polymer communications

Anisotropic phase separation kinetics in a polymer blend solution following cessation of shear studied by light scattering

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A light scattering instrument capable of monitoring the scattering from samples under the influence of a simple shear field has been constructed. The apparatus consists of transparent cone-and-plate fixtures and a two-dimensional charge coupled device array detector. The detector unit is also capable of measuring the scattering patterns as a function of time. The phase separation kinetics of an 8% solution of a polystyrene/polybutadiene (50:50) blend in dioctyl phthalate following cessation of a steady shear is monitored with this instrument. The sample is two-phase in the quiescent state and the applied shear is sufficient to suppress all scattering observed from the quiescent sample (shear-induced mixing). The evolution of the scattering profiles following cessation of shear is quite different parallel and perpendicular to the original flow direction. In the normal direction, a spinodal growth and coarsening mechanism similar to that observed in temperature quench experiments is observed. In the parallel direction, a different mechanism is followed. We believe this is the first report of this type of anisotropic behaviour in the phase separation kinetics of a polymer blend.

(Keywords: polymer blends; light scattering; phase separation kinetics; flow-induced anisotropy)

Introduction

Small angle neutron scattering (SANS) experiments conducted near the phase boundary of a two-component polymer blend have shown distinct differences between the scattering behaviour in the one- and two-phase regions under the influence of a simple shear field[1]. Due to the large size of domains in the two-phase region, examination of two-phase behaviour is better suited to the longer wavelengths utilized in light scattering experiments.

An apparatus has been constructed for conducting light scattering experiments on polymeric samples under the influence of a well defined simple shear using a two-dimensional charge coupled device (CCD) array detector for quantitative measurement of the scattered light intensity. The apparatus consists of transparent cone-and-plate fixtures mounted on a jig boring machine. The instrument is capable of making simultaneous viscosity, first normal stress difference and two-dimensional light scattering measurements. The device can also measure the time evolution of the scattering patterns allowing kinetic studies to be performed. Details of the apparatus will appear elsewhere[2].

The influence of shear gradients on the phase behaviour of binary polymer mixtures is important for both technological and fundamental applications. We will examine the kinetics of phase separation, at a constant temperature, following the shear-induced homogenization of an off-critical polymer blend solution. The solution is initially two-phase and during the application of sufficiently high shear rates, the sample appears to become one-phase. The applied shear rate is then stopped instantaneously and the kinetics of phase separation is monitored utilizing the time resolution capabilities of the light scattering instrument. Prior studies have concentrated on the behaviour of polymer solutions at their critical composition and no reference to anisotropy in the spinodal decomposition kinetics has been reported.

Materials

For these preliminary experiments an 8% solution of a 50:50 blend of deuterated polystyrene (PSD) ($M_w = 8.5 \times 10^4\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.02$) and polybutadiene (PB) ($M_w = 2.2 \times 10^4\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.1$) in dioctyl phthalate was prepared. The critical composition for this particular blend is 35% PSD and 65% PB. A similar sample at the critical composition has been examined by Hashimoto *et al.*[3–5]. The sample which we examined has an optical cloud point of 34°C under quiescent conditions and exhibits upper critical solution temperature behaviour. The shear experiments were conducted at room temperature (22°C), therefore the system is initially well into the two-phase region. Care was taken to insure the two-phase sample was well dispersed into fine droplets before it was placed between the cone and plate. This guarantees a uniform sample composition throughout the sample gap before the start of the experiments.

Results

The data for this study were obtained after a 'shear quench' from a shear rate of $329\,\mathrm{s^{-1}}$. From previous studies[6], we have demonstrated that this shear rate is large enough to suppress all scattering which is observed from the quiescent sample. The shear is applied to the sample for 1 min, which is sufficient for the sample to reach steady state. The motor is then stopped

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instantaneously and the redevelopment of the two-phase state is monitored as a function of time following cessation of the shear flow. The results following cessation of shear are analogous to the temperature jump light scattering experiments of Han and co-workers[7,8] which examine the phase separation kinetics of polymer blends as the temperature of the sample is quenched from the one-phase region to the two-phase region.

