Spin-label study of immiscible polymers: 4. Location of chain ends in blends of poly(methyl methacrylate) and poly(2-ethylhexyl methacrylate)

G. G. Cameron* and D. Stewart
Department of Chemistry, University of Aberdeen, Aberdeen AB9 2UE, UK

and R. Buscall and J. Nemcek
I.C.I. plc, Corporate Colloid Science Group, PO Box 11, The Heath, Runcorn WA7 4QE, UK
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The electron spin resonance (e.s.r.) spectra of nitroxide end-labelled poly(methyl methacrylate) (PMMA) were recorded over a temperature range for the pure, bulk polymer and for 1:1 (w/w) immiscible blends with poly(2-ethylhexyl methacrylate) (PEHMA) and polystyrene (PS). The changes in the e.s.r. spectra brought about by blending and varying the temperature show that chain ends tend to congregate in the interphase region. In the blends of PMMA and PEHMA the chain ends of the PMMA in the interphase are mobilized through plasticization by the rubbery PEHMA. This phenomenon was observed previously in blends of end-labelled PS with unlabelled polyisoprene. Our present results, particularly from the PMMA–PS blends, reveal that an additional enhancement of mobility of chain ends results from the accumulation of free volume in the interphase.

(Keywords: immiscible blends; poly(methacrylates); spin labelling)

INTRODUCTION

Previous papers in this series have reported spin-label investigations on blends of polystyrene (PS) and polyisoprene (PIP)[1,2]. In these studies the PS component was labelled both at chain ends and at in-chain positions, with a nitroxide group. This pair of polymers was chosen because it has some technical importance and also because the two polymers are immiscible on a macroscopic scale[3] and have widely differing glass transition temperatures (T_g). The last reason is of fundamental importance because any significant interaction in a blend of the two polymers was expected to lead to partial plasticization of the PS by the PIP and hence to a detectable influence on the electron spin resonance (e.s.r.) spectrum of labelled PS.

Some interaction was indeed detected in a 1:1 (w/w) freeze-dried blend of end-labelled PS and unlabelled PIP, a proportion of the PS chain ends being rendered more mobile by the low-T_g PIP component. The effect was manifest by the appearance of a motionally narrowed component in the e.s.r. spectrum of the blend at temperatures significantly lower than in pure, bulk PS. The changes observed in the e.s.r. spectra of this blend upon heating were found to be incompletely reversed on cooling, in contrast to what was observed in the spectra of pure PS. The motionally narrowed component persisted on cooling to temperatures well below those at which it was first detected during the initial heat-up procedure and reappeared strongly when reheated[2]. These observations indicate that, upon heating, the original freeze-dried blend reorganizes itself in such a way that more nitroxide-labelled PS chain ends are located in a PIP-rich environment, the so-called interphase region. No similar observations were noted when the end-labelled PS was replaced by a PS sample that was labelled at in-chain positions. Interfacial tension measurements[3] and spin-probe experiments[1] suggested that the interphase was a favoured location for all PS chain ends and not just those carrying nitroxide groups.

These conclusions were interpreted in terms of the theoretical predictions of Helfand on the structure and composition of the interphase region in a blend of two immiscible polymers[4–6]. The spin-label experiments are the first to provide experimental support for Helfand's theory.

In the current work we report a similar study on a two-phase system comprising the two polymers, poly(methyl methacrylate) (PMMA) and poly(2-ethylhexyl methacrylate) (PEHMA), which have structures completely different from those of PS and PIP. However, as before, these were chosen because they are immiscible and have widely differing T_g values (ca. 378 K for PMMA and ca. 263 K for PEHMA). For the first part of this study the PMMA was labelled at chain-end or in-chain positions; the PEHMA was unlabelled.

* To whom correspondence should be addressed

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EXPERIMENTAL

All the methacrylate polymers, with the exception of PMMA labelled at in-chain positions, were prepared by group-transfer polymerization (GTP), according to the method described by Webster *et al.*[7]. The monomers (MMA and EHMA) were distilled twice under vacuum and stored over calcium hydride. Prior to use they were passed through a column of activated alumina (Fisons, Brockmann Type 1, neutral, preheated to 373 K under vacuum for 24 h).

Tetrahydrofuran (THF; BDH, Analar grade) was fractionally distilled from calcium hydride and stored over sodium/benzophenone. Prior to use it was redistilled under vacuum.

Methyl trimethylsilyl dimethylketene acetal (TMS; Aldrich) was distilled twice under vacuum and stored under an atmosphere of dry nitrogen.

Tetrabutylammonium fluoride (TBAF; Aldrich) was used, without further purification, as the catalyst. All polymerizations were carried out in a dry-box flushed with dry nitrogen.

