Late stage spinodal decomposition in an oligomeric blend of polystyrene/polybutadiene: A test of the scaling law for the structure function

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(Received 21 November 1988; accepted 8 February 1989)

The late stages of phase separation by spinodal decomposition have been studied by light scattering in an oligomeric blend of polystyrene (PS) with polybutadiene (PB) as a function of both quench depth and composition. The scattering function $I(q,t)$ follows a dynamical scaling law of the form $S(q,t) = qm(t)^{-3} \tilde{S}[q/qm(t)]$ where the wave vector qm corresponds to the maximum in $I(q,t)$. The profiles of the normalized scaled structure functions are compared with that predicted by Furukawa for critical mixtures (percolation regime) which is given by $\tilde{S}(x) = 4x^2/(3+x^8) [\tilde{S}(1) = 1]$. Apart from one exception, Furukawa's function adequately describes the form of the normalized structure functions for a 60% PS mixture. However there are problems with some of the comparisons with the 50% and 70% PS blends. These disparities may in part be attributable to the fact that some of the data may lie outside the "true" late stages.

I. INTRODUCTION

Theories describing the dynamical behavior of phase separation are generally not concerned with the molecular details of a system, except through macroscopic quantities such as mutual diffusion coefficients, interfacial, and free energy terms. For this reason phase separation dynamics in systems as diverse as metallic alloys, high molecular weight or oligomeric polymer blends, and inorganic glasses can be interpreted using the same theory.

The recent theoretical and experimental interest in the kinetics of phase separation in polymer blends has been somewhat biased towards the early stages of phase separation by spinodal decomposition.¹⁻⁴ The few experimental investigations of the late stages of this process have principally been concerned with the high molecular weight blend of polystyrene/poly(vinyl methylether) (PS/PVME)⁵ although Nose *et al.*⁶ have also studied an oligomeric blend of polystyrene/poly(methyl phenylsiloxane) (PS/PMPS). For both blends attempts have been made to assess the universality of Furukawa's dynamical scaling theory,⁷ this theory having been shown to hold experimentally for phase separating metallic alloys,^{8,9} small molecule liquids,¹⁰ and an inorganic glass system.¹¹ The theory, which will be described in detail below, predicts the form of the scattering function during the late stages of phase separation. Comparison of the theory with experimental data can in principle reveal changes in the morphology of the blend as a function of time, since the shape of the scattering function should be determined by factors such as cluster shape and cluster-cluster interactions. It has, with some reservations, been shown to describe the temperature dependence of the late stage behavior of a critical mixture of PS/PVME.⁵ In PS/PMPS⁶ the wave vector dependence of the scattering function was in accordance with Furukawa's theory for an off-critical

quench (cluster regime) but not for a critical mixture (percolation regime) studied over a limited temperature range.

In this paper we further explore the late stage scaling behavior of polymer blends in an oligomeric mixture of polystyrene/polybutadiene (PS/PB).

The idea of scaling was implicit in Binder and Stauffer's¹² cluster diffusion-reaction theory, whereby clusters increase in size by diffusing through the matrix, coalescing on contact with a second cluster, and in the condensation theory developed by Lifshitz and Slyozov.¹³ In this latter process molecules "evaporate" from the surface of small droplets into the matrix and subsequently are deposited on the surface of a large droplet. Furukawa¹⁴ formulated these proposals in terms of scaling and suggested that the structure factor for a d -dimensional isotropic system should scale as

$$S(q,t) = qm(t)^{-d} \tilde{S}[q/qm(t)] \equiv qm(t)^{-d} \tilde{S}(x), \quad (1)$$

where $q = 4\pi n/\lambda \sin \theta/2$, λ being the wavelength of the incident radiation, n is the refractive index of the medium, and θ is the scattering angle. $\tilde{S}(x)$ is a universal scaling function which is independent of time and varies from zero to unity. The wave vector $qm(t)$ corresponds to the position of the scattering maximum, the time dependence of qm has been shown to follow a simple power law dependence^{5,6}:

$$qm \propto t^{-\varphi}, \quad (2)$$

the intensity of the scattering maximum also follows a power law dependence of the form

$$I_m \propto t^{\theta}. \quad (3)$$

During the late stages of phase separation where no further concentration changes occur in the demixed phases $\theta = -3\varphi$,^{5,6} whereas in the intermediate stages $\theta > -3\varphi$. Values of the exponent φ depend on the nature of the coar-

sensing mechanism and vary from $\varphi = 1/(d+3)$ for the cluster diffusion model at low temperatures (where d is the dimensionality of the system) to $\varphi = 1/(d+2)$ for intermediate temperatures and times increasing to $\varphi = 1/3$ at late times. A time invariant value of $1/3$ is also characteristic of the Lifshitz-Slyozov condensation mechanism.

