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Interface width of low-molecular-weight immiscible polymers

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Abstract

The interfacial width between immiscible low-molecular-weight polymer pairs was investigated using neutron reflection. Deuterated polystyrene (d-PS) and poly(methyl methacrylate) (PMMA) polymers of very low molecular weight (Mw) were used. The interfacial width is seen to increase for the low-molecular-weight cases with respect to the 'infinite'- Mw cases. The time dependence of the formation of the interface was also investigated. The results are compared with the predictions of the self-consistent-field theory with a correction based on capillary-wave fluctuations at the interface.

1. Introduction

The interface of an immiscible polymer blend is characterized by a narrow width and in general exhibits poor mechanical properties. A theory developed by Helfand and Tagami predicts the degree of interfacial mixing of immiscible polymers as a function of statistical segment length and the Flory–Huggins interaction parameter χ [1]. The theory predicts that the volume fraction profile through the interface assumes a hyperbolic tangent form, with a characteristic width w given by $w = 2a/\sqrt{6\chi}$, where a is the polymer statistical segment length. Reliable experimental measurements have been made to test the Helfand and Tagami predictions [2, 3], with the technique of neutron reflection proving to be the most accurate method. Neutron reflectivity (NR) for polymer systems relies on the difference in scattering cross section between hydrogen and deuterium and provides a resolution down to a few Å.

Early NR measurements of immiscible polymer interfaces showed that there was a discrepancy between experimentally measured and theoretically predicted interfacial widths [4, 5]. We have recently shown that the origin of this discrepancy is that the mean-field

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profile predicted by Helfand theory is broadened by a spectrum of thermally excited capillary waves [6].

When corrected for the effect of capillary waves by adding in Gaussian quadrature the theoretical width with the thermal wave broadening, we found a reasonable agreement between the predictions of self-consistent-field theory and experimental measurements of the interfacial widths. The Helfand theory has been found therefore to describe the essential features of high-molecular-weight polymer–polymer interfaces, with χ typically 10^{-2} and monomer segment lengths of 5–7 Å. The assumption of infinite chain length is not accurate for many situations, and a correction to the relation for the interfacial width w for these cases has to be introduced. Anastasiadis *et al* have shown the existence of strong molecular weight effects for chains with molecular weights up to 10^5 [7]. In particular, the interfacial tension was shown to increase with increasing molecular weight of the chains. Very recently, some measurements by Schubert and Stamm of the width of the interface between PS and PMMA, of low molecular weights, have revealed the limit of the assumption of infinite molecular weights when the molecular weights of the polymers are low [8]. The influence of finite chain length on the interfacial width has been considered by several authors, producing different expressions for the interfacial width w and interfacial tension γ [2]. An expression for both quantities in the frame of the mean-field theory has been derived by Broseta *et al* [9]. Considering two segregated homopolymers 1 and 2 with comparably high degrees of incompatibility $w_1 = \chi N_1$ and $w_2 = \chi N_2$, where N_1 and N_2 are the degrees of polymerization of the two polymers, the interfacial width derived by Broseta *et al* is given by

$$w = \frac{2a}{\sqrt{6\chi}} \left(1 + \ln 2 \left(\frac{1}{w_1} + \frac{1}{w_2} \right) \right) \quad (1)$$

and the expression for the interfacial tension is

$$\gamma = \gamma_\infty \left(1 - \frac{\pi^2}{12} \left(\frac{1}{w_1} + \frac{1}{w_2} \right) \right) \quad (2)$$

where γ_∞ is the value of the interfacial tension for the approximation of infinite Mw given in the frame of the Helfand theory by $\gamma_\infty = k_B T \rho a \sqrt{\chi/6}$, and ρ^{-1} is the monomer unit volume.

A conclusion can be drawn from equation (1): the interfacial width is supposed to decrease slowly with increasing molecular weight or incompatibility towards the limit $2a/\sqrt{6\chi}$. The intrinsic interfacial width has to be convoluted—as introduced before—with the contribution from the capillary-wave fluctuations.

To study these effects for polymers with low molecular weights, reflectivity experiments on the d-PS/PMMA interface have been performed.

2. Experimental procedure

Neutron reflection experiments were performed at the ISIS facility, Rutherford Appleton Laboratory (UK), using the reflectometers CRISP and SURF.

