polymer communications

Small-angle neutron scattering studies of a compatible polymer blend, atactic polystyrene—poly(2,6 dimethyl phenylene oxide)*

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In recent years the technique of small angle neutron scattering (SANS) has been used increasingly for the study of chain configuration in bulk amorphous[1–4] and crystalline polymers, in the melt and solid state[5–8]. Samples analysed by this technique are made up of a host polymer matrix in which a small number ($\sim$4%) of isotopically substituted (tagged) polymer molecules are dispersed. The difference in coherent scattering length, b, between deuterium ($b_D = 0.66 \times 10^{-12}$ cm) and hydrogen ($b_H = -0.37 \times 10^{-12}$ cm) results in a marked contrast between hydrogenated and deuterated molecules.

A fundamental assumption on which the scattering theory is based is that the tagged molecules are randomly or statistically dispersed in the host matrix. Any departure from a statistical distribution will invalidate the scattering theory, and lead to anomalies in the scattering pattern. Such anomalies were first reported by Schelten *et al.*[4] for mixtures of deuterated and hydrogenated polyethylene in which they measured (weight-averaged) molecular weights (Σ_0) from the SANS patterns which were many times the true molecular weights (M_w) of the tagged molecules. The high molecular weights were assocated with anomalous values of the radius of gyration $R_g = \langle s^2 \rangle_w^{1/2}$, and were later interpreted in terms of very small deviations (paraclusters) from a statistical distribution of tagged molecules[8]. Model calculations of Σ_0 and R_g were made as a function of the number of molecules diffracting coherently in a paracluster, $n_{cl} = \Sigma_0/M_w$, and were able to reproduce all anomalous features in the measured scattering pattern, resulting from variations of up to three orders of magnitude in n_{cl}. These calculations showed that the SANS technique was very sensitive to small deviations from a statistical distribution and that the apparent molecular weight Σ_0 can be changed to many times its true value with almost no mass transport of the tagged chains. Conversely, in view of the extreme sensitivity of the SANS technique, a measured value of Σ_0 close to the real molecular weight of the tagged chains is conclusive evidence for a random dispersion of tagged molecules in the matrix.

SANS methods were first used to investigate polymer compatibility by Kirste *et al.*[9–11], for both incompatible and compatible blends. The majority of chemically dissimilar polymer pairs are incompatible, and techniques hitherto used to probe this phenomenon (differential calorimetry, optical microscopy etc.) are sensitive to macroscopic fluctuations in composition, from which compatibility at the segmental level must be inferred. Furthermore, these techniques do not provide information on chain configuration in blends, and whether the molecules are perturbed from their configuration in the homopolymer. As pointed out above, the SANS technique is an extremely sensitive test of compatibility at the segmental level, and, by means of SANS measurements, Ballard *et al.*[12] demonstrated that polystyrene and poly(α-methylstyrene) formed a truly compatible mixture. In this communication we report the results of an investigation made on a polymer blend, polystyrene—polydimethyl phenylene oxide (commericially marketed as Noryl), which demonstrates that this system is compatible on a segmental level, and that the chain dimensions are similar to those in the homopolymer.

The neutron scattering samples were prepared by disolving the two polymers in chloroform and precipitating into methanol. After drying the precipitated polymer, films ($\sim$1 mm thick) were made by melt pressing at 300°C for $\sim$3 min and quenching into cold water. Samples were fabricated with a (hydrogenous) poly(dimethylphenylene oxide) (PPO) matrix in which concentrations (1.3, 4.2, and 6.0 wt%) of perdeutero polystyrene (DPS) were dissolved. A PPO matrix was chosen to minimize the contrast due to any residual voids in the system, by means of partial cancellation between the scattering lengths of carbon ($b_c = 0.66 \times 10^{-12}$ cm) and hydrogen ($b_H = -0.37 \times 10^{-12}$ cm)[5]. For each sample, the background matrix scattering was subtracted by performing measurements on a blank sample containing no tagged molecules.

