Small-Angle X-ray Scattering Study of Spinodal Decomposition in Polystyrene/Poly(styrene-*co*-bromostyrene) Blends

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ABSTRACT: Structure factors of polystyrene/poly(styrene-*co*-bromostyrene) blends and their change with time during phase separation were studied by small-angle X-ray scattering. Structure factors in thermal equilibrium show the form given by the random phase approximation. Measurement of absolute scattering intensities for blends of different composition enables a determination of the radii of gyration of the blend components. Evolution of structure after a temperature jump from the mixed state into the two-phase region is in accordance with the predictions of the latest theories. The initial kinetics can be described by an equation of motion that includes relaxation times and a virtual structure factor. Application of the theory enables a determination of relaxation times dependent upon the wave vector. At temperatures near the glass transition, relaxation and growth become nonexponential.

Introduction

Published work on the kinetics of unmixing in polymer alloys[1-3] applies small-angle light scattering and is therefore dealing with the range of smallest values of the wave vector q. Analysis is based on the Cahn–Hilliard theory[4] of spinodal decomposition, which was adapted by de Gennes[5] to the case of polymer blends. As it turns out, this theory provides a satisfactory description for the time dependence of the light scattering curve during the initial stages of unmixing. After a T-jump into the two-phase region a peak develops in the range of smallest q which shows an exponential growth in intensity with time. Processes in this regime are diffusion controlled, thus enabling a determination of diffusion constants.

Recent theoretical studies by Binder[6] and Strobl[7] point at limitations of the Cahn–Hilliard treatment due to the neglect of the random thermal forces. Deviations from the behavior of the Cahn–Hilliard model are expected to occur outside the range of smallest q. In particular, the characteristic point of intersection common to all curves and the intensity decrease at larger wave vectors predicted by the Cahn–Hilliard treatment should not occur; there should be an increase in intensity for all wave vectors. In the revised theories evolution of the structure factor is described by a relaxation equation, which includes a "virtual" structure factor representing the function approached during the initial stages of spinodal decomposition.

A check of the theories is possible by time-dependent small-angle X-ray or neutron scattering experiments. We report in the following the results of an X-ray scattering study on blends of polystyrene (PS) and poly(styrene-*co*-bromostyrene). As described elsewhere in detail,[8] this system exhibits a thermally reversible phase separation below an upper critical solution temperature. Two-phase morphologies, as observed in the polarizing microscope, suggest the occurrence of spinodal decomposition for blends with similar weight fractions of the two components. The critical temperature T_c can be continuously shifted and by that conveniently adjusted through the choice of the molecular weight M and the degree of bromination x. For symmetric blends with an identical degree of polymerization N for both components T_c depends opon the product Nx^2, increasing with N or x^2. For the purpose of the kinetic studies T_c has to be located above the glass temperature (103–145 °C, depending upon the degree of bromination[9]) and below the temperatures of thermal decomposition (>250 °C). As it turned out, for $N \approx 200$ (M(PS) $\approx 20\,000$) mixtures with copolymers with $x \approx 0.30$ show T_c locations in the desired range. As a further advantage, the contrast introduced by bromination enables X-ray scattering experiments.

Work was started with an investigation of the equilibrium concentration fluctuations in the one-phase region. As demonstrated in a number of recent studies,[10-12] fluctuation scattering can be described by the random phase approximation.[13] We have performed absolute intensity measurements and obtained the radii of gyration of the two components. Kinetics of phase separation was studied by time-dependent SAXS measurements; phase separation was initiated through a temperature jump from the one-phase region into the two-phase region to temperatures near T_g. At these temperatures phase separation proceeds sufficiently slow to enable one to follow structure formation through the evolution of the scattering function.

Experimental Section

Polystyrene with molecular weight $M_n = 20\,400$, $M_w/M_n = 1.04$, was purchased from Pressure Chemical Co. Partial bromination of the material was effected by adding Br_2 to a nitrobenzene solution, the degree of bromination being determined by the molecular ratio of styrene units and bromine. Details of the procedure are given elsewhere.[8] It is important to note that bromination occurs exclusively in the para position of the aromatic ring. This can be proved by NMR spectroscopy.

The study was performed for two copolymers: CPI, with $x = 0.30$ and $T_c \approx 90$ °C (estimate, below T_g), and CPII, with $x = 0.33$ and $T_c \approx 155$ °C. The bromination levels x were determined by elemental analysis. It follows from the procedure that the polystyrene and the derived poly(styrene-*co*-bromostyrene) have identical degrees of polymerization. Hence, the blends prepared from the two components were "symmetrical" with well-defined molecular weights.

Blends of different composition were prepared by codissolution in chloroform followed by precipitation in methanol. Precipitates were dried in vacuo at 90 °C for 24 h. Samples for the scattering experiments were prepared in the one-phase region at 170 °C. Pressure was applied in order to remove hole scattering, which can be quite strong for unpressurized samples and then presents a serious problem.