Bilayers of d-PS on h-PMMA were prepared by spin-casting PMMA on a silicon substrate, producing a thick film varying between 2000 Å and 7000 Å. The silicon substrates used were discs polished on one side, of diameter 5 cm and thickness 0.5 cm, with orientation (111). d-PS was first spin-cast on a glass slide and then floated onto the PMMA, producing thickness of around 2000 Å. Smaller thicknesses are difficult to achieve with the floating process for this very low- Mw polymer solution. All the film thicknesses were also measured using ellipsometry. Samples prepared in this way were then dried at 60 °C in a vacuum oven for some time and then annealed at 100, 110 and 120 °C for different lengths of time. The combinations of molecular weights studied for the d-PS and PMMA polymers are given in table 1.

Table 1. Different combinations of molecular weight (M_w) for the d-PS and PMMA pair used for the neutron reflection experiments.

Pair	$M_{w,d-PS}$	$M_{w,PMMA}$
Pair A	10000	7600
Pair B	4500	7600
Pair C	4500	4250

All the polymers used in the experiments were obtained from Polymer Laboratories (UK) and were prepared by anionic polymerizations with M_w/M_n of 1.1 or less.

3. Results

Neutron reflectivities were measured for both the unannealed and the annealed samples. For pair A, the reflectivity curves were taken at different annealing times at a fixed temperature of 120 °C. Figure 1 shows the reflectivity curves for different annealing times (see the scale on the x -axis in figure 2 for the annealing time of the corresponding reflectivity curves). The reflectivities show fringes characteristic of the thickness of the top d-PS layer, since the thickness of the bottom layer was ~ 2200 Å. The thickness of the top layer is slightly different for the different curves, varying by around 100 Å, depending on the sample used. Different samples were prepared from the same polymer solutions and annealed for different annealing times. The solid lines in figure 1 are fits to the data points with a multilayer model with the parameter describing interfacial roughness between the two layers as the only changing variable during the fit. The roughness of the interface between the two polymers layers is described

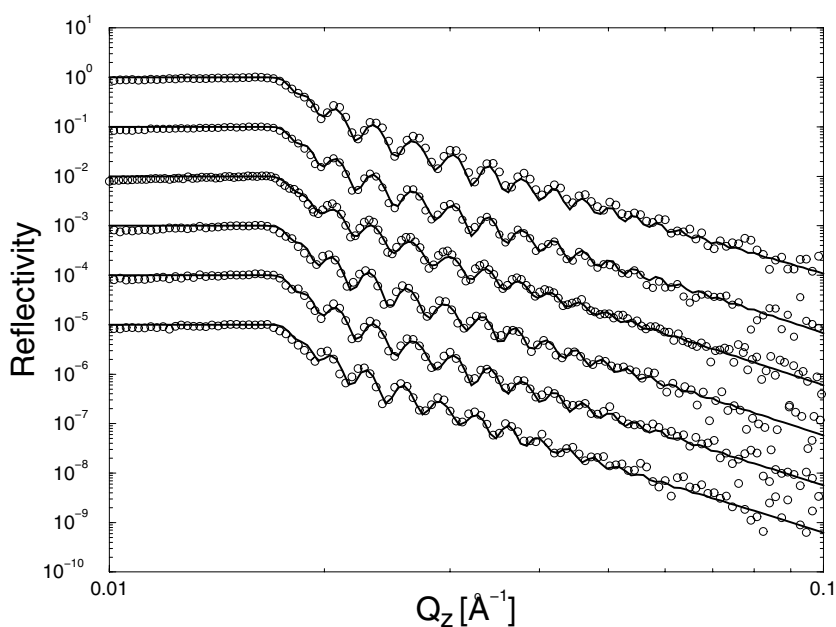


Figure 1. Reflectivity curves for different durations of annealing at a temperature of 120 °C for the 10000 d-PS/7600 PMMA system (see the text for details). The solid lines are fits to the data points using a multilayer model. The curves have been scaled by a factor of 100 for clarity.

