polymer communications

The compatibilizing effect of diblock copolymer on the morphology of immiscible polymer blends

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The morphology of immiscible blends of polystyrene and poly(methyl methacrylate) compatibilized by the addition of poly(styrene-*block*-methyl methacrylate) symmetric diblock copolymers was studied using small angle neutron scattering. From increases in phase dimensions, the reduction in interfacial tension has been calculated. Diblock micelle formation has also been observed.

(Keywords: compatibilization; diblock copolymer; interfacial tension; micelles)

Introduction

Immiscible polymer blends with high interfacial energies suffer from a number of inherent problems which derive from the weak interactions between the phases[1–3]. One way to improve the interfacial situation is by addition of copolymer to the blend[1,2]. The overall macroscopic effect is a drastic improvement in the compatibility of the blend and ultimately in mechanical strength[4–6]. The basis for these improvements is the interfacial activity of the copolymer, which arises from its preferential location at the interphase region[2] causing a reduction in the interfacial tension between the immiscible polymer phases. The success of a copolymer as an interfacial agent is therefore directly related to its ability to segregate to and sit at the interface between the two immiscible polymer phases. Clearly conformational restraints play an important role in the ability of the copolymer to segregate in an ideal morphology at this interface[7]. Using this simple argument it is easy to see that diblock copolymers will suffer less drastic conformational restraints than graft or star copolymers. However, diblock copolymers are prone to aggregation into micelles and to formation of microphase separated layers if present in high concentrations. Once aggregation has occurred the interfacial activity of the copolymers is curtailed[8]. In this communication, we present small angle neutron scattering (SANS) results for blends of polystyrene (PS) and poly(methyl methacrylate) (PMMA) with added poly(styrene-*block*-methyl methacrylate) [P(S-*b*-MMA)] diblock copolymers and discuss the ability of the latter to reduce the homopolymer interfacial tension. We also present results for a higher molecular weight copolymer which aggregates into micelles at low percentage contents and is therefore less useful as a compatibilizing agent.

Experimental

The polymers used were either PS or PMMA, or their deuterated analogues, dPS or dPMMA, together with several copolymers. Two systems were prepared, as summarized in *Table 1*. The first was a 50:50 w/w blend of dPS ($M_w = 1.37 \times 10^5$, $M_w/M_n = 1.31$) and PMMA ($M_w = 1.20 \times 10^5$, $M_w/M_n = 1.71$) with x% of the total mass being one or other of two copolymers. The two P(S-*b*-MMA) symmetric diblock copolymers used were P(S-*b*-MMA)31 ($M_w = 3.15 \times 10^4$, $M_w/M_n = 1.06$) to give blends labelled H31-*x* and the deuterated analogue, dP(S-*b*-MMA)28 ($M_w = 2.84 \times 10^4$, $M_w/M_n = 1.08$) to give blends labelled D28-*x*, where x in both cases is the copolymer percentage. The second system studied was a 25:75 w/w blend of dPMMA ($M_w = 1.61 \times 10^5$, $M_w/M_n = 2.29$) and PS ($M_w = 1.15 \times 10^5$, $M_w/M_n = 1.56$) with x% of the total mass being a hydrogenous symmetric diblock copolymer, P(S-*b*-MMA)85 ($M_w = 8.5 \times 10^4$, $M_w/M_n = 1.08$), to give a blend series labelled H85-*x*. Preparation of blends D28-*x*, H31-*x* and H85-*x* involved solvent casting the blends from 15% w/v toluene solutions in aluminium trays and allowing them to air dry over a period of a week, after which they were transferred to a vacuum oven at 40°C for further drying for 2 days. The samples were then hot pressed into the SANS Al sample holders using a hot press preheated to 120°C applying 7.5 t pressure for 15–20 min. Data collection of neutron scattering profiles were all performed on the LOQ instrument at the ISIS Pulsed Neutron Source at the Rutherford Appleton Laboratory. All data were

Table 1 Summary of the samples used in the SANS experiments together with their classification codes

Sample	Sample code
50:50 w/w dPS/PMMA + x% P(S-*b*-MMA)31	H31-*x*
50:50 w/w dPS/PMMA + x% dP(S-*b*-MMA)28	D28-*x*
25:75 w/w dPMMA/PS + x% P(S-*b*-MMA)85	H85-*x*

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collected at room temperature, and corrected using the COLLETE analysis program package running from the GENIE general utility program[9]. Further treatment of the data was also carried out by COLLETE.