The shape of the structure factor as considered by Furukawa is to some extent again determined by the nature of the coarsening mechanism although his arguments are limited to the cluster diffusion model and should have the following asymptotic limits:

$$\tilde{S}(x) \propto \begin{cases} x^2 & \text{for small } x \\ x^{-\gamma} & \text{for large } x \end{cases}$$

The asymptotic x^2 dependence for wave vectors less than qm , i.e., $x < 1$, is a consequence of the local conservation of particles characteristic of theories based on diffusion-like equations. For $x > 1$, i.e., wave vectors greater than qm , the asymptotic behavior of the structure factor depends on the morphology of the mixture. If the phase separated clusters are isolated then $\gamma = d+1$ ^{15,16} but if the clusters are not isolated but percolate through the structure then $\gamma = 2d$.⁷

By combining these two asymptotic behaviors a universal scaling function $\tilde{S}(x)$ is obtained. It has the form

$$\tilde{S}(x) = \frac{(1 + \gamma/2)x^2}{\gamma/2 + x^{2+\gamma}}, \quad \tilde{S}(1) = 1 \quad (4)$$

with

$$\gamma = \begin{cases} d+1 & \text{cluster regime} \\ 2d & \text{percolation regime} \end{cases}$$

Figure 1 shows an idealized phase diagram with both spinodal and binodal indicated, and the dashed line corresponding to the percolation threshold. Between the percolation threshold and the binodal, droplets or clusters are consid-

FIG. 1. An idealized phase diagram showing the location of the binodal (—), the spinodal (---), and the percolation threshold for developed droplets (-·-). Quenches within the region defined by the binodal and percolation threshold are referred to as off-critical shallow quenches. All other quenches into the two phase region are referred to as either shallow or deep critical quenches depending on the quench depth. The volume fraction of droplets which defines the percolation threshold is approximately $1/6$ (Ref. 20).

ered to be isolated. Below the percolation threshold the clusters are assumed to percolate or ramify through the matrix. It is worth noting that the behavior of a mixture phase separating by nucleation and growth as a result of a deep quench into the metastable gap is no different to that of a mixture in the late stages of spinodal decomposition.

II. EXPERIMENTAL

The polystyrene (PS) sample ($M_w = 2000$, $M_w/M_n = 1.06$) was obtained from Polymer Laboratories Ltd. and the polybutadiene (PB) ($M_w = 960$, $M_w/M_n = 1.12$) was from Goodyear Tire Co. The molecular weights of the components were chosen in order to keep the phase boundary at temperatures near to those of the glass transition temperature of the blend. A consequence of this is to slow down the rate of phase separation particularly for mixtures containing high levels of PS thus enabling the early stages of spinodal decomposition to be observed over comparatively large concentration and temperature ranges.¹⁷

Mixtures were prepared by adding a known weight of PS to a preweighed quantity of PB. A homogeneous melt was produced by stirring the samples in a stoppered tube at 110°C for several minutes. A drop of this fluid when sandwiched between two preheated glass coverslips formed a crude sample cell. The thickness of the resultant film was $20\text{--}100\ \mu\text{m}$. The sample was then cooled to a temperature approximately 20°C above the phase boundary in order to facilitate an efficient temperature jump.

Isothermal kinetic experiments were performed by inserting the sample cell while still hot into a temperature controlled brass block located within a purpose built light scattering apparatus.¹⁸ Cloud point measurements were obtained by cooling the sample at a rate of 1°C min^{-1} until an increase in the intensity of scattered light was observed. Results by this method were reproducible to 0.5°C .