Small-angle X-ray scattering experiments were conducted with the aid of a Kratky camera using Ni-filtered Cu Kα radiation and pulse-height discrimination. Time-dependent measurements were performed either in real time at the chosen temperature using a position-sensitive detector or, after a controlled annealing

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treatment outside the camera, on quenched samples at temperatures below T_g using a proportional counter in a step-scan mode. Comparison of curves proved that for the samples under study quenching resulted in a freezing of the structure. Absolute scattering intensities (eu/nm^3) were obtained by applying a desmearing procedure on the slit-smeared scattering curves[14] and determining the primary beam intensity with the aid of a standard sample.

Scattering in the Mixed State

The scattering function that reflects the equilibrium concentration fluctuations in the one-phase region of a blend can be described by[13]

$$S^{-1}(q = (4\pi \sin \theta)/\lambda) = \frac{1}{N\phi} f_D^{-1}(q^2 R_A^2) + \frac{1}{N(1-\phi)} f_D^{-1}(q^2 R_B^2) - 2\chi \quad (1)$$

R_A and R_B denote the radii of gyration of components A (copolymer) and B (polystyrene) with the volume fractions ϕ and $(1 - \phi)$; χ is the Flory–Huggins interaction parameter. f_D stands for the Debye structure factor of noninteracting ideal chains

$$f_D = \frac{2}{q^2 R^2}(1 - (1 - \exp[-q^2 R^2])/q^2 R^2) \quad (2)$$

It looks like a good approximation to replace eq 1 by

$$S^{-1}(q) = \frac{1}{N\phi(1-\phi)} f^{-1}(q^2 R_\phi^2) - 2\chi \quad (3)$$

where R_ϕ^2 is defined as

$$R_\phi^2 = (1 - \phi)R_A + \phi R_B \quad (4)$$

R_ϕ^2 gives an apparent radius of gyration that depends on the blend composition ϕ. Equations 1 and 3 give in fact identical expressions in the following limits:

$$q^2 R_{A/B}^2 \ll 1 \text{ (Zimm range)}$$

$$S^{-1} N\phi(1-\phi) = 1 + \frac{q^2}{3}((1-\phi)R_A + \phi R_B) - 2\chi N\phi(1-\phi) = 1 + \frac{q^2}{3} R_\phi^2 - 2\chi N\phi(1-\phi) \quad (5)$$

$$q^2 R_{A/B}^2 \gg 1 \text{ (Kratky range)}$$

$$S^{-1} N\phi(1-\phi) = \frac{q^2}{2}((1-\phi)R_A + \phi R_B) - 2\chi N\phi(1-\phi) = \frac{q^2}{2} R_\phi^2 - 2\chi N\phi(1-\phi) \quad (6)$$

It can therefore be expected that eq 3 gives a good approximation of eq 1 for all values of q. Confirmation is provided by the experimental results given below.

The relation between the absolute intensities following from the SAXS measurement, $I(q)$ (eu/nm^3), and the scattering function $S(q)$ appearing in the theoretical formulas is given by

$$I(q) = \Delta\eta^2 V_z S(q) \quad (7)$$

Here V_z denotes the volume per monomer unit (the smaller difference between the styrene and bromostyrene units is neglected). $\Delta\eta$ describes the electron density difference between the two blend components. It can be derived from a measurement of the densities ρ_A and ρ_B.

Figure 1 demonstrates that eq 3 in fact provides an excellent representation of a measured curve. It was obtained for a CPI/PS blend (volume fractions: 0.47/0.53) at T = 125 °C. The theoretical inverse scattering intensity $I^{-1}(q^2 R_\phi^2)$ was fitted in the range $q^2 R_\phi^2 < 10$ to the measured data through separate variations of the scaling factor R_ϕ^2 and χ. By this a value R_ϕ^2 = 13 nm^2 is obtained. The value derived for χ is 7.8×10^{-3}. χ describes the overall interaction between polystyrene and the partially brominated random copolymer. It is a function of the segmental interaction parameter χ_{ab} effective between styrene and bromostyrene units and the degree of bromination x (compare ref 8):

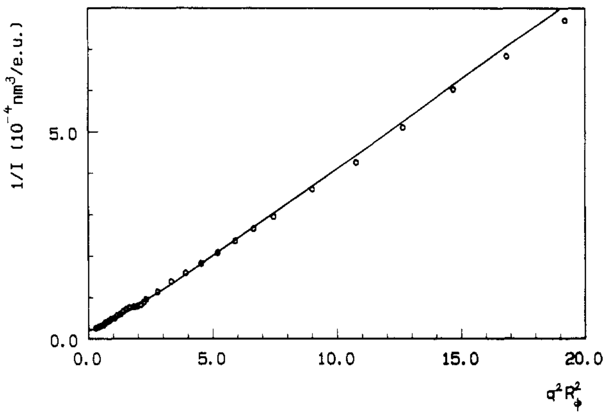

Figure 1. CPI/PS mixture (0.47/0.53) at 125 °C (one-phase region). Fit of measured data by theoretical curve (RPA) in a Zimm plot (R_ϕ^2 = 13 nm^2, χ = 7.8×10^{-3}).