The SANS experiments were performed on a new 5 m instrument in operation at the Oak Ridge Research Reactor[13]. This facility uses 4.8 A neutrons and a two dimensional positron sensitive detector. The scattering patterns from the tagged blends and the blank were each measured over a 32 x 32 array for a period of $\sim$16 h. For each point of the data array, the scattering was corrected for background, sample thickness and transmission and the corresponding scattering from the polymer blank was then subtracted. The resulting two dimensional array of corrected data points was averaged over a ring of constant width as a function of radius from the centre of the beam, to obtain the intensity over a range of scattering vectors, 7×10^{-3} Å$^{-1} \leqslant K = 4\pi/\lambda \sin\theta \leqslant 0.035$ Å^{-1}. These intensities were calibrated by comparison with scattering from water[14], and by direct measurements

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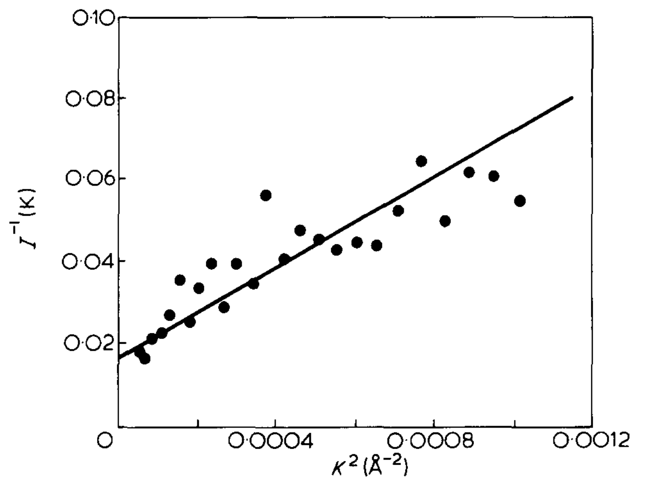

Figure 1 Plot of reciprocal intensity *versus* K^2 for sample containing 6.1 wt % deuterated polystyrene in polydimethyl phenylene oxide. $R_g^z = 98 \pm 20$ Å (experiment); R_g^z = 86–90 Å (bulk polystyrene); $M_w = 70 \pm 15) \times 10^3$ (SANS–ORR); $M_w = 97 \times 10^3$ (g.p.c./osmometry)

Table 1 Measured values of Σ_0 and $R_g = \langle s^2 \rangle_w^{1/2}$ for polydeutrostyrene in polydimethyl phenylene oxide

Sample wt% PDS	$R_g = \langle s^2 \rangle_w^{1/2}$ (Å)	Σ_0 (g)
6.1	98 ± 20	$(70 \pm 15) \times 10^3$
4.2	100 ± 20	$(82 \pm 20) \times 10^3$
2.3	100 ± 20	$(90 \pm 20) \times 10^3$

Tagged molecules (DPS), $M_w = 97 \times 10^3$, $M_w/M_n = 1.1$
Matrix (PPO) $M_w = 46.4 \times 10^3$, $M_w/M_n = 2.7$
R_g of PDS in PSH is 85–90 Å

of the incident beam, and by this means absolute values of Σ_0 were obtained from the SANS data.

Figure 1 is typical of the plots of I^{-1} *versus* K^2 from which the values of Σ_0 and $\langle s^2 \rangle_w^{1/2}$ shown in *Table 1* were obtained. For the tagged molecules the true (weight averaged) molecular weight, M_w was calculated from M_w/M_n determined by g.p.c. methods, and M_n determined by osmometry, prior to blending with the matrix molecules. It is clear that the molecular weights measured by SANS and g.p.c./osmometry are equal within the experimental error (~20%). Schelten *et al.*[8] showed that deviations from a statistical distribution involving less than one monomer unit in one thousand would cause Σ_0 to exceed M_w by a factor ~100. Thus the close agreement recorded above confirms that a statistical distribution of DPS in PPO has been achieved. This conclusion is similar to that resulting from extensive studies of compatibility made on this system by conventional techniques[15–18], and confirms that information on the compatibility of polymer blends on a segmental level can successfully be inferred from these techniques.

The dimensions of DPS in PPO are close to the dimensions of DPS in hydrogenous polystyrene (PSH)[4], although a small expansion of the chain cannot be ruled out within the experimental error. The variation of Σ_0 with concentration indicates a positive second virial coefficient in the range $1 \times 10^{-5} \leqslant 2A_2 \leqslant 1.5 \times 10^{-4}$ cm^3 g^{-2} mol.

Shortly, we will have available a 30 m SANS spectrometer[19] with greatly increased neutron flux and lower fast-neutron background. We propose to extend this study to measure more accurate values of A_2 and also to perform measurements at higher concentrations. However, in view of the extreme sensitivity of Σ_0 to any mass transport of the tagged molecules, the current study is sufficiently accurate to affirm the compatibility of PS in PPO at the segmental level.

During the course of this work our attention has been drawn to a complementary study of the DPS–PPO system by means of SANS methods at a lower molecular weight (R. Kambour *et al. Polymer* 1980, **21**, 133). Similar conclusions were reached concerning the compatibility, positive second virial coefficient and dimensions of DPS in PPO.

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