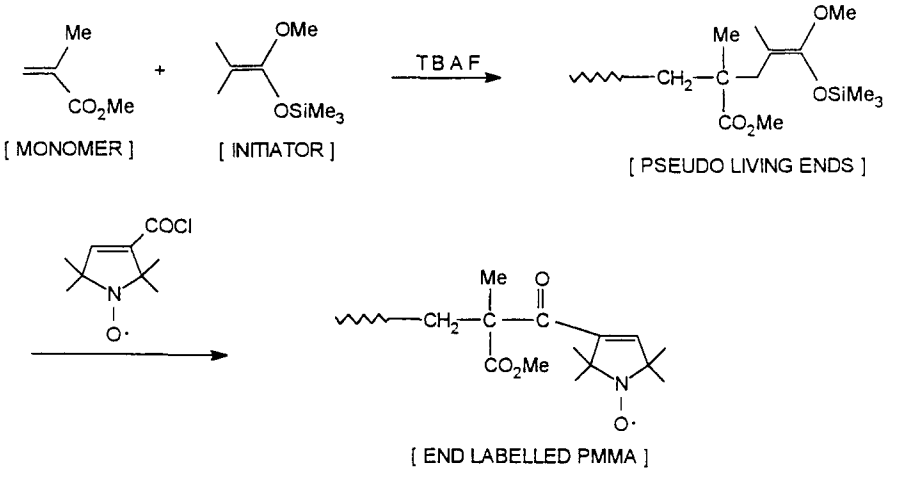
The PEHMA was prepared by terminating with the addition of a 10-fold excess of methanol, whilst nitroxide end-labelled PMMA was prepared by terminating with a benzene solution of 3-chloroformyl-2,2,5,5-tetramethyl-pyrroline-1-oxyl (CHTPO), prepared according to the method of Rozantsev[8]. The reaction sequence is outlined in *Scheme 1*. Gel permeation chromatography (g.p.c.) (PS standards, run in chloroform solution with toluene as the flow-rate marker) of end-labelled PMMA prepared in this way indicated a molar mass (M_n) of 15 300 g mol^{-1} and a dispersity index of 1.16. The unlabelled PEHMA sample had a M_n of 38 500 g mol^{-1} and a dispersity of 1.29.

PMMA labelled at in-chain positions was prepared according to the method described by Elsom[9], outlined in *Scheme 2*. The value of M_n, by g.p.c., was 23 600 g mol^{-1} and the dispersity 1.47.

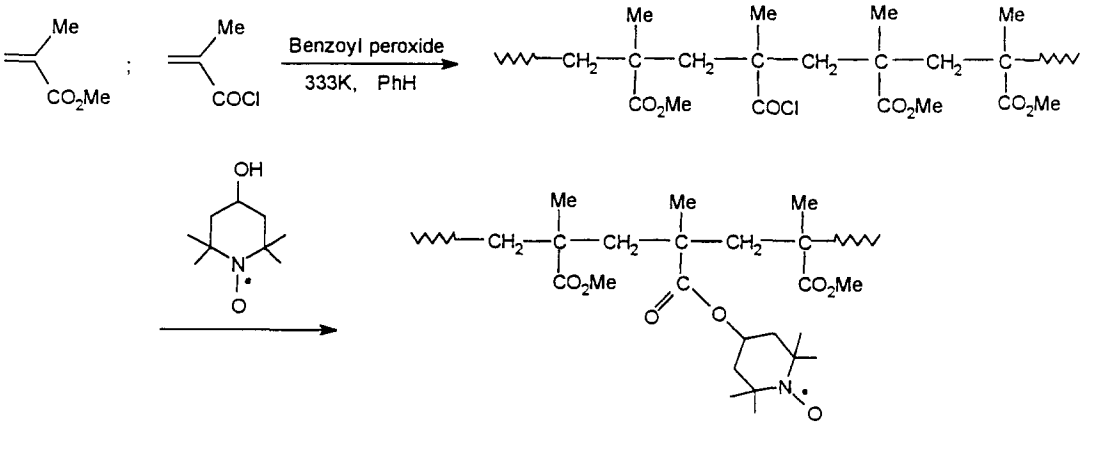
All blends were prepared by freeze-drying a 1% co-solution of the respective homopolymers in benzene. Electron spin resonance (e.s.r.) spectra were recorded with a Varian E-109 ESR spectrometer with variable-temperature accessory.