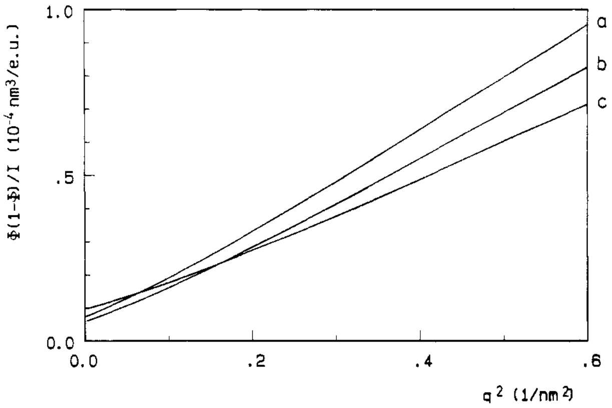

Figure 2. CPI/PS mixtures with volume fractions of CPI ϕ = 0.09 (a), 0.37 (b), and 0.78 (c). Zimm plots of scattering curves at 125 °C.

$$\chi = x^2 \chi_{ab}$$

for χ_{ab} follows a value

$$\chi_{ab} = \chi/x^2 = 3.1 \times 10^{-2}$$

The systematic deviations in the direction of higher intensities showing up in Figure 1 at higher angles are due to Laue scattering associated with the fluctuation of the monomer structure factors.

Analysis of the scattering curves obtained for a series of CPI/PS blends with different composition ϕ at a fixed temperature (125 °C) yields the ϕ dependence of the apparent radius of gyration R_ϕ. Figure 2 shows $I^{-1}(q)$ curves for ϕ = 0.09, 0.37, and 0.78. Figure 3 collects the R_ϕ^2 values thus obtained. The radii of gyration of the individual species follow as

$$R^2(\text{PS}) = R_\phi^2(\phi \rightarrow 1) = 10.5 \text{ nm}^2$$

$$R^2(\text{CPI}) = R_\phi^2(\phi \rightarrow 0) = 15 \text{ nm}^2$$

One notes that bromination leads to a coil expansion. The

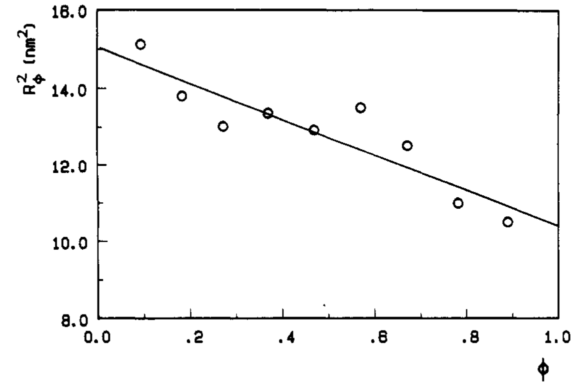

Figure 3. CPI/PS mixtures at 125 °C. Dependence of the apparent radius of gyration R_ϕ^2 on the composition ϕ.

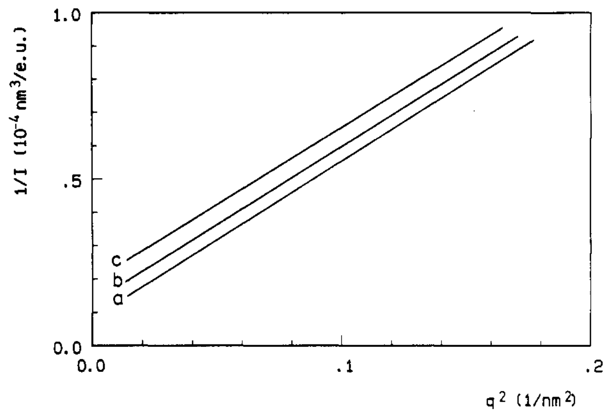

Figure 4. CPI/PS mixtures (0.47/0.53). Zimm plots of scattering curves measured at 125 (a), 145 (b), and 165 °C (c).

value determined for polystyrene is in agreement with that obtained in a Θ solvent (decalin: 10 nm²).

Figure 4 shows the reciprocal scattering intensity, $I^{-1}(q^2)$, measured for a CPI/PS blend (0.47/0.53) at different temperatures, T = 125, 145, and 165 °C. As expected from theory, change of temperature results in the parallel shifts of curves. Similar results were obtained by Shibayama et al.[12] in neutron scattering experiments on PS/PVME blends.