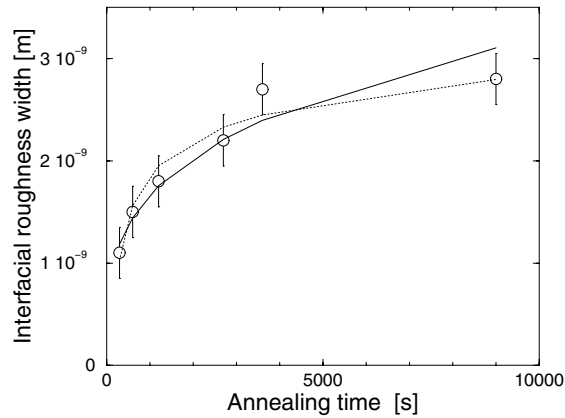


Figure 2. Interfacial roughness as a function of the annealing time extracted from the fits of figure 1 (for the 10 000 d-PS/7600 PMMA system).

by a Debye–Waller factor: the reflectance of this interface is multiplied by $e^{-2k_{\text{PS}}k_{\text{PMMA}}\sigma^2}$, where $k_{\text{PS,PMMA}}$ is the neutron momentum in the PS or PMMA layer and $\langle\sigma\rangle^{1/2}$ is the root mean square roughness at the PS/PMMA interface. In real space, this corresponds to an error function, which has a shape close to the hyperbolic tangent function. The roughness parameter σ (the interfacial roughness width in this paper) must therefore be multiplied by $(2\pi)^{1/2}$ to produce a value comparable with the value extracted from the hyperbolic tangent model (the interfacial width in this paper). The results obtained from the fit for interfacial roughness between d-PS and PMMA are reported in figure 2. The interface roughness width is around 28 \AA , corresponding to a hyperbolic tangent interfacial width of $\sim 70 \text{ \AA}$, after two hours of annealing.

Different samples were prepared for pair B of polymers. The thicknesses of both the d-PS and the PMMA layers were quite large, around 3000 \AA . Different annealing temperatures were used for different annealing times: $100 \text{ }^\circ\text{C}$, $110 \text{ }^\circ\text{C}$ and $120 \text{ }^\circ\text{C}$. Figures 3 and 4 show the roughness parameter Δ extracted from the fitting of the reflectivity curves, as a function of the

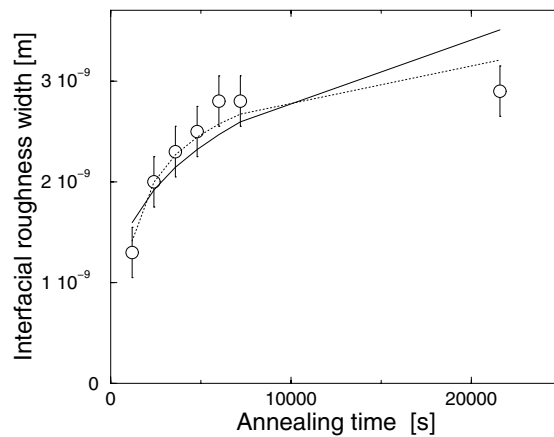


Figure 3. Interfacial roughness as a function of the annealing time for the 4500 d-PS/7600 PMMA system at a temperature of $110 \text{ }^\circ\text{C}$.

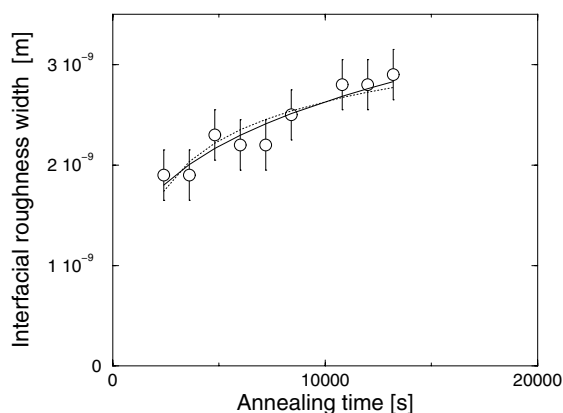


Figure 4. Interfacial roughness as a function of the annealing time for the 4500 d-PS/7600 PMMA system at a temperature of 100 °C.

annealing time, for the annealing temperatures of 110 and 100 °C. The interfacial roughness width parameter is around 30 Å after two hours of annealing time, as shown in the figures. The reflectivity of a 4500 d-PS/7600 PMMA pair when annealed at 120 °C for six hours is 29 ± 3 Å. This value corresponds to an interfacial width of ~ 75 Å, around 50% higher than the value obtained from the infinite- Mw case.

