Scaling analysis in the phase separation of poly(*p*-phenylene benzobisthiazole)/Nylon 66 rigid-rod molecular composites

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The thermally induced phase separation of poly(*p*-phenylene benzobisthiazole)/Nylon 66 molecular composites was followed by small-angle light scattering which showed the development of a scattering ring. The intensity increased and the ring moved towards the main beam as a function of time. The scattering vector q_m and intensity maxima I_m scaled as $q_m \sim t^{-\alpha}$ and $I_m \sim t^{\beta}$ with $\alpha \approx 0.33$ and $\beta = 0.91$–0.95, in close agreement with the cluster dynamics prediction of Binder[18]. However, at longer times, the increase in both q_m and I_m slowed down dramatically indicating a different mechanism. The structure function $\tilde{S}(x)$ was used to test the validity of universal scaling for a rigid-rod/flexible coil polymer blend. At large x, $\tilde{S}(x)$ scaled to the power of -2.4 in x, which is between values predicted for systems with one- and two-dimensional diffusion.

(Keywords: phase separation; molecular composites; blends; poly(*p*-phenylene benzobisthiazole); Nylon 66; small-angle light scattering; scaling)

INTRODUCTION

Rigid-rod molecular composites are blends of two polymers with vastly dissimilar conformations. A high modulus, high strength rigid-rod polymer acting as reinforcer is dispersed in a host matrix of a flexible coil polymer so that reinforcement takes place at the molecular level. This new materials concept was developed at the Air Force Materials Laboratory[1] and has shown excellent mechanical properties[2]. The rigid-rod most studied is poly(*p*-phenylene benzobisthiazole) (PBZT), in combination with a variety of flexible coil polymers, including lyotropic liquid-crystalline polymers, commercial thermoplastics such as Nylon and poly(ether ether ketone), and a bisbenzocyclobutene terminated thermoset[3,4].

An important stage in the development of this new material is the consolidation of the molecular composites into monolithic pieces so that they can be used as structural materials. To date the consolidation steps invariably involve a thermal cycle and the application of pressure. Although the rigid-rod and the coil polymers were processed from a homogeneous ternary solution by rapid coagulation to give good dispersion of the rods, subsequent thermal process can induce phase separation[3] causing the rod molecules to aggregate into μm size domains, thereby diminishing the level of molecular reinforcement to the part of simple particulate reinforcement.

This study addresses the phase separation behaviour due to thermal processes in order to have a better understanding of the phenomena so that consolidation conditions can be suitably controlled and appropriate matrices can be selected to minimize the molecular partition. This study also attempts to understand the critical phenomena of a unique rigid-rod/flexible coil polymer system using time-resolved small-angle light scattering.

EXPERIMENTAL

PBZT with $[\eta] = 21.4\,\mathrm{dl\,g^{-1}}$ was supplied by SRI International and Nylon 66 was Du Pont Zytel 42. Homogeneous solutions were prepared by dissolving PBZT and Nylon 66 in freshly distilled methane sulphonic acid at below the critical concentrations, typically < 3.5 wt%. 45/55 wt% PBZT/Nylon 66 films were made by extruding their solutions through a coat-hanger die onto a rotating drum and coagulating with water to form thin film as previously described[3]. The kinetics of the thermally induced phase separation was studied using small-angle light scattering (SALS) equipped with a sample hot stage and a two-dimensional detector controlled by an EG&G optical multichannel analyser (OMA III). A He–Ne laser with wavelength $\lambda = 632.8$ nm was used as the light source. Kinetics studies were performed by a temperature jump method[5]. The sample was first preheated in a separate hot stage to 220°C, below the phase separation temperature which

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had previusly been determined from the cloud point curve[3]. It was then transferred quickly to the hot stage in the SALS set up at the preset temperature for kinetic measurements. The evolution of the scattering profiles and their intensities were recorded as a function of time.