The amount of shifting depends on the temperature dependence of χ (eq 3 and 7):

$$\frac{dI^{-1}}{dT} = \frac{1}{\Delta\eta^2 V_z^2}\frac{d\chi}{dT} \tag{8}$$

Note that the shift factor dI^{-1}/dT does not depend explicitly on ϕ (only through η) and since

$$\Delta\eta^2 \sim x^2$$

$$\chi \sim x^2 \text{ (compare ref 8)}$$

should also be independent of the degree of bromination x. For the system under study we obtained

$$\frac{dI^{-1}}{dT} = 2.5 \times 10^{-6}\ \frac{\text{nm}^3}{\text{eu °C}} \tag{9}$$

This value will be used later.

The temperature-dependent studies enable an estimate of spinodal temperatures. Figure 5 shows the T dependence of forward scattering in a $I^{-1}(0)$ vs. T plot. The locations of the spinodal T_s for different volume fractions ϕ (0.37, 0.47, and 0.67) follows from the respective intercepts $I^{-1}(T \rightarrow T_s) = 0$. For the sample under study T_s is below T_g and has only a nominal meaning. The large extrapolation distance can only provide a rough estimate.

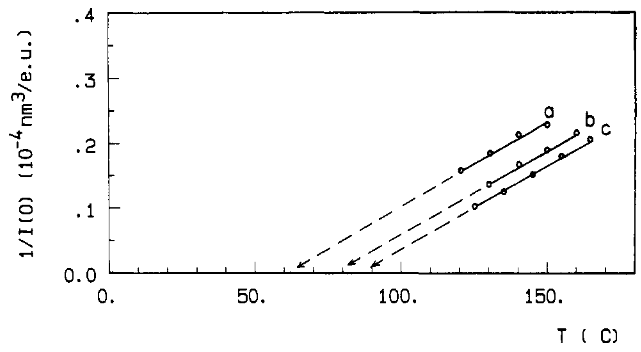

Figure 5. CPI/PS mixtures. Temperature dependence of forward scattering $I(0)$ for CPI volume fractions ϕ = 0.67 (a), 0.37 (b), and 0.47 (c).

Kinetics of Unmixing

Evolution of the structure factor after a temperature jump from the one-phase region into the domain below the spinodal can be described by a first-order equation of motion:[7]

$$\frac{dS(q,t)}{dt} = -2\tau_q^{-1}(S(q,t) - S_\chi(q)) \tag{10}$$

Equation 10 describes the spinodal decomposition in its initial stages. It shows the form of a simple relaxation equation and includes a "virtual" structure factor $S_\chi(q)$ defined by

$$S_\chi^{-1}(q) = \frac{1}{N\phi(1-\phi)} f_D^{-1}(q^2R_\phi^2) - 2\chi \tag{11}$$

Equation 11 is identical with eq 3 and represents a formal extension of the one-phase equilibrium structure factor into the two-phase region. In contrast to the true equilibrium structure factor, which has to be always positive, this virtual structure factor becomes negative for wave vectors q below a critical value q_c. This critical wavenumber q_c is identical with the fixed point with constant intensity in the Cahn–Hilliard theory. τ_q denotes the relaxation time for concentration waves with wave vector q. τ_q changes sign at $q = q_c$, being negative for $q < q_c$ and positive for $q > q_c$.

Binder[6] proposes the following equation:

$$\tau_q^{-1} \simeq \frac{6}{\tau_R} q^2R^2\left(1 - \frac{\chi}{\chi_s} f_D(q^2R^2)\right) \tag{12}$$

Here, τ_R specifies the time required by a chain molecule to diffuse over a length comparable to its own size R (for $R_A \neq R_B$ R is some mean value). χ_s denotes the value of the interaction parameter at the spinodal.

$S_\chi(q)$ and τ_q set together the direction of change of the intensity $S(q,t)$ during the initial stages of phase separation. Since both $S_\chi(q)$ and τ_q change sign at q_c, $S(q,t)$ increases with time for all wave vectors q. Model calculations for demonstration have been performed and were presented elsewhere.[7]

Equation 10 can be transformed into an equation of motion for the reciprocal structure factor $S^{-1}(q,t)$:

$$\frac{dS^{-1}(q,t)}{dt} = 2S^{-1}(q,t)\frac{\tau_q^{-1}}{S_\chi^{-1}(q)}(S_\chi^{-1}(q) - S^{-1}(q,t)) \tag{13}$$

Equation 13 is convenient for a discussion of experimental results.

Figure 6 shows the result of a T-jump experiment. A CPII/PS sample (0.47/0.53) was transferred from 170 °C (one-phase region) to 124 °C (two-phase region). Figure

