatures for the 70/30 mixture and at $T=33$ °C for the 50/50 mixture.

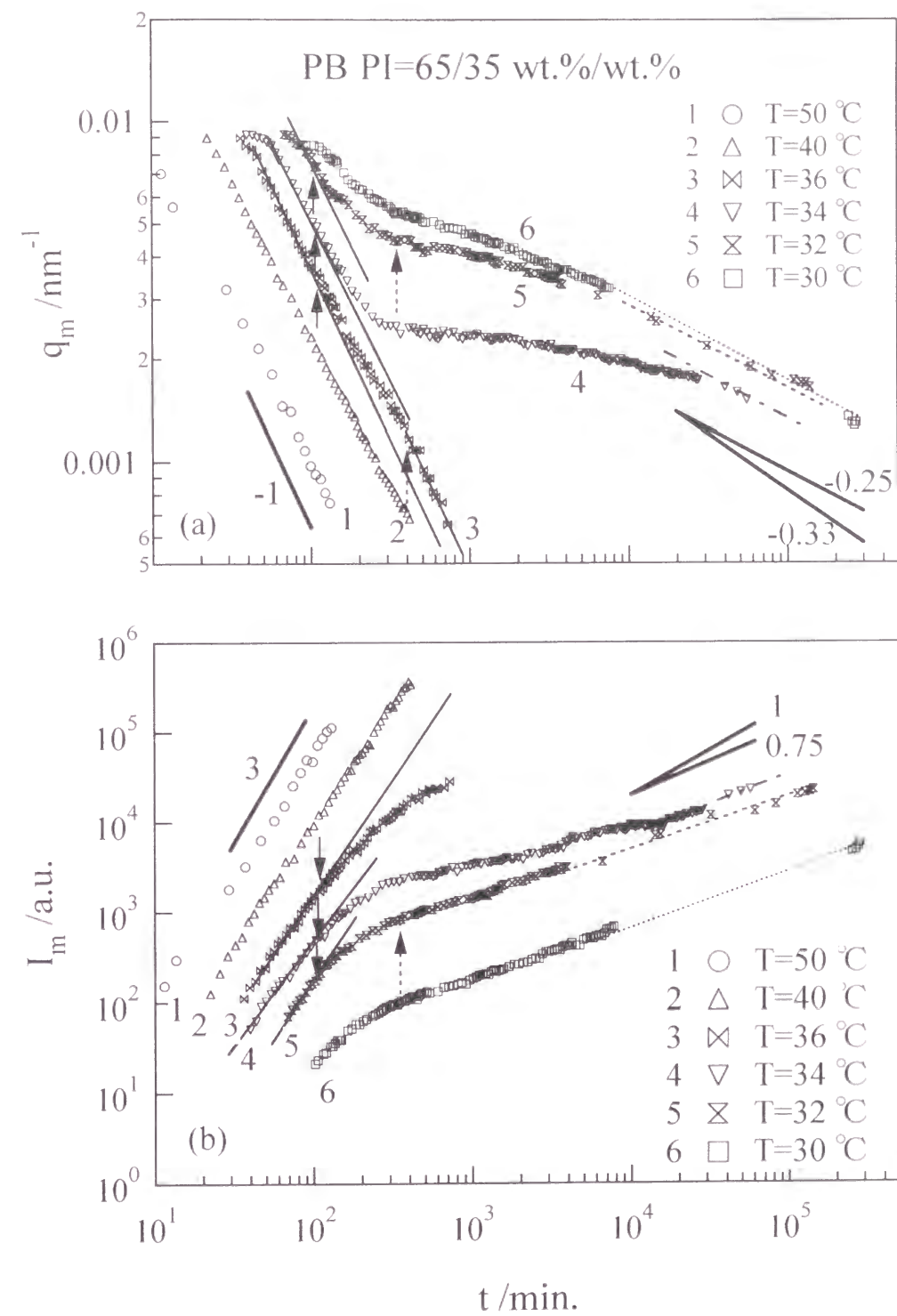


Figure 6-4 Plot of (a) $\log q_m$ and (b) $\log I_m$ versus $\log t$ at various temperatures for the 65/35 mixture.

points at $t \leq 110$ min. with data points at $t > 110$ min. The close observation of q_m vs. t at $T=36$ °C also reveals a similar difference in the time evolution behavior before and after $t \approx 110$ min. (marked by the arrow on the data points of q_m vs. t); the solid line represents the power law obtained at $t \leq 110$ min. The time-evolution of q_m is slightly slowed at $t > 110$ min., although it is much faster than that given by the power law of $\alpha \approx 0.25-0.33$. The behavior of q_m and I_m at 35 °C whose data are not shown in this paper, also shows the same trend as that at 36 °C. The same behaviors as those of I_m and q_m at $T=36$ °C are observed at other temperatures ($T=34$ and 32 °C; see the arrows in Fig. 6-4) too, if we take careful look at Fig. 6-4. This behavior will be further analyzed and discussed in Sec. 6-4-2.

At temperatures of 34 , 32 and 30 °C which are shallower quenches than 50 , 40 and 36 °C, the time-evolutions of q_m and I_m are the same as those at 40 and 50 °C until a certain time of phase separation, but they suddenly slow down beyond this time defined hereafter as t_{slow} . Moreover, the shallower the quench, the earlier the time t_{slow} and the larger the scattering vector q (denoted hereafter as $q_{m,slow}$) at which the slowing down of the domain growth begins. In the slowing-down regime of the domain growth, the values of α and β have quench-depth dependence; the deeper the quench-depths, the smaller the values of α and β become. In the long time scale even in this regime, the domain gradually grows. Then in the much longer time limit the domain grows according to the power law of $\alpha \approx 0.25-0.33$ as observed for the $70/30$ mixture (see the broken lines for visual guides). Thus, the domain-growth behaviors of $65/35$ mixtures show the regime with the scaling law of $\alpha \approx 0.9$ and $\beta \approx 2.7$, that of $\alpha \approx 0.25-0.33$ and $\beta \approx 0.75-1$ and the crossover regime in between the above two scaling regimes.

6-4. Discussion

6-4-1. Time-Evolution of Characteristic Length Scale

In the previous section, we reported on the results of time changes in q_m and I_m for various compositions and quenches. As shown below, our results imply that the phase separation dynamics can be divided into three regimes; (i) “percolation regime” where phase separation dynamics shows the growth law for percolated structure, (ii) “PCT regime” associated with the crossover of the domain-growth behavior induced by PCT, and (iii) “cluster regime” where phase separation dynamics obeys the growth law for cluster of the droplets.

The phase separation behavior of $50/50$ mixture at $T=33$ °C showed the power law of $\alpha \approx 0.9$ and $\beta \approx 2.7$, suggesting that percolated structures grow (*percolation regime*): two coexisting and growing domains are continuous in three dimensional space forming a sponge-like structure.¹⁶⁻²⁰ Namely, the value of $\alpha \approx 0.9$ is close to $\alpha=1$ theoretically predicted for systems with percolation structures in which hydrodynamic interactions are important.²¹ Hence, we expect that the phase-separated structure for the $50/50$ mixture keeps bicontinuous domain structures and hydrodynamic interactions are important in the late time of the phase separation covered in our experiment. On the other hand, the values of α and β for the $70/30$ mixture were $0.25-0.33$ and $0.75-1$, respectively, at all temperatures covered in this experiment (*cluster regime*). Their values obtained are near those expected from the growth of cluster of droplets by vaporization-condensation mechanism (Lifshitz-Slyozov-Wagner law)^{22, 23} and diffusion-coalescence of cluster of droplets with hydrodynamic interactions ($\alpha=1/3$).²²⁻²⁴ The $1/3$ -power law has been reported for non-isometric mixtures of polystyrene/poly(2-chlorostyrene)¹⁰ and deuterated polybutadiene /polystyrene.²⁵

The time evolution of the phase-separated structures for the $65/35$ mixture at $T=40$ and 50 °C revealed the same tendency as that for the $50/50$ mixture,

which means that the phase separated structures form bicontinuous domain structure (percolation regime). On the other hand, at $T=36, 34, 32$ and $30\text{ }^{\circ}\text{C}$, while the phase-separated structure grew according to the power law of percolation regime until a certain time, the slowing down of the domain growth was observed in the course of phase separation (PCT regime). This behavior is considered to be caused by PCT. In fact, the results that $q_{m,slow}$ and t_{slow} were, respectively, larger and earlier for shallower quenches, are consistent with the result of “spontaneous pinning” caused by PCT.^{2,6} In addition, as will be shown in the following section, the scaled structure factor analyses will support the above conjecture of PCT. At $T=34, 32$ and $30\text{ }^{\circ}\text{C}$, in the much longer time scale, the domain grows according to the power law of 0.25-0.33, indicating that the phase separation grows according to the power law of cluster of droplet (cluster regime). Thus, at $T=34, 32$ and $30\text{ }^{\circ}\text{C}$, the phase separation behavior shows three regimes, i.e., (i) the percolation regime before PCT, (ii) PCT regime and (iii) the cluster regime in a much longer time scale.

6-4-2. Scaled Structure Factor

Scaled structure factor $F(x,t)$ is defined as follows.

$$F(x,t) = q_m(t)^3 I(q,t) = \langle \eta(t)^2 \rangle S(x,t). \quad (6-3)$$

$\langle \eta(t)^2 \rangle$ is the mean squared fluctuations of refractive index, and $S(x,t)$ is a scaling function which varies from unity to zero with increasing $x \equiv q/q_m(t)$ from zero to infinity. In the late stage of spinodal decomposition (SD) for critical polymer mixtures, it has been so far reported by numerous experiments^{26, 27} that $F(x,t)$ is universal with time, i.e., dynamical scaling hypothesis²⁴ holds in the late stage of SD.^{28, 29}

In Fig. 6-5, we present a plot of the scaled structure factor $F(x,t)$ vs. x for the 50/50 mixture at $T=33^{\circ}\text{C}$ in the late stage where $F(x,t)$ is shown to be

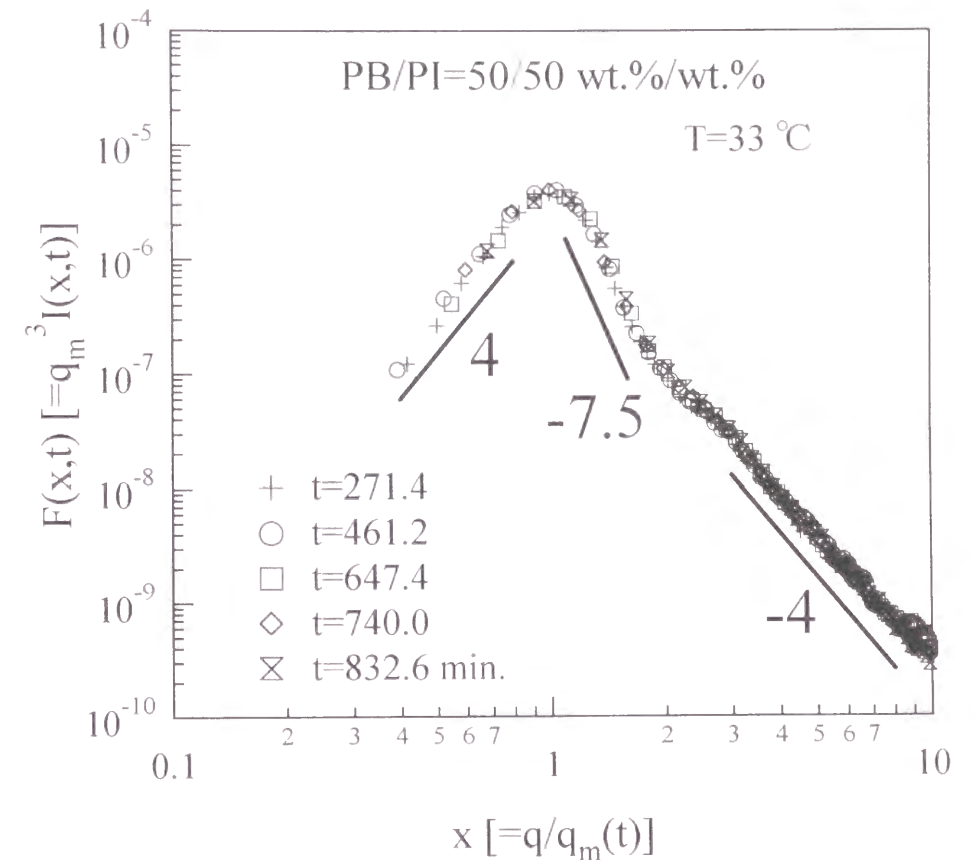


Figure 6-5 Double logarithmic plot of scaled structure factor $F(x,t)$ versus $x=q/q_m$ at $T=33\text{ }^{\circ}\text{C}$ for the 50/50 mixture.

universal with time. The $F(x,t)$ has x^4 dependence for $x < 1$ and $x^{-7.5}$ ($n \approx 7.5$) dependence for $1 < x < 2$. In addition, the $F(x,t)$ has x^{-4} dependence (Porod regime) for $x > 3$. The form of $F(x,t)$ is in agreement with theoretical and other experimental results of $F(x,t)$ for the system whose phase-separated structure forms percolation or bicontinuous domain structure.²⁹⁻³⁶

Next, we present the time change in $F(x,t)$ for the 65/35 mixture at various temperatures. Figure 6-6 shows the time change in $F(x,t)$ for the 65/35 mixture at $T=40\text{ }^{\circ}\text{C}$ in the late stage of SD. The $F(x,t)$ shows universal behavior at time greater than $t=84.6\text{ min.}$, indicating that $\langle \eta(t)^2 \rangle$ reaches an equilibrium value and phase-separated structures grow self-similarly with time. In addition, it is

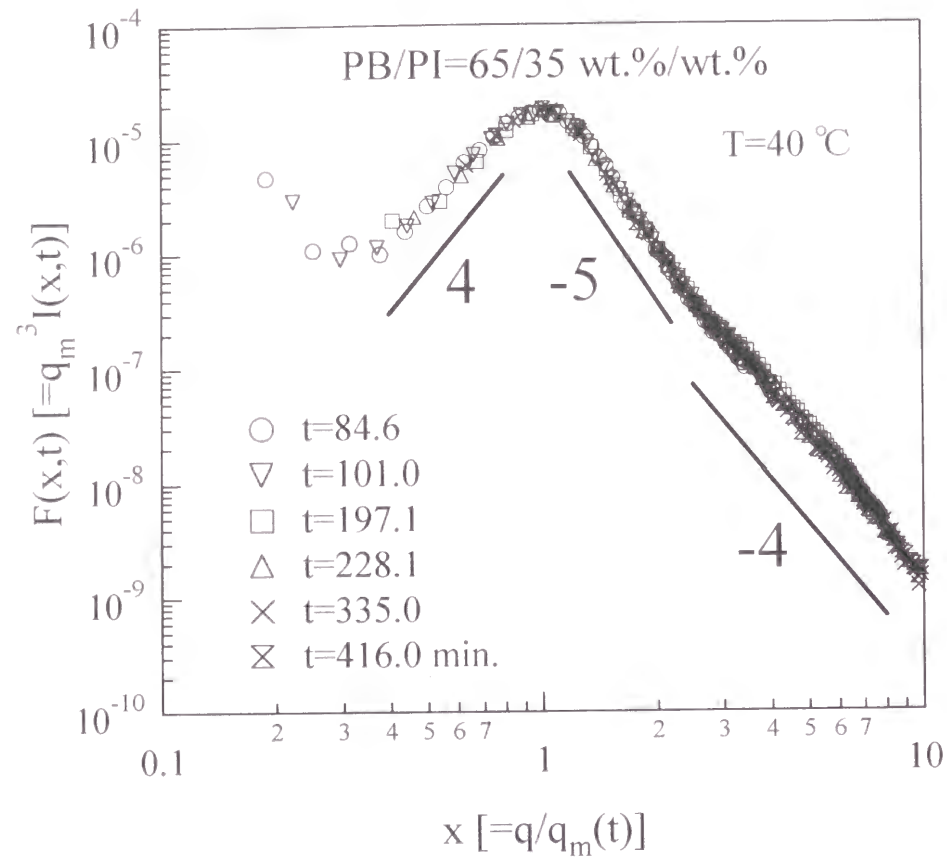


Figure 6-6 Double logarithmic plot of scaled structure factor $F(x,t)$ versus $x=q/q_m$ at $T=40\text{ }^{\circ}\text{C}$ for the 65/35 mixture.

shown that the $F(x,t)$ has x^4 dependence for $x < 1$, x^{-n} ($n \approx 5$) dependence for $1 < x < 2$ and x^{-4} dependence for $x > 3$ as in the case of the 50/50 mixture, except for the fact that the exponent $n \approx 5$ is smaller than $n \approx 7.5$. Nevertheless, the phase-separated structure for the 65/35 mixture at $T=40\text{ }^{\circ}\text{C}$ is expected to be also bicontinuous (percolating network).

Figure 6-7 shows comparison of $F(x,t)/F(1,t)$ vs. x for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$, for the 65/35 mixture at $T=40$ and $50\text{ }^{\circ}\text{C}$ in the late stage, for which phase-separated structures have bicontinuous structures. While the $F(x,t)/F(1,t)$ for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$ (circles) and that for the 65/35 mixture at $T=50\text{ }^{\circ}\text{C}$ (triangles) show the same form, the $F(x,t)/F(1,t)$ for the 65/35 mixture

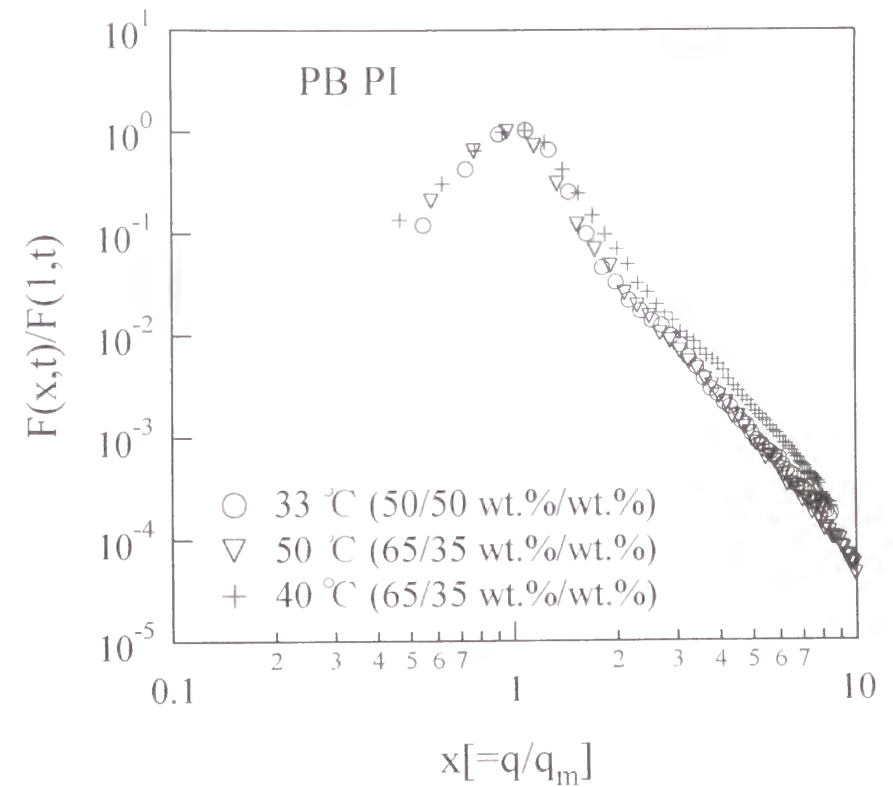


Figure 6-7 Double logarithmic plot of scaled structure factor $F(x,t)/F(1,t)$ versus $x=q/q_m$ at $T=33\text{ }^{\circ}\text{C}$ for the 50/50 mixture, at $T=40$ and $50\text{ }^{\circ}\text{C}$ for the 65/35 mixture.

at $T=40\text{ }^{\circ}\text{C}$ (crosses) is slightly broader than those for the 50/50 mixture at $T=33\text{ }^{\circ}\text{C}$ and for the 65/35 mixture at $T=50\text{ }^{\circ}\text{C}$. The difference may be due to a difference in the relative volume of the two phases.

In Fig. 6-8 we show the time change in $F(x,t)$ at $T=36\text{ }^{\circ}\text{C}$ at which the time evolution of q_m and I_m was slightly slowed down in the course of phase separation. The time change is divided into three regimes. As shown in Fig. 6-8(a), $F(x,t)$ increases with time at whole x region until $t=46.5$ min. Therefore, it is expected that, in this regime, $\langle \eta(t)^2 \rangle$ does not reach the equilibrium value yet and hence becomes larger with time (intermediate regime of SD).²⁶ The scaled structure factors $F(x,t)$ at t between 49.8 (circles) and 114.6 min. (crosses) become nearly independent of time [Fig. 6-8(b)]. Therefore, at $t=50$ min. $\langle \eta(t)^2 \rangle$ is expected to almost attain an equilibrium value. Thus, the system

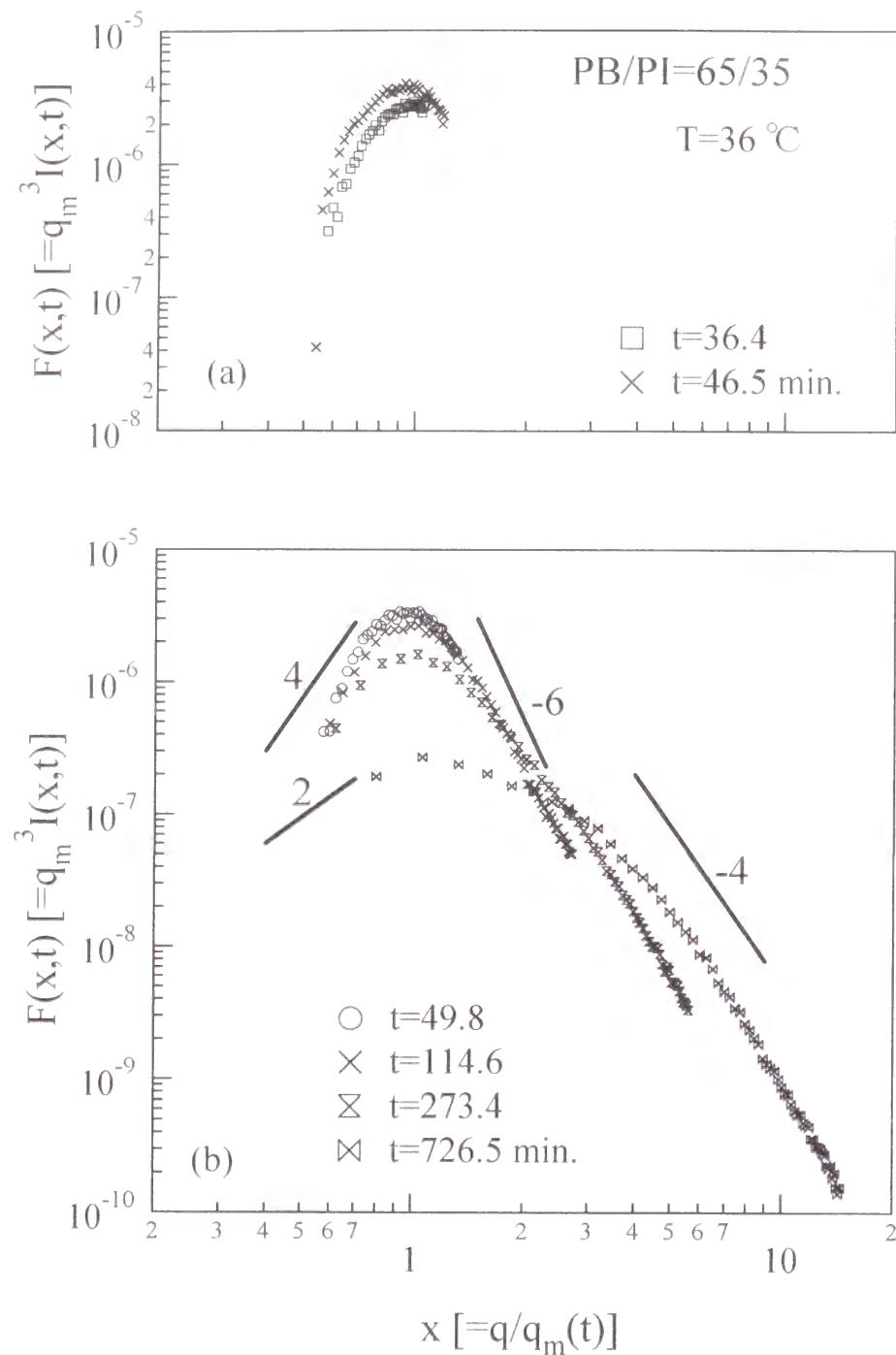


Figure 6-8 Time change in scaled structure factor $F(x,t)$ versus $x=q/q_m$ at $T=36^\circ\text{C}$ for the 65/35 mixture.

reaches approximately the late stage of SD where the dynamical scaling hypothesis is essentially valid (scaling regime).