RESULTS AND DISCUSSION

Figure 1 illustrates the e.s.r. spectra of pure, end-labelled PMMA in the temperature range 248–409 K. These spectra are all of the slow-motion variety, and all the spectral changes brought about by heating are completely reversed on cooling. No signal was detected at temperatures above 410 K because of decay of the nitroxide moiety.



Scheme 1



Scheme 2

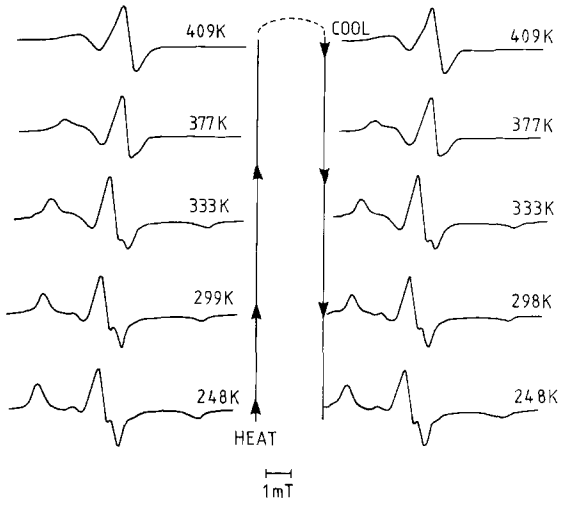


Figure 1 E.s.r. spectra of pure PMMA with nitroxide end labels of the type in *Scheme 1*

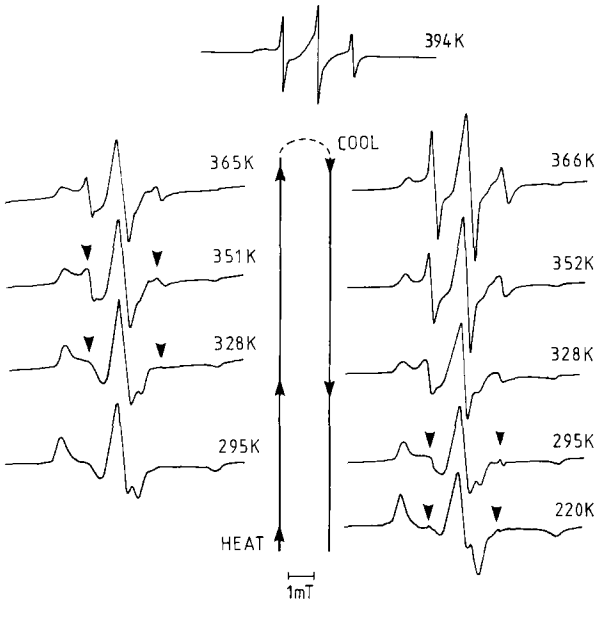


Figure 2 E.s.r. spectra of a 1:1 (w/w) freeze-dried blend of end-labelled PMMA and unlabelled PEHMA. Arrows indicate the appearance of a motionally narrowed component

The e.s.r. spectra of end-labelled PMMA in the 1:1 (w/w) freeze-dried blend with unlabelled PEHMA are illustrated in *Figure 2*. Clearly these are not all of the slow-motion type, and the spectral changes are strongly dependent on the thermal history of the sample. As the sample is heated, a motionally narrowed component appears at ca. 328 K in the spectra of the blend. The intensity of the narrow-line component increases with increasing temperature until the spectrum is almost entirely of the motionally narrowed type at 394 K, just above T_g of PMMA. On subsequent cooling the motionally narrowed component persists at a greater intensity than during the heat-up phase in the cycle, and is still detectable at temperatures where the sample showed only a slow-motion spectrum during the initial heat-up. Significantly, even at ca. 220 K, well below the T_g of PEHMA, the motionally narrowed component is still visible.

Clearly the low-T_g component (PEHMA) exerts a plasticizing effect on the nitroxide-labelled PMMA chain ends, and since the pair of polymers is immiscible we must suppose that the plasticized nitroxide end labels are located in the interphase. On heating to T_g of PMMA, there is an increase in the proportion of nitroxide groups in the interphase as the blend approaches a state of thermodynamic equilibrium. (Freeze-dried blends are generally well removed from thermodynamic equilibrium.)