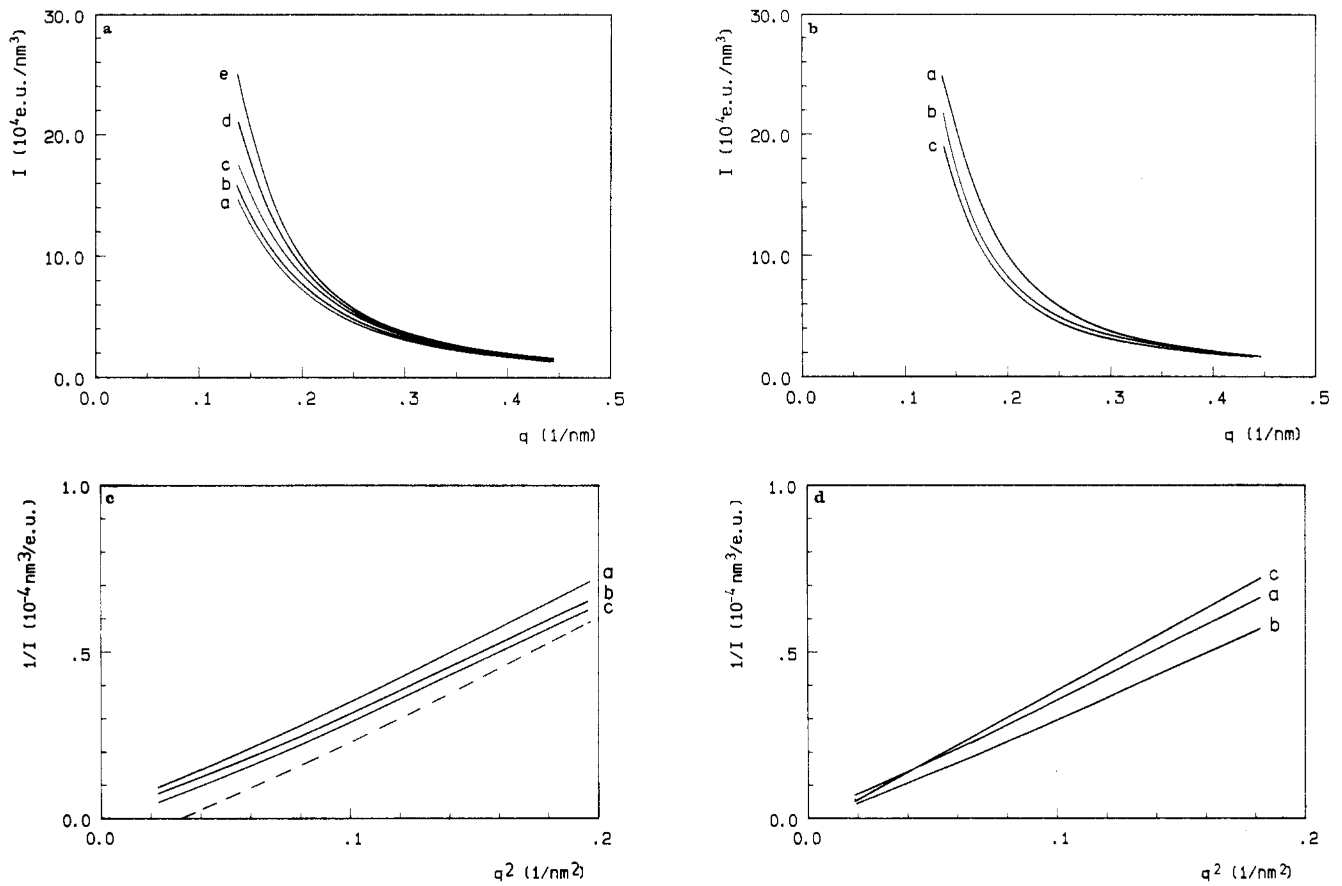

Figure 6. (a) CPII/PS mixture (0.47/0.53). Evolution of structure factor after a T-jump from 170 °C (one-phase region) to 124 °C (two-phase region). Curve a shows the original scattering curve (170 °C). Annealing time at 124 °C: curve b, 10^2 s; curve c, 1.5×10^3 s; curve d, 2.7×10^3 s; curve e, 4×10^3 s. (b) Structure factor after 4×10^3 s (curve a), 2.2×10^4 s (curve b), and 5.8×10^4 s (curve c). (c) Time dependence of reciprocal structure factor: curve a, 0 s (original scattering curve); curve b, 1.5×10^3 s; curve c, 4×10^3 s. Broken line indicates virtual structure factor. (d) Time dependence of reciprocal structure factor: curve a, 0 s; curve b, 4×10^3 s; curve c, 10^5 s.

6a shows the evolution of the structure factor for annealing times up to 4×10^3. During these initial stages of development an increase of the intensity is observed for all wave vectors q. For longer times of annealing, the tendency changes. After passing over a maximum, intensities decrease with time (Figure 6b). Parts c and d of Figure 6 depict this behavior using Zimm plots $I^{-1}(q^2)$. First, the scattering intensities tend toward the virtual structure factor S_χ. It is given by the broken line in Figure 6c. The virtual structure factor has been obtained by extrapolation on the basis of eq 11 through a parallel shift of the initial curve $I^{-1}(q^2,t = 0)$. The shift factor $\mathrm{d}I^{-1}/\mathrm{d}T$ can be taken from the measurements on the one-phase CPI/PS system (eq 9). The resulting shift then becomes

$$I^{-1}(q^2) = 2.5 \times 10^{-6}\,\frac{\mathrm{nm}^3}{\mathrm{eu}\ {}^\circ\mathrm{C}}(170 - 124\ {}^\circ\mathrm{C}) = 0.12 \times 10^{-4}\,\frac{\mathrm{nm}^3}{\mathrm{eu}}$$

which is the value used in Figure 6c. Figure 6d includes in addition to the initial curve (a) and the curve for $t = 4 \times 10^3$ s, where scattering intensities reached their maxima (b), the Zimm plot of the final scattering curve of the equilibrium two-phase structure (c). It was measured after an annealing time of 27.8 h.