After $t=114.6$ min., $F(x,t)$ shows a drastic change with time [Fig. 6-8(b)]. Note that the time 114.6 min. corresponds closely to that where the time-evolution behaviors of $I_m(t)$ and $q_m(t)$ start to change (see the arrows in Fig. 6-4). While $F(x,t)$ around $x=1$ decreases with time in this regime, $F(x,t)$ increases at higher x . (e.g. $x \geq 2$) That is, $F(x,t)$ gradually gets broader as time elapses, and this broadening in $F(x,t)$ continues over the time scale of our experiment (up to $t=726.5$ min.). It is important to follow further changes in $F(x,t)$, and the power law behaviors of $q_m(t)$ and $I_m(t)$ with time, which is left for future studies. The asymptotic behavior of $F(x,t)$ at $x < 1$ [$F(x,t) \sim x^n$] gradually changes from $n=4$ to $n=2$, and that of $F(x,t)$ at $x > 1$ [$F(x,t) \sim x^{-n}$] changes from $n=6$ to $n=4$, suggesting that the broadening in $F(x,t)$ is due to PCT. The PCT appears to continue over the time scale of this experiment (PCT regime).

The result that $F(x,t)$ became broader after PCT occurred was also recently reported by Takenaka et al.⁴ However, the increase of $F(x,t)$ at the high x , as found here in our studies, was not observed in their experiments. This may be simply because their experiment did not cover the high x range. The result illuminated here seems to be quite natural, considering the fact that $\langle \eta(t)^2 \rangle$ does not decrease in the course of PCT because the phase-separated domains almost attained the equilibrium compositions at the time of PCT. That is, the integration of $F(x,t)$ over whole x [which is related to $\langle \eta(t)^2 \rangle$] should be constant with time.

We interpret these results of $F(x,t)$ and the gradual slowing down of I_m after PCT at $T=36^\circ\text{C}$ as follows. The percolated domains will break up into fragments with locally percolated structure, as shown in schematic representation of Fig. 6-9(a), the fragments with wavy interface split into smaller fragments, and they are gradually transformed into droplets with round

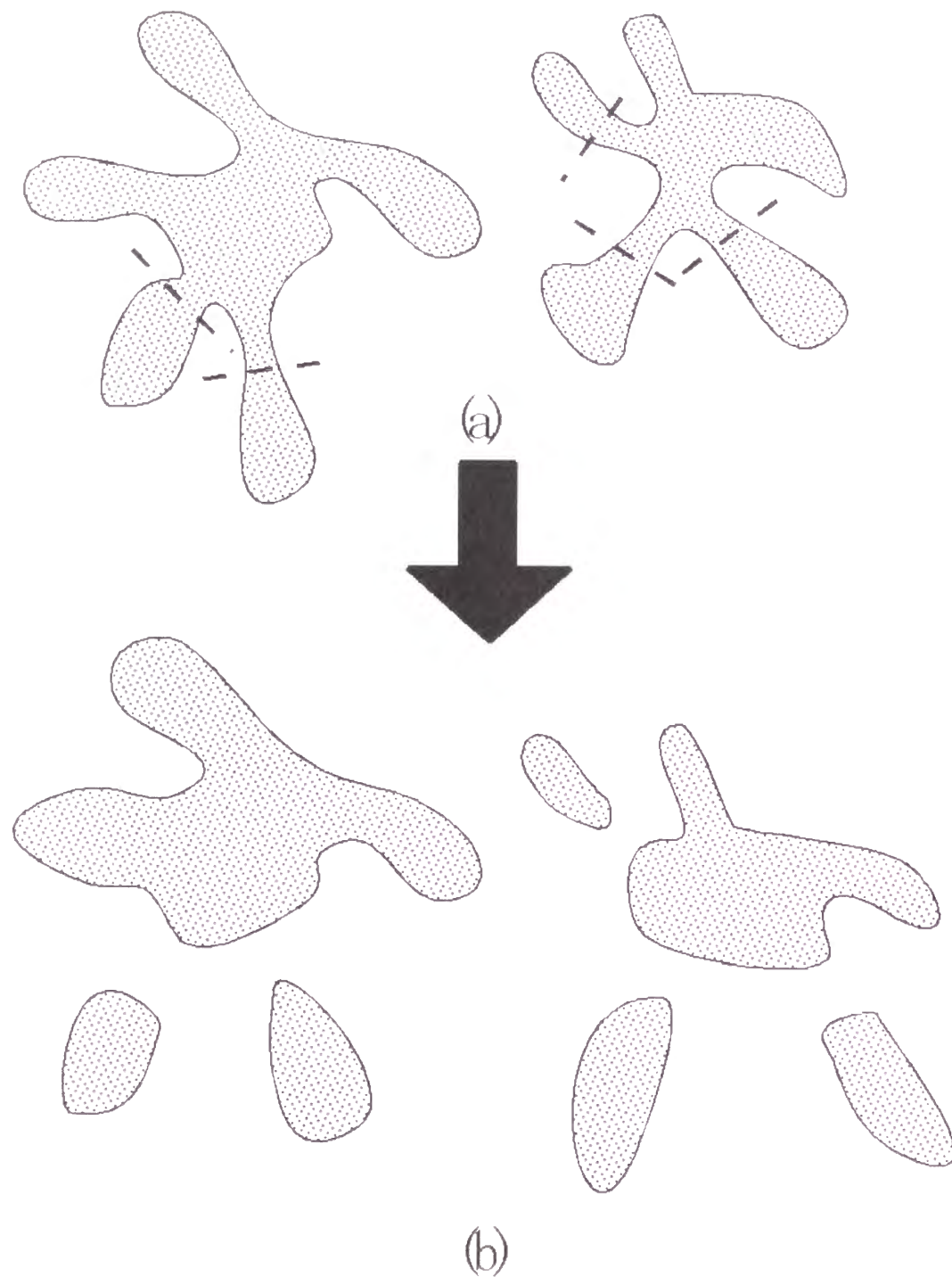


Figure 6-9 Schematic representation in the breakup of phase-separated structures with locally percolated structures (part a) into smaller fragments (part b).

shape to reduce the interfacial energy^{37, 38} as shown in Fig. 6-9(b). During this process, the time-evolution of I_m becomes gradually slow. Since after breakup of the percolated domains the scaled structure factor tends to broaden, and $S(x=1, t)$ decreases.⁴

On the other hand, after the slight slowing down in the time evolution of $q_m(t)$ and hence that of the domain growth starting $t=110$ min. [solid arrows in Fig. 6-4(a)], q_m appears to recover the growth behavior with the power of $\alpha \approx 0.9$, at the time longer than ca. 400 min. [see the dotted arrow in Fig. 6-4(a)]. The interpretation of this behavior cannot be made at present and is beyond the scope of this paper. For the investigation, a real-space observation is crucial.

The time dependence of $F(x, t)$ at $T=32$ °C is divided into four regimes (Fig. 6-10). Until $t=111.4$ min. $F(x, t)$ increases with time in the whole x region covered in our experiment, implying that $\langle \eta(t)^2 \rangle$ increases with time [Fig. 6-10(a)] (intermediate regime of SD). Afterwards, $F(x, t)$ decreases around $x=1$ and slightly increases at high x with time from $t=111.4$ [see the corresponding time marked by solid arrows in Figs. 6-4 (a) and 6-4(b)] to 354.9 min. [see the corresponding time marked by dotted arrows in Figs. 6-4(a) and 6-4(b)] as seen in Fig. 6-10(b). The $F(x, t)$ becomes slightly broader with t . This change in the $F(x, t)$ corresponds to that after onset of PCT at $T=36$ °C. Therefore, we expect that PCT starts to occur at ca. $t=111.4$ min. (PCT regime at $t > 111.4$ min.). As shown in the following section, PCT starts to occur in the intermediate stage of SD, i.e., $\langle \eta(t)^2 \rangle$ still grows with time. However, we should notice that the decrease of $F(x, t)$ around $x=1$ and increase of $F(x, t)$ at high x are very small and the time period over which they are observed is short relative to the corresponding changes at $T=36$ °C. Furthermore, in the time region after $t=354.9$ min., as shown in Fig. 6-10(c), $F(x, t)$ around $x=1$ increases and $F(x, t)$ at high x slightly decreases with time. Namely, in this regime, $F(x, t)$ becomes sharper with time. Moreover, a broad shoulder at $x \approx 2.5$ is observed at $t=3889.7$

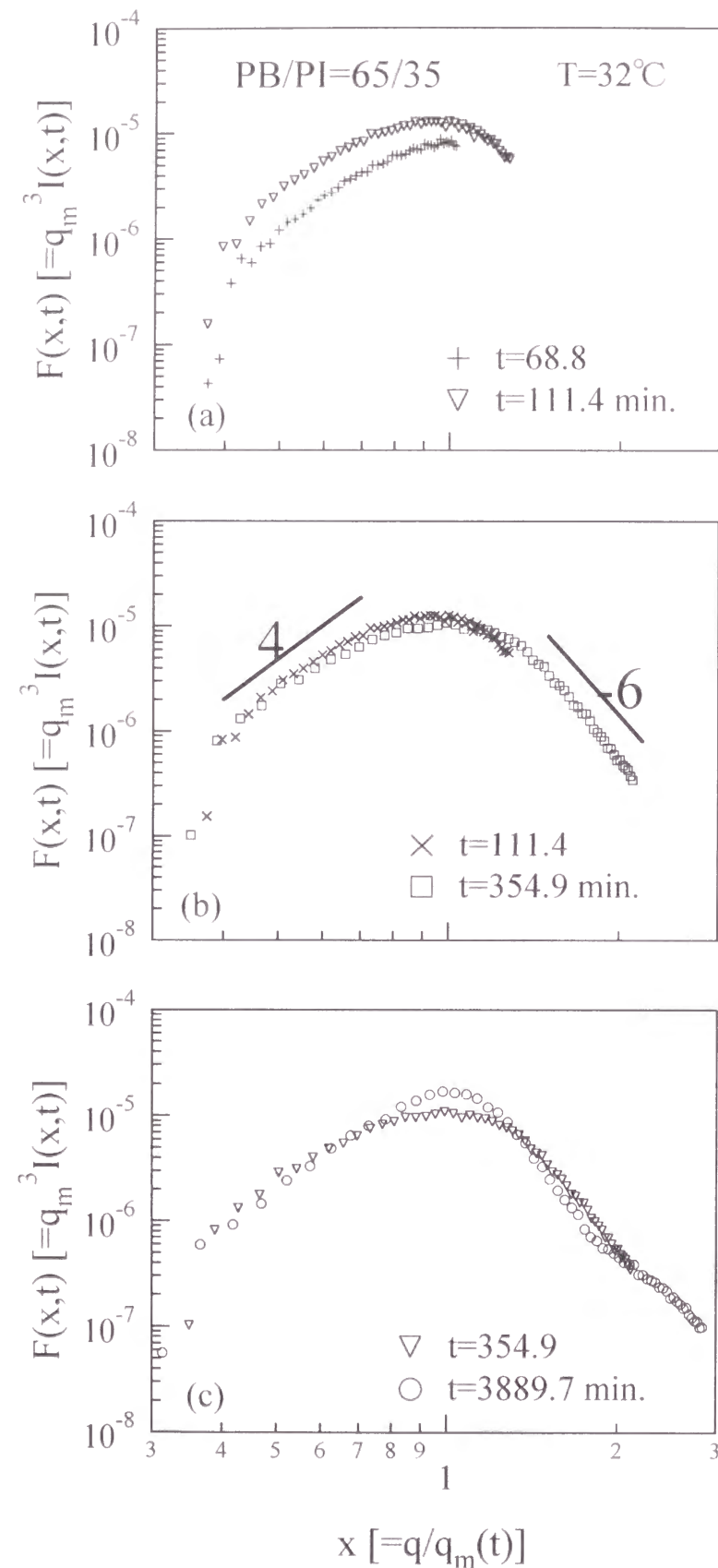


Figure 6-10 Time change in scaled structure factor $F(x,t)$ versus $x=q/q_m$ at $T=32\text{ }^{\circ}\text{C}$ for the 65/35 mixture.

min. In this regime, we speculate that the splitting process as shown in Fig. 6-9 does not occur any longer and the cluster of ramified particles caused by PCT gradually become the cluster of particles of round shape to reduce the interfacial energy and the distribution of the cluster changes so that the cluster size and the spacing among domains become uniform with time. Therefore, $F(x,t)$ is considered to become sharp with time. Furthermore, we conjecture that the shoulder at $x \approx 2.5$ at $t=3889.7$ min. is caused by the scattering maximum from the form factor of the single droplet.

Here, we should notice that the time-evolution of q_m and I_m also become very slow after $t \approx 350$ min., which almost corresponds to the time beyond which $F(x,t)$ starts to become sharper (see the dotted arrow in Fig. 6-4). This change in $F(x,t)$ indicates that the transformation of the cluster of ramified particles into that of round shaped particles and the spatial rearrangement of the cluster are dominant processes relative to the process involving growth of the particles occurring in the earlier stage.

In Fig. 6-11, the comparison of $F(x,t)/F(1,t)$ at $T=36\text{ }^{\circ}\text{C}$ at $t=726.5$ min. (roughly in the middle of PCT regime) and at $T=32\text{ }^{\circ}\text{C}$ at $t=3889.7$ min. (in nearly end of PCT regime) is shown. Clearly, $F(x,t)/F(1,t)$ at $T=32\text{ }^{\circ}\text{C}$ at $t=3889.7$ min. is much sharper than that at $T=36\text{ }^{\circ}\text{C}$ at $t=726.5$ min. and therefore the distribution of the droplet size and the spacing between droplets at $T=32\text{ }^{\circ}\text{C}$ at $t=3889.7$ min. are expected to be much more uniform than those at $T=36\text{ }^{\circ}\text{C}$ at $t=726.5$ min. Afterwards (at $t \geq 4000$ min.), the phase separation process gradually transfers into diffusion-coalescence of droplets or vaporization-condensation mechanism (cluster regime). The behaviors of $F(x,t)$ at $T=34\text{ }^{\circ}\text{C}$ and $T=30\text{ }^{\circ}\text{C}$ whose data were not shown in this paper are essentially same as those at $T=32\text{ }^{\circ}\text{C}$ and $T=36\text{ }^{\circ}\text{C}$.

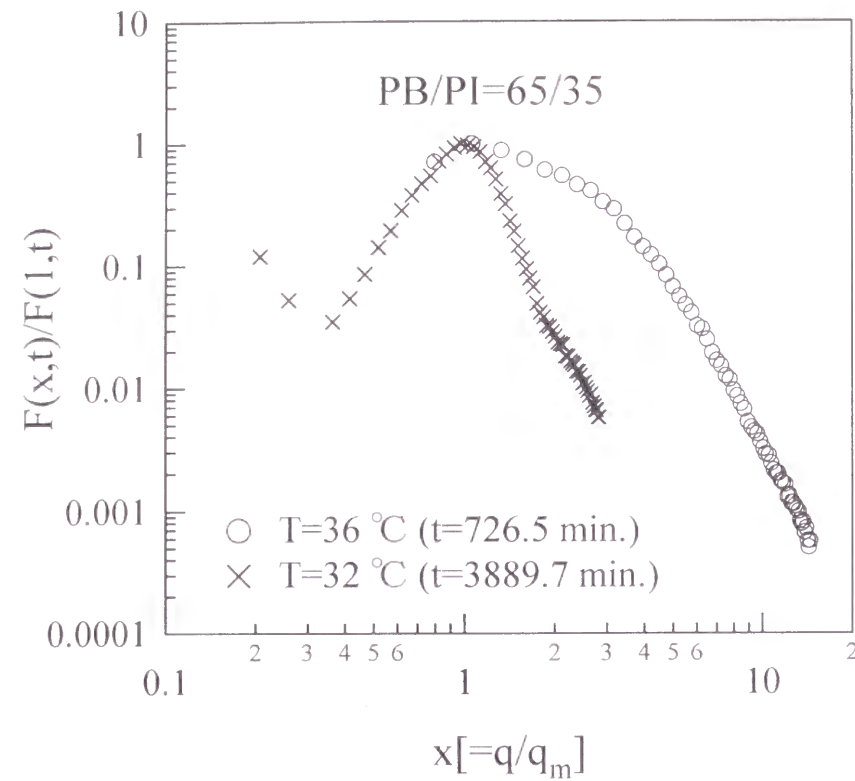


Figure 6-11 Double logarithmic plot of scaled structure factor $F(x,t)/F(1,t)$ versus $x=q/q_m$ at $T=36\text{ }^{\circ}\text{C}$ at $t=726.5\text{ min.}$ and at $T=32\text{ }^{\circ}\text{C}$ at $t=3889.7\text{ min.}$ for the 65/35 mixture.

6-4-3. Time Change in $\langle \eta(t)^2 \rangle$

In Sec. 6-4-1, we discussed that PCT was observed at $T=36, 34, 32,$ and $30\text{ }^{\circ}\text{C}$ for the 65/35 mixture in our experimental time scale. In this section, we investigate time change in $\langle \eta(t)^2 \rangle$ and the stage at which PCT occurs at these temperatures. We can evaluate $\langle \eta(t)^2 \rangle$ by calculating the invariant,

$$\langle \eta(t)^2 \rangle \propto \int_0^{\infty} F(x,t) x^2 dx \approx \int_{x_1}^{x_2} F(x,t) x^2 dx, \quad (6-4)$$

where x_1 and x_2 are, respectively, the upper and lower limits beyond which the integrand becomes negligibly small. Figure 6-12 shows the double-logarithmic

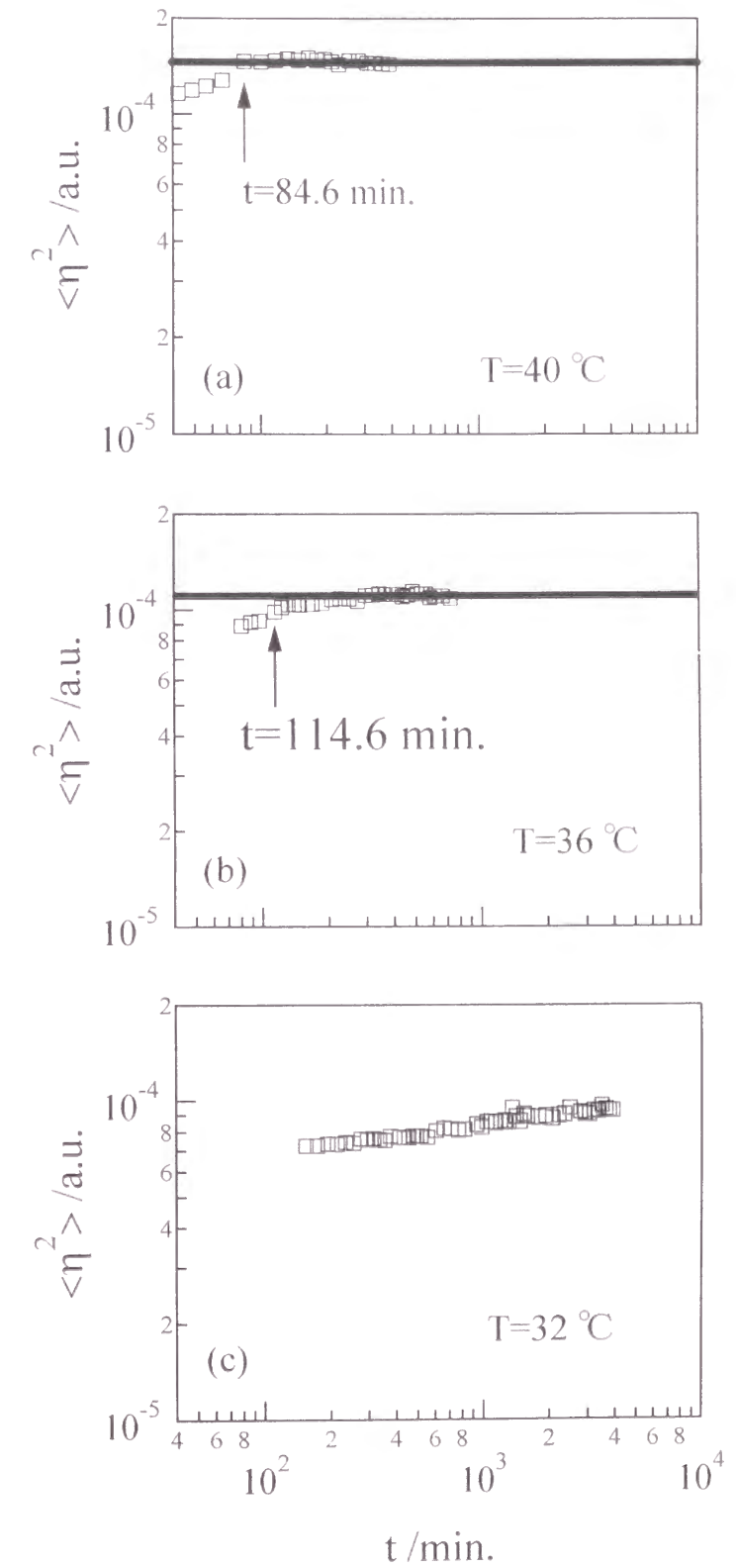


Figure 6-12 Time change in $\langle \eta(t)^2 \rangle$ at (a) $T=40\text{ }^{\circ}\text{C}$, (b) $T=36\text{ }^{\circ}\text{C}$ and (c) $T=32\text{ }^{\circ}\text{C}$ for the 65/35 mixture.

plot of the time change in $\langle \eta(t)^2 \rangle$ at (a) $T=40$, (b) 36, and (c) 32 °C. At $T=40$ °C where PCT does not occur, $\langle \eta(t)^2 \rangle$ becomes constant at the time greater than $t=84.6$ min. and reaches the predicted equilibrium (horizontal line). As was shown in Sec. 6-4-2, at the time greater than $t=84.6$ min. $F(x,t)$ became a universal function. In Fig. 6-12(b) $\langle \eta(t)^2 \rangle$ at $T=36$ °C increases with time until ca. $t=110$ min. and afterwards becomes almost constant expected for the equilibrium value (horizontal line). In the previous section, we showed that PCT appeared to take place after 114.6 min. for this mixture at 36 °C from the behavior of $F(x,t)$. Therefore, it is predicted that PCT at $T=36$ °C occurs in the beginning of the late stage.

On the other hand, time change in $\langle \eta(t)^2 \rangle$ at $T=32$ °C keeps on increasing in the time scale covered in our experiment, indicating that PCT at this temperature occurs in the intermediate stage. $\langle \eta(t)^2 \rangle$ at $T=32$ °C does not reach an equilibrium value³⁹ for a while after PCT.

As shown in the previous sections, the behavior of $F(x,t)$ and the time evolution of phase-separated structure after onset of PCT at $T=36$ °C are different from those at $T=32$ °C. Namely, these results suggest that phase separation dynamics after the onset of PCT is strongly affected by the stage at which PCT occurs.

6-4-4. Reduced Plot on q_m and I_m

Reduced wave number Q_m and reduced time τ are defined, respectively, as follows:

$$Q_m(\tau) = q_m(t) / q_m(0), \quad (6-5)$$

$$\tau = t / t_c, \quad (6-6)$$

and

$$t_c = (D_{app} q_m(0)^2)^{-1}. \quad (6-7)$$

$q_m(0)$ is the characteristic wave number of concentration fluctuations which grow at a maximum rate in the early stage of SD in which the linearized theory of Cahn-Hilliard-Cook is legitimate.^{40, 41} D_{app} is mutual diffusivity of the mixture. If temperature dependence of D_{app} is mainly affected by thermodynamic driving force for the phase separation ε , or temperature dependence of self-diffusivity term in D_{app} is small compared with that of ε over the temperature range covered, the relation between D_{app} and temperature is given as follows in the context of mean-field theory:⁴²⁻⁴⁴

$$D_{app} \propto \varepsilon. \quad (6-8)$$

and

$$\varepsilon = \frac{\chi - \chi_s}{\chi_s} \propto 1/T - 1/T_s, \quad (6-9)$$

where T_s is spinodal temperature, χ is often given by the following form:⁴⁵⁻⁴⁷

$$\chi = A + B/T. \quad (6-10)$$

χ_s is the χ parameter at $T=T_s$. On the other hand, temperature dependence of $q_m(0)$ is presented in the following form:

$$q_m(0)^2 \propto \varepsilon. \quad (6-11)$$

We usually carry out reduced plot Q_m vs. τ by estimating $q_m(0)$ and D_{app} from the linear analysis of the scattering data in the early stage of SD based upon the Cahn's theory.^{33, 35, 48, 49} However, experimental estimations of $q_m(0)$ and D_{app} at all the measurement temperatures are not always feasible. In deep quenches, phase-separation kinetics is so fast that we cannot follow experimentally the early stage. In shallow quenches, the driving force for phase separation is small and hence thermal noise effect cannot be neglected in the phase separation, i.e., we must not use Cahn linearized theory but we should rather use Cahn-Hilliard-Cook theory.⁴¹

For these reasons, we tried to perform the reduced plot using the following method. First we estimated $q_m(0)$ and D_{app} at $T=32^\circ\text{C}$ from the Cahn analysis. Next, as shown in Fig. 6-13, the straight lines for plots of $q_m(0)^2$ and D_{app} vs. $1/T$ can be drawn so that the relations of eqs. (6-8)-(6-11) are satisfied, where spinodal temperature was obtained from the spinodal line in Fig. 6-1. Thus, we can estimate $q_m(0)$ and D_{app} at other temperatures using the straight lines drawn in Fig. 6-13.