Figures 3 and *4* show the e.s.r. spectra of PMMA labelled at in-chain positions both in the pure state and in a 1:1 (w/w) blend with unlabelled PEHMA respectively. In both cases the spectra are essentially all of the slow-motion variety, although at elevated temperatures the spectra of the blend exhibit a small motionally narrowed component. In both figures the spectral changes are reversed completely on cooling and are reproduced exactly on repeating the heat–cool cycle. This behaviour contrasts sharply with what was observed when the PMMA was labelled at chain ends. The small motionally narrowed component in the spectra of *Figure 4* is attributable to a small, but constant, concentration of labelled inner segments in the interphase. There is no evidence to suggest that nitroxide groups in inner segments migrate to the interphase. Indeed, calculation

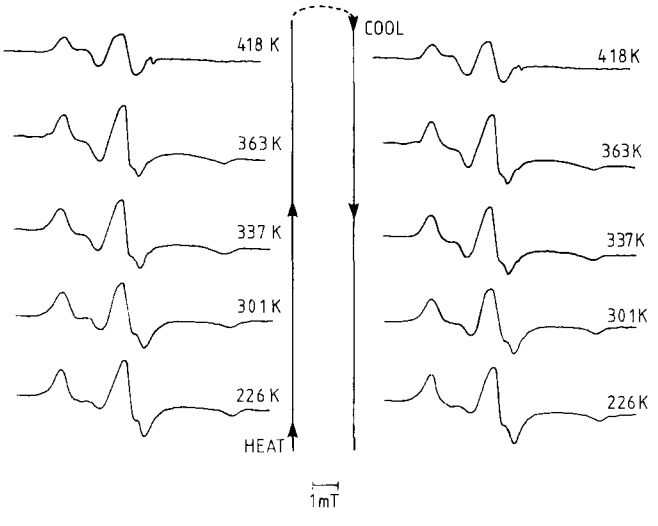


Figure 3 E.s.r. spectra of pure PMMA labelled at in-chain positions, as shown in *Scheme 2*

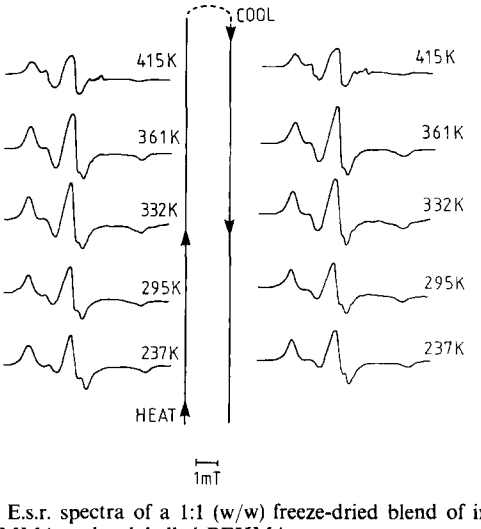


Figure 4 E.s.r. spectra of a 1:1 (w/w) freeze-dried blend of in-chain labelled PMMA and unlabelled PEHMA

of the solubility parameter of both the chain-end and in-chain nitroxides, according to the method of Small[10], gave values of 9.98 and 9.87 (cal $cm^{-3})^{1/2}$ respectively, both of which are closer to the literature value for PMMA (9.6 (cal $cm^{-3})^{1/2}$) than that for PEHMA* (8.4 (cal $cm^{-3})^{1/2}$)[11]. Thus, the migration of nitroxide groups to the interphase occurs not because of their particular chemical structure but because they are located at chain ends.

These observations are an almost exact replica of what we observed with the PS–PIP system[1,2] and lead us to the same conclusion, namely that in a blend of immiscible polymers the interphase is a more thermodynamically favourable location for chain ends than for in-chain segments. This conclusion accords with the theoretical predictions of Helfand[4–6]. Because there are fewer constraints on the mobility of chain ends compared with internal segments, the entropy of mixing at the interphase is maximized if chain ends, rather than in-chain segments, concentrate there. This is the origin of the thermodynamic force that drives chain ends to the interphase at the expense of other segments.

As mentioned above, the motionally narrowed component that appears in the e.s.r. spectra of the blend with end-labelled PMMA (*Figure 2*) persists on cooling to ca. 220 K, a temperature well below the T_g (ca. 263 K) of the rubbery PEHMA. This surprising observation may be explained as follows. Since the interphase is enriched with chain ends at the expense of internal segments, then it follows that the interphase must possess a proportionately greater free volume than either of the two bulk phases. Thus, the interphase is a region where molecular and segmental motion (including motion of the nitroxide-labelled chain ends) is relatively unhindered. It is noteworthy that Monte Carlo calculations on blends of two immiscible polymers have predicted such an accumulation of free volume at the interphase[12].

