Kinetics of phase separation of poly(styrene-co-methyl methacrylate) and poly(styrene-co-acrylonitrile) blends

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Abstract: The phase behavior and kinetics of phase separation for blends of the random copolymer poly(styrene-co-methyl methacrylate) (SMMA) and poly(styrene-co-acrylonitrile) (SAN) were studied by using small-angle laser light scattering. The partially miscible SMMA/SAN blends undergo spinodal decomposition (SD) and subsequent domain coarsening when quenched inside the unstable region. For blends of SMMA and SAN, the early stages of the phase separation process could be observed, unlike a number of other blends where the earliest stages are not visible by light scattering. The process was described in terms of the Cahn–Hilliard linear theory. Subsequently, a coarsening process was detected and the time evolution of \( q_m \) at the beginning of the late stages of phase separation followed the relationship \( q_m \propto t^{-1/3} \), corresponding to an evaporation–condensation mechanism. Self-similar growth of the phase-separated structures at different timescales was observed for the late stage.

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INTRODUCTION

The ability of a copolymer to serve as a compatibilizer in a polymer blend has received much attention both experimentally and theoretically. The different structures of a copolymer may have distinctly different effects on a polymer blend.1 For example, a symmetric ‘A-block-B’ is often added to an essentially immiscible binary A and B blend where it acts as a surfactant to reduce the interfacial tension.2,3 The addition of a random copolymer has been used to enhance the miscibility of binary blends of polymers by either changing the miscibility window, or by altering the phase separation kinetics, thus causing a change in the final phase-separated morphology.1,4 A homopolymer may form a miscible blend with a random copolymer, i.e. a negative interaction parameter of mixing may be obtained when a homopolymer is mixed with a random copolymer in certain copolymer compositions. The driving force for miscibility resides in the repulsive interactions between the two components of the same polymer chain. In the past two decades, extensive studies of the way that the miscibility behavior changes with the copolymer composition in blends containing random copolymers have been reported.5–9 Izumitani and Hashimoto10 studied spinodal decomposition (SD) by light scattering for the copolymer blend of SBR (styrene–butadiene random copolymer) and polybutadiene with upper critical solution temperature (UCST) behavior. The results obtained show that this system exhibits very slow SD and experiences a very long period of early stage behaviour. To date, however, most of the work carried out in this area has concentrated on thermodynamic studies of the phase boundary, and kinetic experiments are less common.

In general, although a number of studies have been carried out to investigate SD in polymer blends, these are still limited to relatively few polymeric systems. The most commonly studied system has been polystyrene (PS) with poly(vinyl methyl ether) (PVME). The earliest stages of phase separation in this system have been observed both by light11–13 and by neutron scattering14 and seem to fall at the limits of light scattering. In another system, poly(methyl methacrylate) with poly(\(\alpha\)-methyl styrene-co-acrylonitrile), the phase separation could barely be observed at all with light scattering but could be followed successfully with neutrons.15 In one recent example of polystyrene with tetramethyl bisphenol-A polycarbonate (TMPC), the light scattering data do

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not show any signal until some considerable time after the blend crosses the spinodal. Neutron scattering and atomic force microscopy, however, show that structures too small for light to observe are developing during this time.\textsuperscript{16} It is clear from these studies that the initial phase seen in SD varies considerably from system to system.