The reflectivity curves measured for pair C are reported in figure 5. The top curve corresponds to the unannealed case and the other three curves to different annealing times

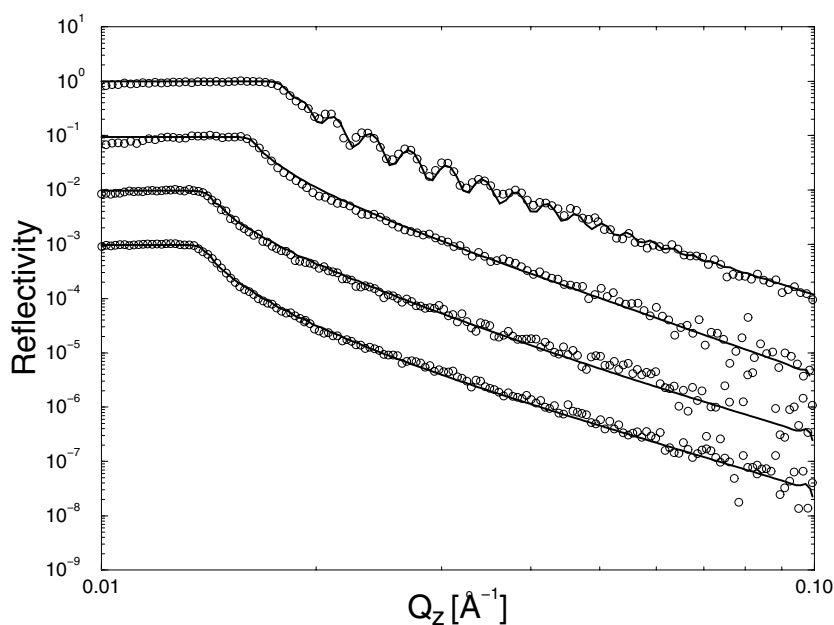


Figure 5. Reflectivity curves for different annealing times at a temperature of 120 °C for the 4500 d-PS/4250 PMMA system (see the text for details). The solid lines are fits to the data points using a multilayer model. The curves have been scaled by a factor of 100 for clarity.

at a temperature of 120 °C. The thickness of the top curve for the d-PS layer was 1400 Å, while the thickness of the bottom PMMA layer was ~5500 Å. For the other three cases the thickness of the top d-PS layer was around 3500–4000 Å, while the thickness of the bottom layer was the same as in the unannealed case. The solid lines in figure 5 are fits to the data. The critical edge clearly shifts for different annealing times, with the scattering length density decreasing from a value of $6.4 \times 10^{-6} \text{ \AA}^{-2}$ for the unannealed sample to a value of around $3.9 \times 10^{-6} \text{ \AA}^{-2}$ for the sample after one hour of annealing. The interfacial roughness width also increases to 52 Å for one hour of annealing; this value has been extracted by fitting the data with a hyperbolic tangent profile between the d-PS and PMMA layer, and corresponds to an interfacial width of 130 Å.

4. Discussion

The interfacial roughness widths extracted from the study of the pair A and B of table 1 are $28 \pm 3 \text{ \AA}$ and $30 \pm 3 \text{ \AA}$ respectively. The interfacial widths are therefore larger than in the case of infinite molecular weight, as expected. To quantify these results, the expression for the bare interfacial width for finite molecular weight as calculated by Broseta *et al* [9] has been applied, and convoluted with the contribution from the capillary-wave part. Using the relation (1), with $a = 7 \text{ \AA}$, $\chi = 0.037$ as used for the infinite-molecular-weight case, and $w_{\text{PS,PMMA}}$ given by $\chi N_{\text{PS,PMMA}}$, values for the interfacial widths for the A and B systems can be calculated. A value of 51.7 Å is extracted for the 4500 d-PS and 7600 PMMA case, and 43.9 Å for the 10 000 d-PS and 7600 h-PMMA, corresponding to values for the interfacial roughness parameter of 20.7 and 17.6 Å respectively. These values are higher than the value of 11.8 Å for the infinite-molecular-weight case. The contribution to the interfacial width due to the capillary-wave fluctuations can be calculated using the following equation [10]:

$$\langle \Delta \zeta^2 \rangle = \frac{k_B T}{2\pi \gamma_{\text{AB}}} \ln \frac{\lambda_{\text{max}}}{\lambda_{\text{min}}} \quad (3)$$

