Phase separation in poly(*p*-phenylene benzobisthiazole)/nylon 66 molecular composite

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Poly(*p*-phenylene benzobisthiazole)/nylon 66 rigid-rod molecular composite undergoes thermally induced phase separation when heated to the nylon melting temperature. The phase-separated domains imaged by back-scattering scanning electron microscopy are 2–7 μm in size. The cloud-point curve is determined by using small-angle light scattering. Above the cloud point, phase separation proceeds with the development of a scattering ring which increases in intensity and moves towards the main beam with time.

(Keywords: poly(*p*-phenylene benzobisthiazole); nylon 66; rigid rod; molecular composite; blend; phase separation)

INTRODUCTION

The phase separation behaviour of polymer blends has been studied extensively in recent years to understand the demixing process. Such studies not only are important from the industrial standpoint for processing but also provide an experimental comparison with the theories on the mechanism and kinetics of phase separation. Numerous studies of the demixing process during heating or cooling of polymer blends have been reported for flexible coil polymers. Cahn–Hilliard[1] and de Gennes' random phase approximation theories[2] were applied to the kinetics during the early stage of phase separation for blends occurring through spinodal decomposition. Phase separation was also reported to occur by a different mechanism of nucleation and growth in the off-critical mixtures with shallow quench depths. Recently, Nakai *et al.*[3] reported the spinodal decomposition of a blend of thermotropic liquid crystalline polymer and poly(ethylene terephthalate). This was the first phase separation study in which one component is a rod-like polymer molecule. In this communication, we report a new system consisting of a blend of true rigid-rod polymers with flexible-coil polymers of poly(*p*-phenylene benzobisthiazole) (PBT) and nylon 66 that can undergo thermally induced phase separation.

PBT is a high performance aromatic heterocyclic rigid-rod polymer developed by the US Air Force. It is a true rod and differs from other rod-like molecules in that conformational flexibility is limited to axial rotations between monomer units; PBT forms a nematic liquid crystal when dissolved in a strong acid. It has excellent mechanical properties and thermal stability. A modulus of 330 GPa and a tensile strength of 3 GPa has been reported for a heat treated PBT fibre[4], making it a potential polymer for many new applications. One of these is the molecular composite in which the rigid-rod molecules are dispersed in a matrix of flexible coil polymer such that the rods act as reinforcing elements. This is similar in character to a chopped fibre composite but with the reinforcement taking place at the molecular level, thus giving a rigid-rod molecular composite.

Several flexible coil polymers[5,6] which are soluble in the common acid solvent of PBT have been used to make molecular composites with significant improvement in the mechanical properties. They were processed by dissolving the polymers in methane sulphonic acid (MSA) to form a ternary system which is a homogeneous solution at low concentration. Above a critical concentration, aggregation of the rod molecules occurs, forming a biphasic solution. Such a critical concentration depends on the axial ratio of the rigid-rod polymer, the contour length of the coil and their compositions[7]. The ternary solution is then processed below this critical concentration into thin films by rapid coagulation with water such that the rod/coil mixture is 'frozen' to overcome the unfavourable thermodynamic driving force for phase separation.

This communication reports the phase separation behaviour of a rigid rod molecular composite of PBT/nylon 66.

EXPERIMENTAL METHODS

PBT/nylon 66 solutions (PBT $[\eta]=21.4\,\mathrm{dl\,g^{-1}}$ was supplied by SRI International and nylon 66 is Du Pont Zytel 42, $M_w=28\,000$ and $M_n=14\,000$) with rod compositions of 10–70 wt% were prepared in freshly distilled MSA at concentrations of 2–3 wt%, well below

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the critical concentration. They were extruded using a coat hanger die into thin films onto a rotating drum and were coagulated with distilled water[8]. The final film thickness was 5–10 μm. The washed and dried films were heated to 280°C, above the nylon peak melting point of 260°C, under N_2 atmosphere for 1.5 h. The morphology before and after heating was examined with an Olympus BH-2 optical microscope and with a JEOL JSM-840 scanning electron microscope (SEM) in the back scattering mode using carbon-coated samples.

The phase separation behaviour was also studied using small-angle light scattering (SALS) at the University of Akron. The SALS system is equipped with a sample hot stage and a two-dimensional detector controlled by an optical multichannel analyser (OMA III). Cloud point measurements were undertaken at a heating rate of 5°C $\min^{-1}$.

