The Local Structure of Miscible Polymer Blends

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1. Introduction
The formation of miscible mixtures of two chemically dissimilar polymers is in general unfavourable. For many materials a single phase is never formed, while for others, the miscible state is only obtained at low temperatures. The classic description of the interaction between two polymers is via the Flory-Huggins theory (for example see [1]) in which $\chi$, the interaction parameter, together with the molecular weight information defines the phase behaviour. This approach has proved very successful in describing both phase boundaries and the nature of the two phase morphologies. Despite this success there is no firm microscopic model on which to base calculation of the interaction parameter. In part, the lack of a microscopic model arises from the paucity of data describing the local structure of miscible blends. It is clear that a range of interactions may exist. For example atactic poly(methylmethacrylate) (PMMA) and atactic poly(styrene) (PS) do not form a single phase unless oligomeric systems are considered. However, copolymerisation of styrene with ~10 mol% acrylic acid leads to a miscible blend with PMMA. The natural conclusion is that the miscible state is stabilised through a dilute set of strong interactions. In contrast, the blend system of PS and poly(phenyleneoxide) exhibits a strongly negative volume of mixing and some evidence for changes to the local structure on mixing [2]. In other words, the system is stabilised by a concentrated set of relatively weak local interactions. If such variations in local structure exist, then clearly, the interaction parameter must embrace many factors.

We have set out to explore the local interactions in miscible blends using a variety of scattering procedures. Broad Q neutron scattering on a series of blends prepared using isotopically substituted polymers provides a direct route to obtaining partial correlation functions which describe the local distributions of the differing chain segments with respect to each other [3]. However, such approach requires the challenging preparation of deuterated and hydrogenated isostructural systems for each polymer in the blend and extensive access to neutron scattering facilities. In this contribution, we explore an alternative approach which utilises conventional laboratory-based x-ray scattering procedures and thus in principle enables a much broader study of differing blend systems.

2. Materials
We have considered two blend systems in this study. The first is based on low molecular weight PMMA and PS. Interaction parameters have been obtained for such systems by Callaghan and Paul [4]. The second system is the widely studied...
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poly(vinylmethylether) (PVME) and PS, for example the studies of Han et al. provides insight into the composition dependence of the interaction parameter [5]. Table 1 contains the characteristics of the parent polymers

Table 1 Characteristics of the Polymers used in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Blend</th>
<th>Mn</th>
<th>Mw</th>
<th>Mw/Mn</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>PS/PMMA</td>
<td>9680</td>
<td></td>
<td>1.02</td>
<td>Polymer Laboratories</td>
</tr>
<tr>
<td>PMMA</td>
<td>PS/PMMA</td>
<td>2400</td>
<td></td>
<td>1.07</td>
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<td>75200</td>
<td>225000</td>
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<td>Aldrich</td>
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<td>33300</td>
<td>112000</td>
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<td>Polysciences</td>
</tr>
</tbody>
</table>

The PS/PMMA blends were cast from a 3% solution of the polymers in THF and vacuum dried at 70°C. The samples were then held in capillary tubes at the required temperature in the single phase region. The PS/PVME blends were prepared by casting from a co-solvent of toluene and vacuum drying at 70°C. The samples were used as prepared at room temperature. The phase behaviour of the blends was established using thermo-optic procedures. The PS/PMMA shows the expected upper critical solution temperature (UCST) behaviour while PS/PVME shows the lower critical solution temperature (LCST) type phase behaviour.