Figure 6-14 shows the reduced plot of Q_m and τ . It is shown in Fig. 6-14 that the reduced curve superimposes onto a single master curve until the slowing down of the time-evolution of Q_m due to the onset of PCT (shown by thick arrows) occurs. However, afterwards, at $T=30, 32$, and 34°C , the reduced curve ramifies into the respective curves, which indicate the slowing down of the domain growth. Namely, while the reduced plot superimposes before PCT, it does not do so after the onset of PCT. In addition, it is shown that the shallower the quench, the larger the reduced wave number $Q_{m, slow}$ at which the slowing down of the domain growth begins, and the earlier the slowing down takes place. This trend is in agreement with the result of "pinning" due to PCT reported by Hashimoto et al.² [see their Fig. 6-12(a)]. After the slowing down of the domain growth, Q_m starts to decrease with time according to the power law

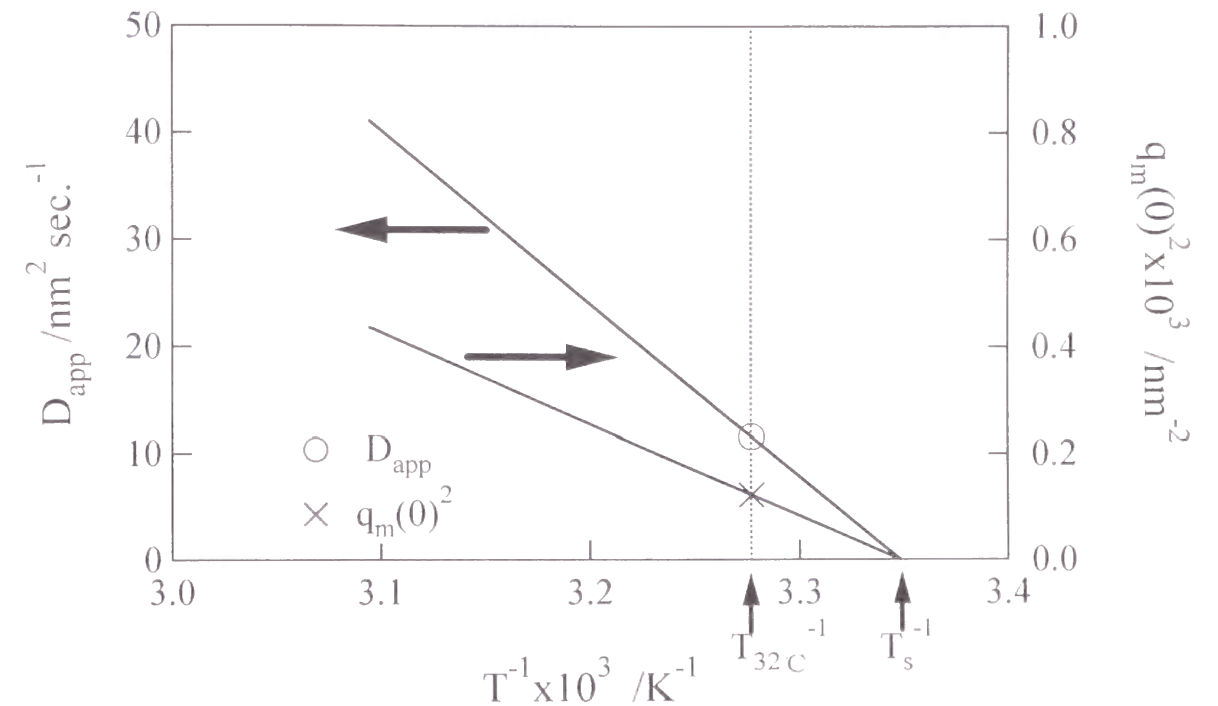


Figure 6-13 D_{app} and $q_m(0)^2$ against reciprocal temperature T^{-1} predicted from eqs. (6-8)-(6-11), where circle and cross points are values of D_{app} and $q_m(0)^2$, respectively, at $T=32^\circ\text{C}$ which were estimated from the Cahn analysis.

of cluster of the droplet (cluster regime). The onset of the cluster regime is shown by thin arrows in Fig. 6-14, and the solid lines in Fig. 6-14 show the power law with slope $-1/4$. After all, the reduced plot is classified into three regimes; (i) percolation regime before PCT where Q_m superimposes onto a single master curve against τ , (ii) the PCT regime where Q_m does not fall onto a single master curve against τ , and (iii) cluster regime in much longer time. It is intriguing to note whether or not the growth behavior in the cluster regime can be described with a single master curve. It is not very clear whether or not the disparity between curves (5) and (6) in the cluster regime is within experimental error. Note that curves (6) and (7) tend to fall onto a single master curve.

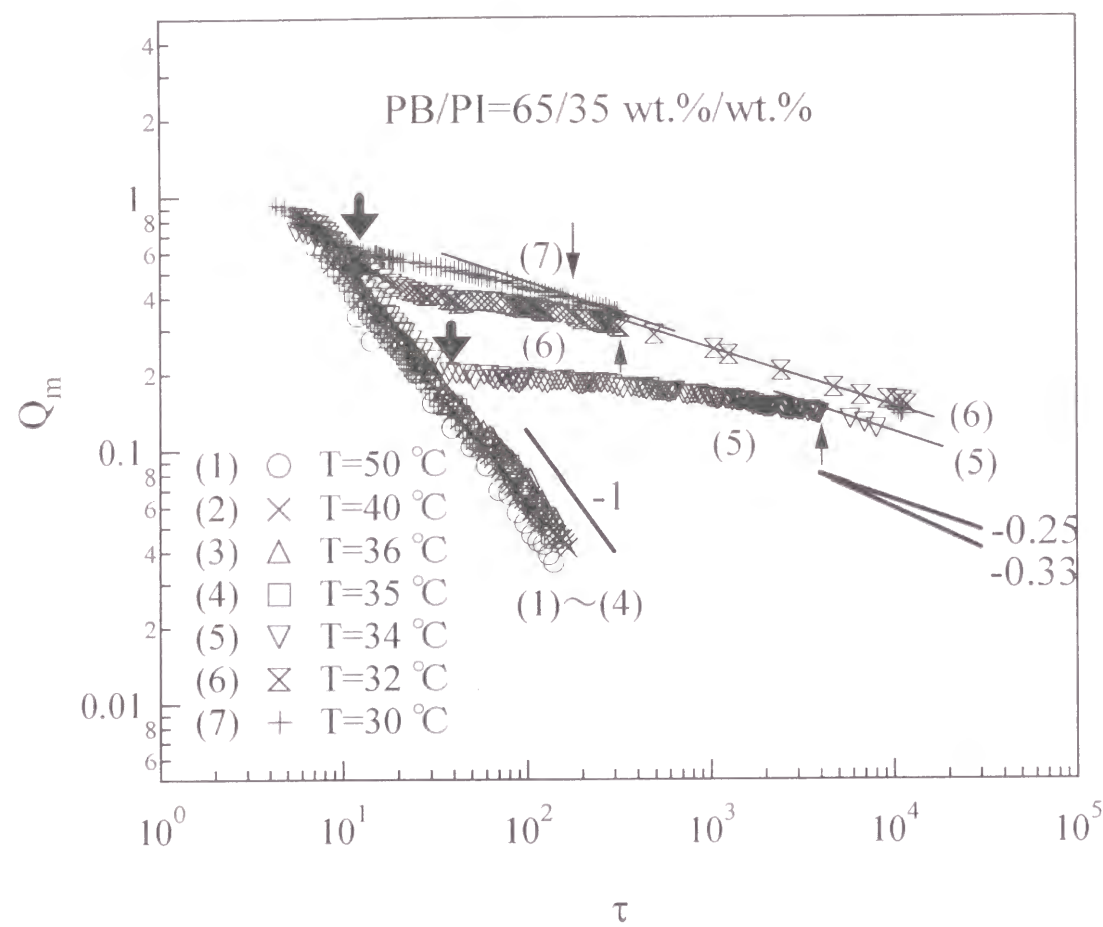


Figure 6-14 Reduced plot of Q_m versus τ for the 65/35 mixture.

Hashimoto et al.'s result showed that the time-evolution of the domain growth can be reduced by the wave number q_{mp} and the time t_p at which "pinning" begins, i.e., the time evolution of the domain growth does not show any quench-depth dependence after the scalings with $q_{m,p}$ and t_p [see their Figs. 6-9 and 6-11(b)]. The similar plot in our experiment does not fall onto a single master curve as shown in Fig. 6-15. The discrepancy may be due to the fact that the time-scale covered in their experiments was not sufficiently large compared to this work and/or that the temperature range studied in their experiments covered only a deep-quench limit. The studies of quench dependence of phase

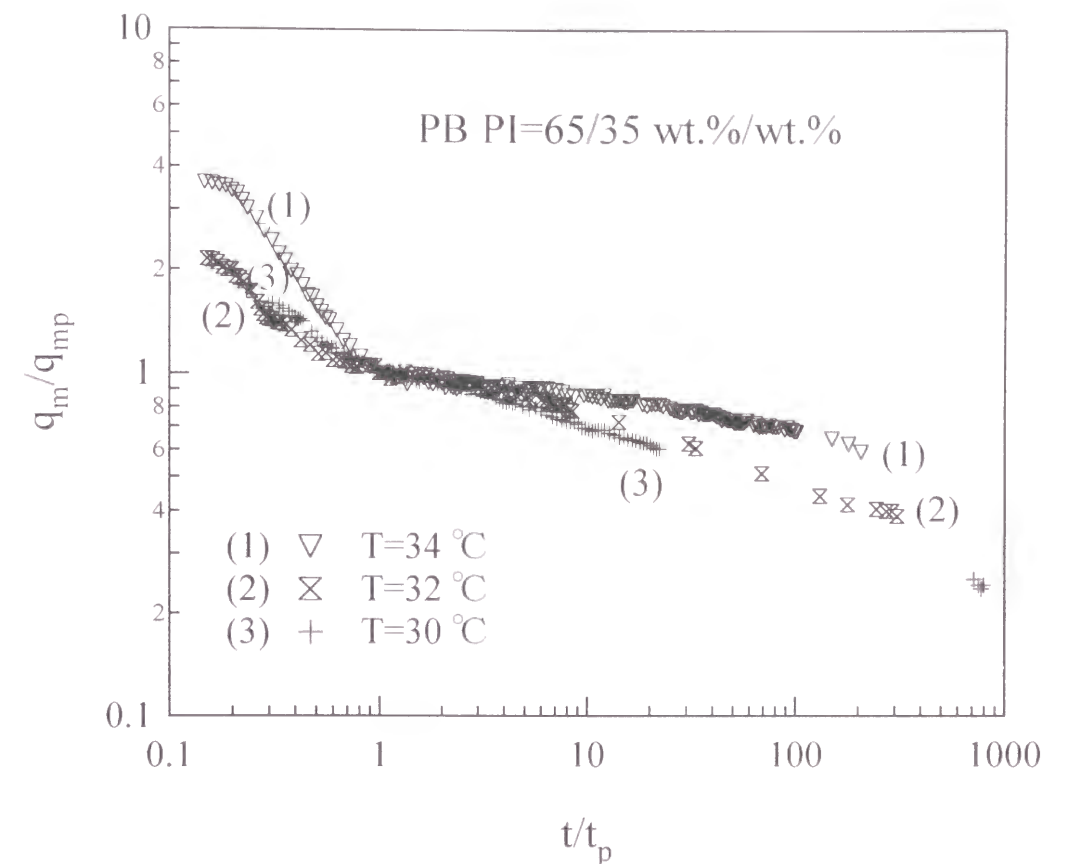


Figure 6-15 q_m/q_{mp} vs t/t_p at $T=34, 32$ and 30 °C for the 65/35 mixture.

separation dynamics in the regime of slowing down of the domain growth will be a subject of future work.

6-5. Conclusion

In summary, we investigated crossover of the domain-growth behavior from percolated structures into droplets structures by using time-resolved light scattering technique. The crossover of the domain-growth occurs as a consequence of percolation-to-cluster transition (PCT) and extends after the onset of PCT before beginning of the cluster regime. Phase-separation dynamics became very slow in regime of the crossover, consistent with the report by Hashimoto et al.² Phase-separation kinetics in the regime of the slow

dynamics has a quench-depth dependence over the quench depths and the time scale covered in this experiments. After the onset of PCT, the time change in the scattering function, which reflected morphology of phase separated structure, was strongly affected by the stage at which PCT started to occur. In addition, it was found that the domain gradually coarsened with time in the long time after PCT and eventually grew according to the power law of the cluster of the droplet.

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Chapter 7

Heterogeneous Percolation-to-Cluster Transition in Phase Separation of a Non-Isometric Polymer Mixture

7-1. Introduction

In the previous chapter we reported that the phase separation dynamics involving percolation-to-cluster transition (PCT) is divided into three regimes by using the light scattering: (i) percolation regime, (ii) PCT regime and (iii) cluster regime. In this chapter in addition to the light scattering, optical microscopy and transmission electron microscopy have been used to observe the morphology of the phase separating domains in each regime.

It is well-known that the phase separation has two types of mechanisms:^{1,2} (i) nucleation and growth (NG) and (ii) spinodal decomposition (SD). In the former, cluster of droplets initially produced by nucleation grow with time through evaporation-condensation process (Lifshitz-Slyosov-Wagner law)^{3, 4} or diffusion-coalescence of the droplets.⁵ In the latter, since even infinitesimal fluctuation leads to decrease in free energy of the system, each phase induced by SD is initially continuous (bicontinuous or percolating).

In critical mixtures, each phase keeps percolation (percolation regime) even in the late stage of phase separation where interface of the phase separating domains is well defined. However, in non-isometric mixtures even when their phase separation takes place via SD, as phase separation proceeds, the minority phase cannot keep percolation any longer, and the system undergoes PCT. In some cases the percolating morphology changes into droplet morphology in quite early stage.⁶ In non-isometric mixtures with a certain composition range, droplet morphology is eventually attained regardless of the phase separation mechanism (SD or NG) and they grow with time (droplet regime).

We will be able to find a boundary (percolation threshold) with respect to composition, below and above which phase-separating domains in the late stage have droplet morphology and percolating morphology, respectively. Slightly below the percolation threshold, we may observe the phase separation process involving PCT in the late stage in which the phase-separating domains change from percolating morphology to droplets morphology. In fact, some researchers have so far argued the PCT from the light scattering behavior⁷⁻⁹, numerical simulation¹⁰⁻¹³ or real space observation.¹⁴⁻¹⁶ Furthermore, the percolation-threshold line in a phase diagram is influenced not only by composition but also by quench depth, because volume fraction of each phase also depends on quench depth.

In this study, we found, at least in the time scale of our observation, the percolation threshold with respect to quench depth for a binary mixture of polybutadiene and polyisoprene having a certain composition. By means of time-resolved light scattering and optical and transmission electron microscopies, we investigated the phase separation process and the morphology above and below this percolation threshold. Slightly below the percolation threshold we successfully observed the PCT process. Furthermore, we found that PCT does not necessarily take place simultaneously and homogeneously over all sample places in the region just below the percolation threshold: PCT takes place *heterogeneously* and *anisotropically*; some regions involves the PCT earlier than the other regions and percolating domains break earlier along the direction normal to the glass surface than along the direction parallel to it.

7-2. Experimental Section

7-2-1. Sample Characterization and Preparation

A system investigated is an non-isometric mixture of polybutadiene (PB) and polyisoprene (PI) with weight-averaged molecular weights of 5.8×10^4 and

10.1×10^4 , respectively. The polydispersity indices for the molecular weight distribution of the PB and the PI are 1.2 and 1.3, respectively. The mixture with a composition of PB and PI with 65/35 wt.%/wt.% was dissolved in toluene solution containing ca. 1 wt. % polymer in total. The solution was filtered by using a milipore film with a pore size 0.45 μm . The solution filtered was cast into film specimens by slowly evaporating solvent and then the specimens obtained were dried in a vacuum oven for ca. 2 days in order to perfectly remove solvent. All these operations were performed at 18 °C where the mixture is in the single-phase state. The sample for the light scattering (LS) measurement was put on a clear glass and then degassed in a vacuum oven for ca. 12 hours in order to avoid bubble formation in the specimens. The sample was then sandwiched between two clear glasses. The sample thickness was 0.5 mm.

7-2-2. Light Scattering

LS measurements were performed using a He-Ne laser with a wavelength of $\lambda=632.8$ nm. LS profiles were measured as a function of time after the sample temperature being jumped from 19 °C in a single phase state into a target temperature in a two-phase state. A fresh, as-prepared sample was used for each measurements of the phase separation. The sample before temperature-jump was preserved at a temperature less than 19 °C to avoid the phase separation. Therefore, there must exist no heterogeneities in the sample before quench.

7-2-3. TEM and OM Observation

For real space observation, the sample undergoing phase separation was quenched into liquid nitrogen to freeze growth of the phase separating structures at a given time after temperature-jump. For this purpose, fresh sample specimens, different from those used in the light scattering measurements, were

used for the observation under transmission electron microscope and transmission optical microscope. The phase separation behavior before freezing was followed by light scattering (not shown here). The time change in the light scattering profiles showed almost the same behavior as that presented in Fig. 7-2. The frozen sample was cut using ultramicrotome at -120 °C and then stained by the vapor of 2 wt.% benzene solution of Osmium tetroxide (OsO₄). The thickness of the ultramicrotomed films is 50 nm and 500-1000 nm for observations under transmission electron microscopy (TEM) and optical microscopy (OM), respectively. OsO₄ stains the PB phase more rapidly than the PI phase, which gives a darker contrast to the PB phase compared with the PI phase.

7-3. Results

7-3-1. Time-Evolution of Light Scattering Profiles

Figure 7-1 shows the cloud points for the PB/PI mixture. We obtained the cloud points by comparing a light scattering profile in a single phase state before annealing with that after annealing at a given temperature for more than one week. The method of the cloud point measurements will be described in details in chapter 8. We believe that since the annealing time is long enough, the cloud points curve obtained using this method are close to the binodal curve.

The binodal and spinodal curves obtained by a fit to the cloud points data in the context of Flory-Huggins theory are also shown.¹⁷ The PB/PI mixture possesses a lower critical solution temperature (LCST) type of phase diagram. The cloud point for the 65/35 mixture is 22.5 ± 0.5 °C. Furthermore, the temperatures where the phase separation behaviors were explored in this study are shown in Fig. 7-1 (cross symbol). By using the lever rule in the binodal curve, we calculated the volume fraction of the minority phase at thermal equilibrium at these temperatures. The result is presented in Table 7-1.

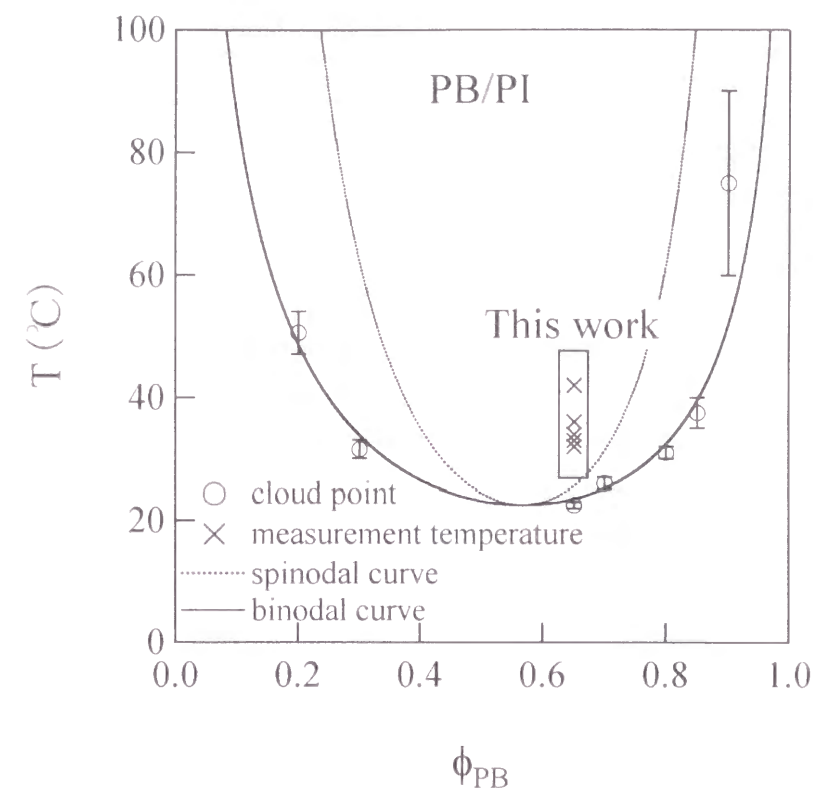


Figure 7-1 Phase diagram for the PB/PI mixtures.

Table 7-1 Volume fraction ϕ_{minority} of the minority phase which is predicted from the binodal curve in Fig. 7-1, at various quench depth at thermal equilibrium.

T (°C)	42	36	34	33	32
ϕ_{minority}	0.339	0.324	0.316	0.311	0.306

Figure 7-2 shows the time change in LS profiles at (a) $T=33$ °C and (b) $T=34$ °C. The data before quench were taken at 19 °C at which the mixture is in a single-phase state. Until a certain time after temperature-jump at both temperatures, a single scattering peak appears and it shifts toward small q with time [$q = (4\pi/\lambda) \sin(\theta/2)$; θ and λ are scattering angle and wavelength in the sample, respectively]. Afterwards, the single peak gradually becomes broad [see a LS profile at $t=307$ min. in Fig. 7-2(a) and that at $t=323$ min. in Fig. 7-2(b)] and eventually splits into a double peak. To our best knowledge this

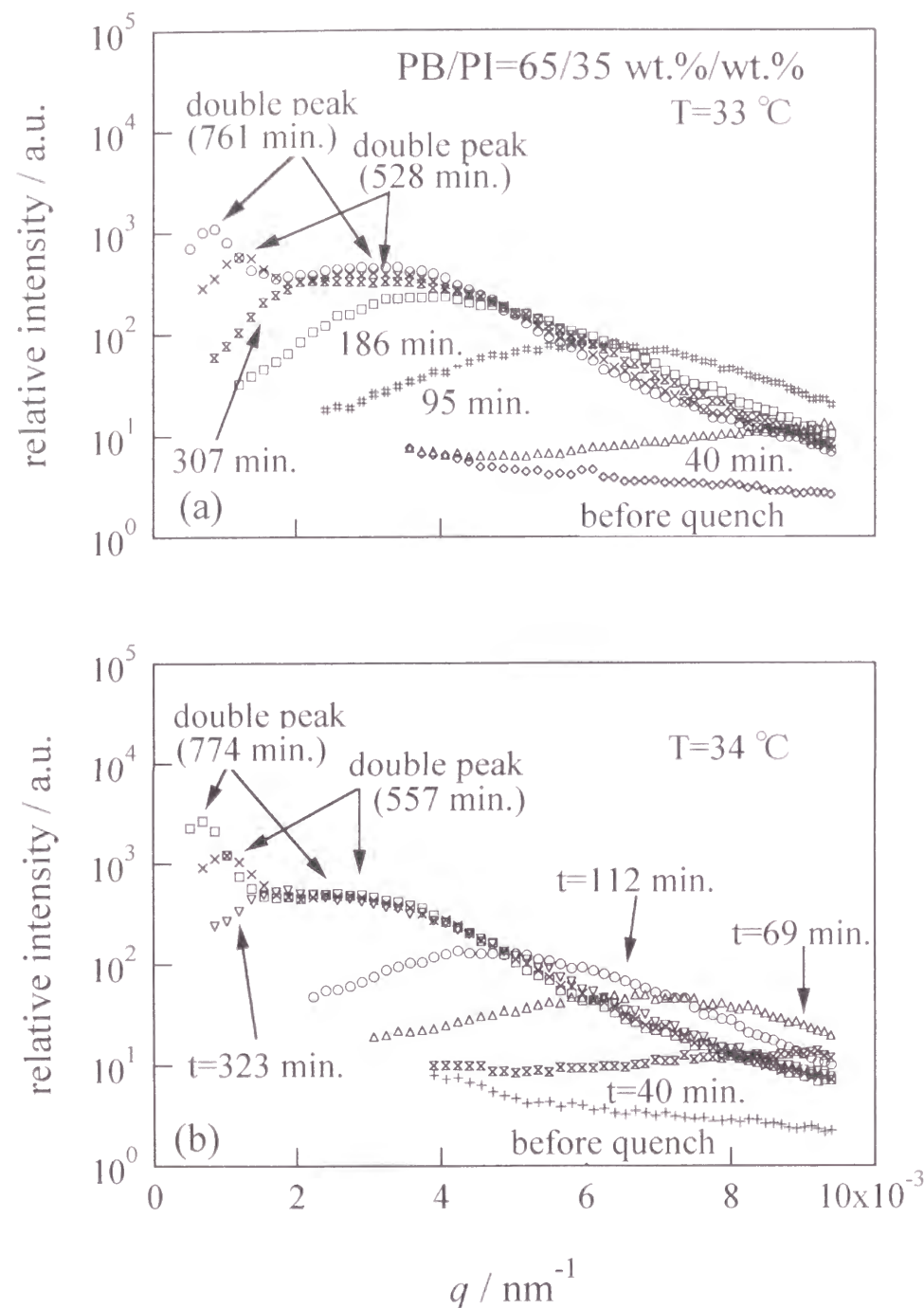


Figure 7-2 Time change in the light scattering profiles after temperature-jump to (a) $T=33\text{ }^{\circ}\text{C}$ and (b) $T=34\text{ }^{\circ}\text{C}$.

splitting process in the scattering profile was found here for the first time. Hereafter, we designate a peak in smaller q as the first peak and a peak in higher q as the second peak. The double peak changes with time with different modes: While the first peak shifts toward small q with a fast rate, the second peak moves toward small q with a very slow rate.