RESULTS AND DISCUSSION

In recent years, there have been numerous experimental studies on the dynamics of polymer blend phase separation[6–11], and significant progress has been made in the understanding of the demixing process both in experiments and theories. However, the experimental studies were carried out mainly with blends of flexible coil polymers. Recently, the spinodal decomposition of a blend in which one of the components is a stiff chain thermotropic liquid crystalline polymer was reported[12]. Blends with such vastly different conformations are interesting because the rigid-rod polymer shows anisotropy in the diffusion coefficients, parallel and perpendicular to the rod axis. This anisotropy can influence the diffusion process and the dynamics during phase separation.

In our laboratory, we have been working on the development of rigid-rod molecular composites. The reinforcing polymer, PBZT, is a true rigid-rod molecule which has only axial rotational conformation freedom and is much more rigid than the extended rod-like thermotropic liquid crystal used in the recent phase separation studies[12,13]. In our previous studies, it was found that when thermoplastics were used as host matrix, the molecular composites underwent thermally induced phase separation[3]. The rods aggregated into μm size domains as evidenced by back scattered (scanning) electron microscopy. The small-angle light scattering pattern was a single ring which developed during phase separation. *Figure 1* shows a typical time evolution of the scattering profile of a 45/55 PBZT/Nylon 66 molecular composite at 262°C. The intensity of the scattering maxima increased and moved towards the main beam very rapidly with time. The scattering profiles were corrected for background and scattering from initial thermal fluctuations.

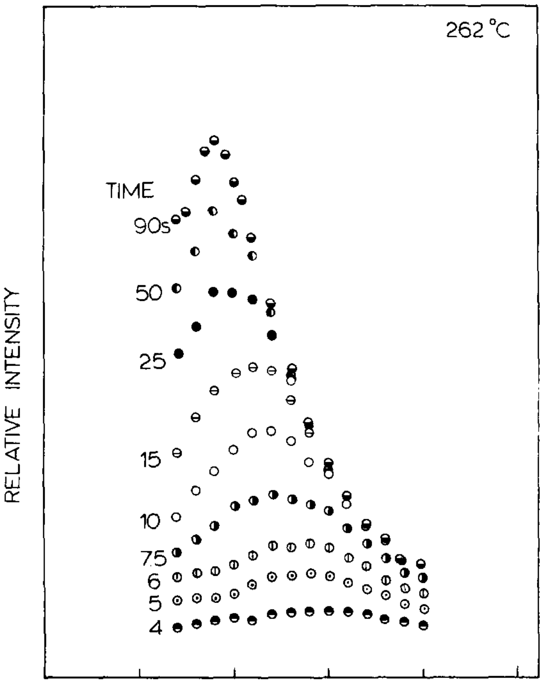

Figure 1 Small-angle light scattering profiles of 45/55 PBZT/Nylon 66 molecular composites as a function of time at 262°C

In polymer blends phase separation is generally slower, due to the size of the larger molecules, compared to blends of small molecules, therefore the early stage can be studied more easily. Several experimental studies were performed using both small-angle light and neutron scattering[6,14–16]. The early stage behaviour was analysed using the linearized Cahn–Hilliard theory[17]. A typical feature of this stage is that the scattered intensity, $I(q, t)$, increases exponentially with time, t:

$$I(q, t) = I(q, t=0)\exp[2R(q)t] \qquad (1)$$

where $R(q)$ is the growth rate and q is the scattering vector. Using this analysis, important information such as the apparent diffusion coefficients, critical growth size and the spinodal temperature could be determined. These parameters are, of course, useful for making comparisons on the phase separation behaviour of different blends and can provide criteria in selecting suitable host matrix for molecular composites.