3. Experimental

In the case of the PS/PVME blends, samples in the form of thin slabs, thickness ~1 mm, were used for the x-ray scattering measurements. X-ray scattering data were obtained using a symmetrical transmission diffractometer equipped with an incident beam monochromator and pinhole collimation. Intensity data were recorded on an equally intervalled Q scale where \( Q = 4\pi \sin \theta / \lambda \), where \( \theta \) is the scattering angle and \( \lambda \) is the incident x-ray wavelength from \( Q = 0.2 \) to 6.2 Å\(^{-1}\) in steps of \( \Delta Q = 0.02 \) Å\(^{-1}\). Count times were selected such that the standard deviation in the intensity data was always less than 1%. These data were corrected for the effects of absorption, polarisation, multiple and incoherent scattering and scaled to electron units using procedures detailed elsewhere [6,7]. The data presented below is the reduced intensity function, that is the scaled and corrected data from which the self-scattering has been subtracted. For the PS/PMMA samples, x-ray scattering data were obtained from samples held in 1mm Lindemann glass capillary tubes mounted within an oven which controlled the temperature to ±0.5°C. The scattering geometry was essentially that used for the PMMA/PS samples, except that the sample did not rotate as in the case of the symmetrical system described above.
Figure 1. Scaled and corrected reduced intensity curves for miscible blends of PS/PMMA

4. Results and Discussion

Figure 1 shows the scaled intensity functions $I(Q)$ for the set of miscible PMMA/PS. The PS system exhibits a broad peak $\sim 1.3 \text{ Å}^{-1}$ arising largely from interactions between phenyl groups and a rather weak peak at $0.7 \text{ Å}^{-1}$, sometimes dubbed the polymerisation peak. This arises from larger scale interactions [8]. PMMA exhibits a rather different scattering curve with a broad interchain peak at $Q \sim 1.0 \text{ Å}^{-1}$ and two intrachain peaks which arise from the curved nature of the chain segments [9]. The scattering patterns for the blends show a continuous transformation between those of the parent polymers. The curves are the scaled and corrected intensity functions from which the self or independent scattering has been subtracted. Despite the rather diffuse nature of the scattering it is clear that different polymer blends, even those of closely related composition, exhibit variations in the scattering curves.

For a multiple component system we can group the contributions in a convenient manner. For example, in a simple binary elemental fluid it is useful to write the observed scattering $I(Q)$ in terms of four partial structure factors $S_{ij}(Q)$ which arises from the correlations between AA, AB, BA and BB. Using the indices i and j to sum over A and B this takes the form:

$$I(Q) - <f^2(Q)> = \sum_i \sum_j f_i f_j c_i c_j S_{ij}(Q)$$
Figure 2. Partial Structure Factor for PS obtained from the data shown in Figure 1 for the miscible blends of PS/PMMA

where $f_{ij}$ are the scattering lengths, $c_{ij}$ are the number densities of atoms types, i and j in the sample. The second term on the left hand side of the above equation is the self-scattering component and does not carry any static structural information. In a consideration of the local structure of a binary polymer blend we can identify the chain segments as the key structural units. Accordingly we write the observed structure factors in terms of partial structure factors which arise from correlations between atoms in the same type of segment of an inter nature. Features of an intra segment nature will scale as $c_i$. In principal the most direct approach to obtaining the partial structure factors from experimental observations is through the use of isotopic substitution and neutron scattering, i.e., modification of the scattering lengths $f_{ij}$ and indeed such work is in progress [3]. In this study we explore the possibility of extracting the partial structure factors by using data with different compositions, i.e., by varying $c_{ij}$. We obtain the partial structure factors by considering experimental data obtained with blends of closely related compositions and solving the linear set of equations defined in the above equation. Of course such an approach requires the partial structure factors to be invariant with composition or at least to change slowly with composition. We have a numerical procedure based on a singular value decomposition technique to solve the linear equations at each value of $Q$. All sets of data for each $Q$ value are considered independently and hence the nature of the partial structure factors themselves provides a useful diagnostic to the procedures and to the correctness of the assumptions made with respect to the composition dependence. The approach depends heavily on high quality data with a high signal/noise ratio.
Using the data shown in Figure 1 we have obtained through the procedures described above, the partial structure factors for the miscible PS/PMMA system. Figure 2 shows the partial structure factor for PS for a number of different compositions from 90 to 50% PS. Our interest focuses on the peaks in the region 0.5 to 2Å⁻¹ since this contains features which are of interchain origin. A series of rather similar structure factors is obtained in that the positions of the diffuse peaks and their intensity ratios are similar. The peak intensity of the broad peak centered on ~ 1.3 Å⁻¹ increases with increasing PMMA content and the width of the peak increases by ~ 15%. In Figure 3 we plot this peak intensity as a function of the composition and the increase in intensity is easily confirmed. We have also plotted in Figure 3 the equivalent results from an analysis of a series of phase separated blends of PMMA/PS. Clearly the expectation would be that this approach would not work since we expect the observed structure factor to vary as cᵢ rather than as cᵢ² and the data shown in Figure 4 reflects this expectation. There is a clear increase in the peak intensity for the PS structure factor and this line of data represents one limiting case of more or less complete non-mixing. In fact, we would expect the intensity ratio to be 2 for 50% PS, and the lower value of 1.85 may arise due to interfacial interactions if the domain size in the phase separated system is small. The data for the miscible PS/PMMA lies below this limiting case but not on the expected unity ratio line. This suggests that there is only limited local mixing even in the miscible state. At higher concentrations of PMMA the assumption of slowly changing partial structure factors breaks down and the numerical solutions are no longer meaningful.
PS/PMMA blends, at 30 °C

