A preliminary study of the dynamics of phase separation in oligomeric polystyrene–polybutadiene blends

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We report here the preliminary results of a study of the kinetics of spinodal decomposition in an oligomeric blend, polystyrene with polybutadiene using small angle light scattering. The data are compared with the theoretical predictions of Cahn–Hilliard and van-Aartsen. The results corroborate the position of the critical point as determined by the pulse induced critical scattering technique.

(Keywords: spinodal decomposition; polymer blends; *UCST*; phase separation; kinetics)

INTRODUCTION

The thermodynamics of polymer miscibility has received a rapidly increasing amount of attention in recent years[1] in contrast to the rather scant attention received by the kinetics of phase separation in polymer mixtures.

Figure 1a shows the phase diagram of a partially miscible oligomeric blend of polystyrene with polybutadiene showing the cloud point curve and the spinodal locus. When a sample of known composition is taken from the one phase region to the two phase region Cahn–Hilliard theory[2,3,4] predicts that phase separation will occur by two distinct mechanisms. If the system is unstable to small concentration fluctuations then the second derivative of the free energy with respect to composition will be negative, i.e. $\partial^2 G/\partial \phi^2 < 0$ and phase separation will occur by spinodal decomposition. This process is spontaneous and unlike nucleation and growth (the other possible mechanism) does not require an activation energy.

Cahn and Hilliard derived the following expression to describe the change in concentration as a function of time during a spinodal process:

$$\frac{d\phi}{dt} = M\frac{\partial^2 G}{\partial \phi^2}\nabla^2\phi - 2MKV^4\phi + \text{non linear terms} \quad (1)$$

where G is the Gibbs free energy of mixing
ϕ is the concentration
M is the diffusional mobility
K is an energy gradient parameter

If the non linear terms are ignored the equation can be solved to give:

$$\phi - \phi_0 = \sum_{\text{all }\beta}\exp[R(\beta)t] \times [A(\beta)\cos(\underline{\beta}.r) + B(\beta)\sin\underline{\beta}.r] \quad (2)$$

where ϕ is the phase concentration
ϕ_0 is the average homogenous phase concentration
$\beta = 2\pi/\lambda$ where λ is the wavelength of a concentration fluctuation
A and B are the Fourier coefficients
t is time

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r is a positional variable
$R(\beta)$ is the rate at which the amplitude of β increases
where

$$R(\beta) = -M[\partial^2 G/\partial \phi^2]\beta^2 - 2MK\beta^4 \quad (3)$$

The energy gradient parameter (K) is very small and at small values of β the term $2MK\beta^4$ can be neglected.

In Cahn's linearized theory only fluctuations with a sufficiently large wavelength, or small wavenumber β less than some critical value β_c, will continue to grow, all others will decay with time.

The amplification factor $R(\beta)$ shows a rather sharp maximum at:

$$\beta_m = \beta_c/\sqrt{2} = \tfrac{1}{2}[-(\partial^2 G/\partial \phi^2)/K]^{1/2} \quad (4)$$

i.e. one particular concentration fluctuation wavelength becomes dominant within the system. The Fourier transform of this situation gives rise to a scattering pattern which shows a well defined peak at wavevector Q_m where

$$Q_m = (4\pi n\sin\theta)/\lambda \quad (5)$$

λ being the wavelength of the incident light, n is the refractive index, taken as 1.50 and θ half the scattering angle. (Substituting Braggs law $(\lambda = 2d\sin\theta)$ into equation (5) we obtain $Q = 2\pi/d$ where d corresponds to a correlation length λ_m. Hence $\beta_m = Q_m$.) Equation (1) is analogous to a conventional diffusion expression:

$$\partial\phi/\partial t = \bar{D}\nabla^2\phi \quad (6)$$

This gives rise to the concept of the Cahn–Hilliard diffusion coefficient $\bar{D}$ where