Low copolymer molecular weight blends

The radially averaged $I(Q)$ *versus* Q data for all the blends H31-x and D28-x show similar behaviour for all values of x, with intense scattering at low Q which drops off sharply, falling to a constant $I(Q)$ value, at large Q. Data at large Q in the range $0.1 < Q < 0.25\,\text{Å}^{-1}$ were analysed in terms of the Porod law which is applicable to a randomly oriented two-phase system of arbitrary particle shape with sharp boundaries. The ordinate axis intercept of a linear fit to a Porod plot of $I(Q)Q^4$ *versus* Q^4 is equal to a parameter κ, which describes the blend morphology and can be expressed as[10]:

$$\kappa = \frac{c_p}{\rho_p} 2\pi(\Delta B)^2 \frac{A_p}{V_p} \tag{1}$$

where A_p/V_p is the surface area to volume ratio of the particles, c_p and ρ_p are the particle concentration and density, respectively, and ΔB is the scattering length density difference.

The dependence of A_p/V_p on copolymer content, x, as calculated from equation (1), is shown graphically in *Figure 1*. The increase in surface area to volume ratio must be a direct result of a reduction in the interfacial tension, γ, between the two phases which can be caused only by the location of the copolymer to this interface. The critical value of x at 10% copolymer addition must therefore represent a saturation point at which no further addition of copolymer to the interface can occur, consequently it can no longer affect γ and A_p/V_p remains constant. It can be shown that the relative reduction in interfacial tension, $\Delta\gamma$, is inversely proportional to the A_p/V_p ratio[11-14], as qualitatively predicted by Leibler[15]. As a first approximation the disperse phase can be assumed to be spherical particles, in which case A_p/V_p is simply equal to $3/r_p$. Using this assumption the values of γ obtained from the A_p/V_p ratio are shown plotted in *Figure 2* as a function of x(%). Although there is an addition of 20% of copolymer to the blend, there is only a maximum reduction in γ of 13% corresponding to a copolymer content of 10%. This behaviour parallels that of the change of the A_p/V_p ratio as a function of x, which showed a maximum effect at $x = 10\%$.

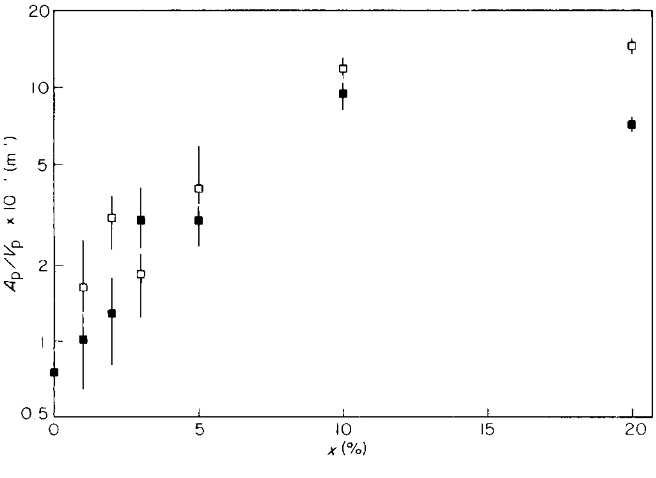

Figure 1 Plot of surface area to volume ratios (A_p/V_p) of the disperse phase regions in a continuous matrix obtained from fits to Porod plots in the Q range 0.1–0.25 Å^{-1} for blends H31-x (□) and D28-x (■)