Although the light scattering apparatus has been described elsewhere,¹⁸ improvements made to the design necessitate a recapitulation. A beam of light from a 5 mW helium-neon laser (vacuum wavelength $6328\ \text{\AA}$) passes through a sample contained within a temperature controlled brass block (stable to within 0.1°C). The scattered radiation is detected by an array of 32 photodiodes set at intervals of 2° spanning the range $5^\circ\text{--}69^\circ$. The array is mounted on an arc of radius 16 cm with respect to the sample location. The voltage output from the photodiodes is digitized and read by a BBC microcomputer at user selected intervals of not less than 3 s. Data are stored on magnetic disk.

The data were corrected for the detector response $I(q, r)$ (determined using the isotropic scattering from a colloidal solution) and the scattering attributable to the empty cell $I(q, e)$, i.e.,

$$I(q, t) = I_c(q, t) = \frac{I_{\text{meas}}(q, t) - I(q, e)}{I(q, r)} \quad (5)$$

Thickness and transmission corrections were considered unnecessary. Values of the refractive indices for the PS were 1.595 and 1.515 for the PB.¹⁹

III. RESULTS

A. Determination of the cloud point curve

The position of the cloud point curve (Fig. 2) was obtained as described above. During the early stages of phase separation the intensity $I(q,t)$ was found to increase exponentially with time for those mixtures containing more than 50% PS. This suggests that the cloud point curve for these compositions lies close to the spinodal.^{18,23} Of course it is possible that the true cloud points may lie at a higher temperature than that reported here, but may not have been observed due to the sluggishness of the PS rich mixtures. To test such a hypothesis intensity measurements were made at constant temperatures to within 0.5 °C of the apparent spinodal temperatures for periods of up to 3 h. The results of these experiments showed no significant change in the scattered intensity.

B. Dynamical scaling of the scattering function

Kinetic experiments were carried out on four compositions containing 52.5%, 60.9%, 70.0%, and 79.9% PS, respectively, over comparatively wide temperature ranges for periods of up to 3 h. Our aim was to collect data for both the early and late stages of spinodal decomposition. However the former proceeded too quickly in the 52.5% mixture for us to follow, while the late states of the 79.9% PS mixture were not obtained due to the very slow rate of phase separation.

FIG. 2. The cloud point curve. The open circles refer to temperatures and compositions where late stage data was obtained.

Figure 3 shows how the scattering profiles change with time for a sample containing 60% PS quenched to 45.9 °C. At times below 100 s the intensity of the data increases exponentially with time in accordance with Cahn-Hilliard³ theory and a scattering maximum develops. With increasing time this scattering maximum becomes sharper and more intense, moving to lower values of q as the interconnected structure fragments and coarsens.

Beyond 100 s there exists a transition period between the end of the early stages of spinodal decomposition and the beginning of the late stages. Over this period it is not possible to interpret the data in terms of either early or late stage theory. The late stages being defined as that period when the data can be scaled according to Eq. (1). For a three-dimensional system the scaled function $F(x)$ is given by

$$F(x) \equiv \tilde{S}(x) = S(q,t)qm^3(t). \quad (6)$$

Figure 4(a) illustrates this point for some intermediate time data showing that scaling is not possible using Eq. (6) as $F(x)$ is time dependent. Figure 4(b) shows that beyond 255 s Eq. (6) is obeyed, i.e., $F(x)$ is now independent of time and late stage theories are applicable.

Prior to comparing the form of the scaled data with that of Eq. (4) it is first necessary to determine an appropriate value for γ . Both the cloud point determinations and the kinetics data from the 60.9% and 70% PS mixtures indicate

FIG. 3. Time evolution of light scattering profiles for a 60% mixture quenches to 45.9 °C. qm is represented by the large open circles.

FIG. 4. (a) Scattering profiles for a 60% mixture quenched to 45.9°C cannot be scaled by a single length parameter according to Eq. (6) at times below approximately 250 s. (b) For times greater than 250 s Eq. (6) is obeyed and the data can be scaled with a single length parameter.

that we are observing phase separation by spinodal decomposition in these compositions and hence $\gamma = 2d$. We have also chosen a value of $2d$ for γ in the case of the 52.5% PS mixture on the basis of the cloud point data and the fact that the quenches are too deep to be described by a γ of $(d + 1)$.