The general behavior corresponds to that expected from theory. During the initial stages of structure development an increase of intensities is observed for all wave vectors q. There is no fixed point with constant intensity as is predicted by the Cahn–Hilliard theory. The scattering curve tends with time toward the virtual structure factor. This becomes particularly clear in the Zimm plots of Figure 6c. According to the equation of motion eq 13, $S^{-1}(q,t)$ approaches with increasing time $S_\chi^{-1}(q)$. Strictly speaking, $S^{-1}(q,t)$ approaches $S_\chi^{-1}(q)$ for $q > q_c$, where $S_\chi^{-1}(q) > 0$; for $q < q_c$ the rate of change $\mathrm{d}S^{-1}/\mathrm{d}t$ goes to zero for $S^{-1}(q,t) \rightarrow 0$ and hence $S^{-1}(q < q_c,t) \rightarrow 0$. The observed changes are in general agreement with these anticipations.

Validity of the equation of motion eq 10 is restricted to the early stages of structure formation where the concentration fluctuations $\delta\phi$ are small compared to the width of the coexistence curve[6]

$$\langle \delta\phi^2 \rangle \ll (\phi_\mathrm{I} - \phi_\mathrm{II})^2$$

(ϕ_I and ϕ_II denote the points at the binodal). The later stages are controlled by ripening processes which finally lead to the new two-phase equilibrium. Therefore the initial increase of the scattering intensities has to be followed by a decrease. This is in accordance with the observation.

The scattering curve measured for the two-phase equilibrium at 124 °C is a superposition of the structure factors of the two phases I and II. Each of the individual structure factors can be described by the random phase approximation. For the blend under study the binodal is roughly symmetrical, $\phi_\mathrm{I} \approx (1 - \phi_\mathrm{II})$. In this case the reciprocal value of the total structure factor is given to a good approximation by

$$S^{-1}(q) = \frac{1}{N\phi_\mathrm{I}(1 - \phi_\mathrm{I})} f_\mathrm{D}^{-1}(q^2\overline{R^2}) - 2\chi \qquad (14)$$

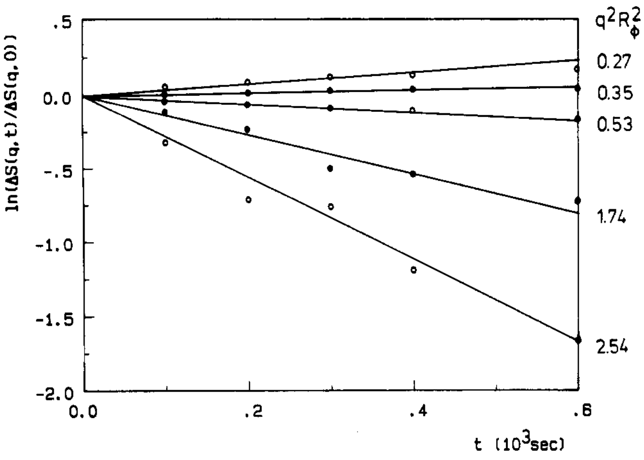

Figure 7. CPII/PS mixture (0.47/0.53). Relaxation of structure factor after T-jump from 170 °C (one-phase region) to 132 °C (two-phase region).

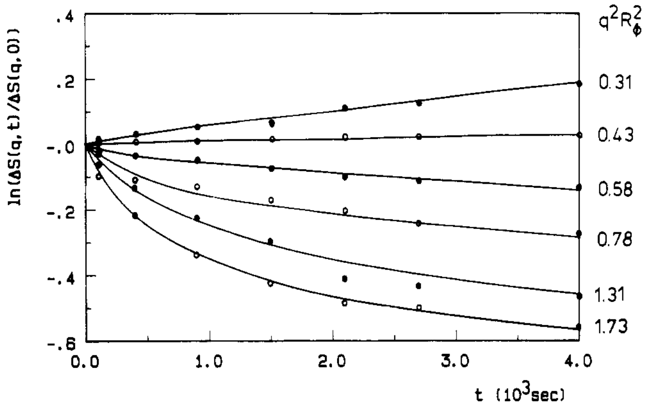

Figure 8. CPII/PS mixture (0.47/0.53). Relaxation of structure factor after T-jump from 170 to 124 °C.