However, in the PBZT/Nylon 66 system, the demixing process was very rapid when the temperature was above the Nylon melting point. A scattering maxima developed immediately and moved to the lower scattering angle. Therefore the early stage was too fast to follow accurately for Cahn–Hilliard type of analysis. At temperatures <250°C, i.e. below the Nylon peak melting point, there was a short duration of approximately 20 s in which the scattered intensity indeed increased exponentially. However, there were uncertainties associated with such observations. It was not certain that 20 s allowed in the temperature jump before scanning began was sufficient to attain temperature equilibration. This, however, will not pose a problem for the late stage results. At the lower temperatures, the Nylon was only partially melted and the unmelted crystals could contribute to the intensity changes due to an annealing effect. In fact, when a pure Nylon 66 film was examined, the intensity increased by $\approx 10\%$ before it diminished to the background level on complete melting. For these reasons, the kinetic experiments were performed above the Nylon melting point. Due to the unfavourable thermodynamics of blending rod and coil polymers, once the mobility constraints were removed through melting, demixing occurs rapidly. The early stage could not be distinctly observed, therefore only the late stage results are presented here.

Scaling with power laws

Theories and computer simulations have been developed to describe late stage phase separation in terms of power laws, using both the scattering intensity maxima $I_m(t)$ and the scattering vector maxima $q_m(t)$ as follows:

$$q_m(t) \sim t^{-\alpha} \qquad (2)$$

$$I_m(t) \sim t^{\beta} \qquad (3)$$

Binder[18] used a kinetic Ising model in which two different atoms are allowed to exchange randomly, and this stochastic interchange of atoms led to the formation of clusters and a final evolution of a cluster pattern. It was shown that the growth of the clusters can be described by power laws with indices $\alpha = 1/3$ and $\beta = 1$. This prediction has the same result as the Lifshift and Slyozov[19] constant volume evaporation–condensation model in which a droplet size also grows according to the power law with $\alpha = 1/3$, even though molecular details were not considered. At a later stage, these growing domains coalesce into larger ones, and the total free energy is reduced from the decrease in surface area. However, the above models did not account for the hydrodynamic effect which plays a part in the coalescence of the growing domains in which the suspending component between them has to be squeezed out. Such a consideration was treated by Siggia[20], and α becomes unity when this occurs. With the different mechanisms operating, it is expected that the power law would not cover the whole range of phase separation. The power indices are therefore expected to change when there is a cross-over of mechanisms.

Figures 2 and *3* show the plots of log $q_m(t)$ vs. t and log $I_m(t)$ vs. t respectively at 262, 267 and 272°C. There were two distinct regions at which power laws were valid implying that two mechanisms of domain growth were involved.

In *Figure 2*, at 262°C, the earlier region showed $\alpha = 0.23$, lower than those observed at the higher temperatures of 267 and 272°C which have $\alpha \simeq 0.33$, as predicted by Binder[18]. The same phenomenon was observed in log $I_m(t)$ vs. t plots of *Figure 3*. At 262°C, $\beta = 0.59$, considerably below the theoretical prediction. Only at the higher temperatures did β approach 1 and $\beta \simeq 3\alpha$. The deviation at the lower temperature could be due to the incomplete melting of Nylon. Mobility constraints were not totally removed for the diffusion and clustering of the rod molecules. At the higher temperatures where Nylon was completely melted, the clustering mechanism dominates and the experimental observations agree well with the theoretical prediction of Binder.