RESULTS AND DISCUSSION

The PBT/nylon 66 films processed by extrusion and rapid coagulation are optically clear and did not show gross phase separation in an optical microscope. Dark field transmission electron microscopy of a film with 55/45 composition processed this way showed homogeneous dispersion of crystals 5–10 nm in size[9] using the 0.35 nm reflection of PBT for imaging. An SEM study of the fracture surface of the film also did not show phase separated domains[9]. Thus it was concluded from the microscopy studies that films processed by rapid coagulation of the ternary solution are not phase separated, in contrast to films cast by solvent evaporation and coagulation from solution above the critical concentration[10], which showed micrometre size phase separated domains.

Figure 1(a) shows the back scattering SEM micrograph of an as-processed 70/30 PBT/nylon 66 specimen before heating above the nylon melting point. The back scattering mode is useful in detecting the aggregation of the PBT molecules larger than 0.1 μm since the heavy sulphur atoms provide high contrast should there be PBT-rich domains. No specific domain features can be identified in the initial sample except for weak contrast from surface topological variations. After heating to 280°C, above the peak melting point of nylon 66, distinct phase separated PBT-rich domains 2–7 μm in size appear as bright areas in the micrograph, *Figure 1(b)*. This suggests that thermally induced phase separation occurs during heating.

The films with PBT composition from 10–70 wt % were heated at 5°C $\min^{-1}$ from 200°C in a hot stage mounted in the SALS setup. When phase separation occurs an isotropic scattering ring develops and then moves towards the main beam with heating. The intensity at a scattering vector q was plotted as a function of temperature. The intensity stays constant initially; the temperature at which there is a sharp increase in intensity is considered the cloud point, as shown in *Figure 2*.

For the rod/coil system, the curve is concave with a minimum at about 45 % rod content and at a temperature of 233°C, well below the peak melting point of nylon 66. Differential scanning calorimetry showed that, for the films studied, the onset of the melting endotherm begins at about 225°C and is broad with a peak at 260°C. Even though the peak melting point is not reached, phase separation occurs when the nylon chains have some mobility due to partial melting. This temperature is, however, much higher than the nylon glass transition, where the segmental motion alone is insufficient to cause phase separation. The temperature at which this occurs depends on the rod content. The concavity of the cloud point curve is similar in shape to a lower critical solution temperature (LCST). However, it should not be interpreted as an equilibrium phase diagram for reasons discussed below.

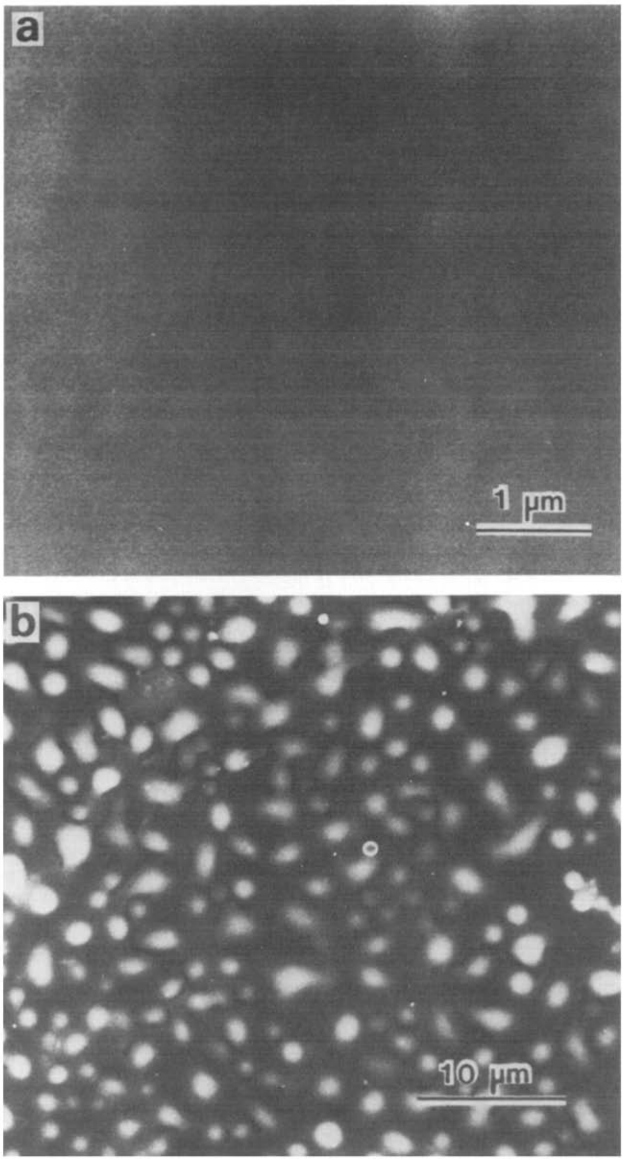

Figure 1 Back scattering electron micrographs of a 70/30 PBT/nylon 66 film (a) before and (b) after heating to 280°C for 1.5 h