In order to facilitate comparison of the experimental data with an equation of the form given in Eq. (4) it is necessary to normalize the scaled structure factors according to the definition given by Marro and co-workers^{20,21}:

$$\tilde{F}(x) = \frac{F(x)}{\int_{q_{\min}}^{q_{\max}} q^2 I(q, t) dq} \cdot \int_{x_{\min}}^{x_{\max}} x^2 \tilde{S}(x) dx. \quad (7)$$

With $F(x)$ defined as in Eq. (6), $x_{\min}$ and $x_{\max}$ were set to experimentally accessible limits of $x = q/q_m$ of 0.5 and 1.5, respectively.

The factor $\int x^2 \tilde{S}(x) dx$ eliminates the effect of finite limits of the sum in the denominator and ensures that $\tilde{F}(1) = 1$.⁸

Equation (4) may be written as

$$\tilde{S}(x) = \frac{4x^2}{3 + x^8} \quad (\text{critical mixtures, percolation regime}), \quad (8)$$

which ensures that $\tilde{S}(1) = 1$.

Figures 5, 6, and 7 show experimental structure factors as a function of temperature for three compositions which have been scaled according to Eq. (6) and subsequently normalized using Eq. (7).

The normalized structure factors for the 60% PS mixture are compared with the predicted structure function [Eq. (8)] for a critical composition mixture in Fig. 5. The model adequately describes the data with the exception of that obtained for the deepest quench at 28.7°C. However, there are indications of a disparity for $x > 1$ which might

suggest that the model structure function is insufficiently broad.

For the 70% PS mixture in Fig. 6 the quality of the fit improves with increasing quench depth, the fit at temperatures close to the spinodal being quite poor. For deeper quenches there is again a suggestion that the model function is not sufficiently broad to describe the data for $x > 1$.

A comparison of the model function with the normalized 52.5% PS data is shown in Fig. 7. In these data it seems that the factor $\int x^2 \tilde{S}(x) dx$ is not sufficiently large to ensure that $\tilde{F}(1) = 1$ and again the fit is particularly lacking when $x > 1$.

IV. DISCUSSION

Although Furukawa's function for percolating structures apart from one exception adequately describes the form of the normalized structure function for the 60% PS mixture, there are clearly problems with the comparisons for both the 50% and 70% PS blends.

Bearing in mind that Furukawa's function is an empirical function joining two asymptotic limits it is instructive at this stage to look in more detail at the asymptotic behavior of the experimental structure factors. Figures 8, 9, and 10 shows double logarithmic plots of $\tilde{F}(x)$ against x for the three compositions for values of both $x < 1$ and $x > 1$. Equations (4) and (8) predict that the slopes of critical quenches in the region $x > 1$ should be -6 and although the latter behavior is clearly shown by the 60% PS mixture at temperatures close to the phase boundary, the data are less convincing for deeper quenches. For the 70% PS mixture the slopes in this region are all somewhat shallower than -6 . The slopes of the 50% PS blends may be somewhat steeper than -6 although there is some ambiguity in interpreting

FIG. 5. The scaled structure factor $\bar{F}(x)$ for data normalized to Eq. (7) for a 60.9% PS mixture as a function of temperature and elapsed time after quenching. The solid line corresponds to the theoretical structure factor $\bar{S}(x)$ for a critical mixture [Eq. (8)].

FIG. 6. The scaled structure factor $\tilde{F}(x)$ for data normalized to Eq. (7) for a 70.0% PS mixture as a function of elapsed time and temperature after quenching. The solid line corresponds to the theoretical structure factor $\tilde{S}(x)$ for a critical mixture [Eq. (8)].