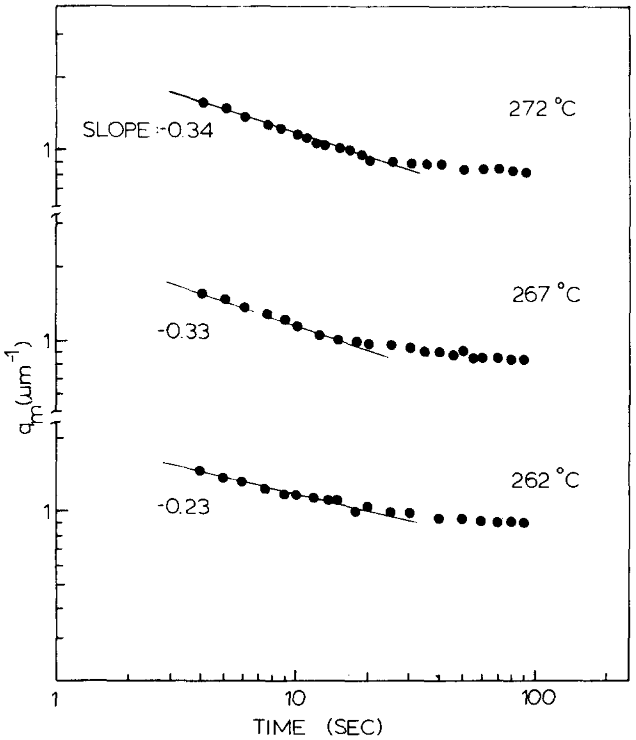

Figure 2 Power law plot of log q_m vs. log t

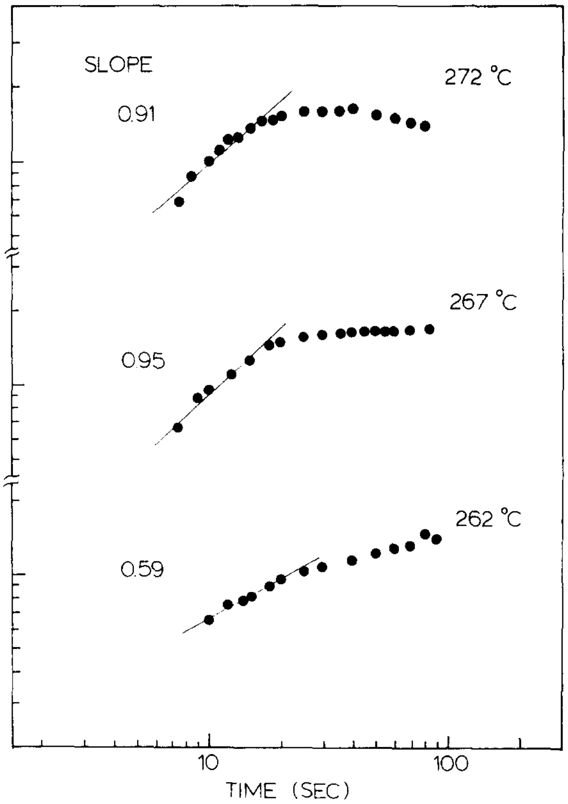

Figure 3 Power law plot of log I_m vs. log t

According to Siggia[20], at a later time of phase separation coalescence of domains occurs such that α becomes one. This phenomenon had been observed in several polymer blends[9]. However, it was not observed in the present system. Instead there was a distinct change of the slopes to smaller α and β, showing that both the increase of q_m and I_m slowed down greatly. This implied that the domain growth slowed down and coalescence was not a dominating mechanism. A possible explanation for this observation is that when phase separation occurs, the system does not undergo true liquid–liquid phase separation as in flexible coil blends. Since the melting point of PBZT is unknown but very high (above its degradation temperature of 700°C), only Nylon 66 is in the melt state at the phase separation temperature. At its inception the rods are released from the constraints by the melting of Nylon to allow the aggregation of the rods. Because of the extremely high undercooling of the rods, aggregation is accompanied by ordering of rod molecules. PBZT forms two-dimensional order crystal with a translational disorder along the chain axis. Only for a short period of time, the aggregated domains can grow by assimilating the adjacent rod molecules available as shown by the movement of the scattering maxima to lower q. Once the ordered/aggregated rod domains are formed, coalescence becomes difficult because the rods are no longer able to rearrange into larger domains since they had become essentially a 'solid' phase. Therefore, phase separation slowed down dramatically. This behaviour contrasts with flexible coil polymer blends which undergo liquid–liquid phase separation and therefore can coalesce, lowering the overall free energy by minimizing the surface area. The slowing down of q_m and I_m has also been observed in the late stage phenomenon in blends of thermotropic liquid crystal and PET[10], suggesting that this might be typical in blends of rod-like/coil polymers.