The mixing of a rigid-rod and a coil polymer is thermodynamically unfavourable due to the low combinatorial entropy. This is dictated by both the length and the volume fraction of the rod. The longer the rod, the more unfavourable is the mixing. For a given rod length, increasing the volume fraction will cause alignment, as in the formation of an anisotropic phase of a lyotropic liquid crystal[11]. In this two-component system, we have the rods in a matrix of flexible-coil polymer in which entanglement of the rods is possible. They form a blend only through the rapid coagulation process from a common solvent. Thus there is no true thermodynamic

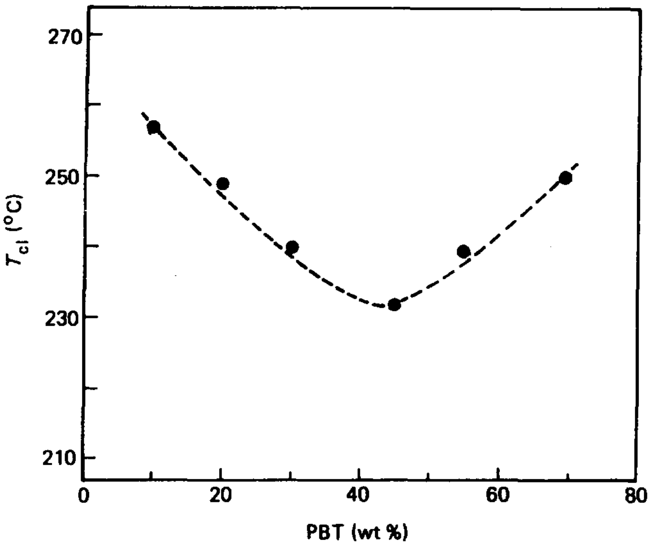

Figure 2 Cloud point curve of PBT/nylon 66 molecular composite determined by small-angle light scattering

LCST for such a system. An example of miscibility through rapid quenching was recently reported for polypropylene/EPR[12]. The true phase diagram is not known, but it could be shaped like an hour glass, with limited miscibility at very low rod content. With the compositions studied, the rod contents are high enough that the blend is in an unstable state. The cloud point curve merely reflects the drive towards phase separation as demanded by the unfavourable thermodynamics when sufficient mobility is imparted to the system.

This particular rigid-rod/coil system is further complicated by nylon 66, which is crystallizable as a competitive process for demixing during the coagulation. Indeed differential scanning calorimetry (d.s.c.) showed that about 35% of the nylon is crystalline, which precludes mixing with the rods. Some fractions of the PBT do aggregate by virtue of their volume fraction, as is evidenced by the dark field TEM imaging of the 5–10 nm crystals. Thus the true composition of the rod/coil blend is affected by these factors and is not readily accounted for in the cloud point curve which depicts the overall compositions. Additional scattering can arise from the density fluctuation between the nylon crystalline and amorphous regions. The effect of annealing of the nylon crystals during heating is not readily separable from the aggregation of the rods during phase separation, and this can contribute to the actual measured cloud point. Despite these shortcomings, the cloud point curve reported here represents the first example for a rigid-rod/coil system. It is important for molecular composite applications in which the consolidation process for fabrication as a structural material and the final use temperature are defined by the cloud point curve.

In the SALS studies, it was also found that the isotropic ring developed during phase separation, *Figure 3*(*a*), formed a four-lobe clover pattern for H_V scattering, *Figure 3*(*b*). Such a pattern persisted when heated to 285°C, well above the nylon 66 melting point, and after cooling to room temperature. This strong depolarized H_V scattering arises from the aggregated PBT rod molecules, which are anisotropic. Such depolarized scattering was predicted in the scattering theory of an anisotropic system and was also observed recently by Nakai *et al.*[3] in the liquid crystal/coil polymer system.