In this instrument geometry, the flow direction is defined along the x-axis while the gradient direction is along the y-axis. The incident beam is parallel to the y-axis and the scattering from the sample is collected in the xz-plane. Sector averages of the scattering data normal (along the z-axis) and parallel (along the x-axis) to the original flow direction were obtained for each time frame. Examples of the scattering patterns as a function of time after the shear quench are shown in *Figure 1*. The times indicate the time after the quench. For times <60 s, the normal scattering intensities are greater than the parallel intensities. At times >60 s, the scattering pattern is isotropic with respect to the original flow direction. The contours in both directions exhibit a peak which migrates to lower scattering vector, q, as a function of time, t. The magnitude of q is defined as $(4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident radiation and θ is the scattering angle. The intensity of

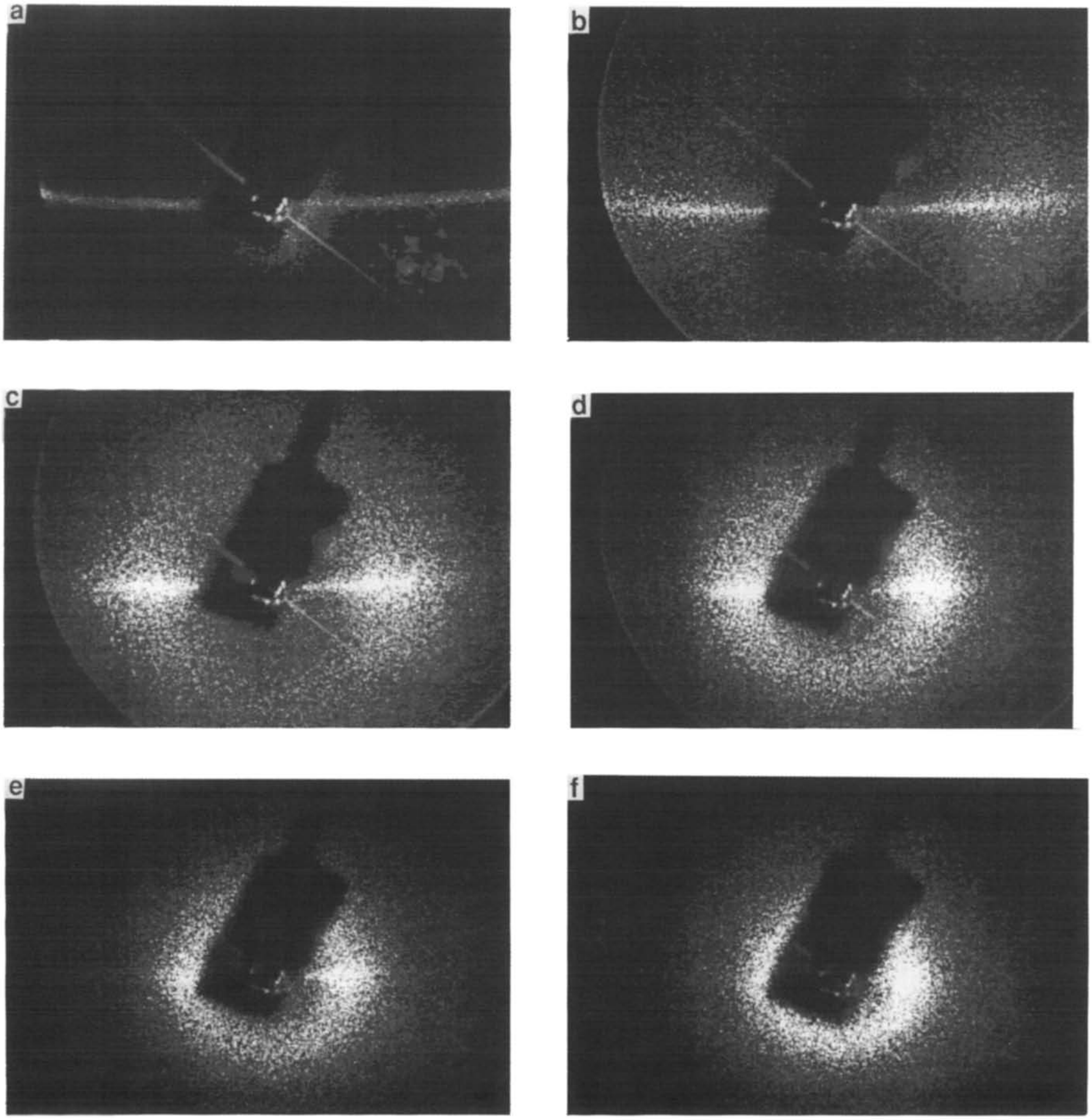

Figure 1 Scattering patterns as a function of time following cessation of shear. Time lapsed following cessation of shear: (a) 2.3 s; (b) 8.7 s; (c) 13.5 s; (d) 19.9 s; (e) 24.7 s; (f) 31.1 s. Original flow direction is vertical. The diagonal streak observed in the early time plots is spurious scatter from the beamstop