Scaling with reduced parameters and dynamic scaling

It has been proposed that the phenomenon of phase separation involves similar dynamics irrespective of the type of the blends[11]. Using reduced scattering vector, Q_m, and time, τ, defined as follows:

$$Q_m = q_m \xi(t=0) \tag{4}$$

$$\tau = tD(t=0)/\xi^2(t=0) \tag{5}$$

where D is the coefficient of diffusion, and ξ is the concentration correlation length when phase separation begins as a result of periodic concentration fluctuation, and

$$\tilde{I}_m = I_m q_m^3(t=0) / \int_{x_{min}}^{x_{max}} x^2 \mathrm{F}(x)\mathrm{d}x \tag{6}$$

differences in the length and time scales are reduced so that they can be compared not only within the same blend at different phase separation temperatures but also between different blends. The power laws are rewritten as[21]:

$$Q_m \sim \tau^{-\alpha} \tag{7}$$

$$\tilde{I}_m \sim \tau^{\beta} \tag{8}$$

Using these reduced parameters, Meakin and Snyder[11] showed that the dynamics of phase separation were indeed universal for blends ranging from inorganic glasses, metal alloys, liquid mixtures and polymer blends. Hashimoto *et al.*[21] also showed that in the phase separation of PS/PVME blend, three stages were involved and each stage can be characterized by a single τ for all the temperatures studied. This approach is useful to characterize and for making better comparisons among molecular composites of different matrices. However, it was not used because of the difficulties in determining some of the parameters experimentally. It invariably requires the analysis of the early stage to determine D and ξ, which in this case is difficult to follow with a good precision because of the uncertain early stage.

However, the universality of phase separation was investigated using the scaling function $\tilde{S}(x)$ proposed by Furukawa[22] in which the late stage can be scaled by a single length parameter $R(t)$:

$$\tilde{S}(x) \sim \frac{x^2}{\gamma/2 + x^{2+\gamma}} \tag{9}$$

where d = dimensionality; $x = qR(t)$ and

$$\gamma = \begin{cases} d+1 & \text{off-critical mixture (cluster regime)} \\ 2d & \text{critical mixture (percolation regime)} \end{cases}$$

From equation (9) the asymptotic form of $\tilde{S}(x)$ is

$$\tilde{S}(x) \sim \begin{cases} x^2 \text{ for small } x \\ x^{-\gamma} \text{ for large } x \end{cases} \tag{10}$$

This analysis had been applied in the demixing of Al–Zn and Al–Zn–Mg alloys[23], and in polymer blends of PS/PVME at a critical concentration mixture[21]. The asymptotic behaviour of the scaled function agreed well between experiment and theory at small quenched depth and showed the universality of the phase separation process.

In order to analyse our data using this scaling function, one must first show that the system can indeed be scaled with a single length parameter by examining $\tilde{S}(x)$ at either different phase separation times, t, or reduced times, τ. Since $\tilde{S}(x)$ is a Fourier transform of the space correlation function of the composition, it is related to the scattered intensity $I(q, t)$:

$$\tilde{S}(x) \sim I(q) q_m^3(t) = F(x) \tag{11}$$

and

$$x = q/q_m$$

By plotting $F(x)$ vs. x as in *Figure 4*, the scattering profiles of *Figure 1* which showed varying intensities and scattering maxima at various phase separation times were reduced to a single curve. Thus they can indeed be scaled with a single length parameter.

Figure 5 shows plots of log F(x) vs. log x at temperatures of 262, 267, and 272°C to examine the asymptotic form of $\tilde{S}(x)$. Only plots of large q are shown since in the small-angle region, parasitic and void scattering prevent analysis. It was therefore difficult to scale at low q. At temperatures above 256°C, $\tilde{S}(x)$ scales to slopes between -2.3 to -2.5, between -2 and -3 as would be expected from a cluster structure with 1 and 2 dimensional diffusion according to equation (10). An off-critical mixture is assumed here since the mixing of rod and coil molecules resulted from rapid quenching of a homogeneous solution. Such a system does not have a lower critical solution temperature and is therefore in the off-critical region at all mixtures. Our results showed that the scaling deviated from theoretical predictions. This could be due to the failure of dynamic scaling at deep quenching. However, for all the temperatures studied, γ is $\simeq 2.4$ in all cases. This suggests that the dynamics of their cluster formation must be similar.