$$\bar{D} = M(\partial^2 G/\partial \phi^2) \quad (7)$$

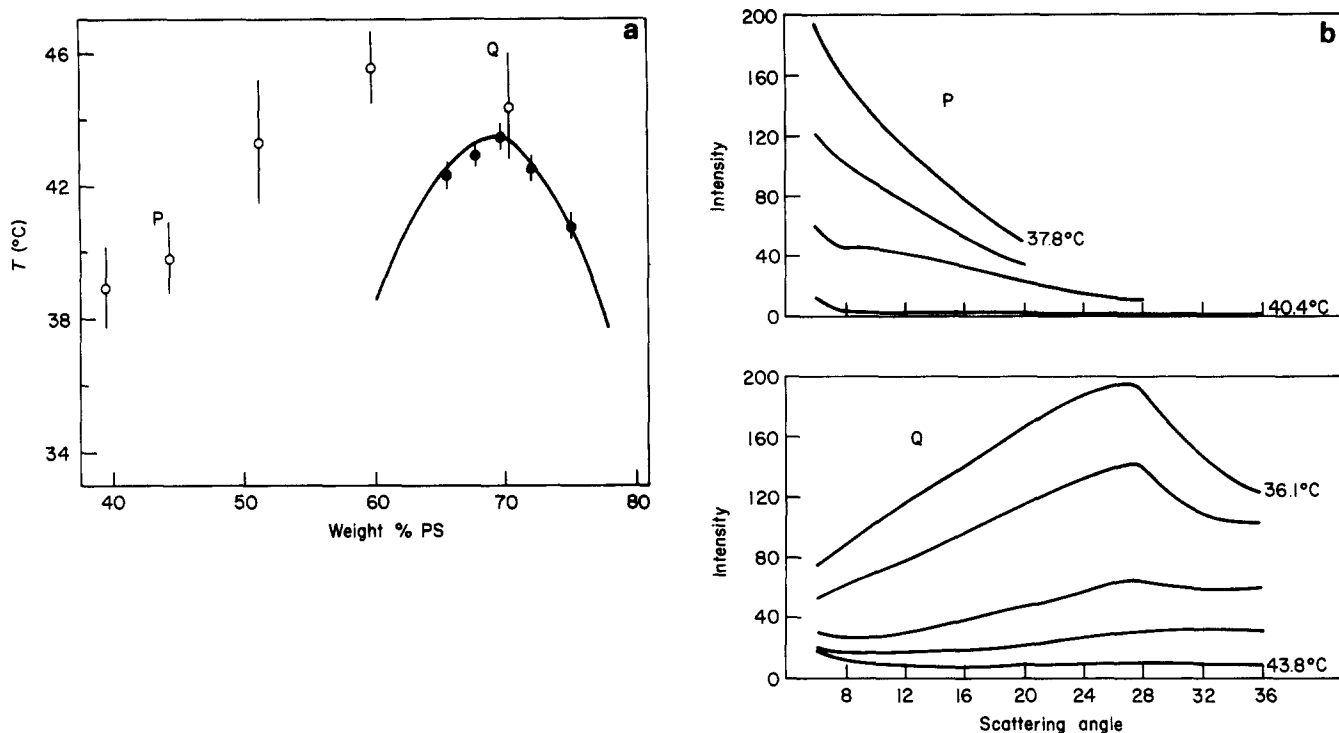$\bar{D}$ can be calculated from the growth rate of the wave

Figure 1 (a) Cloud point curve and spinodal locus for the system. The spinodal locus has been redrawn from Atkin *et al.*[12] (○)=cloud point; (●)=spinodal point. (b) Scattered intensity as a function of angle for compositions P and Q and shown in *Figure 1a*. Cooling rates are 0.37°C min⁻¹ for point P and 0.78°C min⁻¹ for point Q

vector at maximum, β_m. Combining equations (3) and (4) gives

$$R(\beta_m) = -2M\beta_m^2(\partial G/\partial\phi^2) \qquad (8)$$

and hence

$$\bar{D} = -2R(\beta_m)/\beta_m^2$$

Stein[5] has shown that the scattered intensity (I) of Q_m for a mixture undergoing spinodal decomposition is given by

$$I(Q_m) \propto \exp 2R(Q_m)t \qquad (9)$$

Thus at early times where the non-linear terms are unimportant spinodal decomposition is characterized by the exponential growth of a single scattering maximum which remains at fixed position. Such behaviour[6,7] has recently been observed in high molecular weight blends of polystyrene with poly(vinyl methyl ethers) PS/PVME). However at later times there is no longer exponential growth and the scattering maximum shifts to smaller wavevectors. If $\partial^2 G/\partial\phi^2$ is positive then the system is stable to small concentration fluctuations but not to large perturbations. Phase separation occurs in this metastable region by a nucleation and growth mechanism. Generally nucleation and growth is indistinguishable from the late stages of spinodal decomposition.