The phase-separation process is usually divided into three stages, i.e. early, intermediate and late stages. The Cahn–Hilliard linear theory, based upon a diffusion equation, has been widely used to describe the kinetics of the early stages of phase separation.\textsuperscript{17} The key parameter determining the fastest growing wave vector, \( q_m \), is the second derivative of the free energy of mixing, which is essentially determined by the length of the molecules and by the interactions between them. Most of the polymers used in the reported literature are of similar molecular weights and thus this factor seems unlikely to explain the large variation in \( q_m \), but one possibility for the variation in the initial phase size must be the difference in the nature and strength of the interactions. For example, PS/PVME has a weak specific interaction, probably enthalpic in nature. The isotopic blend, poly(ethylene propylene) (PEP) and deuterated poly(ethylene propylene) (d-PEP) has a small positive interaction, which is almost entirely enthalpic in origin.\textsuperscript{18} There have been a number of compilations and reviews of the interactions driving polymer–polymer miscibility,\textsuperscript{19} but to date there has been no attempt to correlate the information on the nature of the interaction with the early spinodal decomposition behavior of the same systems. We believe that this is because, as yet, there have been studies of spinodal decomposition in only a relatively small range of systems. Polymer blends comprising random copolymers where the specific interactions may be quite strong, and arise from the reduction in unfavorable intramolecular enthalpic contacts at certain copolymer compositions, provide yet another example of different types of interactions to add to this limited sample set.

In this paper, we present the results obtained for the de-mixing of blends of two random copolymers, i.e. poly(styrene-co-methyl methacrylate) (SMMA) and poly(styrene-co-acrylonitrile) (SAN), where there is a specific interaction arising from intramolecular repulsion causing a lower critical solution temperature (LCST) phase behavior (see Tang et al.\textsuperscript{20}) and show that the blends follow spinodal phase separation kinetics. The characteristics of the SD process were observed by using light scattering and data compared with the Cahn–Hilliard linear theory for the early stages and with dynamic scaling laws for the late stages, respectively.

**THEORETICAL BACKGROUND**

In the very early stage of SD, according to the Cahn–Hilliard linear theory, the intensity of the scattered light should follow an exponential growth with time:\textsuperscript{17}

\[
I_q(t) = I_q(0) \exp[R(q)t]
\]

where \( q = (4\pi n)/\lambda \sin(\theta/2) \) is the magnitude of the scattering wavevector, \( n \) the refractive index of the blend, \( \lambda \) the incident-beam wavelength and \( \theta \) the scattering angle. The growth rate of the amplitude of the concentration, \( R(q) \), is given by the following:

\[
R(q) = \frac{q^2 D_{\text{app}}(1 - q^2/2q_m^2)}{2}
\]

\[
q_m = \sqrt{\frac{1}{2} \left( K \frac{\partial^2(\Delta G_m/RT)}{\partial q^2} \right)^{1/2}}
\]

where \( D_{\text{app}} \) is the apparent diffusion coefficient, \( \Delta G_m \) the free energy of mixing and \( K \) is related to the free energy in the concentration gradients. The characteristic wave number, \( q_m \), which is related to the domain spacing, \( \lambda_m \), is independent of time, as follows:

\[
\lambda_m = 2\pi/q_m
\]

The Cahn–Hilliard theory also predicts that \( R(q)/q^2 \) should vary linearly with \( q^2 \), and so \( D_{\text{app}} \) and \( q_m \) can be obtained from the intercept and slope, respectively, by plotting \( R(q)/q^2 \) versus \( q^2 \), as indicated above Equation (2). The growth rate, \( R(q) \), can be estimated from the slope of \( \ln I_q(t) \) versus time, according to Equation (1).

After the early stages of phase separation, subsequent coarsening of the phase-separated domains takes place, driven by chemical potential gradients at the interfaces. The size of the phase-separated domains (proportional to \( q_m^{-1} \)) satisfies the relationship: \( q_m \propto t^{\alpha} \). In this regime, there is no simple scaling law and the power \( \alpha \) changes with time, reflecting various coarsening mechanisms. The Lifshitz–Slyozov model, based upon the vaporization–condensation mechanism, predicts the following:\textsuperscript{21}

\[
q_m \propto t^{-1/3}
\]

At the same time, in the late stages of the phase-separation process, the structures developed at different times show 'self-similarity', and satisfy the Furukawa dynamical scaling law. The scaled structure factor, \( F(x) \), in this regime is given by the following:\textsuperscript{22}

\[
F(x) = I_{q_m}^3, \quad x = q/q_m
\]

**EXPERIMENTAL**

A copolymer of SMMA (with 27 % volume fraction of styrene) was synthesized by free-radical polymerization in toluene solution using azobisisobutyronitrile (AIBN) as the initiator. The weight-average molecular weight, \( M_w \), of the SMMA copolymer was 66 700 g mol\(^{-1}\). SAN (75 % volume fraction of styrene) was purchased from Aldrich \((M_w = \)...
150 000 g mol⁻¹). The glass transition temperatures (Tg) for SMMA and SAN are 385 and 386 K, respectively, measured by differential scanning calorimetry (DSC) at a rate of 10 K min⁻¹.

