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Spin-label study of immiscible polymers: 5. Blends of labelled poly(2-ethyl hexyl methacrylate) with poly(methyl methacrylate) and polystyrene

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The electron spin resonance (e.s.r.) spectra of poly(2-ethyl hexyl methacrylate) (PEHMA) spin-labelled with nitroxide end groups were recorded over a temperature range for both the pure, bulk polymer and for 1 : 1 (w/w) immiscible blends with poly(methyl methacrylate) (PMMA) and polystyrene (PS). Both PMMA and PS have significantly higher glass transition temperatures than PEHMA, with which they are immiscible. Nevertheless, the glassy component of these blends exerts a retarding effect on the motion of a portion of the spin labels on the PEHMA, as evidenced by the presence of a persistent slow-motion component in the e.s.r. spectra of the blends. These experiments complement our earlier work in which the spin label was attached to the chain ends of the glassy component in a binary blend. The results support our previous conclusion that in a blend of two immiscible polymers, chain ends tend to congregate in the interphase where they experience the combined influences of accumulated free volume and the presence of the other polymer.

(Keywords: immiscible polymers; blends; spin labelling)

INTRODUCTION

Previous papers in this series have reported spin-label investigations on both the polystyrene (PS)–polyisoprene (PIP) system[1,2] and the poly(methyl methacrylate) (PMMA)–poly(2-ethyl hexyl methacrylate) (PEHMA) system[3]. These pairs of polymers were chosen initially because of some technical importance (PS–PIP), but also because the respective components in each blend are immiscible on a macroscopic scale[4] and have widely differing glass transition temperatures, T_gs (T_g for PS is 370 K and for PIP is 200 K; similarly T_g for PMMA is 378 K and for PEHMA is 265 K). The latter reason is of fundamental importance because any significant interaction between any of the respective pairs of polymers was expected to lead to partial plasticization of the high T_g component (PS or PMMA) by the lower T_g component (PIP or PEHMA) and hence to a detectable influence in the electron spin resonance (e.s.r.) spectrum of the labelled component.

In each investigation[1–3], the high T_g component was labelled both at chain ends and at in-chain positions with a stable nitroxide radical. The evidence from the spin-label experiments carried out on these two systems revealed that the mobility of a proportion of chain ends of the high T_g component was greatly enhanced by the presence of the second lower T_g component. These observations are a result of a thermodynamic driving force towards enrichment with chain ends of the so-called interphase region, which exists between two immiscible polymers, in accord with the model of the interphase described by Helfand and co-workers[5–7]. Observed changes in the e.s.r. spectra of end-labelled PMMA in blends with unlabelled PEHMA and with PS led to the conclusion that, concomitantly with the accumulation of chain ends in the interphase, free volume also concentrates in this region[3]. The enhancement of free volume at the interphase has been given theoretical support from Monte Carlo calculations performed on blends of immiscible polymers[8].

The present paper is concerned with complementary experiments in which the low T_g component (PEHMA) is labelled, at both chain ends and in-chain positions, with a nitroxide radical.

EXPERIMENTAL

Preparation of end-labelled PEHMA (*Structure 1*) was accomplished as for PMMA[3] by group transfer polymerization[9]. Gel permeation chromatography (g.p.c.) (PS standards, run in chloroform with toluene as the flow-rate marker) of end-labelled PEHMA indicated a molar mass (M_n) of 31 700 g mol^{-1} and

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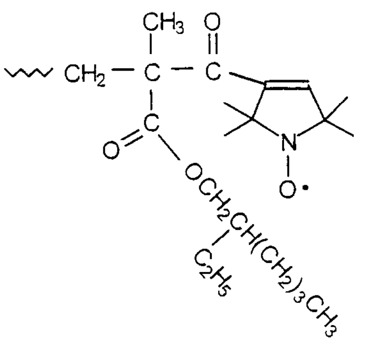
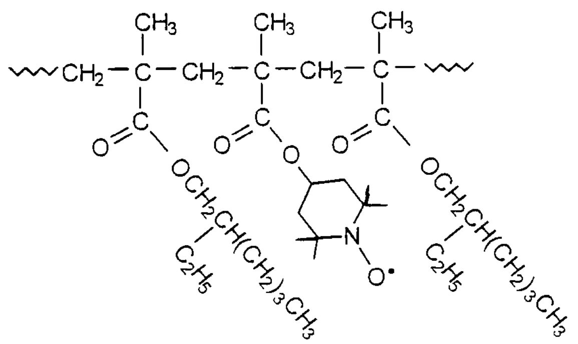