since the thicknesses of the two layers are $\geq 1400 \text{ \AA}$, and the upper limit cut-off on the capillary wave is of the order of a few μm . λ_{min} and λ_{max} are the minimum and the maximum wavelengths of the fluctuations (λ_{max} is limited by the lateral coherence length of the neutrons and it is of the order of μm , and the intrinsic width is a good estimate of λ_{min}). The interfacial tension has to be estimated in order to calculate the contribution to the interfacial width of the capillary-wave term. An extension to the self-consistent-field theory for finite chain length has been proposed by Helfand *et al* [11]. An expression for the interfacial tension is given by

$$\gamma = \left(\left(\frac{\chi}{6} \right)^{1/2} a \rho k_B T \right) \left(1 - \frac{N_\gamma}{N} \right) \quad (4)$$

where $N_\gamma = 2 \log 2 / \chi$ and is a characteristic degree of polymerization of the order of $N_\gamma a^2 \sim w^2$ (w is the interfacial width). The term that multiplies the factor $(1 - N_\gamma / N)$ in equation (4) is the infinite interfacial tension which is 1.7 mJ m^{-2} . N is given by $N = (N_1 + N_2) / 2$. Using expression (4), values of the interfacial tension can be estimated. They are 0.52 mJ m^{-2} for the 4500 d-PS and 7600 PMMA, and 0.86 mJ m^{-2} for the 10 000 d-PS and 7600 PMMA, for a temperature of 120 °C. Using expression (2), the interfacial tension between PS and PMMA for low molecular weight can be estimated: values of 0.175 mJ m^{-2} for the 4500 d-PS and 7600 PMMA, and 0.7 mJ m^{-2} for the 10 000 d-PS and 7600 PMMA are obtained for a temperature of 120 °C. It is possible to observe that there is a clear difference between the values of the interfacial tension extracted with the Helfand and Broseta expressions for the lower- Mw combination, while the values agree better for the 10 000 d-PS and 7600

PMMA system. Experimental results on the interfacial tension between the two polymers are quite sparse: low values of the interfacial tension are quite difficult to measure in a polymer melt. This is mainly due to their high viscosity and also their low molecular weights. Using the interfacial tension values estimated from the Helfand and the Broseta theories, the capillary-wave contribution can be calculated using equation (3). The total roughness parameter can be compared with the experimental values. These are reported in table 2. A sufficiently good agreement is obtained between the experimental and theoretical results for the 10 000 d-PS and 7600 PMMA combination, with an experimental interfacial roughness width of around 28 Å and a theoretical one of around 35 Å, using the two different values of the interfacial tensions. For the low-molecular-weight combinations, the calculated values are much larger than the experimental values. This polymer blend Mw combination is nearer to the critical point, where the theories described above do not hold.

Table 2. Experimental (Δ_e) and theoretical (Δ_t) predictions of the roughness interfacial parameter for low-molecular-weight d-PS and PMMA pairs. The theoretical predictions are described in the text. H. stands for Helfand and B. for Broseta (equations (2) and (4) corresponding to the Broseta and Helfand predictions respectively for the interfacial tension needed in equation (3) have been used, as described in detail in the text).

Mw_{d-PS}	Mw_{PMMA}	Δ_e (Å)	Δ_t (Å), H.	Δ_t (Å), B.
10000	7600	28(3)	34	36
4500	7600	30(3)	42	67

There are three possible explanations. The first is that the Broseta theory overestimates the increase in interfacial width that results from finite Mw . The second is that our estimation of the interfacial tension is too low. The third is that the upper cut-off length l that we have chosen is too large, either because we have overestimated the lateral coherence length of the neutrons, or because the sample has not yet reached equilibrium.