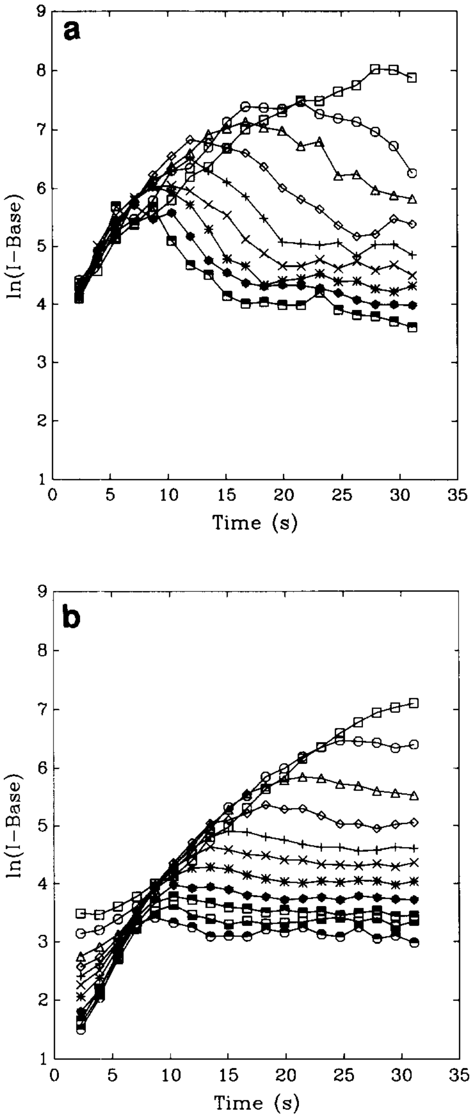

Figure 2 Ln[$I(q)$-baseline] *versus* time as a function of q. All q values in nm^{-1}. (a) Normal to the original flow direction. Values of q: (□) 1.36×10^{-3}; (○) 1.63×10^{-3}; (△) 1.89×10^{-3}; (◇) 2.14×10^{-3}; (+) 2.39×10^{-3}; (×) 2.62×10^{3}; (✱) 2.85×10^{-3}; (◆) 3.07×10^{-3}; (⬒) 3.28×10^{-3}. (b) Parallel to the original flow direction. Values of q: (□) 1.19×10^{-3}; (○) 1.47×10^{-3}; (△) 1.73×10^{-3}; (◇) 1.99×10^{-3}; (+) 2.24×10^{-3}; (×) 2.48×10^{-3}; (✱) 2.71×10^{-3}; (◆) 2.94×10^{-3}; (⬒) 3.15×10^{-3}; (⬓) 3.36×10^{-3}; (◓) 3.55×10^{-3}

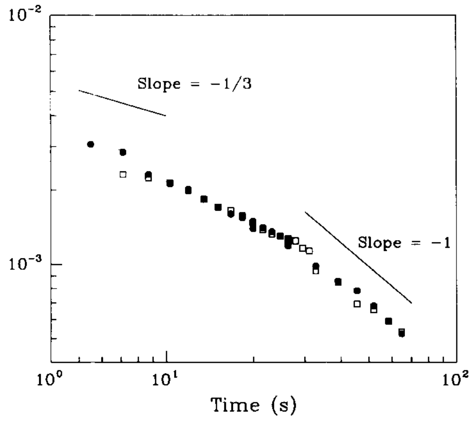

Figure 3 Logarithmic plot of q_m *versus* time: (□) parallel direction; (●) normal direction