$\overline{R^2}$ has to be calculated as an average over the values R_ϕ^2 of the two phases

$$\overline{R^2} = \tfrac{1}{2}((1 - \phi_{\mathrm{I}})R_{\mathrm{A}}^2 + \phi_{\mathrm{I}}R_{\mathrm{B}}^2 + (1 - \phi_{\mathrm{II}})R_{\mathrm{A}}^2 + \phi_{\mathrm{II}}R_{\mathrm{B}}^2) = \tfrac{1}{2}(R_{\mathrm{A}}^2 + R_{\mathrm{B}}^2)$$

Equation 14 shows that the slope of the Zimm plot, $\mathrm{d}S^{-1}/\mathrm{d}q^2$, is affected by ϕ_{I}. The observed higher slope of the two-phase scattering curve (Figure 6d, curve c) compared to that of the original one-phase scattering curve (Figure 6d, curve a) is due to the change in ϕ from $\phi = 0.47$ to $\phi = \phi_{\mathrm{I}} \approx 0.30$.

Relaxation Times

Equation 10 shows that relaxation times τ_q can only be derived from the experiment if the virtual structure factor $S_\chi(q)$ is known. The situation is different from that found in the analysis of light scattering data, where the effect of $S_\chi(q)$ becomes negligible for $t\tau_q^{-1} \gg 1$;[7] the scattering intensities then show an exponential growth $S(q,t) \sim \exp(2\tau_q^{-1}t)$. The required virtual structure factor $S_\chi(q)$ cannot be measured directly. It is defined and has to be determined by an extrapolation procedure, which can be performed as described above. Having determined $S_\chi(q)$, one can use the general solution of eq 10

$$S(q,t) - S_\chi(q) = (S(q,0) - S_\chi(q)) \exp(-2\tau_q^{-1}t) \quad (15)$$

and derive τ_q from a plot of ln $(\Delta S(q,t)/\Delta S(q,0))$ vs. t $(\Delta S(q,t) = S(q,t) - S_\chi(q))$.

Figures 7–9 shows this kind of drawing for the T-jump experiment 170 → 124 °C presented above (Figure 8) and for two further experiments, a T-jump 170 → 132 °C (Figure 7) and a T-jump 170 → 120 °C (Figure 9). Relaxation behavior is shown for different values of $q^2R_\phi^2$ ($R_\phi^2 = 14.0$ nm^2). The characteristic values $q_c^2R_\phi^2$ where τ_q changes from negative to positive values are determined by the locations q_c of the singularity of the virtual structure factors, $S^{-1}(q_c) = 0$. q_c shifs to higher values with decreasing temperature. It is principally impossible to derive q_c directly from an experiment (as was originally suggested by the Cahn–Hilliard theory where it was given by the fixed point with constant intensity). As expected from theory (eq 12), relaxation rates increase with q for $q > q_c$. For $q < q_c$ growth rates increase with the distance from q_c. The growth rate maximum apparently lies just outside the experimental range at slightly lower angles. Comparison of Figures 7–9 shows that there is a general decrease of relaxation rates with decreasing temperature.

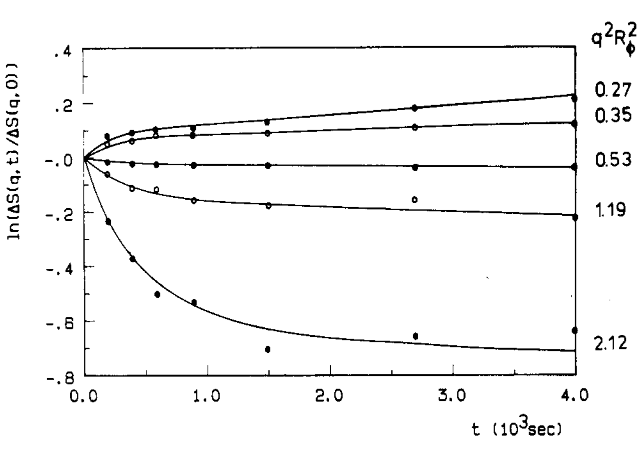

Figure 9. CPII/PS mixture (0.47/0.53). Relaxation of structure factor after T-jump from 170 to 120 °C.

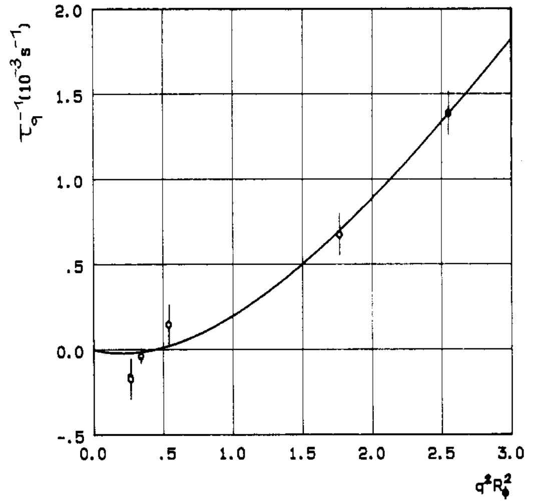

Figure 10. Relaxation times derived from Figure 7. Comparison with theoretical curve (eq 12, $\tau_R = 4.7 \times 10^3$ s, $\chi/\chi_s = 1.15$).