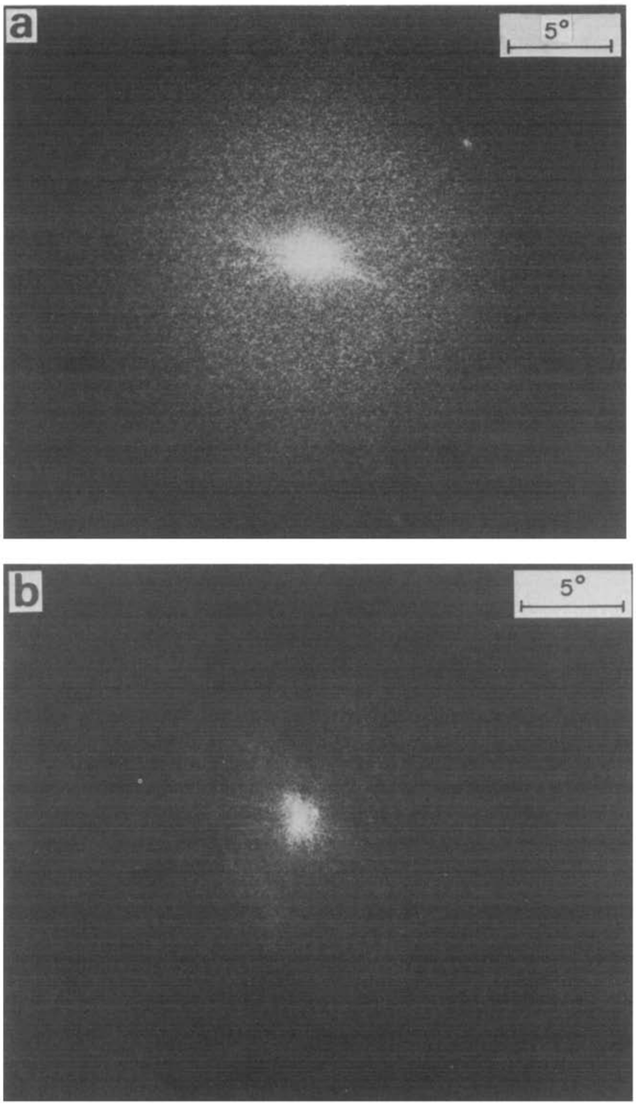

Figure 3 Light scattering of a phase separated PBT/nylon 66 film: (a) V_v and (b) H_v scattering

The development of a scattering ring and its time evolution of intensity in the time-resolved SALS studies indicate that demixing of the rigid-rod/coil blend follows the criteria of spinodal decomposition despite its complicated morphology. To avoid the complication of crystallizable nylon 66, a study has been performed using an amorphous nylon as the flexible component. The results will be reported in a separate communication.

CONCLUSION

This communication is the first to demonstrate the thermally induced phase separation of a rigid-rod/flexible-coil polymer blend in which the rod molecules can form lyotropic liquid crystals. Demixing occurs when sufficient mobility is imparted to the system at below the peak melting point of the flexible coil polymer. The rod molecules aggregate into domains with size determined by both the temperature and the time at which separation occurs. Because of the unfavourable thermodynamic driving force for such a system, phase separation proceeds rapidly.

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REFERENCES

1 Cahn, J. W. and Hilliard, J. E. *J. Chem. Phys.* 1958, **29**, 258
2 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, New York, 1979
3 Nakai, A., Shiwaku, T., Hasegawa, H. and Hashimoto, T. *Macromolecules* 1986, **19**, 3010
4 Allen, S. R. *et al. J. Mater. Sci.* 1985, **20**, 2727
5 Hwang, W-F. *et al. J. Macromol Sci.* 1983, **B22**, 231
6 Hwang, W-F. *et al. ACSD Div. Org. Coat. Appl. Polym. Eng. Sci.* 1983, **48**, 929
7 Flory, P. J. *Macromolecules* 1978, **11**, 1138
8 US Air Force Technical Report AFWAL TR-81-4156
9 Kumar, S., personal communication
10 Krause, S. *et al. J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 1991
11 Flory, P. J. and Ronca, G. *Mol. Cryst. Liq. Cryst.* 1979, **54**, 289
12 Inaba, N., Sato, K., Suzuki, S. and Hashimoto, T. *Macromolecules* 1986, **19**, 1690