FIG. 7. The scaled structure factor $\tilde{F}(x)$ for data normalized to Eq. (7) for a 52.5% PS mixture as a function of temperature and elapsed time after quenching. The solid line corresponds to the theoretical structure factor $\tilde{S}(x)$ for a critical mixture (Eq. (8)).

the limited data of the deeper quenches. For any particular temperature there is a tendency for the slope of the longer time data to approach the theoretical limit of -6 as, for example, in the case of the 38.5°C quench of the 70.0% PS blend. When $x < 1$ the asymptotic behavior of the experimental structure factors should be 2 according to Eq. 8. This is the case for the shallower quenches of the 60% PS mixture and for the deeper quenches of both the 50% and 70% PS blends. It is evident that with the exception of the 60% mixture the slopes become steeper with increasing quench depth. For any particular temperature there is a tendency for

the slope of the longer time data to approach the theoretical limit of 2, this is particularly noticeable in the 28.2°C quench of a 50% blend.

The rate at which a mixture phase separates depends on the second derivative of the Gibbs free energy with respect to composition and on a mobility term which relates to the viscosity of the material.¹⁷ The molecular weight of the components used in this study were chosen so as to phase separate at temperatures near to the composition dependent glass transition temperature of the blend. In this way the rate of phase separation is reduced which allows the early stages of

FIG. 8. The asymptotic behavior of the scaled structure factor $\bar{F}(x)$ for a 60.9% PS mixture (symbols) and the theoretical structure factor $\bar{S}(x)$ (solid lines). The symbols have the same meaning as those in Fig. 5. (a) for $x < 1$ the theoretical slope is 2, (b) for $x > 1$ the theoretical slope for a critical mixture is -6.

spinodal decomposition to be followed. However a consequence of this action is that for deeper quenches the increase in the thermodynamic driving force favoring phase separation is opposed by a reduction in the mobility term as the glass transition temperature of the blend is approached. It is therefore quite likely that for some of the deeper quenches we have data which does not quite fall into the time-dependent regime described by late stage theory. This may also be the case for some of the data obtained for very shallow quenches where the rate of phase separation depends on a large mobility term and a small thermodynamic driving

force. This would explain the tendency of the slopes of some of the data to approach the theoretical limits of 2 and -6 only at longer times.

Slopes of < 2 have also been observed by Nose *et al.*⁶ for a UCST mixture of PS/PMPS which are apparently unaffected by quench depth although in this study the maximum quench depth was only 0.5 °C. In the region $x > 1$ the slope was < 6 and again apparently independent of quench depth. Hashimoto *et al.*⁵ in their investigation of an LCST critical mixture of PS/PVME observed slopes of 2 at temperatures close to the spinodal which fell to < 2 for deeper quenches.

FIG.9. The asymptotic behavior of the scaled structure factor for a 70.0% PS mixture (symbols) and the theoretical factor $\tilde{S}(x)$ (solid lines). The symbols have the same meaning as those in Fig. 6. (a) for $x < 1$ the theoretical slope is 2, (b) for $x > 1$ the theoretical slope for a critical mixture is -6 .

In the region $x > 1$ the slope of -6 become shallower with increasing quench depth. The maximum quench depth of this study was 11 °C.

Furukawa has recently proposed²² that for a deep quench $\tilde{S}(x)$ should be of the form

$$\tilde{S}(x) = \frac{3x^3}{2 + x^9}$$

which gives an asymptotic limit of x^3 rather than x^2 for $x < 1$.

Although Hashimoto *et al.* have indicated that the asymptotic x^3 behavior could describe their data for shallow quenches it is quite clear that such a function would not adequately describe the data presented here.

In summary we have again demonstrated that the time-dependent structure factors of the late stages of spinodal decomposition can be scaled according to a simple relationship given by Eq. (2). We have also shown that Furukawa's equations can be used to describe the profile of normalized structure factors for critical mixtures although in some cases

FIG. 10. The asymptotic behavior of the scaled structure factor $\tilde{F}(x)$ for a 52.5% PS mixture (symbols) and the theoretical structure factor $\tilde{S}(x)$ (solid lines). The symbols have the same meaning as those in Fig. 7. (a) for $x < 1$ the theoretical slope is 2, (b) for $x > 1$ the theoretical slope for a critical mixture is -6 .

there is a considerable disparity between the theoretical behavior of the structure factor and that obtained experimentally. However some of this disparity may well be due to the fact that some of the data may lie outside the "true" late stages.

ACKNOWLEDGMENT

P. E. T. wishes to acknowledge the support of the SERC over the period during which this work was carried out.

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