More insight is obtained when the dynamics of the formation of the interfaces is considered. In the limit of large degrees of immiscibility, a narrow intrinsic interface may come to equilibrium quite rapidly as the formation of such an interface—whose width is much smaller than the overall chain dimension—will be governed by the polymer motion on the segment level rather than by the diffusion of the whole chains. On the other hand, the broadening of the interface by capillary waves will take much longer, as the growth of these waves requires hydrodynamic flows of the polymer melt. In fact, on dimensional grounds, one can argue that the largest wavelength of capillary wave $l(t)$ that has had time to come to equilibrium after time t must scale like $l(t) \sim (\sigma/\eta)t$ where η is the viscosity of the polymer and σ is the interfacial tension. The prediction is then that the interface width grows logarithmically with time, as we have in fact observed for high- Mw PS/PMMA systems [12]. The situation can be different for polymer pairs closer to the critical point, where the initial diffusive broadening of the interface must be significant. Here theory predicts that the broadening of the interface follows a power-law dependence with exponent 0.25 [13]. Figures 2, 3 and 4 show that an interfacial roughness value of around 10 Å is obtained rather rapidly, with a subsequent increase towards the equilibrium value over a time of the order of an hour or so. We can interpret this in terms of the capillary-wave picture by assuming that the intrinsic interface width is achieved relatively fast, and that the subsequent slow rise in interfacial thickness is due to capillary waves of progressively larger wavelength coming to an equilibrium. We can interpret equation (3) as applying to the non-equilibrium case by assuming that the cut-off length $\lambda_{max} = l(t)$ is to be interpreted as a time-dependent length representing the longest wavelength that has had a chance to come to equilibrium. This predicts a logarithmic dependence on time; the solid

lines in the figures show the best fit of such a law to our data, showing satisfactory agreement. If the dependence of the cut-off length on time is linear, the fits imply an interfacial tension of $\sim 0.43 \text{ mJ m}^{-2}$ for the 10 000 dPS/7600 PMMA system, and $\sim 0.28 \text{ mJ m}^{-2}$ for the 4500 d-PS/7600 PMMA, of the right order of magnitude but somewhat smaller than we estimated above. We should, however, be cautious about this interpretation, as it is difficult on the basis of limited data to distinguish between logarithmic growth and a weak power law. The dotted line shows a best power-law fit, with a growth proportional to $t^{0.26}$ and $t^{0.28}$ for the pairs A and B respectively. Both exponents are close to the value 0.25 predicted for the growth of interfacial width in near-critical interfaces [13].

Thus it is difficult with the present set of data and our current level of theoretical understanding to distinguish definitely between these two approaches.

From the result of the reflectivity data fitting for the 4500 d-PS and 4250 PMMA pair, a wider interface was observed after one hour of annealing at 120°C . The interfacial roughness width is observed to be 52 \AA , corresponding to an interfacial width of 130 \AA . From figure 5, it is also clear that the density of the top layer decreases to just above half the value for the unannealed case.

If the Flory–Huggins theory is considered, stability in a miscible polymer blend is obtained if the second derivative of the free energy of mixing with respect to the volume fraction of polymer 1 is positive:

$$\frac{1}{k_B T} \frac{\partial^2 \Delta G}{\partial \phi_1^2} = \frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_1} - 2\chi > 0 \quad (5)$$

with χ the interaction parameter. As was seen before, in the case of low-molecular-weight polymers, the combinatorial entropy of mixing becomes larger and miscibility can also occur for positive values of χ , as for the case of PS/PMMA blends at temperatures between 100 and 200°C . The minimum value of the line of stability, the spinodal, is obtained from

$$\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}} \right)^2 \quad (6)$$

with N_1 and N_2 the degrees of polymerization of the two polymers. The χ_c -value depends only on the molecular weight of the two components. For the 4500 d-PS and 4250 PMMA system this value is ~ 0.057 (the same calculation for the other combinations gives results of 0.04 for the 4500 d-PS and 7600 PMMA, and 0.026 for the 10 000 d-PS and 7600 PMMA). The value of 0.057 is similar to the values for the pairs used by Shearmur *et al* [14], where total miscibility was observed. According to the work published on similar combination polymers by Russell *et al* [15] and Callaghan and Paul [16], this value of χ_c corresponds to a value of the critical temperature T_c (above which miscibility occurs) of below -100°C . This is in contrast to other work by Stühn [17] and Kressler *et al* [18] in which the χ_c -value would correspond to a critical temperature above 200°C . The observation of an interface width of 130 \AA after one hour of annealing would support the miscibility case.

5. Conclusions

In conclusion, the interfacial width is seen to increase for low-molecular-weight d-PS/PMMA systems with respect to the infinite- M_w case. The prediction of the interfacial width using a correction due to the low molecular weight involved is also compared with the experimental data. The results obtained agree well for the higher-molecular-weight polymer system, but not for the other two low- M_w polymer combinations. The kinetics of formation of the interface have also been investigated.

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