An elegant technique for determining the position of spinodal points is Gordon's pulse induced critical scattering (PICS)[8,9]. This technique involves measuring the light scattered from a sample in both stable and metastable states at fixed angle. By extrapolating a plot of the reciprocal of the intensity, I, against temperature to the point where $1/I$ is zero an accurate estimate of the spinodal temperature is obtained. Phase separation does

not occur in the metastable region because the sample is temperature jumped into and out of it before any nucleation and growth can take place. For practical reasons this technique has only been widely applied to binary oligomeric mixtures[12] or polymers in solvents[10].

This paper reports an investigation into spinodal decomposition in oligomeric blends of polystyrene and polybutadiene in which the spinodal locus has been determined by PICS. This blend is also being studied as a model system for measuring the thermodynamic interaction parameter χ as a function of temperature in the one phase region.

EXPERIMENTAL

The polystyrene (PS) sample ($M_w = 1460$, $M_w/M_n = 1.09$) was obtained from Polymer Laboratories Ltd. and the polybutadiene (PB) sample ($M_w = 2660$, $M_w/M_n = 1.06$) was from Goodyear Tyre Co.

Samples were made by adding the desired weight of PS to a preweighed quantity of PB. A homogenous fluid was produced by stirring the samples in stoppered tubes at 120°C for several minutes. A drop of this fluid when sandwiched between two preheated coverslips formed a crude sample cell, the thickness of the resultant film being 20–100 μm.

A detailed description of the purpose built light scattering apparatus is given elsewhere[11]. Briefly a beam of light (vacuum wavelength $\lambda_0 = 6328$ Å) from a 5 mW helium-neon laser source passes through the sample which is contained within a temperature controlled brass heating block (stable to within ± 0.1°C). The scattered radiation is detected by an array of sixteen photodiodes which simultaneously record scattering within a 32° segment (*Figure 2*). The position of the photodiode array can be manually adjusted to detect scattering in the range 0–90°.
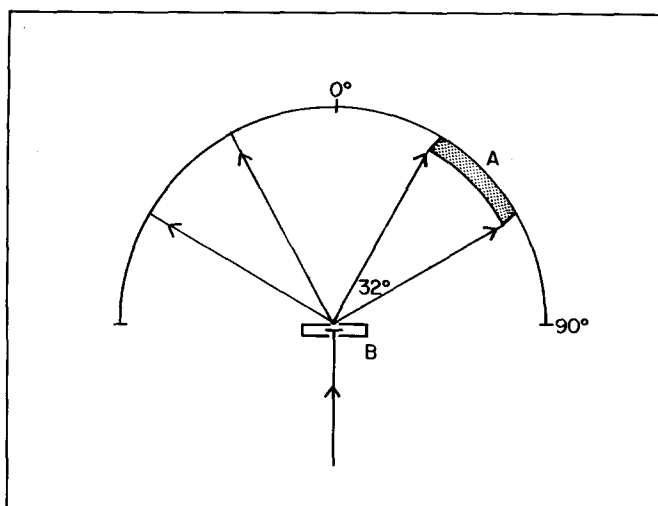
Figure 2 Schematic diagram of the small angle light scattering apparatus. A—photodiode array; B—sample holder

The voltages from each diode are measured and stored by a BBC microcomputer which takes approximately 100 ms to read the contents of the array. The interval between repeat measurements is set by the user and has a minimum value of 0.5 s.

Cloud point measurements were made by loading the brass heating block with a sample cell at temperatures some 20°C above the expected cloud point. The block was subsequently cooled at a known rate until an increase in the scattered light was observed. The cloud point was taken to be the point at which the scattered light intensity began to increase on an intensity against temperature plot. The results obtained by this method were found to be reproducible and independent of the cooling rate.