For a simple relaxation process, as described by eq 15, relaxation curves ln $(\Delta S(q,t)/\Delta S(q,0))$ vs. t should be linear. This is in fact observed for the T-jump 170 → 132 °C (Figure 7). Lowering the temperature leads to a change. The relaxation curves in Figures 8 and 9 are no longer linear, the curvature being more pronounced at the lower temperature, 120 °C. Hence, at temperatures below 130 °C relaxation behavior becomes nonexponential. The reason for this is certainly the neighborhood of the glass transition and the interference of related volume relaxation phenomena. Different effects can be invoked for explaining the deviations from nonlinearity. If the volume relaxation after the T-jump occurs with similar relaxation times as the unmixing, the interaction parameter χ, the related virtual structure factor $S_\chi(q)$, and also the basic time constant τ_R (eq 12) have to be considered as time-dependent. Another possible reason is the increase of T_g with increasing volume fraction of the brominated component. As a consequence, the kinetics could get progressively slower during unmixing. It appears difficult, to discriminate between the different effects on the basis of the presented results alone.

Relaxation times can only be derived for the T-jump 170 → 132 C from Figure 7. The values obtained are shown in Figure 10. They are compared to a theoretical curve following from eq 12. The parameters used in order to adjust the theoretical curve to the measured data were $\tau_R = 4.7 \times 10^3$ s and $\chi/\chi_s = 1.15$. The curve provides a reasonable fit to the measured data. The deviation at low wave vectors could be due to errors introduced by hole scattering.

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Light Scattering from Polymer Blend Solutions. 4. Data Analysis for Asymmetrical Dilute Systems

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ABSTRACT: The second virial coefficient B_{12} between unlike polymers 1 and 2 is assumed to be, as suggested by the Flory–Krigbaum theory, of the form $B_{12} = \text{const} \times h_0(\bar{Z}_{12})$, where h_0 is the same function as for the coefficient between like polymers. The argument $\bar{Z}_{12}$ is determined so as to be consistent with the first-order perturbation theory of B_{12}. Thus-determined $\bar{Z}_{12}$ is largely different, especially for highly asymmetrical systems, from the corresponding argument of the Flory–Krigbaum function, which is virtually the only theory available to date to describe ternary solutions of chemically different polymers. Also, the modified Kurata–Yamakawa function is adopted for h_0. As to mixtures of homologous polymers differing in molecular weight, this treatment gives numerical results generally close to those given by the Padé approximant due to Tanaka and Šolc. On the basis of this B_{12} function, a simple procedure is proposed to analyze light scattering data for the "net" interaction parameter $\chi_{12}°$ between unlike polymers. It is applied to experimental data for ternary solutions of varying degrees of asymmetry to give the most satisfactory results thus far obtained.

Introduction

In previous papers dealing with light scattering from two polymers dissolved in an optical Θ solvent,[1-3] it has been established that the Flory–Huggins[4] (FH) interaction parameter χ_{12} between unlike polymers is generally a function of chain length, concentration, and solvent power (see note 5 for the definition of the χ parameters). Thus, χ_{12} in a ternary solution is merely an apparent quantity and cannot be used for, e.g., quantitatively predicting the miscibility of the polymers in the bulk or in the presence of a solvent at a given fraction. However, if adequate solution data are available, it should be possible, at least in principle, to convert χ_{12} into a more quantitative piece of information on the polymer–polymer interaction.

As to infinitely dilute solution, the problem is directly concerned with the description of the second virial coefficient B_{12} between different polymers.[6] For homologous monodisperse polymers, fairly successful theories of the second virial coefficient are available to date.[7] Thus, if the ternary solution considered is symmetrical with respect to the two polymers, viz., the same size and the same affinity for the solvent, those theories may be applied for the mentioned purpose. This approach has been taken to analyze the χ_{12} data for some reasonably symmetrical systems.[1,3] On the other hand, there as yet seem to be no adequate theories applicable to asymmetrical systems, and this imposes a severe constraint not only on the application of the proposed particular light scattering technique[1-3,8] but also on solution approaches in general for determining polymer–polymer interactions.

In this paper, we propose a simple treatment based on the perturbation theory on B_{12} combined with an already-established closed-form expression for the second virial coefficient for homologous monodisperse systems. The expression for B_{12} or χ_{12} resulting from this treatment is entirely different, especially for highly asymmetrical systems, from that due to Flory and Krigbaum,[10] which is virtually the only theory thus far available to describe ternary systems composed of chemically different polymers. On the basis of this B_{12} function, a simple procedure will be proposed to analyze ternary-solution light scattering data for the "net" interaction parameter $\chi_{12}°$ which is considered to characterize the interaction between the given polymer pair. The validity of this procedure will be

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