7-3-2. Time Change in q_m and I_m

In the scattering experiments, phase separation dynamics is characterized by the time change in peak wave number q_m and peak intensity I_m . The time evolutions of q_m and I_m often obey the power law;

$$q_m(t) \sim t^{-\alpha} \quad (7-1)$$

and

$$I_m(t) \sim t^{\beta}. \quad (7-2)$$

The scaling exponents α and β are related to the mechanism of phase separation.

Figure 7-3 shows the double logarithmic plots of (a) q_m vs t and (b) I_m vs t at various temperatures. In Fig. 7-4 we show the comparison between q_m and I_m at $T=33\text{ }^{\circ}\text{C}$ and those at $T=34\text{ }^{\circ}\text{C}$, where q_m and I_m at $T=34\text{ }^{\circ}\text{C}$ were shifted by 10 times relative to those at $T=33\text{ }^{\circ}\text{C}$ so that they can be easily compared. At deep quench ($T=42\text{ }^{\circ}\text{C}$, data points indicated by number 1), q_m and I_m grow with the exponents of $\alpha \approx 0.9$ and $\beta \approx 2.7$, respectively, over the time scale covered in this experiment. At $36\text{ }^{\circ}\text{C}$ (the data points indicated by number 2), in some period after onset of the phase separation, the time change in q_m and I_m is characterized by the same exponents α and β as those at $42\text{ }^{\circ}\text{C}$ [see the straight lines drawn on the basis of the data points at $t \leq 110$ min. in Figs. 7-3(a) and 7-3(b)] and then they are slowed down after ca. 110 min. as shown by the arrows pointing at 110 min.

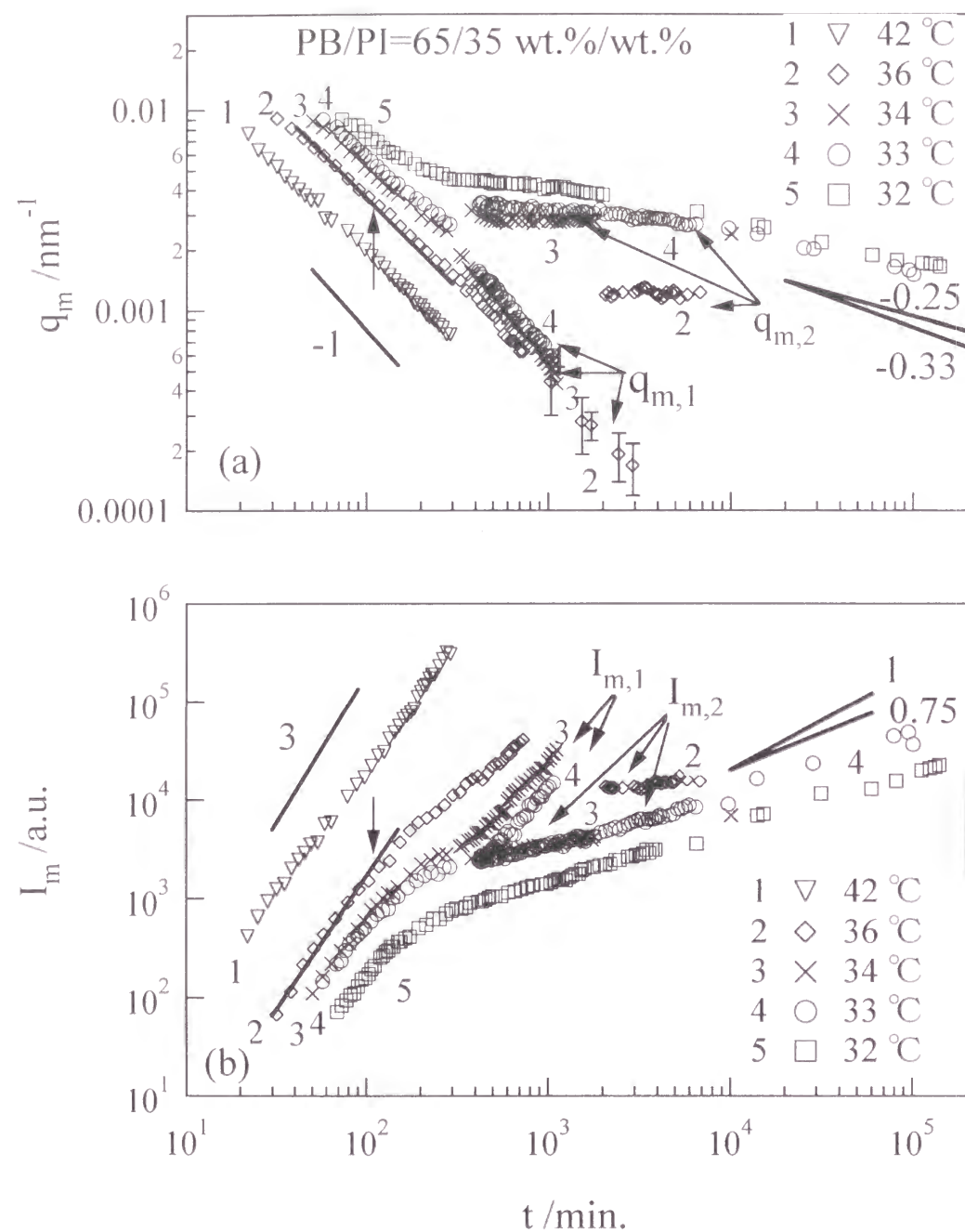


Figure 7-3 Double logarithmic plots of (a) q_m vs t and (b) I_m vs t at various temperatures.

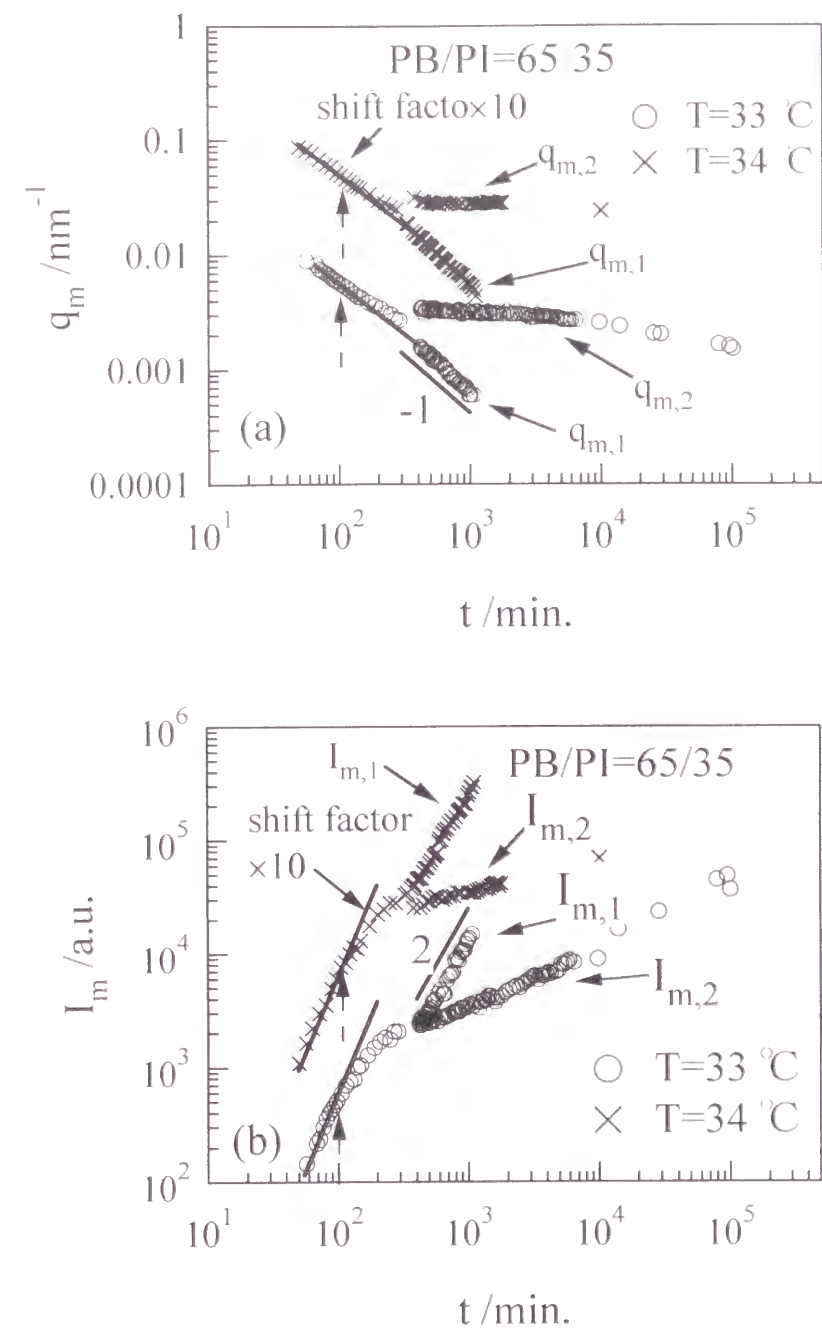


Figure 7-4 Comparison between the plots of (a) q_m vs t and (b) I_m vs t at $T=33$ and those at $T=34$ °C. In the figure, q_m and I_m at $T=34$ °C are shifted by 10 times relative to those at 33 °C.

The behaviors of q_m vs t and I_m vs t at 36 °C are similar to those reported previously.⁹ However, in this study, we further investigated the time change in the light scattering behavior in a much longer time scale than that in the

previous study. After $t \approx 750$ min. q_m becomes very small and reaches beyond the small q -limit of our light scattering photometer (ca. $4 \times 10^{-4} \text{ nm}^{-1}$). Consequently we could not estimate q_m with our photometer in our previous study. However, in this study we estimated the q_m from the position of the spinodal ring projected on a screen. To our surprise we found a double peak in the scattering profile at the long time scale newly covered in this study. In the long time scale, the time-evolution of q_m shows a recovery of the growth behavior of the percolated domains with $\alpha = 1$. In addition to the peak in the very small q , the second peak was observed at higher q ($q \approx 0.0012 \text{ nm}^{-1}$) at $t \approx 2080$ min. The growth of the second peak is very slow and is similar to that of the second peak at 33 and 34 °C (the data points indicated by number 4 and 3, respectively) shown below. This phenomenon seems to be identical to that found by Okada et al.,¹⁵ except for the value of α for the time evolution of the second peak wave number and for the fact that they could not simultaneously observe the two peaks in a given time period.

At both temperatures of 33 °C and 34 °C, double peak was newly developed and able to be simultaneously observed in the q -window of our photometer (ca. 1×10^{-2} to $4 \times 10^{-4} \text{ nm}^{-1}$), for the first time.¹⁸ At $T=33$ °C (number 4), q_m and I_m change with time with the exponents of $\alpha \approx 0.9$ and $\beta \approx 2.7$ until ca. $t=105$ min. (see broken arrows in Fig. 7-4), respectively. However, the phase separation dynamics becomes a little slow at $t \geq 105$ min. just as in the case found at $T=36$ °C after $t=110$ min. Moreover, at $T=33$ °C, after ca. $t=425$ min., the double peak appears and the first peak wave number $q_{m,1}$ and the peak intensity $I_{m,1}$ change with time with the exponents of $\alpha \approx 1.0$ and $\beta \approx 2.0$, respectively. Here, it is important to note that β is not 3.0 but 2.0. On the other hand, the second peak wave number $q_{m,2}$ and its peak intensity $I_{m,2}$ evolve very slowly compared with the evolutions of $q_{m,1}$ and $I_{m,1}$.

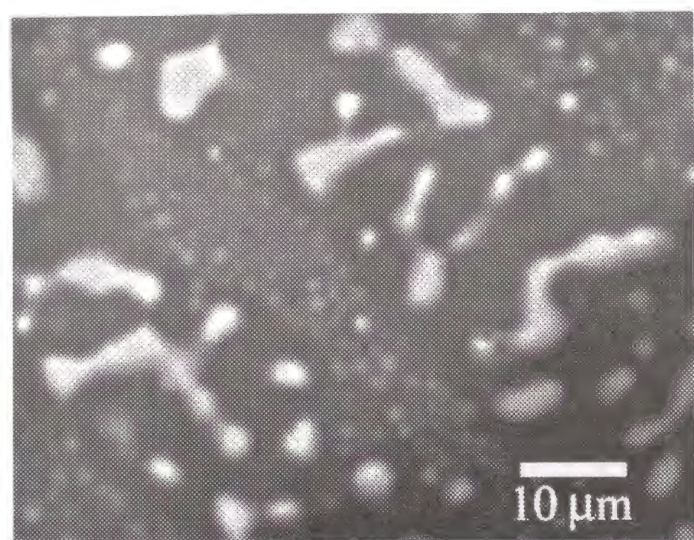
At $T=32$ °C (the data points indicated by number 5), until $t \approx 100$ min. q_m and I_m evolve with exponents of 0.9 and 2.7, respectively. After $t \approx 100$ min., they become a little slow and then very slow from $t \approx 350$ min. to $t \approx 6500$ min. In the late time after $t \approx 6500$ min., the time-evolutions of q_m and I_m are characterized with exponents of 0.25-0.33 and 0.75-1, respectively. The double peak was not observed in this case.

7-3-3. Real Space Observation

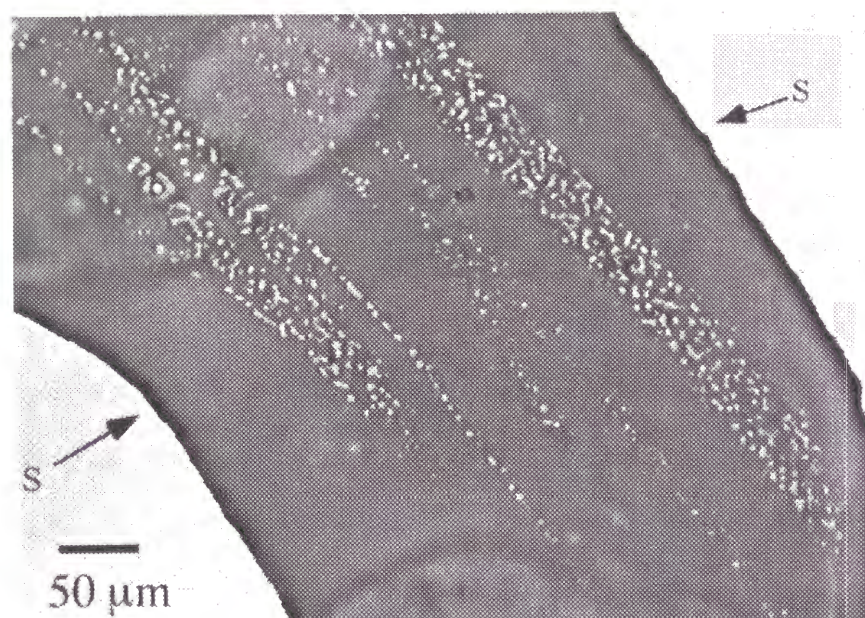
Figure 7-5(a) shows an OM image on the cross-section of the specimen at $t=817$ min. after temperature-jump to $T=34$ °C when the double peak in the LS profile was simultaneously observed. It is shown in Fig. 7-5(a) that large percolated structures (which appeared to be percolated only in local scale but not macroscopically) and cluster of small spherical droplets coexist.

Figure 7-5(b) shows the OM picture on the cross-section of the specimen at low magnification where S denotes the sample surface.¹⁹ The image demonstrates the coexistence of the percolating structures and cluster of the droplets: The large percolating structures can be seen as bright sheet-like objects running parallel to the film surface S, while the cluster of the small spherical droplets cannot be clearly observed in this picture because of the low magnification: in fact they exist in the interstitial region between the sheets. To our surprise, the sheets containing the percolating structure extend over several hundred microns parallel to film surfaces but only 10 to 50 μm in the direction perpendicular to it.

In Fig. 7-6, we show a TEM picture on the specimen phase-separated for $t = 94$ min. after a temperature-jump to $T=33$ °C. At $t = 94$ min. the scattering profile has only a single peak and the time-evolution of the phase separated domains obey the growth law of the percolating domains according to the light scattering result (Fig. 7-4). The TEM picture shows that some of the phase-



(a)



(b)

Figure 7-5 (a) OM image on the cross-section of the sample annealed for $t=817$ min. at $T=34$ °C and (b) the OM image at a lower magnification under the same condition as in (a).

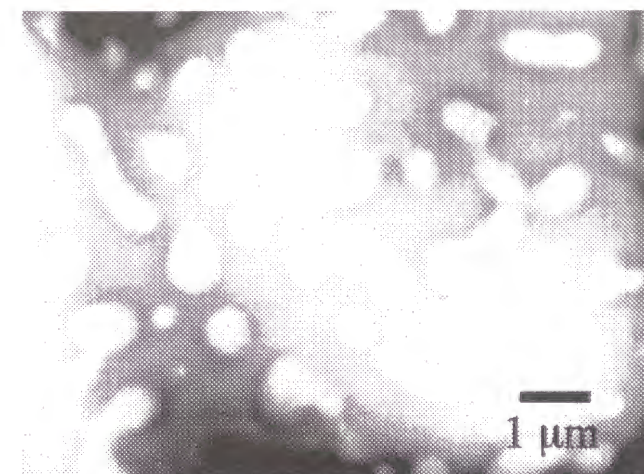
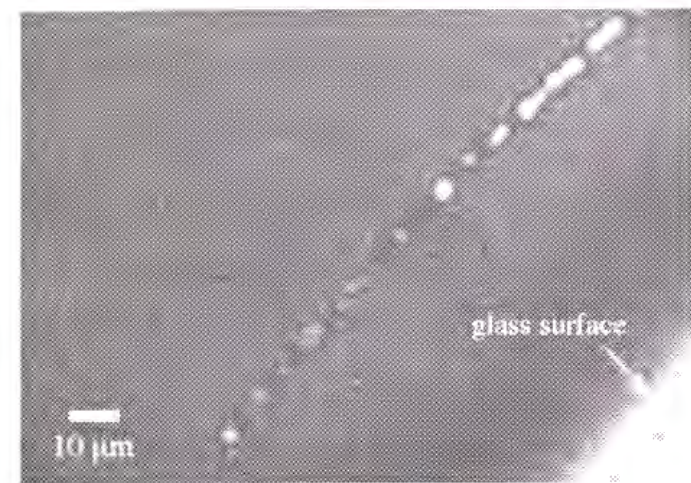


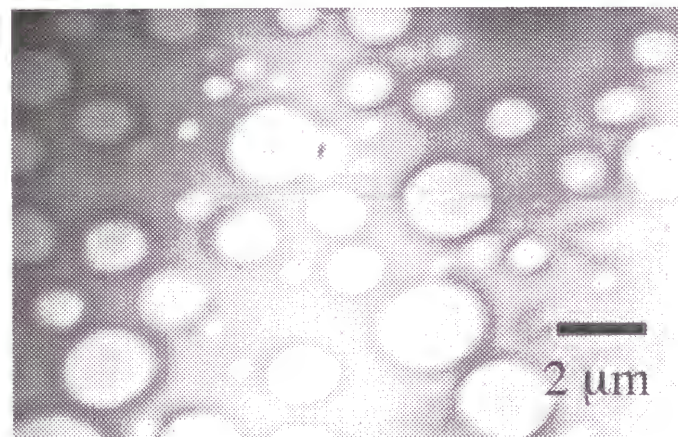
Figure 7-6 TEM image on the cross-section of the sample annealed for $t=94$ min. at $T=33$ °C (before PCT).

separated domains are interconnected, while others are not. Though some of the domains do not appear to be interconnected, we guess that they are interconnected for the reason as will be discussed in Sec. 7-4-2. Furthermore, the size of each domain is moderately uniform: the size of the domain spacing is ca. $1.0 \mu\text{m}$. The remarkable difference in domain size as observed in Figs. 7-5(a) and (b) was also not observed in other areas of TEM images. These domains are so small that they were not clearly seen under OM.

Figure 7-7(a) shows an OM picture on the cross-section of the specimen annealed for $t = 766$ min. at $T=33$ °C. Under this condition the scattering shows the double peak (Fig. 7-4). Similar to the picture in Fig. 7-5(b), the picture also reveals the coexistence of the sheet-like grains comprised of percolating domains, running parallel to the film surface, and cluster of the droplets (the arrow on the right bottom in the figure shows the position of the film surface). The sheet-like grains extend over several hundred microns parallel to the film surface but no grains exist in a direction perpendicular to the film surface. We expect the percolation exists two-dimensional space in the sheet, as will be clarified later in Sec. 7-4-1 and 7-4-3. Because of the low magnification, we



(a)



(b)

Figure 7-7 (a) OM and (b) TEM images on the cross-section of the specimen at $t=766$ min. after temperature-jump to $T=33$ °C.

cannot clearly observe cluster of the droplets. For a clear observation of it TEM was used [Fig. 7-7(b)]. The TEM image reveals that the droplets are spherical and the radii and the spacing among these droplets are $0.5 - 2 \mu\text{m}$ and $1 - 2 \mu\text{m}$, respectively.

7-4. Discussion

7-4-1. Time-Evolution of Phase-Separated Domains Involving Percolation-to-Cluster Transition

As reported in Sec. 7-3-2, at $T=42$ °C (number 1 in Fig. 7-3), q_m and I_m evolve with the exponents of $\alpha \approx 0.9$ and $\beta \approx 2.7$, respectively. These exponents are the same value as those for the near critical mixture with the composition of 50/50.^{9, 20} Siggia theoretically predicted the growth law with the exponent of $\alpha=1$ for binary fluids with percolated structures in regime in which hydrodynamic interactions are effective.²¹ Therefore, at $T=42$ °C, the phase separated structures are expected to be bicontinuous.