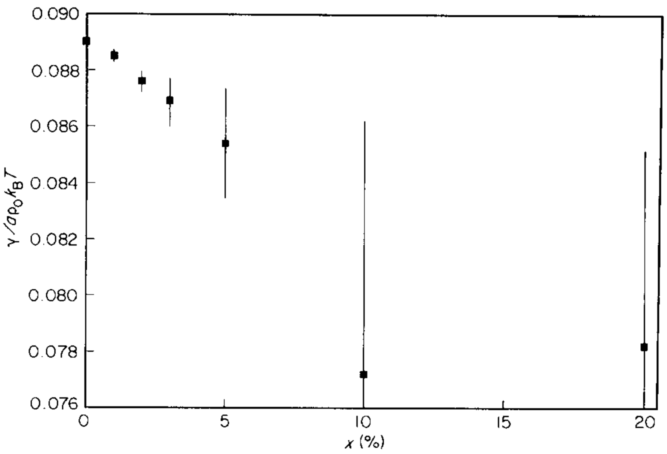

Figure 2 Interfacial tension, γ, between the two immiscible homopolymers PS/PMMA as a function of copolymer content, x%. The interfacial tension has been calculated using average values of the A_p/V_p ratio obtained from blends H31-x and D28-x at each value of x

When copolymer is located at the interface, the sharp boundary assumed by the Porod law will become diffuse, and the formulations, described above, must therefore be modified to account for this. Boundaries of finite width can be incorporated into the Porod law by convoluting with a smoothing function[16], which allows determination of the interphase thickness, d. By incorporation of such a smoothing function Richards and Thomason[17] have shown that the scattering behaviour depends on whether the morphology of the system is spherical ($\eta = 4$), cylindrical ($\eta = 3$) or lamellar ($\eta = 2$) and can therefore be expressed in the general analytic relationship:

$$\ln[I(Q)Q^{\eta}] = \ln \kappa_m - \sigma_d^2 Q^2 \tag{2}$$

where κ_m is a morphological parameter describing the dimensions of the different particle shapes according to the value of η, and σ_d determines d from the relationship[17].

$$d = 12^{1/2}\sigma_d \tag{3}$$

Equation (2) was compared to the SANS data in the Q range 0.05–0.12 Å^{-1} for the various values of η. Only when $\eta = 2$ do plots of $\ln[I(Q)Q^{\eta}]$ *versus* Q^2 for all of the H31-x and D28-x blend samples have a negative gradient which is necessary to satisfy equation (2), therefore suggesting that a lamellar morphology is present in all blends. Fitting in this Q range we now see across the copolymer lamella whereas before with the normal Porod, at higher Q only one face of this lamella is observed. This lamella structural behaviour is strongly influenced by the copolymer, and is well described by the so-called LOW theory[18] and experimental observations by Kinning *et al.*[19]. Lamellar formation can be understood in terms of the interface curvature and packing requirements of the blocks of the copolymer in a dry brush environment[20]. For both blend systems d varies randomly with x, with an average value for H31-x and D28-x of $d = 22.3$ and $25.3\,\text{Å}$, respectively. These values of d can be compared to a theoretical infinite molecular weight value predicted by Helfand and Tagami[21] using the relationship $d = 0.2887\pi a/\chi_{ab}^{1/2}$. With appropriate values for the average statistical segment length[22], $a = 6.85\,\text{Å}$, and an interaction parameter[23] $\chi_{ab} = 3.79 \times 10^{-2}$, Helfand's theory predicts a value of $d = 31.9\,\text{Å}$.

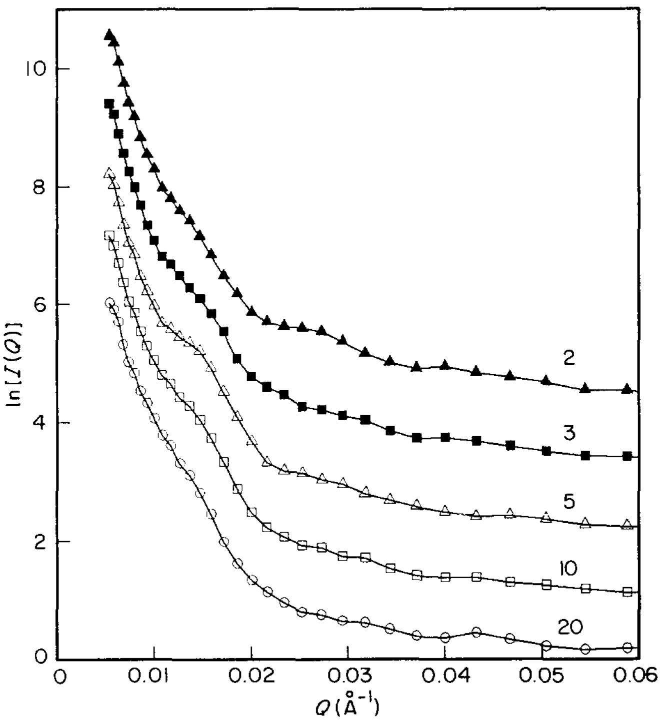

Figure 3 $\mathrm{Ln}[I(Q)]$ *versus* Q behaviour of H85-x blends ($x \geqslant 2\%$) showing oscillatory behaviour characteristic of the presence of spherical micelles. The number above each curve is the percentage of copolymer in the blend. The curves have been translated in the y-axis for clarity