For the light scattering (LS) experiments, copolymer blends of SMMA and SAN were prepared by solution casting from tetrahydrofuran (THF) (5 % (wt/vol)). The solutions were cast on a 16 mm diameter microscope glass cover slip and dried in a vacuum oven at least 20 K above the glass transition temperatures of the blend for three weeks.

The cloud points and SD kinetics of the SAN/SMMA blends were measured by using a home-built light scattering apparatus. A He–Ne laser of 633 nm wavelength is directed onto the sample and the scattered light detected by an array of 32 photo diodes, aligned above the sample in an arc from 5 to 67°. The cloud points were obtained from experiments conducted at different heating rates and then extrapolated to zero rate. Kinetic experiments were carried out by using a temperature-jump technique.

RESULTS AND DISCUSSION

Phase diagram

The cloud point curve obtained from light scattering for the SMMA/SAN system is shown in Figure 1. The miscibility and the phase diagram have been investigated in detail in our recent published work. It is evident that SMMA (27 vol% S) and SAN (75 vol% S) form partially miscible blends and exhibit lower critical solution temperature (LCST) behavior. For this copolymer system, the critical point corresponds to a 40 vol% SAN composition and to a cloud point value, TCP, equal to 431 K.

Spinodal decomposition kinetics

Early stage

A near-critical composition, 60/40 (SMMA/SAN), with TCP = 431 K, was chosen for this study. The isothermal phase separation was carried out by using a temperature jump at 448 K, indicated by an arrow in Figure 1. Figure 2 shows the growth of intensity in four time ranges—Figure 2a the early stage from 0 to 450 s, Figures 2b and 2c the intermediate–later stages and Figure 2d the very late stages.

There is no sign of the spinodal peak for the first 25 min or so, and in other systems this arises because the peak is growing at q values outside the experimental range. However, in this case although the peak cannot be distinguished, the analysis below in terms of Equation (2) gives the fastest growing wave vector as 0.013 nm⁻¹, which is where the peak eventually becomes visible in Figure 2c. There are other unusual features (described below) of the data presented here and one factor we must take into account when attempting to explain them is the unusually large quench depth.

In order to obtain R(q), we plot ln(I) against time t, as shown in Figure 3. In the early stages, according to Cahn–Hilliard (C–H) theory, the scattered intensity shows an exponential increase with time. Figure 3 shows that considerable care needs to be taken to ‘catch’ the early stages as the growth rate quickly slows down. The rather abrupt slope change at around 450 s is unexpected and will be briefly discussed later. From the slopes in the first 450 s, shown in more detail in the inset of Figure 3, we obtain the growth rates presented in Figure 4. These are very scattered because of the rather low intensity of the scattering at this early stage, but there is indication of a rather broad and shallow maximum at around q = 0.013 nm⁻¹.

Figure 5 contains plots of R(q)/q² to allow values of Da and gm to be obtained from the intercept and slope, following Equation (2). In this case, the value of Da is 5.1 × 10⁻¹⁷ m² s⁻¹ and gm is 0.013 nm⁻¹, giving a fastest growing wavelength of 480 nm. If we had not observed the earliest stages in Figure 2a and taken the growth rates from the next time range, we would have obtained an equivalent plot to Figure 5, as shown in Figure 6, which is not only highly curved and therefore clearly not conforming to C–H theory but also gives a much smaller value of Da (7.9 × 10⁻¹⁸ m² s⁻¹) and a somewhat different value of the initial fastest growing wavelength (419 nm).