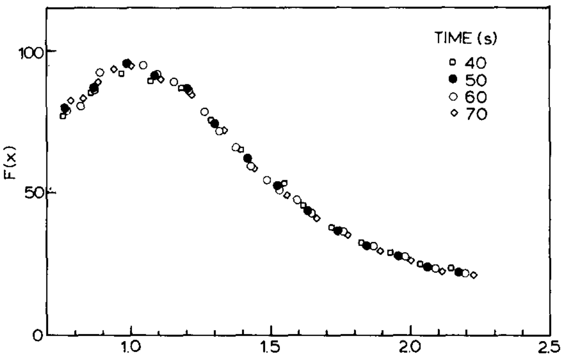

Figure 4 Reduced scattering curves of $F(x)$ vs. x at different phase separation time at 262°C

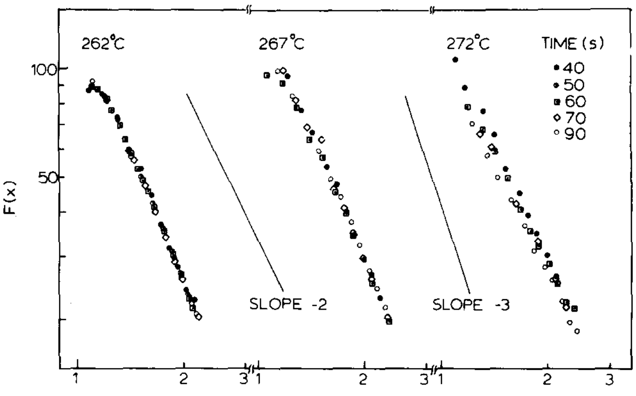

Figure 5 Plots of $F(x)$ vs. x for different time at phase separation temperatures of 262, 267, and 272°C

A possible explanation for the observed $\gamma \simeq 2.4$ is due to the anisotropy of the rod polymer. The coefficient of diffusion D, parallel to the rod axis, is much higher than D perpendicular to the rod axis[24], so that it is easier for a rod to move in a direction parallel to its axis. When Nylon melts, it is likely that at local level the aggregation of the rods proceeds largely through translational motion along the chain axis, which is a pseudo-one dimensional diffusion. This is further complicated by the flexible coils mutually diffusing away from the rods, resulting in a mixed mode of diffusion. Such complication can cause the observed deviation from the theoretical prediction which does not account for anisotropy in the components.

It must be recognized that the rigid rod/flexible coil blend is a unique system. Although there have been rapid advances in the theoretical treatment of polymer blend phase separation, no treatments exist with the extra orientational order parameter from the rod molecules. Recent papers by Doi *et al.*[24,25] on kinetic equations for the spinodal decomposition of stiff polymer solutions are major steps in the understanding of phase separation behaviour of the now widely-studied liquid crystalline polymers.

CONCLUSIONS

The late stage phase separation behaviour of a 45/55 PBZT/Nylon 66 molecular composite was studied using small-angle light scattering. When phase separation occurred, a scattering ring developed. Its intensity increased and the scattering maxima moved to a lower q as a function of time. Power laws were used to scale q_m and I_m with time. At temperatures where the Nylon was completely melted, the indices are $\alpha = 0.33$ and $\beta = 0.91$–0.95, in close agreement with those predicted by Binder[18]. A second stage was observed in which the growth of q_m and I_m slowed down dramatically to a near halt. This is in contrast to the prediction of $\alpha = 1$ observed in flexible coil polymer blends where coalescence of growing domains occurred. In this system the aggregated rod domains do not coalesce due to the simultaneous ordering of the rod molecules in the aggregates from extreme undercooling. The structure function $\tilde{S}(x)$ was scaled to test the universality of phase separation dynamics. At large x, $\tilde{S}(x)$ was scaled to the power of -2.4 of x in between those predicted for systems with one and two-dimensional diffusion as a result of the anisotropy of the rods.

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