Structure 1 Nitroxide end-labelled PEHMA



Structure 2 PEHMA labelled at in-chain positions

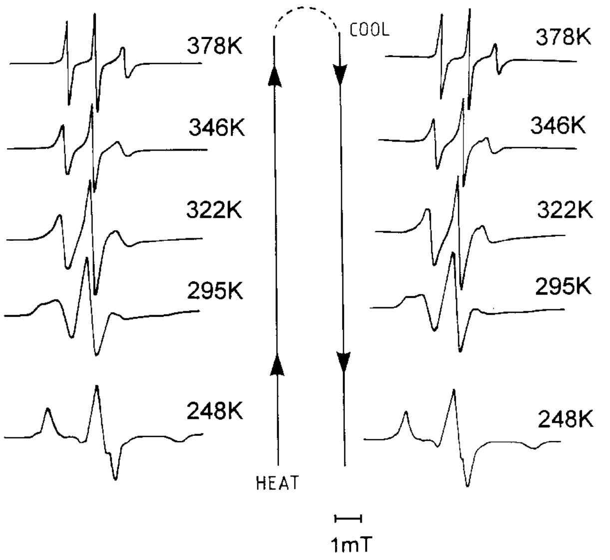


Figure 1 E.s.r. spectra of pure PEHMA with nitroxide end labels of the type shown in *Structure 1*

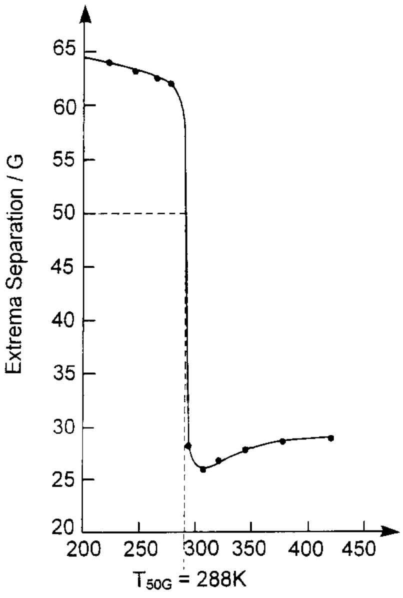


Figure 2 Plot of extrema separation *versus* temperature for pure end-labelled PEHMA, illustrating T_{50G} at 288 K

dispersity index of 1.44. The unlabelled PMMA sample prepared had a M_n of 13 900 g mol^{-1} and a dispersity index of 1.29.

PEHMA labelled at in-chain positions (*Structure 2*) was prepared according to the method described by Elsom[10] and as outined in the previous paper[3]. The value of M_n, by g.p.c., of the in-chain labelled sample was 33 100 g mol^{-1}.

All blends were prepared by freeze-drying a 1% co-solution of the respective polymers in benzene. E.s.r. spectra were recorded with a Varian E-109 e.s.r. spectrometer equipped with a variable temperature accessory.

RESULTS AND DISCUSSION

Figure 1 illustrates the e.s.r. spectra of pure, end-labelled PEHMA in the temperature range 248–378 K. At the lower end of this range a typical broad-line, slow-motion spectrum, with an extrema separation of *c.* 65 G (10 G = 1 mT) is observed. Upon heating, the outer extrema in the spectrum move inwards and eventually the spectrum collapses to the familiar motionally narrowed form, with an extrema separation of *c.* 25–30 G. Such changes in the extrema separation with temperature, which are typical of a nitroxide spin-labelled or spin-probed polymeric material[11] are illustrated in a plot of extrema separation *versus* temperature (*Figure 2*), from which a value of *c.* 288 K was estimated for T_{50G} (the temperature at which the extrema separation is 50 G[11]). The spectral changes in *Figure 1* were completely reversed on cooling and all the spectra are exactly reproduced at particular temperatures upon repetition of the heat-cool cycle.

The e.s.r. spectra of end-labelled PEHMA in a 1 : 1 (w/w) freeze-dried blend with unlabelled PMMA are illustrated in *Figure 3*. These spectra differ in a number of significant ways from those of unblended, end-labelled PEHMA (*Figure 1*). First, the gradual inward shift and narrowing of the outer lines shown in *Figure 1* does not occur. Instead, we see the persistence of a slow-motion spectrum to relatively high temperatures and the appearance of a second, fast-motion component starting at *c.* 333 K. Thus, instead of a single spectrum at each temperature, as occurs in *Figure 1*, the spectra of the blend above *c.* 333 K become composite spectra consisting of a slow-motion and a fast-motion component. The latter increases in intensity, at the expense of the slow-motion component, with increasing temperature until at 402 K the spectrum appears to consist almost entirely of the motionally narrowed form. (However, computer simulations show that spectra such as that at 402 K may contain as much as 30% slow-motion component[12].)