The kinetic experiments were performed by setting the temperature of the heating block to a point just below that of the spinodal. Sample cells approximately 20°C above the spinodal, when loaded into the block were thus quenched to the set temperature reaching equilibrium within 5–10 s. With the temperature remaining constant the scattered light intensity was monitored as a function of time.

RESULTS AND DISCUSSION

Cloud points obtained using the light scattering instrument were well defined. In all cases the scattering curve remained constant until at the cloud point when the scattered intensity started to rise steeply particularly at small angles. This is illustrated in *Figure 1b*. At one composition the development of a scattering maximum was observed. A nucleation and growth mechanism would not be expected to give rise to a scattering maximum unless a large number of identical nuclei were present in the original mixture. In contrast spinodal decomposition always gives rise to a scattering maximum. Since in general we do not see a peak developing in the scattering pattern we infer that the cloud point corresponds to the binodal and not the spinodal. This is presumably due to the high diffusion coefficients of the oligomers. In contrast high molecular weight blends generally show little or no phase separation until the spinodal. The 70/30 PS/PB composition where a scattering maximum was seen to develop would then correspond

to the critical point where the spinodal and binodal meet. The position of the spinodal locus for this system as determined by Atkin *et al.*[12] using the PICS technique is shown in *Figure 1a*. The close proximity of the cloud point to the spinodal at the 70/30 composition indeed suggests this composition might lie close to the critical value.

Conventional cloud point measurements were carried out at a fixed angle. Our experiments clearly demonstrate the advantage of using a multi-angle system in determining the position of the critical point.

Unlike most PS/PB mixtures the phase boundary is at a comparatively low temperature and the critical point is at a fairly high PS concentration. Using the Gordon–Taylor[13] expression for estimating the glass transition temperature (T_g) of a polymer blend and assuming 90°C and $-100°C$ for the T_g's of PS and PB gives the T_g of the critical composition to be $\sim 33°C$. It follows that at temperatures below the cloud point this composition will be fairly immobile making it an ideal system in which to study phase separation.

We now look in detail at phase separation within the spinodal at the critical composition. Equation (9) predicts that if $R(Q_m)$ is positive then the scattered intensity should grow exponentially. *Figure 3* shows a plot of $\ln I(Q_m)$ against time for the fastest wave-vector (Q_m). As expected for early times the plot is linear (and λ_m as shown in *Figure 6* is time invariant). Such behaviour has also been observed in metallic alloys and glasses. From equation (9) it can be seen that the slope of the plot gives the growth rate $R(Q_m)$. Values for $R(Q_m)$, λ_m and $\bar{D}$ are listed in *Table 1* for several temperatures.

The initial temperature dependent correlation length $[\lambda_m(\text{initial})]$ is equal to $2\pi/Q_m$ and is approximately 1 μm. This is much larger than predicted from the expression derived by van Aartsen[14]:

$$\lambda_m = 2\pi L \left[3\left(1 - \frac{T}{T_s}\right) \right]^{-1/2} \qquad (8)$$

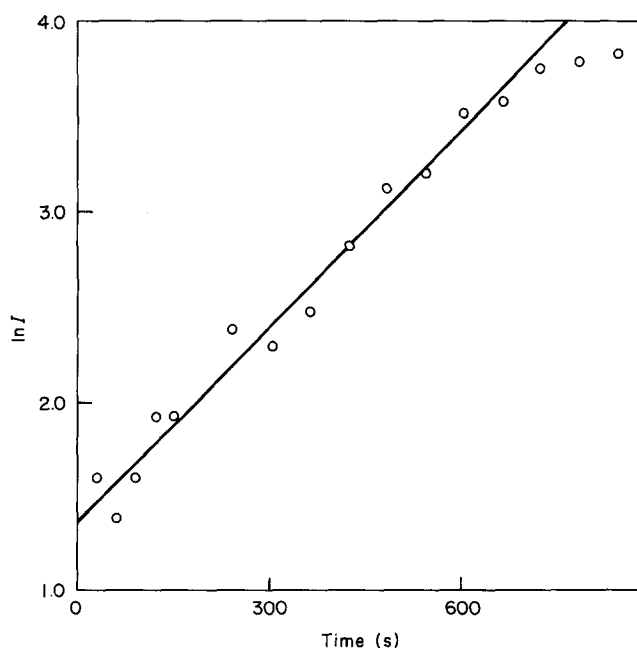where T = temperature (K)
T_s = spinodal temperature (K)