Let us first discuss the time-evolutions of I_m and q_m at $T=33$ (number 4) and 34 °C (number 3). At these temperatures the phase separation dynamics shows a quite normal behavior with growth law of the percolated domains ($\alpha \approx 0.9$ and $\beta \approx 2.7$) until a certain time. An unusual scattering behavior was newly observed afterwards, i.e., the double peak appeared simultaneously within the q -window of our observation in the course of phase separation process, and each peak evolved with a different rate. The appearance of the double peak with different evolution rates suggests that the phase-separated structures have two different characteristic lengths and that time-evolution of each occurs with a different rate. The double peak suddenly came out by a split of a single peak as shown in Fig. 7-2. Therefore, we emphasize that the phase-separating domains with two different characteristic lengths did not exist from the early times of the phase separation process but was suddenly born. Here, we must draw attention to the fact that before the double peak was observed, the evolutions of q_m and I_m become slightly slow from the evolution law with exponents of $\alpha \approx 0.9$ and $\beta \approx 2.7$. (see the dotted arrows and the solid lines drawn for the sake of convenience in Fig. 7-4) As discussed in the previous chapter,⁹ this behavior is considered to be caused by the onset of PCT. The double peak is considered to

appear after the onset of PCT and the process leading to the double peak was illuminated here for the first time.

Time-evolution of the first peak wave number $q_{m,1}$ obeys the evolution law of percolating domains ($\alpha \approx 1.0$). However, the characteristic exponent β for the time-evolution of $I_{m,1}$ is not 3.0 but 2.0, although generally in the late stage of spinodal decomposition the relation $\beta = 3\alpha$ holds. We consider two possibilities for this reason: (i) the volume fraction of the percolated domains decreases with time during the course of PCT and (ii) the domains which causes the first peak percolate not three-dimensionally (3D) but more or less two-dimensionally (2D), along the planes parallel to the glass surface, as shown in [Fig. 7-7(a)]. We speculate these two possibilities occur generally in real systems.

The scenario for the latter possibility (ii) may be detailed as follows. The mixtures have 3D percolating domains before PCT. During the course of PCT, the percolation structures break earlier along the direction normal to the glass surfaces than along the direction parallel to it. The percolation is maintained for a longer time in the latter direction than in the former direction. This process results in the percolating domains with the larger characteristic length in the sheet-like grains parallel to the glass surface, because the domains grow much more rapidly when they are percolated than when they are droplets. The process involves a crossover from 3D growth of domains (with 3D percolation) to 2D growth of domains (with more or less 2D percolation), which in fact gives rise to a crossover of the exponent β for 3 to 2.

On the other hand, time-evolutions of the second peak wave number $q_{m,2}$ and the peak intensity $I_{m,2}$ are very slow compared with those of $q_{m,1}$ and $I_{m,1}$. The behavior of the slowing down of the domain growth is consistent with that caused by the onset of the PCT ("spontaneous pinning of the domain growth"^{7,9,14}). After all, the first peak and the second peak in the light scattering

profiles are expected to originate from the percolated domains before the onset of PCT and cluster of the domains after the onset of PCT, respectively. Namely PCT is expected not to take place simultaneously and homogeneously overall sample space. It rather occurs *heterogeneously*: some regions involves PCT earlier than the others, which results in the unique coexisting domain structures composed of small droplets in one area and the large more or less percolated domains in other area. The former area is the one where PCT occurs earlier than the latter. Moreover this PCT does not occur isotropically but it rather occurs anisotropically, generating the unique sheet-like grains. This speculation from the LS results is confirmed by the OM observation as shown in Figs. 7-5(b) and 7(a). However, its physical interpretation, especially that for the anisotropic PCT, is totally left as future works.

Now let us next discuss the time-evolution of the I_m and q_m at 36 °C. After onset of phase separation, the system at $T=36$ °C attains such time-evolutions of q_m and I_m as characterized by the growth of percolated domains. This growth behavior is maintained until ca. $t = 110$ min. ($\alpha \approx 0.9$ and $\beta \approx 2.7$). Afterwards, it becomes a little slow, reflecting the onset of PCT.⁹ Furthermore, in the long time scale, after $t \approx 2080$ min. the second peak was simultaneously observed in higher q : main peak (first peak) in the smaller q evolved according to the growth law of the percolated domains, while the evolution of the second peak was very slow. These trends are similar to the evolution behavior of $q_{m,1}$ and $q_{m,2}$ at 33 °C and 34 °C. Thus PCT is expected to take place *heterogeneously* and *anisotropically* at 36 °C as well. In fact, coexistence of the large percolated domains and the cluster of the small droplets was observed by using OM at 36 °C, though we do not show the picture in this chapter.

Although the second peak appeared soon after PCT for the system phase separated at 33 and 34 °C, at 36 °C the second peak was not observed for long time after the onset of PCT. We speculate this difference as follows. As the

system at 36 °C is in deeper quench than those at 33 °C and 34 °C, the volume fraction of the minority phase at 36 °C is larger (see Table 7-1) than those at 33 °C and 34 °C. Therefore, we expect a larger volume fraction of the percolated domains at 36 °C than at 33 and 34 °C, giving rise to a higher intensity $I_{m,1}$. Consequently, the second peak with intensity $I_{m,2}$ may be hidden by the scattering from the large percolated domains which is the origin of the first peak. The scattering intensity in higher q from the large percolated domains decreases with time as their domain size becomes larger, so that the second peak is considered to appear in the long time scale.

Okada et al.¹⁵ also inferred existence of the double peak in the LS profiles with the aid of TEM micrographs for a non-isometric mixture of polystyrene and poly(2-chlorostyrene). They found the following: Initially the first peak evolved according to the power law of percolated structures ($\alpha \approx 0.96$ and $\beta \approx 2.2$); then the second peak emerged in a higher q (while the first peak disappeared in their q -window of observation); This second peak obeyed the growth law with an exponent of 1/3 ($\alpha \approx 0.33$ and $\beta \approx 0.79$). In their result β/α for the first peak was 2.3 which is smaller than 3, similar to our result. In their study, they did not either observe the double peak simultaneously in a single light scattering profile or a splitting process of a single peak into double peak. Furthermore, they did not show any direct proof that double peak appears after the onset of PCT. Here in this work we presented the direct proof by showing the slight slowing down in time-evolutions of q_m and I_m from the evolution law with exponents of $\alpha \approx 0.9$ and $\beta \approx 2.7$ (see the dotted arrows and the solid lines in Fig. 7-4) and broadening of the scaled structure factor (Fig. 7-8), as will be described in Sec. 7-4-3, before appearance of the double peak. Moreover, the time change in $q_{m,2}$ in their system did not show such characteristic slowing down as that observed in the process of “spontaneous pinning of the domain growth” but obeyed the growth law with an exponent of 1/3. As indicated from

the phase separation behavior at 33 and 32 °C, the growth of cluster of the droplets with an exponent of 1/3 is expected to take place in the much longer time scale in our system.

Finally let us discuss the system at $T = 32$ °C (the data indicated by number 5) where only the single scattering peak was observed. The phase separation dynamics at $T=32$ °C can be divided into three regimes as discussed in the previous chapter: ⁹ (i) “*percolation regime*” before the onset of PCT occurs, in which the phase separation dynamics obeys the growth law of percolated structures ($\alpha \approx 0.9$ and $\beta \approx 2.7$); (ii) “*PCT regime*” occurring some period after the onset of PCT, in which α is very small relative to α in percolation or cluster regime described below; (iii) “*cluster regime*” occurring in much longer time scale than PCT regime, in which the phase separation kinetics obeys the power law for droplet growth ($\alpha = 1/4-1/3$ and $\beta = 3/4-1$). The single scattering peak before and after PCT reveals that PCT occurs homogeneously at this temperature (or phase volume fraction).

At $T = 33$ °C in the much longer time scale, the time-evolution of $q_{m,2}$ shows the value of α near to that at 32 °C in cluster regime. After all, the time-evolution of $q_{m,2}$ at 33 °C is very similar to that at 32 °C after the onset of PCT: it can be divided into PCT regime and cluster regime. The time-changes in $q_{m,2}$ at 34 and 36 °C showed only the behavior in PCT regime. If we observe the phase separation behavior in the longer time scale than that in this study, we will be able to observe a crossover from PCT regime to cluster regime.

7-4-2. Observation of Morphology of the Phase-Separated Domains with Two Different Characteristic Lengths

In Sec. 7-3-3, in Fig. 7-5 we showed the OM image on the cross-section of the specimen annealed for $t = 817$ min. at $T = 34$ °C which clearly demonstrated the coexistence of the sheet-like percolating domains parallel to

the film surface and cluster of the spherical domains. The spacings estimated from the OM images are consistent with those estimated from $q_{m,1}$ and $q_{m,2}$ in the LS profile (8.3 μm and 2.0 μm , respectively). Therefore, the large locally percolated structures and cluster of the droplets are concluded to be the origin of the first peak and that of the second peak, respectively.

One may consider that the locally percolating domains and cluster of the droplets correspond to the structures close to the glass surface and those in the bulk, respectively, which are caused by wetting effect, as reported by Cumming et al.²² However, it must be noted that the percolated structures parallel to the glass surface are located in the place away from the glass surface by more than at least 50 μm . Therefore, we stress that the locally percolated structures are observed *in the bulk* as typically shown in Fig. 7-5(b).

Okada et al. also observed the coexistence of the percolated structures and cluster of the droplets by TEM for the non-isometric mixtures of polystyrene and poly(2-chlorostyrene).^{15, 23} Some domains in their pictures also percolate locally and anisotropically, although they do not give any comments on the orientation of the percolated grains or their locations with respect to the sample wall.

The TEM image on the cross-section of the specimen annealed for $t = 94$ min. at $T = 33^\circ\text{C}$ in Fig. 7-6 (in the percolation regime before PCT) exhibited that some domains are interconnected, while others are not. We conjecture that in fact, these domains are infinitely interconnected (percolated) but they do not appear interconnected, because the thickness of the ultrathin section for the TEM observation is very thin (ca. 50 nm) compared with the size of the phase separated structures (ca. 1.0 μm) and therefore some of the interconnected domains may be apparently separated in the cross-section of the ultrathin section.

Furthermore, the OM picture of the phase-separated domains annealed for $t = 766$ min. at $T = 33^\circ\text{C}$ in Fig. 7-7 also showed coexistence of the locally percolated structure parallel to the film surface and cluster of the spherical droplets, similar to the picture at $T = 34^\circ\text{C}$ in Fig. 7-5. Comparing Fig. 7-7(a) with Fig. 7-5(b), the volume fraction of the locally percolated domains at $T = 33^\circ\text{C}$ [Fig. 7-7(a)] is smaller than that at $T = 34^\circ\text{C}$ [Fig. 7-5(b)]. This difference can be explained by the volume fraction of the minority phase, i.e., since the system at 33°C is at shallower quench than that at 34°C , the volume fraction of the minority phase at 33°C is expected to be smaller than that at 34°C (Table 7-1) and likewise, the volume fraction of the percolating domains at 33°C is expected to be smaller than that at 34°C . Moreover, as discussed in Sec. 7-4-1, the volume fraction of the percolated structures at $T=36^\circ\text{C}$ which is deeper quench than 33°C and 34°C was expected to be larger than that at $T=33$ and 34°C .

7-4-3. Time Change in Scaled Structure Factor

Scaled structure factor $F(x,t)$ is defined as follows,

$$F(x,t)=q_m^d(t)I(q,t) \quad (7-3)$$

with

$$x=q/q_m(t), \quad (7-4)$$

where d is the dimensionality of the scattering structure. It has so far been confirmed that $F(x,t)$ becomes a universal function with time in the late stage of spinodal decomposition (SD), because the phase separated structures grow with dynamical self-similarity in the late stage of SD.²⁴⁻²⁶

Figure 7-8 shows the time change in the scaled structure factor before observation of the double peak at $T=33^\circ\text{C}$. All the profiles of $F(x,t)$ obtained

from $t = 72$ min. to $t = 103$ min. can be superimposed, though only the two profiles are shown in the figure, and become a universal function with t , as observed in the late stage of spinodal decomposition. However, after $t=103$ min., the $F(x,t)$ is shown to become broad with time. This behavior is considered to be caused by PCT, on the basis of the earlier reports on PCT.^{8,9} Therefore, at $T=33$ °C, the onset of PCT is considered to occur at $t \cong 103$ min. This result is consistent with the time change in q_m and I_m : As described in Sec. 7-3-2,

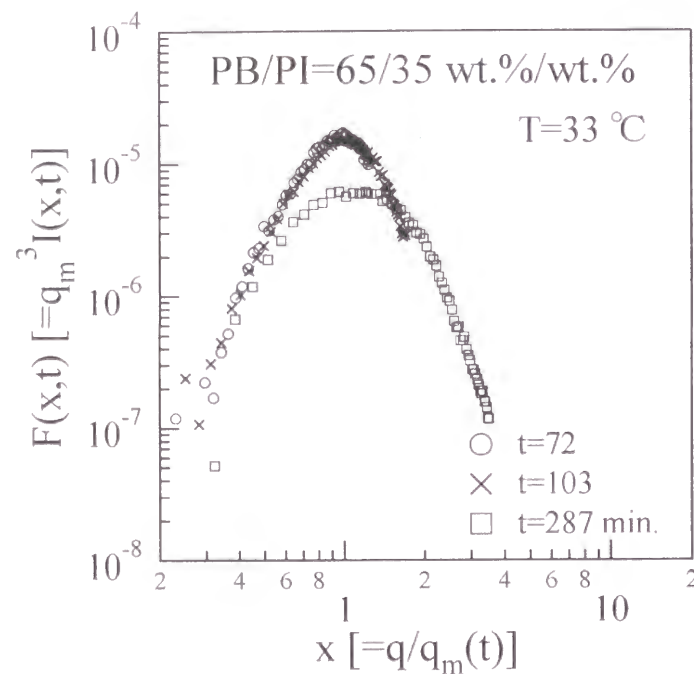


Figure 7-8 Time change in the scaled structure factor $F(x,t)$ vs x ($=q/q_m$) at $T=33$ °C before the double peak observed.

after $t \approx 105$ min., the time-evolutions of q_m and I_m become slightly slow from the growth law of percolating domains.

After the onset of PCT, the scaled structure factor becomes broader and broader, and eventually double peak is observed at $t \cong 426$ min. (Fig. 7-9). After the double peak appeared, the system has two distinct characteristic lengths. Therefore, we can obtain two kinds of scaled structure factors which are reduced

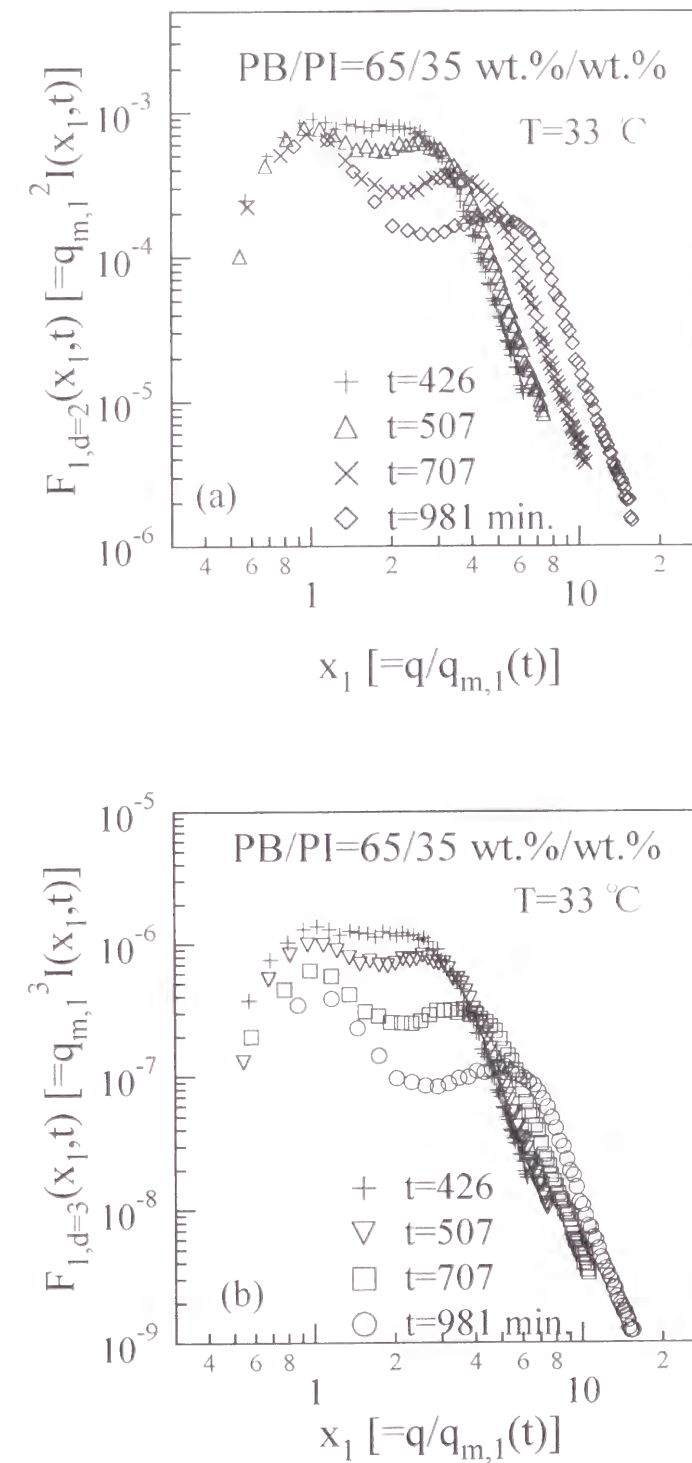


Figure 7-9 Time change in the scaled structure factor at $T=33$ °C (a) for two dimensional structures, $F_{1,d=2}(x_1,t)$ and (b) for three dimensional structures, $F_{1,d=3}(x_1,t)$ reduced with $q_{m,1}$.

with $q_{m,1}$ and $q_{m,2}$, respectively. For the scaled structure factor analysis with $q_{m,1}$, we tried to obtain the scaled structure factor for the two dimensional structures [$F_{1,d=2}(x_1,t) \equiv q_{m,1}^2 I(x_1,t)$ vs $x_1=q/q_{m,1}$] and for the three dimensional structures [$F_{1,d=3}(x_1,t) \equiv q_{m,1}^3 I(x_1,t)$ vs x_1] as respectively shown in Figs. 7-9(a) and (b). The former scaled structure factor is for the percolating domains which extend parallel to the glass surface and form the sheet-like grains as shown in Figs 7-5(b) and 7-7(a).

In Fig. 7-9(a), the $F_{1,d=2}(x_1,t)$ around $x_1=1$ is shown to slightly decrease from 426 min. until 707 min. and afterwards to have almost no change with time. On the other hand, the $F_{1,d=3}(x_1,t)$ around $x_1=1$ largely decreases with time. We consider the following two factors as the cause of the decrease in $F_{1,d=2}(x_1,t)$ and $F_{1,d=3}(x_1,t)$ around $x_1=1$: (i) the volume fraction of the percolated domains decreases with time in the time region covered in this study and (ii) as suggested by Figs. 7-5(b) and 7-7(a), the domains based upon the first peak percolate not three-dimensionally but more or less two-dimensionally, or the domains change from three-dimensionally percolating structures to two-dimensionally percolating structures with time after the onset of PCT. The fact that $F_{1,d=2}(x_1,t)$ at $x_1 \approx 1$ is less time-dependent than $F_{1,d=3}(x_1,t)$ at $x_1 \approx 1$ implies that the percolating domains observed in the time scale of Fig. 7-9 are more 2D-like than 3D-like and this is especially so at $t \geq 707$ min. For both the 2D and 3D structure factors scaled with $q_{m,1}$, the structure factors at the reduce wave vector $x_1 = q_{m,2} / q_{m,1}$, corresponding to the scattering maximum from the cluster of the droplets, strongly depends on time and hence far from universal with time. This suggests the droplet growth cannot be scaled with $q_{m,1}$. The two length scales have more or less independent scaling laws.

Figure 7-10 shows the time-evolution of the 3D scaled structure factor reduced with $q_{m,2}$, $x_2 = q/q_{m,2}$ and $F_{2,d=3}(x_2,t) \equiv q_{m,2}^3 I(x_2,t)$. Note that the maximum due to $q_{m,1}$ is seen at $x_2 \approx 0.4$ only for the structure factor at $t = 426$

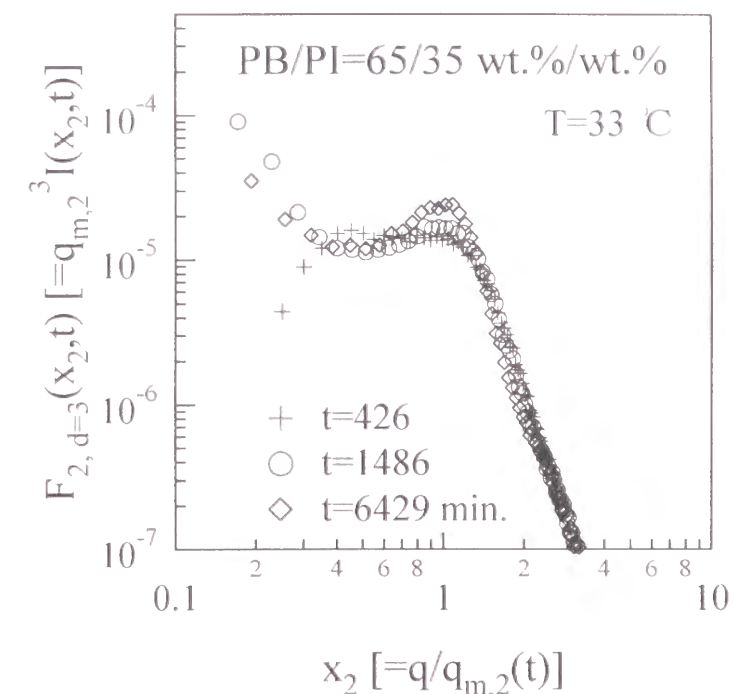


Figure 7-10 Time change in the scaled structure factor $F_{2,d=3}(x_2,t)$ at $T=33$ °C for three dimensional structures reduced with $q_{m,2}$.

min. and that it is out of our observation window ($x_2 < 0.2$) for the structure factor at $t \geq 1486$ min. The $F_{2,d=3}(x_2,t)$ around $x_2=1$ increases and becomes sharp with time, indicating that the size of the droplets and the spacing among the droplets are predicted to become uniform with time. The trend similar to $F_{2,d=3}(x_2,t)$ was also observed for $F(x,t)$ at $T=32$ °C in the long time scale after the onset of PCT occurred.⁹

The time changes in three kinds of $F(x,t)$ [$F_{1,d=2}(x_1,t)$, $F_{1,d=3}(x_1,t)$ and $F_{2,d=3}(x_2,t)$] at $T=34$ °C after appearance of the double peak show the same trend as those at $T=33$ °C.

In summary, the appearance of the double peak is considered to be caused by the *heterogeneous* PCT. Namely, because of the difference between the growth rate of the percolated domains and that of cluster of the droplets, the

difference in the size of these structures becomes large with time after the onset of PCT. Furthermore, the deeper the quench, the larger the volume fraction of the percolating domains, because the volume fraction of the minority phase is larger for the deeper quench. The phase separation behavior near the critical threshold, below and above which PCT takes place and does not, respectively, is very sensitive to the quench depth. This is because the quench depth determines the volume fraction of the minority phase and the volume fraction is sensitive to PCT.

7-5. Conclusion

By means of light scattering (LS), optical microscopy (OM) and transmission electron microscopy (TEM), we investigated the phase separation behavior for an non-isometric mixture of PB and PI which involves PCT in the coarsening process of phase-separating structures. Under a certain condition as discussed in this work, the double peak in the LS profile was simultaneously observed after the onset of PCT. The OM and the LS analyses show that sheet-like grains composed of percolating domains coexist with cluster of the droplets. Furthermore, the sheet-like grains tend to orient parallel to the glass surface. The above results demonstrate that PCT takes place not homogeneously and isotropically, but it rather occurs *heterogeneously* and *anisotropically*.

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- ¹⁸ In the previous chapter we did not notice the double peak at $T=34^\circ\text{C}$. However, repeated experiments and close observation reveal the double peak. As a matter of fact, at $T=34^\circ\text{C}$, the clear double peak were observed in five measurements among six. At $T=33^\circ\text{C}$, the clear double peak after the onset of PCT was observed in five measurements among eight. These results seem to indicate that the phase separation behavior near percolation threshold is very sensitive to the subtle difference in experimental conditions and it seems to fluctuate around the most probable phase separation behavior.
- ¹⁹ The geometry of the cut film is as follows: as described in Sec. 7-2-1, the sample for the phase separation experiment was sandwiched between two glasses during annealing. On the other hand, the film for the optical microscopy observation was cut perpendicularly to the glass surface and therefore, in Fig. 7-5(b), the edge of the cut film had touched the glass surface.
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Chapter 8

Intermittency of Droplet Growth in Phase Separation of Non-Isometric Polymer Mixtures

8-1. Introduction

In the previous studies (chapters 6 and 7), we investigated the growth and morphology of the phase separating domains for mixtures of polybutadiene (PB) and polyisoprene (PI) (PB/PI) with compositions of 50/50, 65/35 and 70/30 in weight percent. In this chapter we studied the phase separation process for the mixture of the PB/PI with a composition of 80/20 wt%/wt%. From the results of chapters 6-8, the phase separation dynamics in polymer blends is shown to strongly depend on the composition and quench depth.