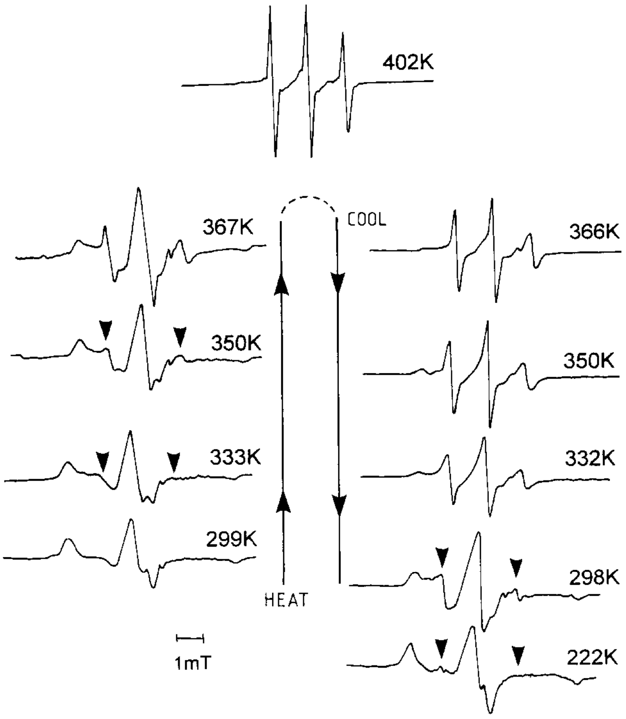


Figure 3 E.s.r. spectra of a 1 : 1 (w/w) freeze-dried blend of end-labelled PEHMA and unlabelled PMMA. Arrows indicate the appearance of a motionally narrowed component

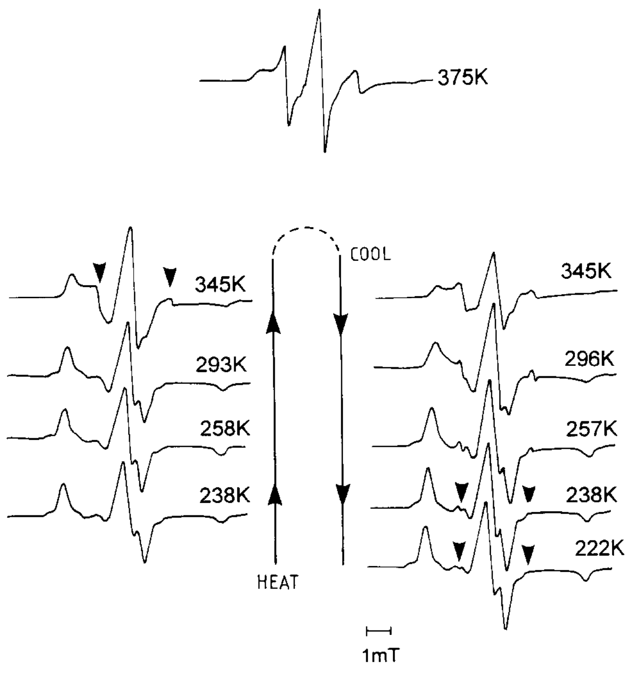


Figure 4 E.s.r. spectra of a 1 : 1 (w/w) freeze-dried blend of end-labelled PEHMA and unlabelled PS. Arrows indicate the appearance of a motionally narrowed component

Second, unlike the spectra in *Figure 1*, at any specified temperature the spectra in *Figure 3* differ depending on whether they were recorded on the heating or the cooling part of the cycle (see, for example, the two spectra at 350 K in *Figure 3*). It is particularly noteworthy that the fast-motion component is still visible in an otherwise slow-motion spectrum as low as 222 K, well below the T_g of PEHMA. On reheating, this fast-motion spectrum builds up again rapidly. Indeed, after heating the blend to 402 K it appears that the system is close to thermodynamic equilibrium since the spectra on the right-hand column of *Figure 3* are reproduced simply by setting the temperature. However, at any specified temperature, the proportion of slow motion in the spectra in *Figure 3* is always greater than it is in *Figure 1*, thus providing evidence that the glassy PMMA exerts a stiffening effect on a proportion of chain ends of the more flexible PEHMA. This is precisely the converse of the plasticizing effect observed when PEHMA was blended with end-labelled PMMA[3] and is wholly in accord with our interpretation that such effects derive from a mutual interaction of chain segments, particularly chain-end segments, in the interphase.

The persistence of a very small proportion of the fast-motion spectrum down to as low as 222 K is not inconsistent with the above interpretation and can be accounted for by a small proportion of nitroxide end labels occupying regions of relatively high free volume in the interphase. It has already been shown that the mobility of labelled chain ends of polymer A in the interphase is influenced by two factors: the existence of segments of polymer B and the concentration of free volume in the interphase. When polymer A is glassy and polymer B is rubbery, the latter exerts a plasticizing influence on polymer A so that the two factors reinforce each other. However, when polymer A is rubbery and polymer B is glassy, as in the present case, the two factors oppose each other. At temperatures as low as 222 K both polymers are in a glassy state and hence the free volume effect can be seen in isolation. Interestingly, the rapid-motion components in both systems–end-labelled PMMA/unlabelled PEHMA[3] and end-labelled PEHMA/unlabelled PMMA–are just visible at *c*. 220 K.