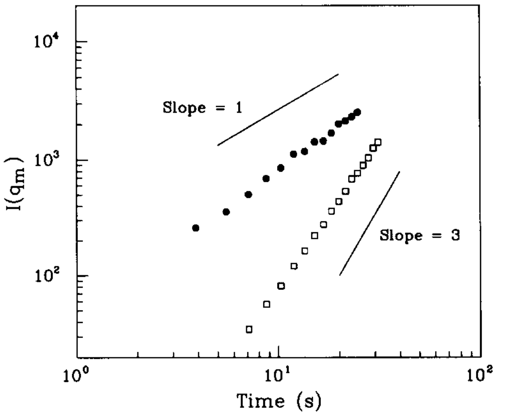

Figure 4 Logarithmic plot of $I(q_m)$ *versus* time. Symbols as in *Figure 3*

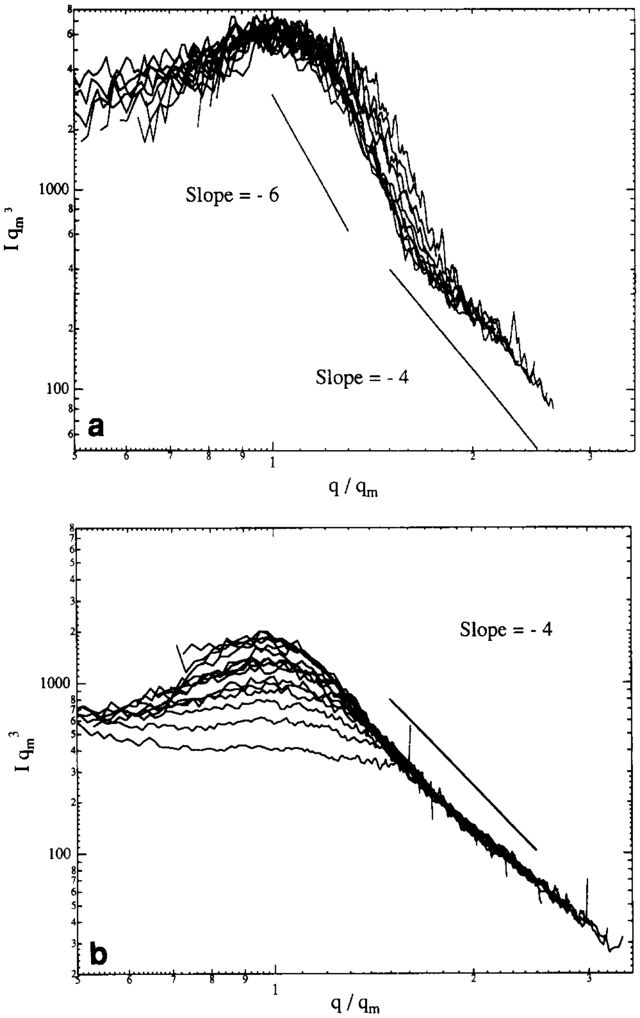

Figure 5 $I(q)q_m^3$ *versus* q/q_m. (a) Normal and (b) parallel to original flow direction

the peak also increases with increasing t. At a given q value, the intensity normal to the original flow direction increases to some maximum value then decreases as a function of t to a constant value (*Figure 2a*). By comparison, the intensity parallel to the original flow direction increases to a constant value as a function of t without passing through a maximum for a given q value (*Figure 2b*). These results are qualitatively different from the results of Hashimoto *et al.*[3,5] who observed a uniform ring of scattered light which collapses to smaller scattering angles with increasing t following the shear quench.

For the analysis of this data, logarithmic plots were constructed for the position of the peak maximum, q_m, as a function of t (*Figure 3*) and the intensity of the peak maximum, $I(q_m)$, as a function of t (*Figure 4*). Limiting slopes for the predicted behaviour are shown for reference. Also, plots of $I(q)q_m^3$ *versus* q/q_m were prepared for the sector averages normal to flow (*Figure 5a*) and parallel to flow (*Figure 5b*). These types of plots have been used previously by Han and co-workers in the analysis of the phase separation kinetics of polymer blends[7,8].

Despite the difference in peak intensities, the positions of q_m were invariant relative to the original flow direction as a function of t (*Figure 3*). From *Figure 3*, q_m does not scale with t as a simple power law but varies between the two limiting cases for intermediate stage ($t^{-1/3}$ dependence) and late stage kinetics (t^{-1} dependence). The logarithmic plots of $I(q_m)$ *versus* t show the growth of the intensity at q_m is faster in the parallel direction than the normal direction for the intermediate time range, $t \leqslant 30$ s (*Figure 4*). Normal to the flow direction, $I(q_m)$ scales as $t^{1.3}$, which is consistent with the scaling behaviour of q_m *versus* t over the same time interval. However, parallel to flow, $I(q_m)$ scales as $t^{2.5}$, which is inconsistent with the scaling behaviour of q_m with t.

The plots of $I(q)q_m^3$ *versus* q/q_m show important differences between the parallel and normal directions. Data taken at all times in the normal direction appear to scale onto a master curve. This curve appears to have a region at high q/q_m which approximates a q^{-6} dependence, which is typical for self-similar structural coarsening observed for spinodal decomposition. At even higher q/q_m the curve appears to scale roughly as q^{-4}, which is consistent with flat interfacial scattering in the Porod regime. The data in the parallel direction do not scale onto a single curve. The peak intensity grows with t but does not reach the level of intensity observed normal to flow. Only a regime proportional to q^{-4} is observed at high q/q_m, in the parallel direction.

A more detailed analysis of these results will be presented in a later publication. However, we believe this is the first report of this type of anisotropic behaviour in the phase separation kinetics of a polymer blend system. Normal to the original flow direction, a spinodal growth and coarsening mechanism similar to that observed in temperature quench experiments is observed. The growth mechanism in the parallel direction is different from conventional spinodal decomposition. An earlier SANS study[1] of polymer blends under the influence of shear in the one-phase region indicated a suppression of concentration fluctuations parallel to the flow direction and these results are consistent with those findings.

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