Phase separation kinetics in polymer mixtures has been extensively studied by numerous researchers in the past few decades.¹⁻³ Time evolution of phase separating domains is traditionally characterized by scaling law:

$$q_m \sim t^{-\alpha} \quad (8-1)$$

$$I_m \sim t^{\beta} \quad (8-2)$$

where q_m and I_m are the peak wave number and the scattering maximum, respectively. α and β are the scaling exponents characterizing the time-evolution. In the intermediate stage of spinodal decomposition (SD), as the characteristic wavelength and amplitude of the concentration fluctuations increase with time, the relation between α and β is given by

$$\beta > 3\alpha. \quad (8-3)$$

On the other hand, in the late stage of SD, the amplitude of the concentration fluctuations reaches the equilibrium value determined by the coexisting curve. Therefore, the relation between α and β is given by

$$\beta = 3\alpha. \quad (8-4)$$

The scaling postulate in the phase separation process was proposed by Langer-Bar-on-Miller (LBM) and Chou-Goldburg (CG).^{4,5} Namely, the plot between the wave number $Q_m [= q_m/q_m(0)]$ and the time $\tau [= t/t_c]$ reduced by a characteristic wave number $q_m(0)$ and a characteristic time t_c , respectively, at various quench depth superimposes onto a single master curve.

In addition, the scaled structure factor $F(x,t)$ is defined by⁶

$$F(x,t) = q_m(t)^3 I(x,t) = \langle \eta^2(t) \rangle S(x,t), \quad (8-5)$$

and

$$x = q/q_m(t). \quad (8-6)$$

$I(x,t)$ and $\langle \eta^2(t) \rangle$ are the scattering function and the space-averaged square of refractive index fluctuations at a given time t , respectively. $S(x,t)$ is a scaling function at time t which characterizes a shape of growing structure. q is wave number which is defined by $q = (4\pi/\lambda) \sin(\theta/2)$, where θ and λ are the scattering angle and the wavelength in the medium, respectively. In the late stage, if the kinetics of phase separation obeys the dynamic scaling hypothesis, $\langle \eta^2(t) \rangle$ becomes constant with t , and $S(x,t)$ becomes independent of t , and hence $F(x,t)$ becomes an universal function.

According to Flory-Huggins model^{7,8} based on mean-field theory, the free energy $f(\phi_A)$ per lattice site of polymer mixtures on mixing is given by

$$\frac{f(\phi_A)}{k_B T} = \frac{\phi_A \ln \phi_A}{N_A} + \frac{(1-\phi_A) \ln(1-\phi_A)}{N_B} + \chi \phi_A (1-\phi_A), \quad (8-7)$$

where N_i and ϕ_i are degree of polymerization and volume fraction of i th component ($i = A$ or B), respectively, ($\phi_A + \phi_B = 1$). χ is the Flory-Huggins interaction parameter. k_B and T are used in the usual meaning. χ parameter is often described by the following experimental form:

$$\chi = s + \frac{h}{T}. \quad (8-8)$$

Spinodal points which show stability limit can be calculated from eq. (8-7), i.e.,

$$\frac{\partial^2 f(\phi_A)}{\partial \phi_A^2} = 0 \text{ at spinodal point.}$$

In the region inside spinodal curve, phase

separation takes place via spinodal decomposition (SD).⁹ Here, even infinitesimal concentration fluctuations lead to decrease of free energy of the system and therefore grows with time. In the region between binodal and spinodal curve, phase separation occurs according to nucleation and growth (NG).¹⁰ Here, the disordered state is metastable, i.e., thermally activated small concentration fluctuations decay because they increase the free energy of the mixture, while thermal concentration fluctuations greater than a critical one cause decrease of free energy, and therefore they grow with time.

Phase separation dynamics is strongly affected by the mechanism of the phase separation. Therefore, a change in phase separation mechanisms, if it occurs, causes the change in the phase separation dynamics. However,

crossover phenomena from one mechanism to another have not been sufficiently understood at present. In the previous paper, we reported on the crossover in the dynamics from that relevant to a growth of percolated morphology to that relevant to a growth of droplet morphology, i.e., crossovered dynamics associated with percolation-to-cluster transition (PCT).¹¹ Before the PCT takes place, the phase separation grows according to the power law with an exponent of $\alpha=0.9$ which is close to that predicted for the growth of percolated morphology.¹² After the PCT occurred, the phase separation kinetics became very slow.^{11, 13, 14} Afterwards, in the much longer time, the kinetics proceeds with the growth law of droplets ($\alpha = 1/4-1/3$).^{6, 15, 16}

In this chapter, we report on a new crossover phenomena where the phase separation kinetics becomes very slow in non-isometric quenches (“intermittency” of the domain growth). At first sight, this crossover phenomenon appears to be the same behavior as that caused by PCT. However, it is shown that the intermittency of the domain growth is not caused by PCT, if we elaborately analyze the results.

8-2. Experimental Section

8-2-1. Sample Preparation and Characterization

PB and PI were polymerized by living anionic polymerization. The PB has a weight-averaged molecular weight (M_w) of 5.8×10^4 and the polydispersity index for the molecular weight distribution M_w/M_n of 1.2, respectively, where M_n is a number-averaged molecular weight. The PI has a M_w of 10.1×10^4 and M_w/M_n of 1.3, respectively. The microstructures of the PB and PI were reported in the previous paper.¹¹ Blend specimens were dissolved in toluene in ca. 2-3 % by total polymer weight fraction. After the solution was filtered by a milipore film with a pore size of 0.45 μm , solvent was slowly evaporated. In addition, the films prepared were dried under vacuum for two days in order to perfectly

remove the solvent. The films were put on a clear glass plate and then degassed under vacuum for ca. 12 hours in order to remove bubbles. The films were sandwiched between two clear glass plates for light scattering measurements and the thickness was 0.5 mm.

8-2-2. Cloud Points

Cloud points were determined by using light scattering. As the kinetics of phase separation in the PB/PI mixtures is very slow, especially in the non-isometric mixtures, we determined the cloud points by comparing a scattering profile in a homogeneous state with that after annealing for more than one week at a given temperature. Namely, if the scattering intensity after annealing at a given temperature increased more than that before annealing, we assessed that the mixture was in two-phase region at this temperature. Otherwise, it was assessed to be in single-phase region. Cloud points were obtained by carrying out such measurements as described above for various compositions and temperatures.

8-2-3. Time-Resolved Light Scattering

By using time-resolved light scattering method, we studied time-evolution of phase separation after the mixture was transferred from a homogenous state into a two-phase state by a temperature jump. Measurements were performed for PB/PI mixtures having compositions of 74.7/25.3 and 80/20 wt%/wt%. Hereafter, we designate the composition of A/B wt %/wt % as A/B for simplicity. The time-evolution of the domain growth for the 50/50, 65/35, and 70/30 mixture was reported in chapter 6.¹¹

The scattering profile, $I_s(q)$, in the single-phase state before quench into the two-phase region was measured for each quench experiment. The measured scattering profile $I_s(q)$ was subtracted from the scattering profiles after quench,

$I(q,t)$, in order to remove the scattering due to artifact, e.g., impurities in sample and so on. All the scattering data shown in the following sections, except for scattering profiles in Fig. 8-2, are corrected for the scattering profile in the single-phase state $I_s(q)$.

8-3. Results and Discussion

8-3-1. Calculation of Binodal and Spinodal Curves

Cloud points for the PB/PI mixtures are shown in Fig. 8-1 (open circles). As shown in the Fig. 8-1, the mixtures have a lower critical solution temperature

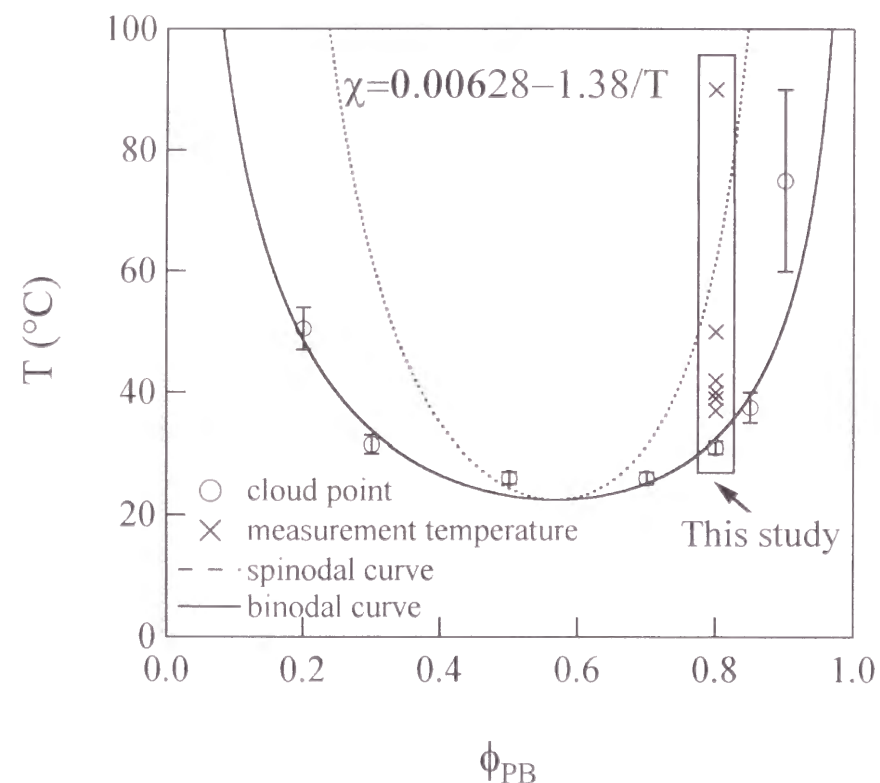


Figure 8-1. Cloud points, spinodal and binodal curves. The latter two curves were calculated in the context of Flory-Huggins theory based on the assumption that χ parameter is independent of composition. The phase separation experiments were carried out at the points marked by $\times$.

(LCST) type phase diagram, i.e., while at temperatures below the cloud point the mixture is in the single-phase state, at temperatures above the cloud point the mixture is in the two-phase state. In addition, we show the binodal curve which was obtained by a best fit of Flory-Huggins theory to the measured cloud points. s and h of eq. (8-8) are parameters for the fit. The values of s and h obtained are 0.00628 and -1.38, respectively. These values are close to those obtained by small-angle neutron scattering (SANS) measurement for a blend of the same PI as that used in this study and deuterated PB (DPB) which has almost the same microstructure and molecular weight as those of the PB used in this study. The values of s and h obtained by the SANS measurement for the DPB/PI 50/50 mixture are 0.00454 and -1.02, respectively.¹⁷ Moreover, mean-field spinodal curve in the context of Flory-Huggins theory was calculated by using the values of s and h (Fig. 8-1). However, we should notice that in fact, it is very difficult to directly determine spinodal points from the phase separation process, i.e., distinction of SD from NG near the spinodal curve is difficult as Binder pointed out.¹⁸

8-3-2. Time-Evolution of Scattering Profiles

Figure 8-2 shows time-evolution of scattering profiles after quench into two-phase region for the 80/20 mixture at (a) $T=39$ °C and (b) $T=90$ °C. Cloud point for the 80/20 mixture is $T=31 \pm 1$ °C. It is shown in Fig. 8-2 that, at both temperatures, a scattering maximum appears, and it increases and shifts toward low q with time. At $T=39$ °C, the peak shift toward low q with time becomes slow after $t=604.3$ min. However, at $T=90$ °C, such slowing down of the peak shift is not observed. The time change in q_m at these temperatures will be reported in details in the following section. Furthermore, the scattering peak at $T=39$ °C is broader than that at $T=90$ °C.

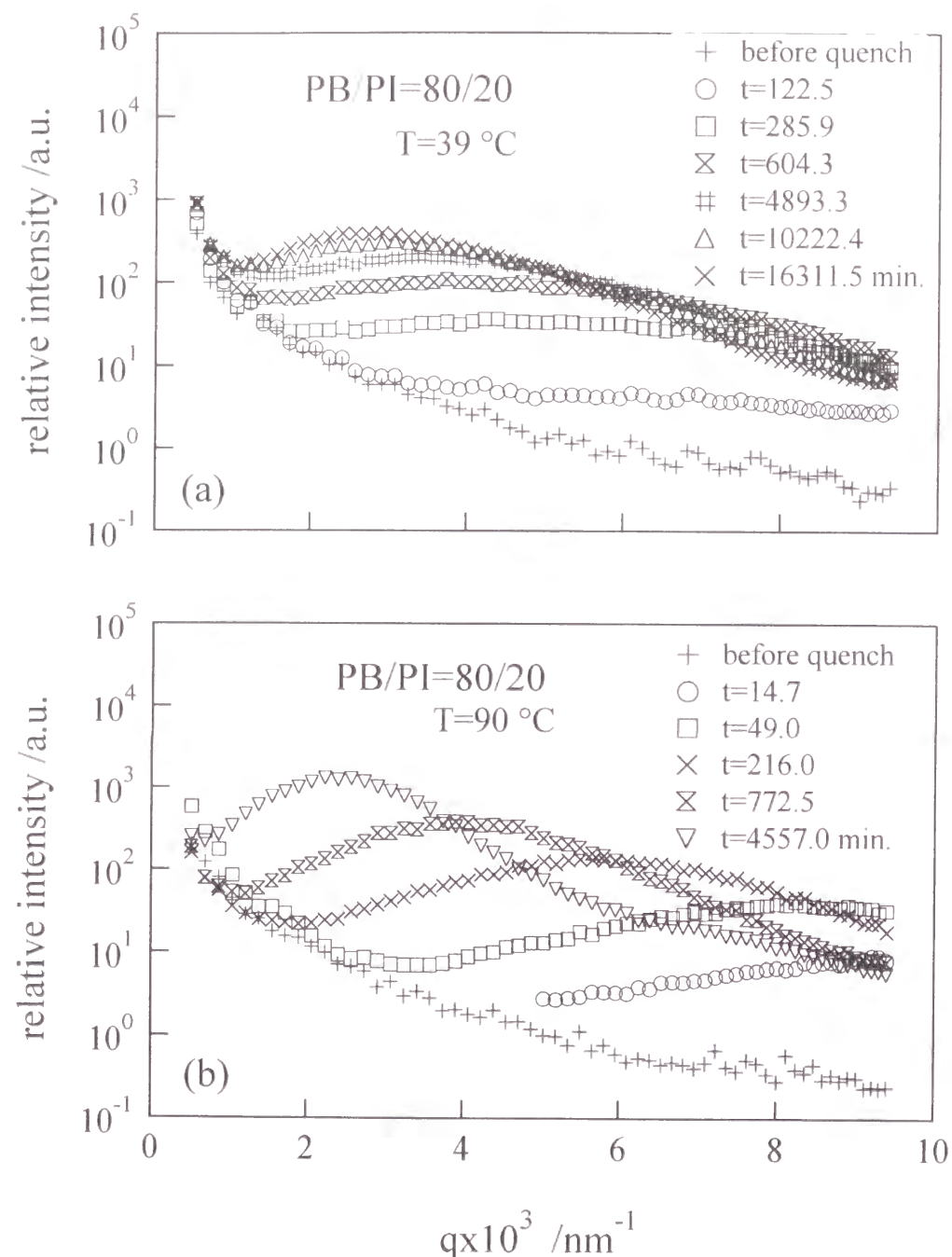


Figure 8-2. Time evolution of scattering profiles for 80/20 wt.%/wt.% (a) at $T=39\text{ }^{\circ}\text{C}$ and (b) $90\text{ }^{\circ}\text{C}$.

8-3-3. Time-Evolution of q_m and I_m

Figure 8-3 shows double logarithmic plot of (a) q_m versus time t and (b) I_m versus t for the 80/20 mixture at deep quenches ($T = 50$ and $90\text{ }^{\circ}\text{C}$). The exponents α and β in eqs. (8-1) and (8-2) at both temperatures show 0.25-0.33 and 0.75-1, respectively, in the late time. The same trend was observed for the 70/30 mixture.¹¹ The exponents α and β for the 70/30 mixture showed the same values, or 0.25-0.33 and 0.75-1, respectively, in both shallow and deep quenches ($T = 30 - 90\text{ }^{\circ}\text{C}$) in the long time limit covered in our experiment.¹¹ Their values are close to those expected from the growth of droplets by evaporation-condensation mechanism (Lifshitz-Slyozov-Wagner law) or diffusion-coalescence of droplets with hydrodynamic interactions ($\alpha=1/3$)^{6, 15, 16}. This $1/3$ power law has also been experimentally found by Okada et al.¹⁹ and L. Sung et al.²⁰ for non-isometric mixtures of polystyrene/poly(2-chlorostyrene) and deuterated polystyrene/polybutadiene, respectively. Therefore, the phase-separated structures at these temperatures for the 80/20 mixture are expected to form droplets morphology.

On the other hand, the time changes in q_m and I_m at shallow quenches ($T=42, 40, 39$ and $37\text{ }^{\circ}\text{C}$) for the 80/20 mixture are quite different from those at deep quenches ($T = 90$ and $50\text{ }^{\circ}\text{C}$). As shown in Fig. 8-4, the time change in q_m at (a) $T=42$, (b) 40 , (c) 39 and (d) $37\text{ }^{\circ}\text{C}$ can be divided into three regimes [regime (I)-(III)]. Similarly, Fig. 8-5 shows that the time change in I_m at (a) $T=42$, (b) 40 , (c) 39 and (d) $37\text{ }^{\circ}\text{C}$ can also be divided into three regimes. In regime (I), α and β have 0.32-0.37 and 1.70-2.50, respectively, as shown in Fig. 8-6(a). The relation between α and β fulfills inequality (8-3) [Fig. 8-7(a)]. Therefore, in regime (I), concentration fluctuations do not reach an equilibrium value yet and hence increases with time. In another words, the growing droplets have not reached the equilibrium compositions yet. In regime (II), the growth of

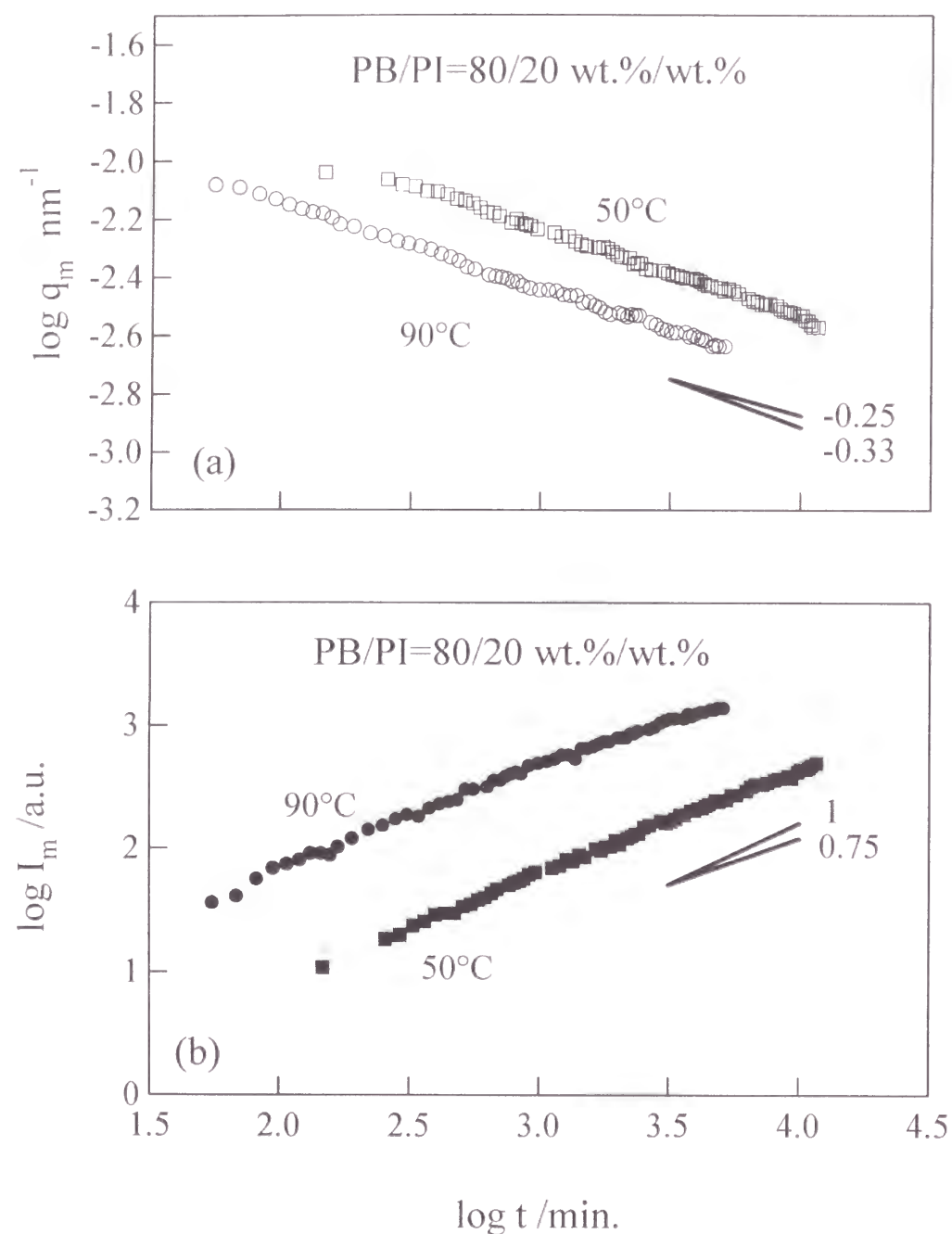


Figure 8-3. Time evolution of (a) q_m and (b) I_m for 80/20 wt.%/wt.% at deep quenches.

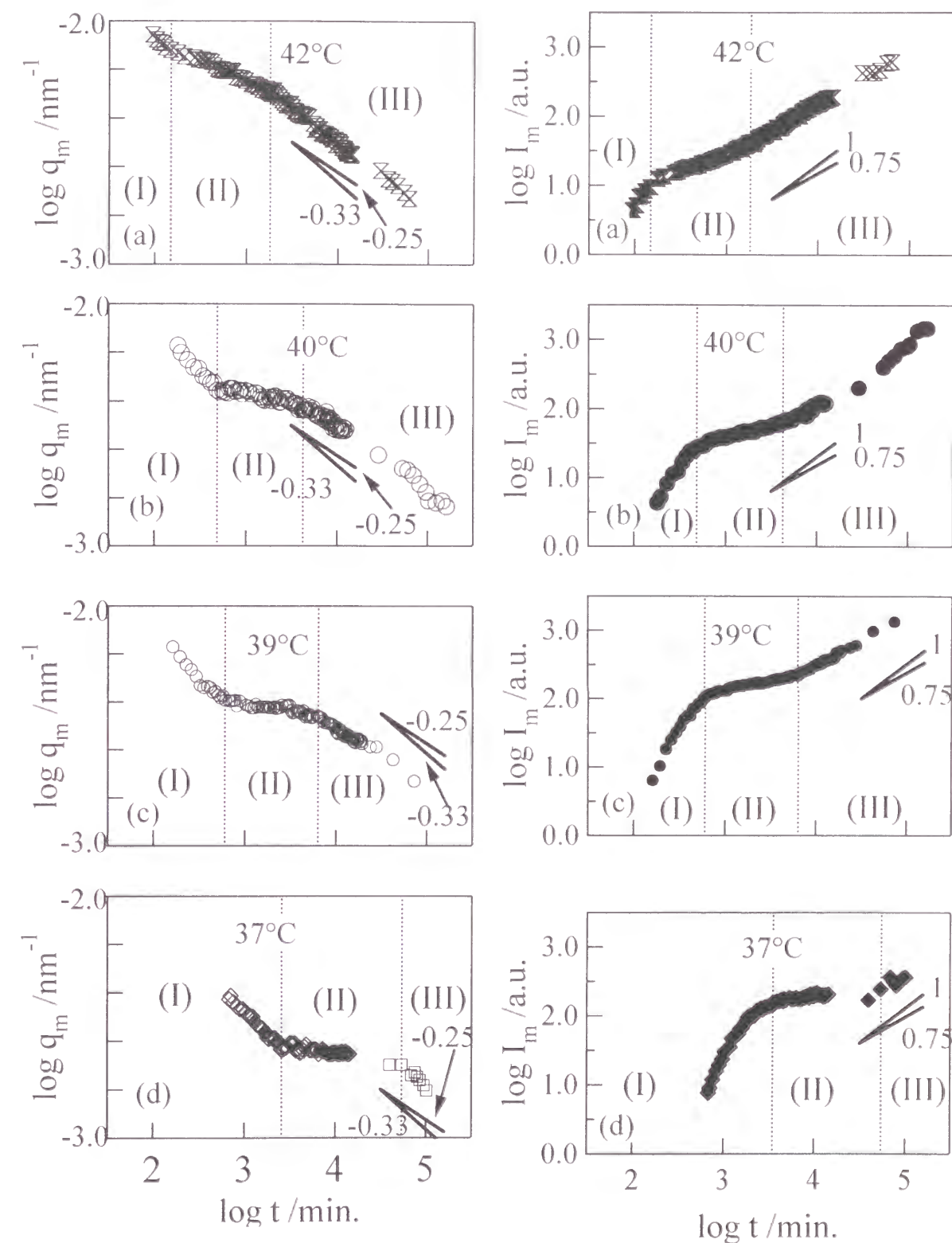


Figure 8-4. Time evolution of q_m for 80/20 wt.%/wt.% at shallow quenches. Figure 8-5. Time evolution of I_m for 80/20 wt.%/wt.% at shallow quenches.

the phase-separated structure becomes very slow (intermittency of the droplet growth). Namely, α and β are very small and they are 0.04-0.18 and 0.18-0.51, respectively, as shown in Fig. 8-6(b). Here, it is important to note that the values of α and β in regime (II) depend on quench depth. The shallower the quench (the lower the temperature), the smaller the values of α and β , i.e., the slower the time-evolution of phase separation. Moreover, the shallower the quench, the longer the regime (II), as may be recognized in Fig. 8-4.