If this model of the structure of the interphase is valid, then we should observe the effect of free volume at the interphase in blends of other pairs of immiscible polymers. Thus, in favourable circumstances, the e.s.r. experiment might show the existence of free volume in a blend of two polymers each with comparable T_g values. This idea is put to the test in *Figure 5*, which shows spectra of a 1:1 (w/w) blend of end-labelled PMMA and unlabelled PS (T_g ca. 370 K). As the temperature of the blend is raised, a motionally narrowed component in the spectrum appears at ca. 255 K, the intensity of which increases with increasing temperature. A greater degree of fast motion is evident in the spectrum at 298 K after the sample has been heated to 376 K than was seen at this temperature before commencement of the heat–cool cycle. This observation is wholly consistent with the idea that, upon heating a freeze-dried blend, thermodynamic equilibrium is attained through enrichment of chain ends at the interphase.

The contrast between *Figure 5* and *Figure 1* (for pure end-labelled PMMA) is quite dramatic. It shows that the process of blending two glassy polymers produces a system with regions—presumably the interphase—where polymer chain ends have relatively high rotational freedom. This freedom is detectable at 120°C below the

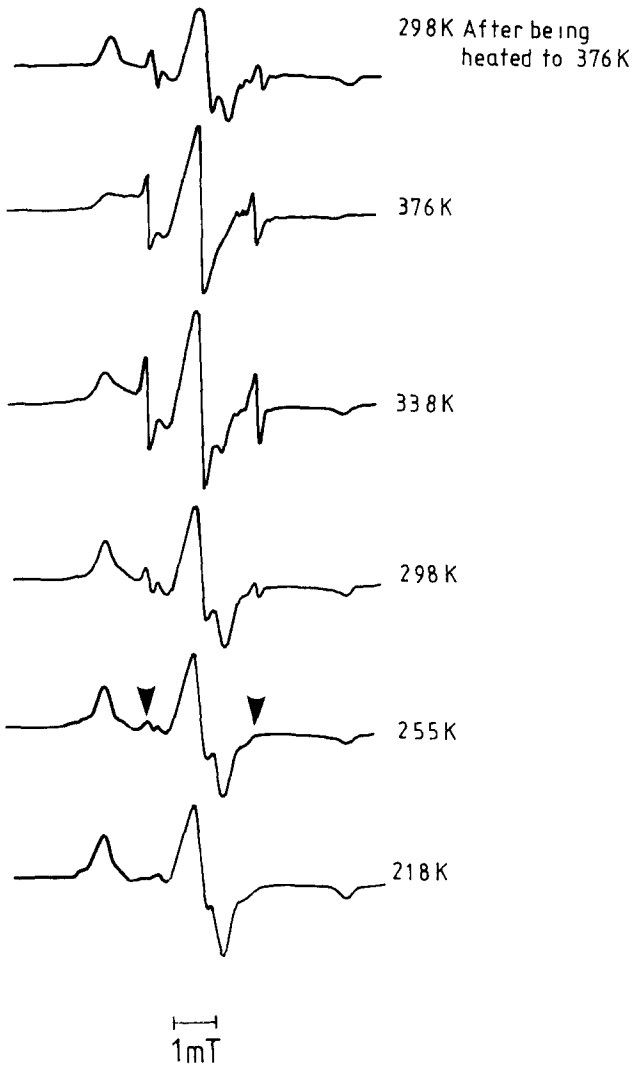


Figure 5 E.s.r. spectra of a 1:1 (w/w) freeze-dried blend of end-labelled PMMA and unlabelled PS. Arrows indicate the appearance of a motionally narrowed component

T_g values of the constituent polymers. The appearance of this motionally narrowed component in the e.s.r. spectra of the PMMA/PS system gives a 'visible' indication of the accumulation of free volume within the interphase.

Thus, there are two effects that influence the mobility of chain ends when located in the interphase region of a blend of two immiscible polymers: plasticization of the component of higher T_g by the low-T_g component (and presumably vice versa), and the accumulated free volume that results when chain ends are thermodynamically driven to the interphase. These two effects are additive and are both detectable by the above spin-label experiments.

An intriguing feature of this and the previously published paper on PS/PIP blends[2] concerns the relative proportion of fast and slowly tumbling chain ends as revealed by the e.s.r. spectra. At thermodynamic equilibrium, attained through heat treatment, the proportion of rapidly moving chain ends increases and decreases with rise and fall in temperature. Spectral simulation (by computer superposition of fast and slow spectra) indicates that the proportion of mobile chain ends may well exceed 25% at high temperatures. This observation raises the questions as to how the interphase

*No value could be found for the solubility parameter of poly(2-ethylhexyl methacrylate), so a value of 8.4 (cal $cm^{-3})^{1/2}$, the same as for structurally similar poly(octyl methacrylate), was assumed[11]

may (i) change in thickness with temperature and (ii) accommodate such a high proportion of chain ends.

These questions will be addressed in future papers, where we will also consider the correlation times of label rotation and the effects of attaching the chain-end spin label to the component of low T_g.

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