The two experimental points at very small q values (q < 1 × 10⁻² nm⁻¹) in Figure 5 deviate from linearity. Similar behaviour has been observed in the literature for other blends. It is commonly believed that this may be due to experimental difficulties in obtaining, at small q values, scattered intensities that are free from ‘parasitic’ scattering. Deviations from linearity may also be a consequence of experimental failures to detect an early enough stage of SD. Such curvature is seen much more strongly in Figure 6.

![Figure 1. Cloud point curve, extrapolated to zero heating rate for SMMA/SAN blends.](image-url)
Figure 2. Time-evolution of LS profiles during isothermal SD at 448 K for the blend of SMMA/SAN (60/40) for various 'un-mixing' times, t(s), shown by various symbols: (a) very early stages; (b) intermediate–later stages; (c) later stages; (d) very late stages.

Figure 3. Scattered intensity (logarithmic scale) versus time for a critical blend of SMMA/SAN (60/40), during the early–intermediate stages of the SD process, following a temperature jump at 448 K (for clarity, we have not included error bars). The inset displays examples of linear fitting in terms of Equation (1) to obtain \( R(q) \) in the first 450 s, where the vertical axes, \( \ln I \), have been shifted up by 0.2 and 0.4 for \( q = 0.0082 \) and \( 0.0072 \) nm\(^{-1} \), respectively, for clarity. The data symbols used in the latter represent the same values of \( q \) as those in the main figure.

Figure 4. Dependence of \( q \) on the growth rate \( R(q) \) at 448 K for SMMA/SAN (60/40) in the first 450 s of Figure 3.

for this copolymer blend where we have plotted the slightly later stages of the phase-separation process. We believe in the case of this blend that we have been able to track phase separation from the earliest stages. There are three criteria that are used to determine if the true early stages of SD, as described in the C–H linear theory, have been observed. The first is that the intensity should grow exponentially with time, and we do appear to have observed this, as seen in the inset of Figure 3. The second is the observation of the spinodal peak appearing and remaining at a fixed wavenumber.
Figure 5. \( R(q)/q^2 \) as a function of \( q^2 \), corresponding to Figure 4, at 448 K for SMMA/SAN (60/40) in the first 450 s of Figure 3.

Figure 6. \( R(q)/q^2 \) as a function of \( q^2 \) at 448 K for SMMA/SAN (60/40) at the early–intermediate stages (450–1200 s) of Figure 3.

Figure 7. Variation of \( q_m \) with time during isothermal SD at 448 K for SMMA/SAN (60/40).

Figure 8. The scaled structure, \( F(x) = I q_m^3 \), for SMMA/SAN (60/40) at 448 K for various ‘un-mixing’ times, \( t \)(s), shown by various symbols.

Discussion

From the results presented here it appears that the phase-separation process after a deep quench for copolymer blends of SMMA and SAN with LCST phase behavior follows the expected SD mechanism. Both early and late stages of the SD process could be

mechanism (Equation (5)), but later no clear value of the exponent can be extracted.

However, as shown in Figure 8, when the LS curves are plotted as the scaled structure factor, \( F(x) \), versus \( x = q/q_m \) (see Equation (6)) at different times, reasonable superposition is achieved, in the late stages of the SD process. This suggests that dynamic self-similarity is preserved throughout the phase-separation process.

Late stages

In Figure 2d we showed the very late stages of phase separation where the spinodal peak is clearly visible. The \( q_m \) value corresponding to the maximum intensity, \( I_m \), shifts to lower \( q \) values as phase separation proceeds, i.e. domains of size \( \lambda_m \) grow with time, indicating various coarsening mechanisms in the late stage of SD. The time evolution of the dominant phase separation domain, \( q_m \), indicated by filled symbols in Figure 2d, is reported in Figure 7. The results indicate that no simple scaling relationship characterizes the time dependence of \( q_m \). An initial \( t^{-1/3} \) dependence is suggested by the data, as expected from the vaporization–condensation
resolved by LS measurements, although the spinodal peak took a very long time to become visible.