The quench-depth dependence of α and β implies that the validity of LBM and CG scaling postulate^{4, 5} does not hold for the 80/20 mixture. This behavior is largely different from that for the critical mixture of the same PB/PI²¹ and other critical mixtures²²⁻²⁴ in which LBM and CG scaling postulate holds.

Here, it might be possible to consider that the intermittency of the droplet growth in regime (II) is related to the “spontaneous pinning of the domain growth” caused by PCT.^{11, 13} However, we should notice that the behavior is different from that due to PCT in some respects. As the quench-depth becomes shallower, the $q_{m,II}$ at which regime (II) begins, becomes smaller. Moreover, the time t_{II} , at which regime (II) begins, is later in shallower quench (Figs. 8-4 and 8-5). These results are quite opposite to those caused by PCT. In the case of PCT, the shallower the quench-depth, the earlier PCT occurs, and the larger the $q_{m,p}$ at which PCT takes place.^{11, 13} In addition, PCT took place for the 65/35 mixture of the PB/PI in our light scattering experiment.^{11, 25} It is predicted from these results that the intermittent growth in regime (II) is not caused by PCT. In regime (III) which is the long time limit covered in these measurements, the phase separation dynamics shows the same behaviors as those at deep quenches for the 80/20 mixture and for the 70/30 mixture. Namely, the scaling exponents α and β show 0.25-0.33 and 0.75-1, respectively, in the long time as shown in

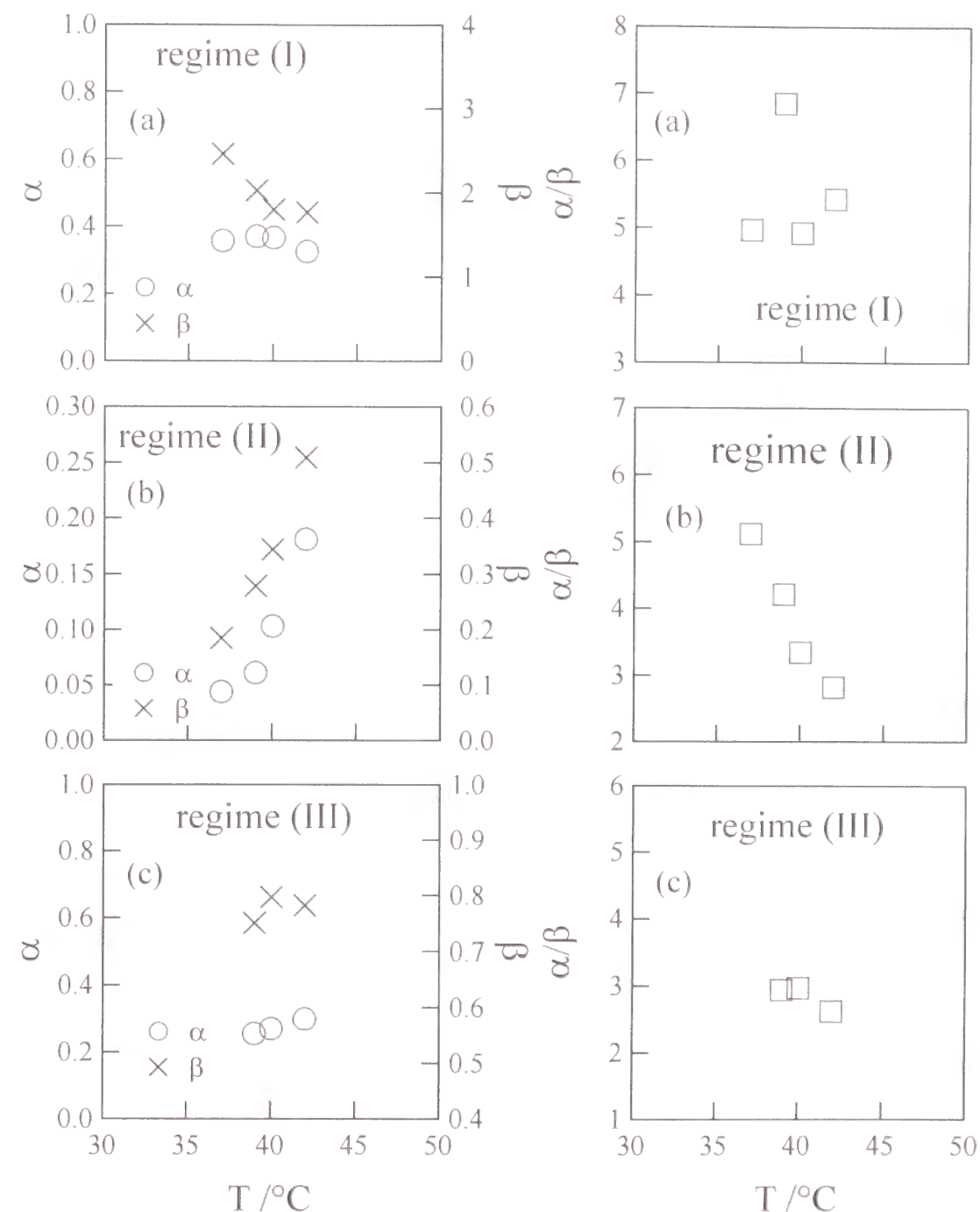


Figure 8-6. Scaling exponents α and β as a function of temperature in each regime.

Figure 8-7 α/β as a function of temperature in each regime.

Fig. 8-6(c). It is shown in Fig. 8-7(c) that β/α is almost equal to 3 at all temperatures in regime (III). Hence the growing droplets have reached equilibrium compositions in regime (III).

8-3-4. Scaled Structure Factor at Deep and Shallow Quenches

We present time change in the scaled structure factor $F(x,t)$ for the 80/20 mixture at $T=50^\circ\text{C}$ (a deep quench) in Fig. 8-8. In Fig. 8-8(a) obtained at $t \leq 393.2$ min., $F(x,t)$ increases with time at whole x region, indicating that $\langle \eta^2(t) \rangle$ grows with time. Figure 8-8(b) shows that $F(x,t)$ in the late time $t \geq 905.5$ min. becomes an universal function. Apart from the form of $F(x,t)$, this universal behavior in the late time is similar to that for the critical mixture.²¹

Figures 8-9(a) to 8-9(c) show the double logarithmic plot of $F(x,t)$ vs x in regime (I) to (III), respectively, at $T=42^\circ\text{C}$ (a shallow quench) for the 80/20 mixture. Similar plots at $T=40^\circ\text{C}$ (a shallow quench) are shown in Figs. 8-10(a) to 8-10(c). In Figs. 8-9(a) and 8-10(a), $F(x,t)$ increases with time at whole x region in regime (I), suggesting that $\langle \eta^2(t) \rangle$ becomes larger with time as expected from eq. (8-5). In regime (II), the $F(x,t)$ is independent of t at $x \geq 1$, while the $F(x,t)$ is nonuniversal with t at $x < 1$ [Figs. 8-9(b) and 8-10(b)]. It is predicted from this result that $\langle \eta^2(t) \rangle$ reaches the value near to an equilibrium one in regime (II). However, the scattering function cannot be scaled with the peak wave number q_m . We predict that, in regime (II), the droplets which almost reached the equilibrium compositions, change the spatial distribution with time. In regime (III), $F(x,t)$ is universal with t at whole x region [Figs. 8-9(c) and 8-10(c)], which implies that, in regime (III), $\langle \eta^2(t) \rangle$ reaches an equilibrium value and the phase separated structures can be scaled with a single characteristic parameter $\Lambda=2\pi/q_m$. Here, it is important to notice that the system which forms droplets has at least two characteristic length, i.e., interdroplet distance and droplet radius. The peak at $x=1$ is considered to be due to the interference of

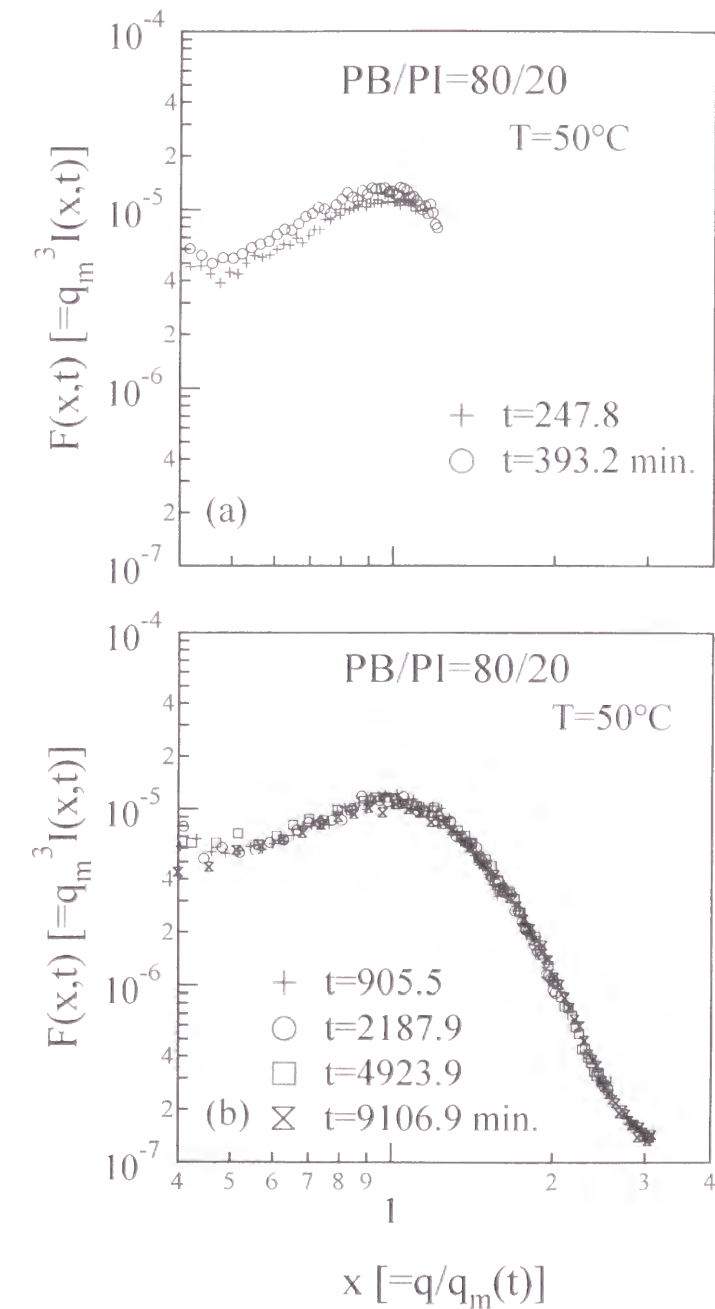


Figure 8-8. Time change in scaled structure factor $F(x,t)$ at $T=50^\circ\text{C}$.

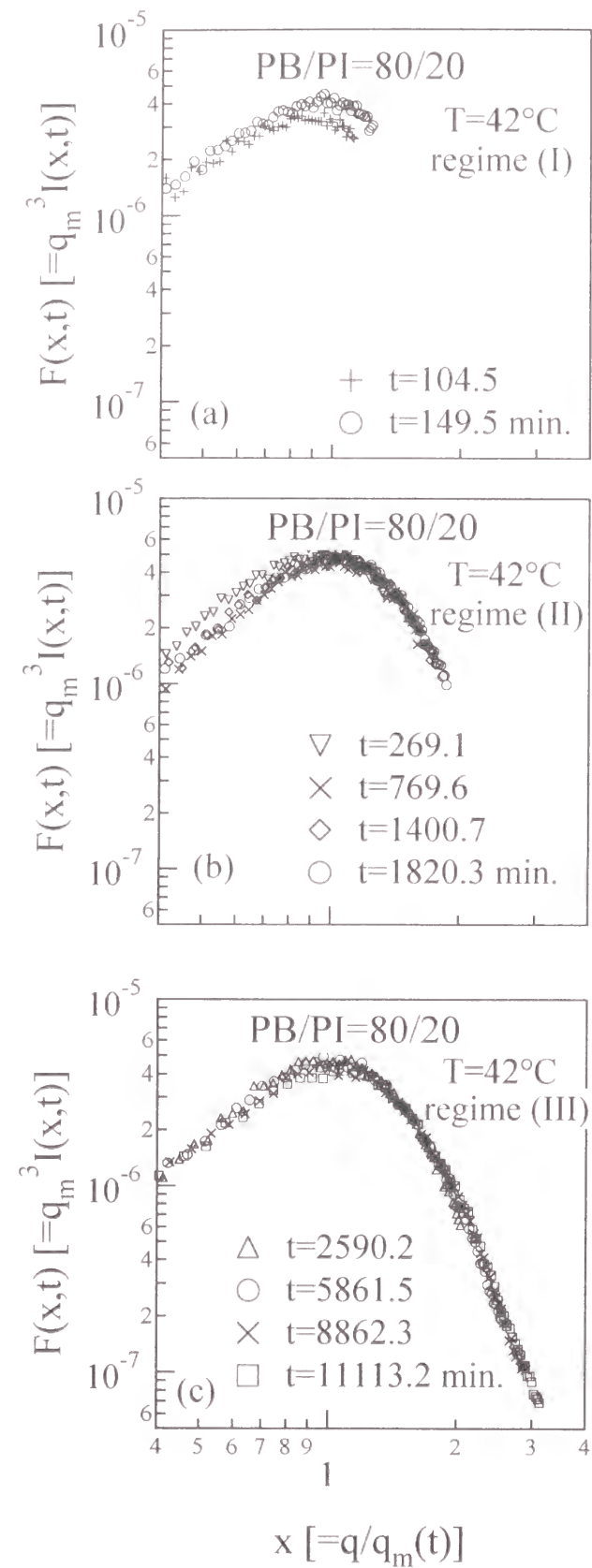


Figure 8-9. Time change in scaled structure factor $F(x,t)$ in each regime at $T=42^\circ\text{C}$.

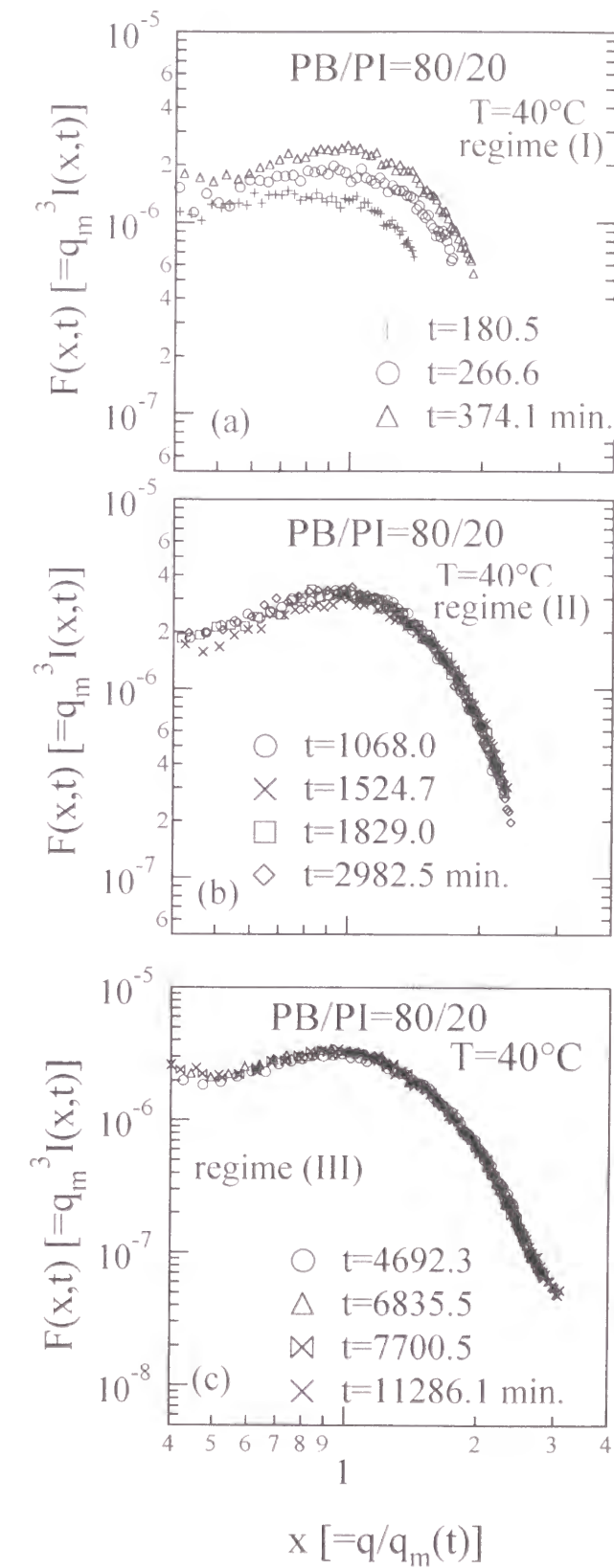


Figure 8-10. Time change in scaled structure factor $F(x,t)$ in each regime at $T=40^\circ\text{C}$.

scattered waves from droplets. This consideration is based upon the fact that the peak caused by form factor of single droplets was observed in higher- q at $T=37^\circ\text{C}$ and $T=39^\circ\text{C}$ in the late time. This result about the scattering of single droplets will be described in the following section.

From the results of the time change in q_m , I_m , and $F(x,t)$, we interpret the behaviors in each regime as follows. In regime (I), as $\langle\eta^2(t)\rangle$ does not reach an equilibrium value, droplets are expected to grow mainly by diffusion of PI molecules from the matrix into droplet phase (PI-rich phase). In regime (III), $\langle\eta^2(t)\rangle$ reaches an equilibrium value and droplets grow according to the diffusion-coalescence of droplets or Lifshitz-Slyozov-Wagner law. We will show our speculation of regime (II) in Sec. 8-3-7.

8-3-5. Scattering Maximum Arising from Form Factor of Single Droplets

Figure 8-11(a) shows the scattering profiles after $t=1749.1$ min. for the 80/20 mixture at $T=37^\circ\text{C}$. In addition to a large peak at $q \approx 0.002\text{ nm}^{-1}$ due to the interdroplet interference effect, a small peak appears at $q \approx 0.009\text{ nm}^{-1}$. We conjecture that the small peak is caused by the scattering maximum from single droplets. The value of the peak wave number at $t=1749.1$ min. corresponds to the droplet radius $0.64\text{ }\mu\text{m}$ under the assumption that the single droplet is spherical. Figure 8-11(b) presents magnification around the small peak. As shown in Fig. 8-11(b), the peak intensity increases with time and the peak wave number slightly shifts toward small q , i.e., droplet size gets larger with time. Time-evolution of radii of the droplets, R is presented as follows,

$$R \sim t^{0.025}. \quad (8-9)$$

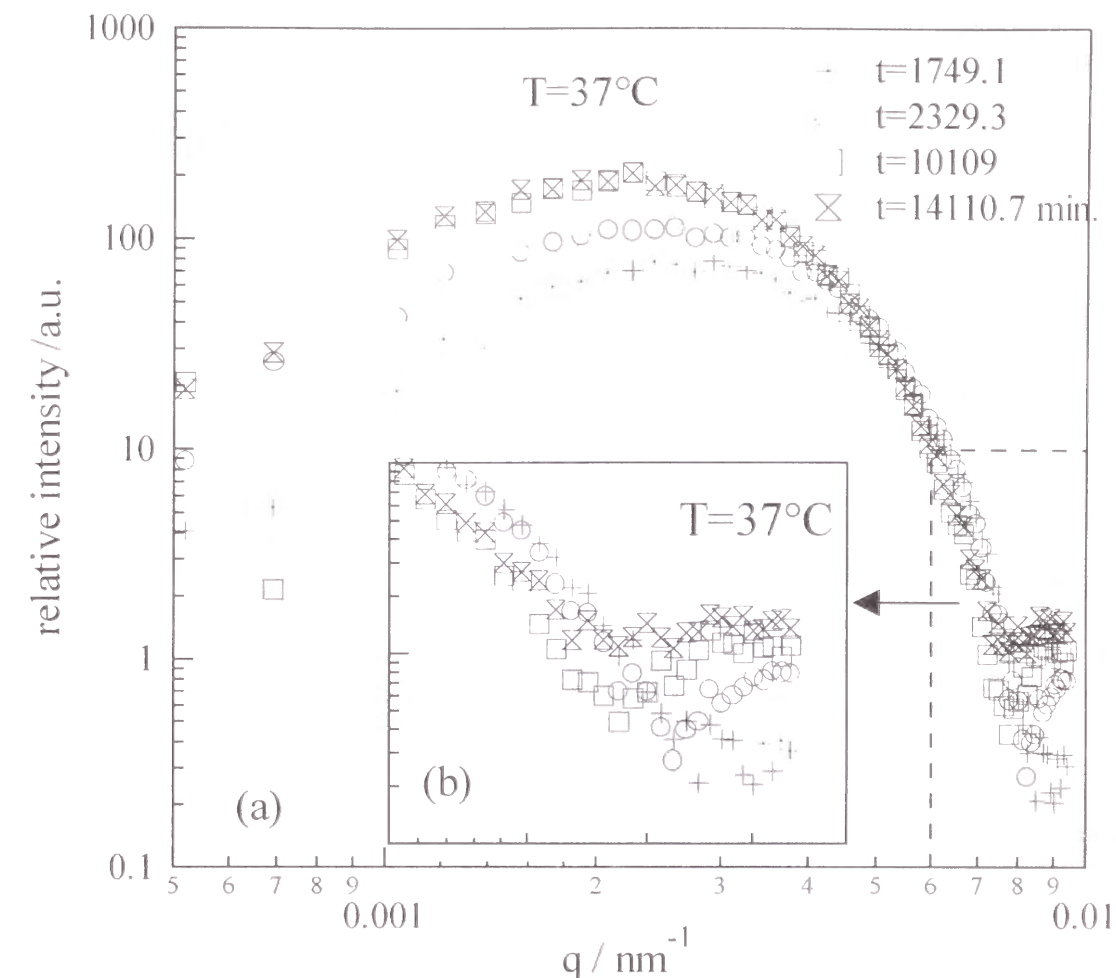


Figure 8-11. (a) Scattering function showing the scattering maximum from the form factor of single droplets and (b) the magnification around the scattering maximum.

8-3-6. Quench-Depth Dependence of Scaled Structure Factor

Figure 8-12 shows double logarithmic plot of scaled structure factor $F(x,t)$ in the late time, which is normalized by $F(x=1,t)$ for the 80/20 mixture at various quenches, vs x . For the comparison, the $F(x,t)/F(1,t)$ for the 50/50 mixture at $T=33^\circ\text{C}$ is also shown in Fig. 8-12. All the $F(x,t)/F(1,t)$ data except for that at $T=37^\circ\text{C}$ in Fig. 8-12 are observed in regime (III) where $F(x,t)$ is independent of time. Therefore, in the time region, the size and spatial distributions of the droplets are expected not to change with time for a given ΔT .