Replacing PMMA by PS as the glassy component of a blend with end-labelled PEHMA produces spectra (*Figure 4*) broadly similar to those in *Figure 3*. In particular, the spectra consist mainly of a superposition of fast- and slow-motion spectra. The persistence of the latter, even at relatively high temperatures, indicates, as before, the stiffening of a proportion of the labelled chain ends by the glassy polymer, and the persistence of the former down to very low temperatures indicates the presence of free volume in the interphase. Again, the rapid-motion component is just visible at 222 K.

In an earlier paper[2] we used the value of T_{50G} of blends of the immiscible pair PS/PIP, where the chain ends of the PS were labelled, to calculate the composition in the interphase in the region of PS chain ends. This calculation, however, took no account of any contribution to chain-end mobility other than the presence of the rubbery component PIP. The existence of a free-volume effect shown here and in the preceding paper[3] shows that such calculations are invalid, and accordingly the figures quoted in the earlier paper on PS/PIP blends[2] are meaningless.

The mutual interaction of the polymers in the interphase can only be observed (in the e.s.r. experiment) when the spin label is situated at the chain end. *Figures 5* and *6* are sets of spectra of PEHMA labelled with nitroxide groups in the side chain in the pure and blended (50 : 50 with PMMA) states, respectively. The two sets of spectra are virtually identical. There are

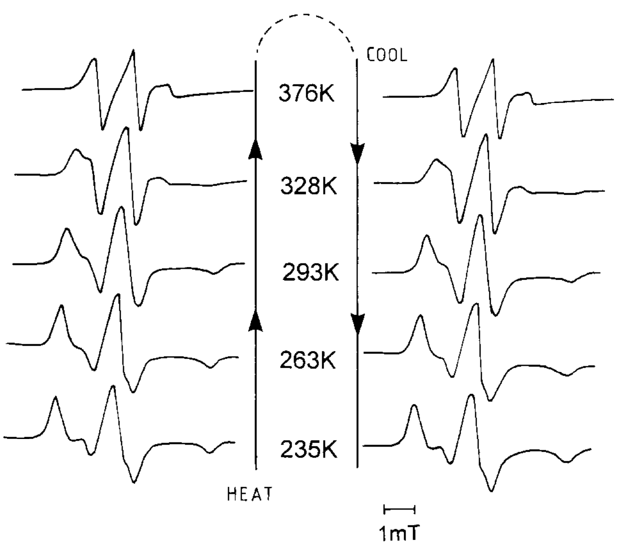


Figure 5 E.s.r. spectra of pure PEHMA labelled at in-chain positions, as illustrated in *Structure 2*

neither signs of stiffening nor of the persistent narrow lines which reveal free volume in the interphase.

CONCLUSIONS

The spin-label experiments with blends containing end-labelled PEHMA provide support for the conclusions in our earlier papers[1–3], namely that in binary blends of immiscible polymers, chain ends of each type tend to migrate to the interphase, where they experience the combined effects of accumulated free volume and the presence of the second polymer. Our results are consistent with the theoretical predictions of Helfand and co-workers[5–7] and Karasz[8].

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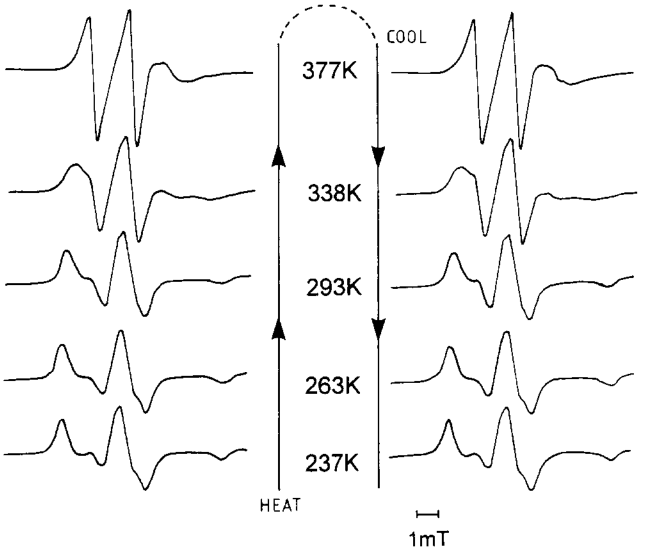

Figure 6 E.s.r. spectra of a 1 : 1 (w/w) freeze-dried blend of in-chain labelled PEHMA and unlabelled PMMA

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