High copolymer molecular weight blends

With the exception of H85-1 the H85-x blend series do not show the same $I(Q)$ *versus* Q characteristics as observed for the D28-x and H31-x blends. The intense scattering at low Q does fall rapidly with increasing Q, but for $x \geqslant 2\%$ this decrease in intensity is not smooth and shows oscillatory behaviour, as shown in *Figure 3*. Blend H85-1 does not show this oscillatory behaviour and was treated using Porod and modified Porod plots to give $A_p/V_p = (1.21 \pm 2.67) \times 10^6\,\mathrm{m}^{-1}$ and $d = 36.20 \pm 4.99$ Å. As observed before, modified Porod plots were only valid when $\eta = 2$ (lamellar).

The oscillatory behaviour in $I(Q)$ *versus* Q observed for H85-x in the range $x \geqslant 2\%$ is characteristic of microphase copolymer structure[24]. The structure most likely formed in this blend situation is that of spherical micelles of the P(S-*b*-MMA)85 copolymer present in the dPMMA matrix phase. For micelles to have formed, the critical micelle concentration (CMC) in the dPMMA phases must have been exceeded at some copolymer concentration in the range $1 < x(\%) < 2$. The radii of these micelles can be determined from the minima (Q_{min}) in the $I(Q)$ *versus* Q data, using the relationship derived from the spherical particle form factor to give[25].

$$Q_{\mathrm{min}} R_{\mathrm{m}} = 4.49n \tag{4}$$

where $n = 1, 2, 3$, etc. The values of R_{m} determined from the H85-x blends using equation (4) show that R_{m} remains essentially constant with x, varying about a statistically averaged value of 416 Å. These experimentally determined values of R_{m} can be compared to the theoretical value, $R_{\mathrm{m}} = 389$ Å, obtained from a mean-field calculation assuming monodisperse micelles[26]. The most likely explanation of the differences in experimental and theoretical micelle size is inclusion of PS homopolymer matrix chains within the PS micelle core, as observed by Inoue *et al.*[27] and Moritani *et al.*[28]. The transition from lamellar to spherical structure at $1 < x(\%) \leqslant 2$, must correspond to interfacial saturation. Further addition of copolymer can only be accommodated in one or other of the matrix phases, with as little as 2% causing the CMC in the dPMMA to be exceeded.

Conclusions

The effect of copolymer on the PS/PMMA blend is to increase the surface area to volume ratio of the homopolymer domains by more than an order of magnitude. The increase in this ratio, consistent with a reduction in phase dimensions, is ultimately associated with preferential segregation of the copolymer to the PS/PMMA interface. By assembling in a lamellar morphology at the interface, the copolymer molecules reduce the interfacial tension between the homopolymers and thereby allow a reduction in phase size. The maximum reduction of phase size corresponds to a 13% reduction in the interfacial tension. The maximum increase in surface area to volume ratio corresponding to the greatest reduction in interfacial tension is observed at 10% copolymer content for the low molecular weight copolymer of $M_{\mathrm{w}} \sim 30\,000\,\mathrm{g\,mol}^{-1}$. Further addition of this copolymer to the system provides no additional reductions in the interfacial tension, indicating a saturation level for this system at 10% copolymer addition. Micelle formation by the high molecular weight copolymer ($M_{\mathrm{w}} = 1.15 \times 10^5$) in the PMMA homopolymer phase is observed at copolymer contents of $> 2\%$. This indicates a CMC value of $\leqslant 2\%$. The micelles formed are larger than theoretical predictions using mean-field calculations, suggesting inclusion of homopolymer within the core. In further publications we will discuss the location of copolymer at the interface, and the conformation of the copolymer segments.

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