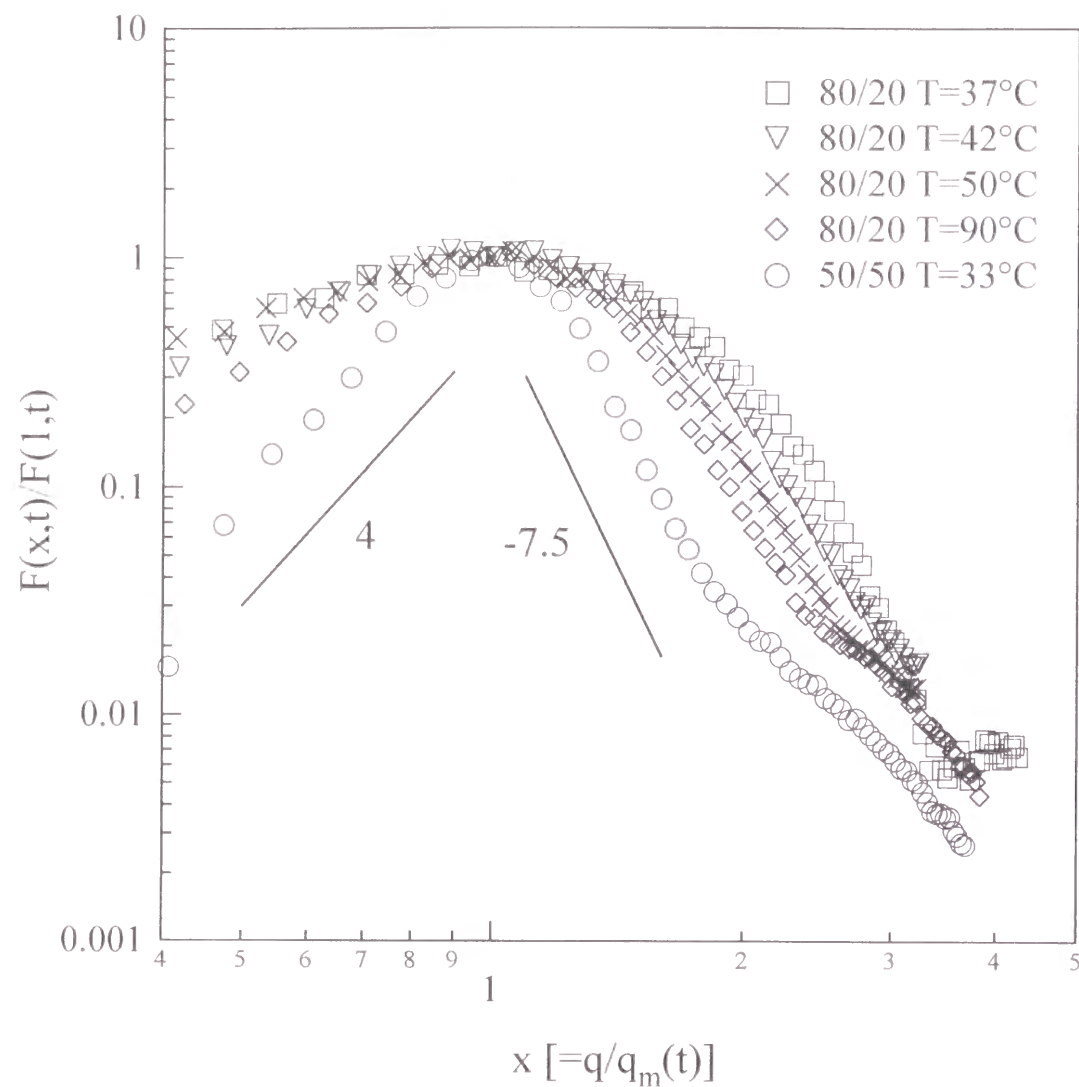


Figure 8-12. Scaled structure factor $F(x,t)$ normalized by $F(x=1,t)$ for the 80/20 mixture at various quench depths.

However, they may depend on ΔT . The form of $F(x,t)/F(1,t)$ for the 80/20 mixture is broader than that for the 50/50 mixture. The $F(x,t)/F(1,t)$ for the 50/50 mixture shows the $x^{-7.5}$ dependence at $1 < x < 2$ and x^4 dependence at $x < 1$, which implies that the phase separated structure is bicontinuous.¹¹ On the other hand, the $F(x,t)/F(1,t)$ for the 80/20 mixture depends on quench-depth. The form of the $F(x,t)/F(1,t)$ is broader, as quench is shallower. The result is

different from that for the 50/50 mixture which is near the critical mixture. In the 50/50 mixture, the scaled structure factor normalized by $\langle \eta^2(t) \rangle$ was universal with quench depth.²¹

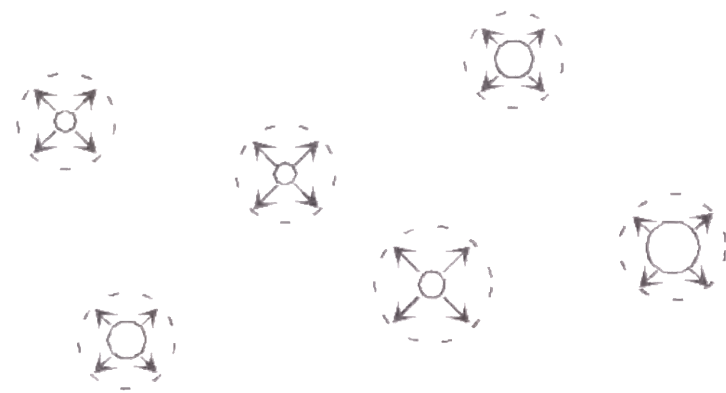
We believe that our observation on the broadening of the scaled structure factor with decreasing the quench depth results from a decreasing volume fraction of droplets. It is well expected from the phase diagram shown in Fig. 8-1 that the volume fraction of the droplets phase decreases with decreasing the quench depth. The trend we observed was able to be qualitatively confirmed even by the simplest model of Debye hard spheres. In the model the scattering function is given by

$$I(q) \sim \langle \eta^2 \rangle V_s \Phi V_{drop} P^2(u) \{1 - 8\Phi P(2u)\}. \quad (8-10)$$

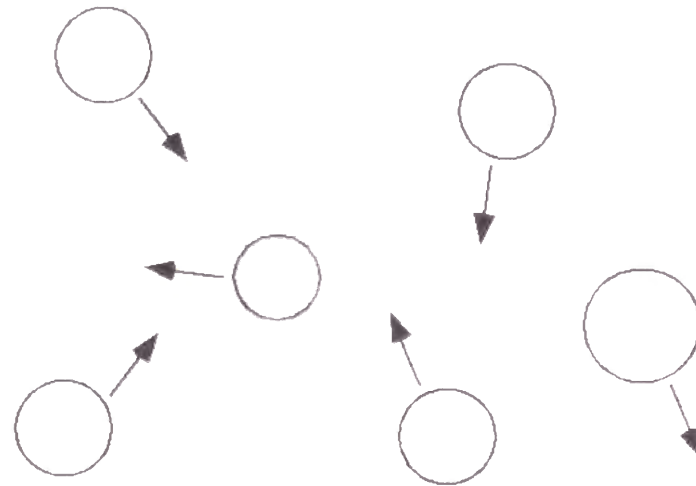
V_s is the total volume of the system, Φ is the volume fraction of spheres, V_{drop} is volume of a sphere and $P^2(u)$ is the form factor of single spheres ($u=qR$; R is radius of sphere). Based on eq. (8-10), we clearly found the observed trend that the scaled structure factor calculated from eq. (8-10) broadens with decreasing Φ , although the results are not included here.

8-3-7. A Possible Model for Intermittent Growth

At this stage we present our speculation about a possible model of the intermittent growth of droplets in Fig. 8-13. The droplets (PI-rich phase) may be developed via nucleation and growth. They have a composition very close to an equilibrium composition but the composition of the matrix phase (PB-rich phase) is still far from an equilibrium composition. They grow as a consequence of diffusion of PI molecules in the matrix phase into them but their centers of mass may be essentially fixed (see the growth of the droplets from the particles shown by solid lines to those shown by broken lines in part a). The



(a) regime (I)



(b) regime (III)

Figure 8-13. A possible model for the intermittent growth. (a) Nucleation of droplets and growth of droplets in regime (I) before the two phases attain the equilibrium compositions; in this process centers of droplets may be essentially fixed, and the PI droplets grow via diffusion of PI molecules in the matrix to the droplets. (b) Diffusion-coalescence of droplets in regime (III) after both the droplets and matrix attain the equilibrium compositions. The intermittency of the growth occurs as a result of a switching of the growth mechanism from that in regime (I) to that in regime (III).

growth of the PI droplets due to the absorption of PI in the matrix may be much faster than the rate of translational diffusion of droplets themselves. This process causes the PB-rich matrix phase to attain equilibrium composition. After the system (closely) attains the equilibrium composition, the droplets may grow via the mechanism of diffusion-coalescence of droplets as schematically shown in part b. A switching of the growth mechanism (from that shown in part a to that in part b) may possibly explain the intermittency. If this is the case, the intermittent time, t_{int} , may correspond to an average time required for the diffusion of particles over an averaged nearest-neighbor distance $\Lambda_{m,II}$ ($=2\pi/q_{m,II}$) at the end of regime (I) {at the beginning of regime (II)}:

$$t_{int} \approx \Lambda_{m,II}^2 D_{drop}^{-1} = (2\pi/q_{m,II})^2 D_{drop}^{-1}, \quad (8-11)$$

where $q_{m,II}$ and D_{drop} are a characteristic wave number and a translational diffusivity of the droplets formed in the system at the end of regime (I). The model explains the experimental observations that t_{int} decreases as T increases, i.e., as T increases (quench becomes deeper), $q_{m,II}$ and D_{drop} increases and therefore t_{int} decreases. Furthermore, we estimated D_{drop} at each temperature where regime (II) was observed, from the following equation:

$$D_{drop} = k_B T / (6\pi \eta R_{drop,II}), \quad (8-12)$$

where k_B and η are the Boltzmann constant and the viscosity of the matrix, respectively. $R_{drop,II}$ is radius of the droplet at the end of regime (I). As for the value of η , we used the magnitude of complex dynamic viscosity of the neat PB in the low angular frequency region which were obtained from the dynamic mechanical measurements. On the other hand, as we could not estimate $R_{drop,II}$ at each temperature, we assumed that $R_{drop,II}$ at each temperature equals that (0.6

μm) at $T=37^\circ\text{C}$. Here, we estimated the value of $R_{\text{drop,II}}$ at $T=37^\circ\text{C}$ from the peak position of the single droplet as shown in Sec. 8-3-5. Thus, estimated D_{drop} , t_{int} , $D_{\text{drop}} t_{\text{int}}$ and $A_{\text{m,II}}^2$ at each temperature are summarized in Table 8-1. In Table 8-1 $D_{\text{drop}} t_{\text{int}}$ is shown to be approximately close to $A_{\text{m,II}}^2$ at each temperature, supporting qualitatively our model.

One may wonder if the droplets growth according to the scheme shown in Fig. 8-13(a) can account for the decrease of q_m in regime (I). The trend of the decreasing q_m value with the growth of droplet radii can be predicted even by the simplest model of Debye's hard sphere as discussed in Sec. 8-3-6. As radii increase, the form factor $P^2(u)$ shifts toward a small q and the interference part $\{1-8\Phi P(2u)\}$ shifts slightly toward a large q side [see eq. (8-10)]. The two factors give a shift of q_m toward a small q . In fact, we can calculate the first moment of the intensity distribution of q -fourier mode, $\langle q \rangle$, as functions of R

Table 8-1 Characteristic parameters estimated from eq. (8-12) and the light scattering analysis.

$T(^{\circ}\text{C})$	D_{drop} ($10^{-18} \text{ m}^2 \text{ s}^{-1}$)	t_{int} (10^5 s)	$D_{\text{drop}} t_{\text{int}}$ (10^{-14} m^2)	$A_{\text{m,II}}^2$ (10^{-14} m^2)
42	8.66	1.00	0.866	0.69
40	8.47	2.28	1.93	2.03
39	8.37	3.49	2.92	2.42
37	8.21	31.2	25.6	7.30

and Φ from the model of Debye's hard sphere [eq. (8-10)], where $\langle q \rangle$ is defined by

$$\langle q \rangle = \frac{\int_0^\infty q I(q) q^2 dq}{\int_0^\infty I(q) q^2 dq} \quad (8-13)$$

The $\langle q \rangle$ calculated for some sets of (R, Φ) is plotted against R in Fig. 8-14. (Note that R and Φ are not independent in our scheme shown in Fig. 8-13(a), i.e., $\frac{R_2^3}{R_1^3} = \frac{\Phi_2}{\Phi_1}$ for arbitrary sets of (R_1, Φ_1) and (R_2, Φ_2) holds.) The value $\langle q \rangle$ is

shown to decrease with increase of R , by about the same order of magnitude on the results shown in regime (I) in Fig. 8-4. Thus, the decrease of q_m in the regime (I) can be explained even in the simple model of Debye's hard sphere apart from the value of the scaling exponent α .

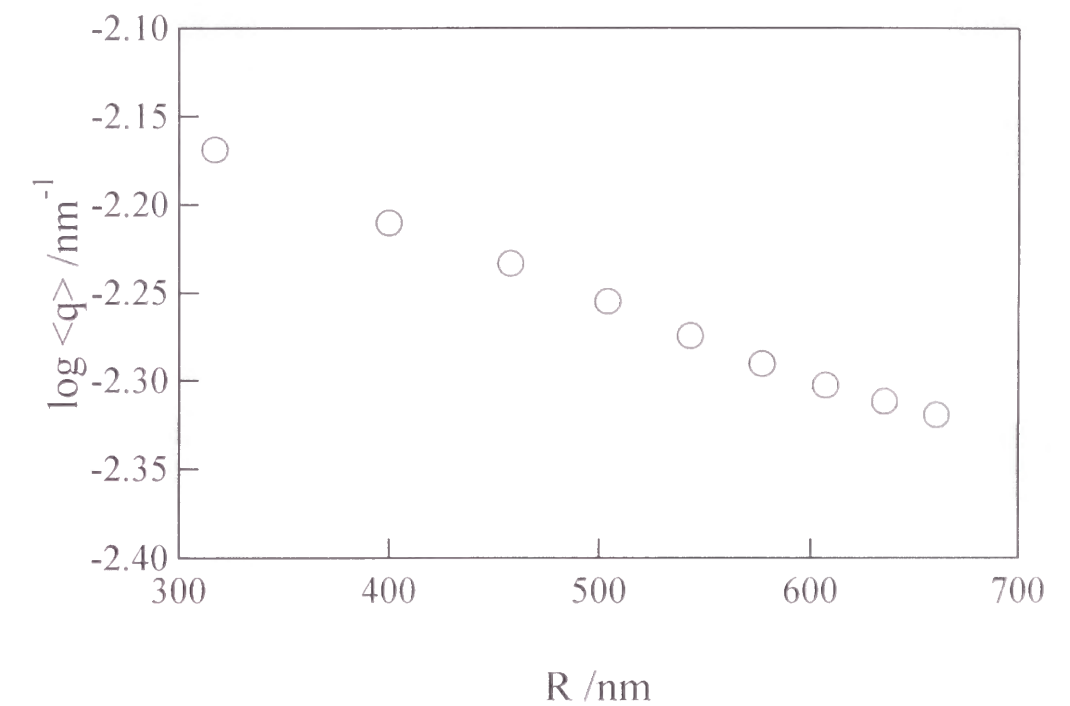


Figure 8-14. Plot of $\langle q \rangle$ calculated on the basis of hard sphere model for some sets of $(R, \Phi) [= (317, 0.01), (400, 0.02), (458, 0.03), (504, 0.04), (543, 0.05), (577, 0.06), (607, 0.07), (635, 0.08) \text{ and } (660, 0.09)]$ against R .

Furthermore, a very simple model in Fig. 8-13(a) assumes no coalescence of droplets or vaporization-condensation mechanism. However, in real systems

the mechanisms discussed above may take place to some degree even in regime (I), in addition to the primary mechanism of diffusion of PI molecules in the matrix phase into the droplets.

The above factor(s) are expected to shift q_m toward small q in regime (I). As the future work for the check of our speculation we need real-space observation.

8-4. Conclusion

The phase separation dynamics for non-isometric mixtures of PB and PI was investigated by means of time resolved light scattering. For the 80/20 mixture, the phase separation at shallow quenches seemingly occurs via nucleation and growth (NG) process, and after all, the process can be classified into four regimes, i.e., (i) early stage (nucleation stage), (ii) intermediate stage, (iii) intermittent stage, (iv) late stage. In this study, the early stage where nucleation takes place, is not observed. For the study of the nucleation stage, we should investigate the scattering in higher q , e.g., by using small-angle neutron scattering or X-ray scattering. In intermediate stage after nucleation stage which corresponds to regime (I), droplets rich in PI grow through the diffusion of PI molecules in the matrix to the droplets, i.e., mean square of refractive index fluctuations increase with time. In late stage which corresponds to regime (III), the exponents, α and β show 0.25-0.33 and 0.75-1, respectively. That is, the droplets and matrix attain their equilibrium composition, and the droplets grow according to diffusion-coalescence with hydrodynamic interactions or Lifshitz-Slyosov-Wagner law. In the intermittent stage, the phase separation dynamics becomes very slow at shallow quenches. The intermittent growth may be caused by the switching of the growth mechanism from that in the intermediate stage to that in the late stage.

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Summary

In chapter 2, the influence of change in chemical structure of polymers on the miscibility of polymer mixtures was investigated by means of small-angle neutron scattering (SANS) technique. Modification of the end-group of polymer chains or subtle modification of main chain with an incorporation of *a small amount of* comonomer by copolymerization gave rise to a large change in the miscibility of the polymer mixtures. The result can be explained by “ χN effect” which is one of the unique properties in the miscibility of polymer mixtures.

In chapter 3, the Ginzburg criterion for mixtures of three kinds of deuterated polybutadienes (d-PBs) and polystyrene (PS) were investigated by using SANS. The d-PBs have the same degree of polymerization but differ in the microstructure, e.g., the content of the 1,4 and 1,2 units. Consequently, it was shown that the Ginzburg criterion for the polymer mixtures depends upon the microstructure of the constituent polymer, which is inconsistent with theoretical prediction by de Gennes and others. Furthermore, in this study, the Ginzburg criterion was suggested to be affected by the free volume change upon mixing.

In chapter 4, high pressure cells for SANS and light scattering (LS) studies were constructed to investigate the effect of pressure on the miscibility of polymer mixtures or diblock copolymers. In the cells, pressure up to 200 MPa can be applied to the cells through a pressurizing liquid. In a preliminary experiment using the SANS pressure cell, the miscibility of a diblock copolymer with a lower critical order-disorder transition temperature was shown to increase with pressure.

In chapter 5, SANS has been used to investigate the thermal concentration fluctuations in the single-phase state for two types of polymer mixtures, in a wide temperature range from far above the glass transition temperature (T_g) of mixtures to below the T_g . One of the two types of polymer mixtures is characteristic of having a large difference in the T_g 's of the pure components, while the other has a

small difference in the T_g 's of the pure components. The structure factors in the small q for the former type mixtures were more suppressed than that predicted by RPA near the T_g , while the structure factors for the latter type mixtures did not show any deviation from the scattering function predicted by RPA even near the T_g . As a result of an elaborate analysis, it was found that, for the former type mixtures, a negative contribution to the χ parameter arose near the T_g and it increased more and more upon approaching the T_g . Further, the χ parameter with the negative contribution has a interaction range over a few nanometer.

In chapter 6, the phase separation dynamics involving a morphological change from percolation to cluster of droplets, i.e., percolation-to-cluster transition (PCT), has been investigated by means of time-resolved light scattering technique. The phase separation dynamics can be classified into three regime: (i) percolation regime, (ii) PCT regime and (iii) cluster regime. In percolation regime, the phase separation dynamics obeys the growth law of percolation ($q_m \sim t^{-0.9}$). In PCT regime after the onset of PCT takes place, the phase separation dynamics becomes very slow or is apparently stopped. In cluster regime which is long-time limit, the phase separation dynamics proceeds according to growth law of droplets ($q_m \sim t^{-0.25 \sim -0.33}$).

In chapter 7, the phase separation dynamics and the morphology under the condition very close to the percolation threshold were studied. Just below the percolation threshold, after the onset of PCT occurred, we observed the coexistence of the sheet-like grains composed of percolating domains and cluster of droplets in bulk for long time. The sheet-like grains have a tendency to orient parallel to the glass surface. Thus, it was found that PCT did not occur homogeneously and isotropically but *heterogeneously* and *anisotropically*.

In chapter 8, I studied the phase separation process seemingly caused by nucleation and growth for non-isometric polymer mixtures. The phase separation dynamics in the long time limit obeys the growth law of droplets ($q_m \sim t^{-0.25 \sim -0.33}$),

independent of quench depth. Before the long time limit, intermittency of the domain growth was observed under a certain condition. In the region of the intermittent growth, the power law of the domain growth depends on quench-depth. Namely, the phase separation dynamics does not obey the scaling postulate proposed by Chou and Goldburg (CG) and Langer-Bar-on-Miller (LBM), which holds in the phase separation process for isometric mixtures.

List of Publications

1. "Microstructural Effects on the Ginzburg Number and the Crossover Behavior in d-PB/PS Blends"
Phys. Rev. Lett., **73**, 3427 (1994)
D. Schwahn, H. Takeno, L. Willner, H. Hasegawa, H. Jinnai, T. Hashimoto and M. Imai
(Chapter 3)
2. "Critical Crossover Phenomena in Compatible Polymer Blends Studied with SANS"
Physica B, **213&214**, 685 (1995)
D. Schwahn, S. Janßen, L. Willner, T. Schmackers, T. Springer, K. Mortensen, H. Takeno, H. Hasegawa, H. Jinnai, T. Hashimoto and M. Imai
(not included in this thesis but related to chapter 3)
3. "Small-Angle Neutron Scattering Study of Anomalous Mixing Behaviors in Deuterated Polystyrene/Poly (vinyl methyl ether) Mixtures near the Glass Transition Temperature"
Macromolecules, **29**, 2440-2448 (1996)
H. Takeno, S. Koizumi, H. Hasegawa and T. Hashimoto
(Chapter 5)
4. "Microheterogeneities of Polymer Blends near the Glass Transition Temperature"
Kobunshi Ronbunshu, **53**, 846 (1996)
H. Takeno, S. Koizumi, H. Hasegawa and T. Hashimoto
(not included in this thesis but related to chapter 5)

5. "Crossover of Domain-Growth Behavior from Percolation to Cluster Regime in Phase Separation of an Off-Critical Polymer Mixture"
J. Chem. Phys., **107**, 1634 (1997)
H. Takeno and T. Hashimoto
(Chapter 6)
6. "High Pressure Cell for Small-Angle Neutron and Light Scattering Studies of Phase Transitions in Complex Liquids"
Polym. J., **29**, 931 (1997)
H. Takeno, M. Nagao, Y. Nakayama, H. Hasegawa, T. Hashimoto, H. Seto and M. Imai
(Chapter 4)
7. "Intermittency of Droplet Growth in Phase Separation of Off-Critical Polymer Mixtures"
J. Chem. Phys., **108**, 1225 (1998)
H. Takeno and T. Hashimoto
(Chapter 8)
8. "Heterogeneous Percolation-to-Cluster Transition in Phase Separation of an Off-Critical Polymer Mixture"
J. Chem. Phys., **110**, 3612 (1999)
H. Takeno, E. Nakamura and T. Hashimoto
(Chapter 7)

9. "Small-Angle Neutron Scattering Studies on the Miscibility of Deuterated Polysulfone and Modified Polysulfone Blends"
Polymer, **41**, 1309 (2000)
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(Chapter 2)

10. "Small-Angle Neutron Scattering Studies on Phase Behavior of Block Copolymers"
J. Phys. Chem. Solids, **60**, 1307 (1999)
H. Hasegawa, N. Sakamoto, H. Takeno, H. Jinnai, T. Hashimoto, D. Schwahn, H. Frielinghaus, S. Janßen, M. Imai and K. Mortensen
(not included in this thesis but related to chapter4)

11. "Laser Scanning Confocal Microscopy Analysis in Spinodal Decomposition involving Percolation-to-Cluster Transition"
Macromolecules (to be submitted)
M. Iwata, H. Takeno, M. Takenaka and T. Hashimoto
(not included in this thesis but related to chapters 6 and 7)

12. "Viscoelastic Effects in Relaxation Processes of Concentration Fluctuations in Asymmetric Polymer Blends"
Phys. Rev. E (to be submitted)
M. Takenaka, H. Takeno, H. Hasegawa, S. Saito, T. Hashimoto and M. Nagao
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