The growth rates presented in Figure 3 show a rather abrupt change of slope after the initial few hundred seconds and it is interesting to speculate as to whether this is a signal that the early stages are over. Two subsequent stages can be imagined. First, the amplitude of the growing fluctuations achieves the values of the equilibrium phase concentrations. Thereafter, the interfaces between the phases sharpen but the domain sizes remain unaltered. In a second stage, the coarsening processes outlined in the introduction take over. The phase separation is quite slow in this system which is only 60 K above the glass transition temperature of the blend, and it is possible that, unusually, the point at which sharpening of the interfaces begins gives a clear time signal. This would account for the fact that the spinodal peak shown in Figure 2c still appears to be growing at a fixed q, despite the change of slope shown in Figure 3 which indicates that the early stages are over.

On the other hand, these data follow an unusually deep quench and it is always questionable how ‘cleanly’ the sample has passed through the intermediate temperatures. Although the furnace temperature of the samples equilibrates within a few seconds, unusual effects may result from a ‘memory’ of the passage through these temperatures. There is a suspicion that phase separation may start as soon as the phase boundary is crossed. This would give rise to long wavelength fluctuations growing at small q values, while at the higher temperatures and deeper quench depth eventually reached, shorter wavelength fluctuations would grow at higher q values. Could the signal in the experimental range be the memory of the original crossing the phase boundary, while a second set of wavelengths is growing ‘off-scale’, only to move ‘on-scale’ eventually? This might be another explanation of the origin of the abrupt change of slope in Figure 3. Izumitani and Hashimoto\(^1\) carried out light scattering on a phase-separating sample at deep quench depths and did not report such slope changes. However, their system was rather different. They were working with a UCST blend, at 300 K below the calculated cloud point temperature, the samples were ‘homogenized’ at room temperature from unmixed blends, and the spinodal decomposition was then followed. This was extremely slow as the samples were close to the \(T_g\) of the polymers. In this case, the samples arrived inside the spinodal by a different route than our temperature jump and so a different behavior might be expected. In order to clarify if anything is happening ‘off-scale’, other techniques will be necessary—X-ray or neutron scattering, for example. However, the former will show very little contrast between these hydrocarbon polymers, while the latter relies on isotopic substitution of deuterium for its contrast. Unfortunately, it is well reported that deuterium substitution may well shift the phase boundary by some tens of degrees and therefore change the experimental situation. We have recently had some success in following these early stages with atomic force microscopy (AFM) and this looks a promising tool for cases where light scattering cannot detect the early stages.\(^1\) The question of what might be happening outside the light scattering range for these samples remains for the present unanswered. However, if the spinodal peak at 0.013 nm\(^{-1}\) is indeed attributable to our deep quench, the implication is that the temperature-dependence of the free energy derivative in Equation (3) is rather weak, which may be a relevant observation with respect to the repulsive interactions driving mixing in these copolymer blends.

**CONCLUSIONS**

Using laser light scattering, we have observed partially miscible blends of the random copolymer SMMA and SAN undergoing spinodal decomposition and subsequent domain coarsening when quenched inside the unstable region. We thus add a new system to the relatively limited number in the literature whose phase separation kinetics have been studied. The data for the SMMA/SAN blend reported here show two unusual features. The early stages of the process could be observed by light scattering, unlike a number of systems reported, and the growth rate shows an abrupt slowing down after an initial period of around 400s. We are inclined to attribute both these observations to the very deep quench depth inside the spinodal which was used in these experiments. This deep quench leads to a wide difference in the concentration of the new growing phases, and hence to a large refractive index difference and a large light scattering signal, while the rather high glass transition temperature relative to the phase boundary slows down the motion of the polymers and allows the process to be observed. We also speculate in the discussion above that the growth rate change might be a signal of the end of the early stages when the interfaces between phases begin to sharpen.

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