Figure 3 Ln I as a function of time for the fastest growing wavevector (Q_m) at 43.5°C

Table 1 $R(Q_m)$, $\bar{D}$ and λ_m(initial) as a function of temperature

Temperature $\pm 0.5°C$	$2R(Q_m) \times 10^{-3}s^{-1}$	$\bar{D} \times 10^{-13}cm^2 s^{-1}$	λ_m(initial)μm
46.2[a]	–	–	–
43.4	1.7	−3.1	0.85
42.25	6.0	−10.8	0.65
42.0	7.5	−9.7	0.71
38.8	2.1	−2.2	0.65
35.2	2.2	−2.1	0.61

[a] The mixture does not phase separate at this temperature
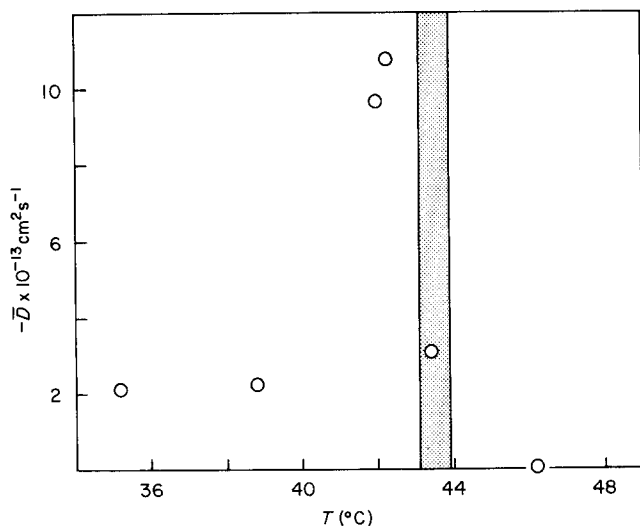

Figure 4 Effect of temperature on $\bar{D}$. Normally at temperatures away from the spinodal $\bar{D}$ is primarily dependent on the value of $\partial^2 G/\partial\phi^2$, i.e. it should drop to zero at the spinodal temperature (marked by the vertical bar on the Figure). However, as the temperature approaches the blend T_g ($\sim 33°C$) $\bar{D}$ falls again because of decreasing chain mobility as reflected in M (equation (7))

which is based on Flory–Huggins[15,16] and Cahn–Hilliard theory. In this expression L, the Debye[17] interaction length should be approximately the same size as the radius of gyration of the oligomers, i.e. 25 Å. Hence the initial correlation length would be about 500 Å and unobservable by small angle light scattering. λ_m(initial) decreases slightly for deeper quenches into the spinodal, however the magnitude of this effect is never large enough for λ_m to approach this value. This discrepancy could arise from a temperature dependence of L, or result from the comparative slowness of the quenches relative to the phase separation process.

Cahn[18], assuming regular solution theory predicted that the Cahn–Hilliard diffusion coefficient should extrapolate back to the temperature of the spinodal at $\bar{D}=0$. This analysis assumes that the driving force for phase separation results from a reduction in the entropy of mixing term $(T\Delta S_m)$ on lowering the temperature. An identical prediction can be made for polymer mixtures using both Flory–Huggins and Cahn theory. This method enables the spinodal to be obtained from measurements in the unstable region of the phase diagram, in contrast to the PICS technique which relies on data collected in the stable and metastable zones. Snyder et al.[7] have recently determined the spinodal in PS/PVME mixtures by extrapolating $\bar{D}$ to zero. A plot of $\bar{D}$ against temperature is shown in Figure 4. Clearly the plot does not extrapolate back to the spinodal. We believe this is due to the fact that the extrapolation procedure assumes that the thermody-

namic driving force in equation (7), i.e. $\partial^2 G/\partial\phi^2$, dominates the phase separation process and that the diffusional mobility term, M does not change significantly with temperature. As the T_g of the blend is approached however the mobility of the chains will be significantly reduced causing the plot of $\bar{D}$ against temperature to curve, and in Figure 4 even to form a maximum.