Figure 3. A plot of the intensity at Q=1.3Å⁻¹ of the PS partial structure factor as a ratio to the structure factor for PS (Filled circles correspond to the phase separated system and the open circles to the miscible blend samples) for the PS/PMMA blends.

Figure 4 shows the scaled data obtained for miscible PS/PVME blends. There is a smooth transition from the characteristic peaks of PS to the those of PVME. Figure 5 shows the PS partial structure factors obtained for the PS/PVME system.
The reduced structure factor for miscible PS/PVME blends

Figure 4. Scaled and corrected reduced intensity data from miscible blends of PS and PVME
Figure 5. PS partial Structure Factors obtained from the data in Figure 4

Figure 6. A plot of the intensity at $Q=1.3\text{Å}^{-1}$ of the PS partial structure factor as a ratio to the structure factor for PS for the PS/PVME miscible blends
In contrast to the PS/PMMA system, reasonable structure factors are obtained at all compositions. This, in itself, suggests that the PS/PVME blends follow rather different mixing rules than the PS/PMMA system. We have plotted the peak intensities of the partial structure factors for PS in Figure 6.

The data presented in Figure 6 are clearly very different from that displayed in Figure 3. The continuous reduction in the ratio of the partial structure to that of the pure component with increasing concentration of PMMA indicates a more extensive local mixing than that exhibited by the PS/PMMA system. Of course with the PS structure factors at Q=1.3Å⁻¹ there will be element of intrachain scattering and the scaling used for the coefficients in the linear equations will be inappropriate. However, this would tend to overestimate the partial structure factor (as in the case of phase separated PS/PMMA mixtures) and thus the real reduction of the structure factor with composition may be more substantial. Analysis by Dudowicz and Freed [10] of small-angle neutron scattering has suggested that PVME is a very good solvent for PS since the PS chain dimensions expand on mixing. The data shown in Figure 6 support this notion in that clearly the PS segments are favouring PS-PVME interactions at the expense of PS-PS interactions. In other words there is clear mixing of the PS with PVME.

5. Summary
We have explored the possibility of extracting partial structure factors from a series of miscible blends through the use of the composition dependence of the observed scattering. The preliminary results are encouraging and we plan to apply the procedures to a broader range of polymers. Clearly, the mixing in PS/PMMA single phase blends is less than random, whilst the mixing in PS/PVME suggests a strong preference for PS-PVME interactions rather than PS-PS contacts.

6. Acknowledgements
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References

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5. C.C.Han et al Polymer 29 2002 (1988)