The late stages begin when the scattered intensity stops growing exponentially. A variety of coarsening mechanisms take place during this period, which include Ostwald ripening[19], coalescence[20] and a viscous flow process[21]. The primary driving force for particle coarsening is no longer the thermodynamic term $\partial^2 G/\partial\phi^2$ but the surface tension contribution to the free energy which becomes less as the surface area to volume ratio decreases. Q_m therefore moves to smaller wavevectors. Plots of intensity as a function of Q at different times are shown in Figure 5.

A plot of the correlation length (λ_m) against log time is shown in Figure 6. Most of the coarsening mechanisms proposed predict a constant scaling law, i.e. $\lambda_m \propto t^\gamma$ where γ is 1/3 for both Ostwald ripening and coalescence. Clearly, apart from the early stages where λ_m is constant, no power
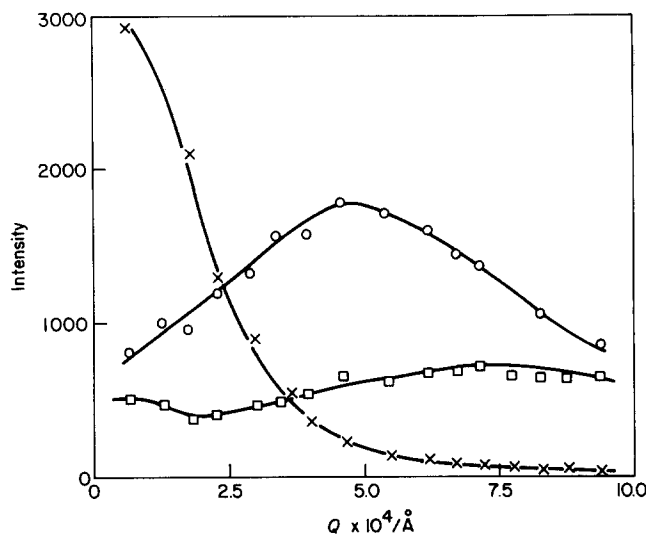

Figure 5 Intensity vs. Q at various times after jumping into the unstable region. ($\square$)=540 s; ($\bigcirc$)=900 s; ($\times$)=3720 s
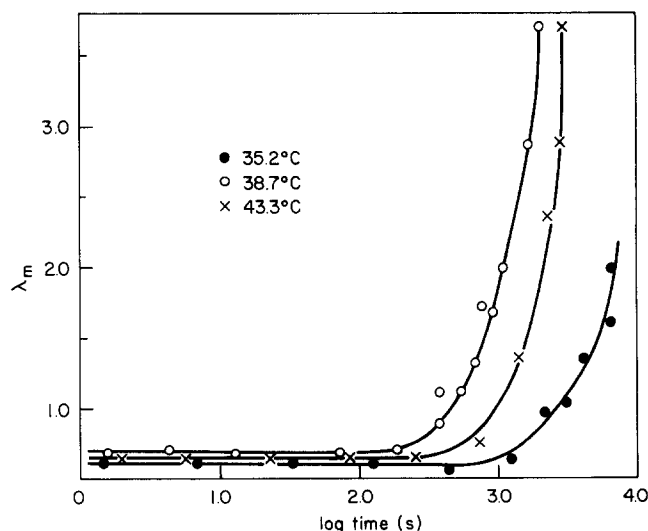

Figure 6 Time dependence of the correlation length λ_m for different temperatures within the unstable region—the early stages where λ_m is constant are clearly seen. ($\bullet$)=35.2°C; ($\bigcirc$)=38.7°C; ($\times$)=43.3°C

law behaviour is observed in *Figure 6* since the relationship between λ_m and (log) time is non-linear. These results are in agreement with those obtained by Snyder *et al.*[7] for PS/PVME blends. A probable reason for the non-linearity of these plots is that several coarsening mechanisms act simultaneously.

SUMMARY

The results presented here provide strong, though incomplete evidence for spinodal decomposition in oligomeric mixtures of PS/PB. To prove unequivocally that spinodal decomposition is taking place would require evidence that the concentration of the two phases being formed changes continuously with time as demonstrated by Nishi *et al.*[22] for high molecular weight mixtures of PS/PVME. The results confirm the position of the critical point as predicted by the PICS technique.

ACKNOWLEDGEMENTS

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