Spin-label study of immiscible polymers: 3. Location of chain ends in a blend of polystyrene and polyisoprene

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Electron spin resonance (e.s.r.) spectra of polystyrene (PS) samples labelled at chain ends or at in-chain sites with nitroxide radicals were recorded over a temperature range. Up to 423 K for the end-labelled PS and 453 K for the in-chain labelled PS, the spectra are essentially of the broad-line type and in both cases the spectral changes are reversed exactly on cooling. Both labelled PS samples were blended with polyisoprene (PIP) (1:1, w/w). The e.s.r. spectra of the blend of the in-chain labelled PS are identical to those of the bulk labelled PS. The e.s.r. spectra of the blend of the end-labelled PS reveal, as previously, that PIP plasticizes PS chain ends. Also, for this blend, the spectral changes produced on heating are not reversed exactly on cooling, and even at room temperature a motionally narrowed component persists. It appears that after heating, the original freeze-dried polymer is reorganized so that more nitroxide chain ends are located in a PIP-rich environment. It is concluded that the e.s.r. experiments confirm the theoretical prediction of Helfand that at thermodynamic equilibrium the interphase in a blend of immiscible polymers contains more than the statistical concentration of chain ends.

(Keywords: spin-labelled polystyrene; plasticization; polystyrene–polyisoprene blends)

INTRODUCTION

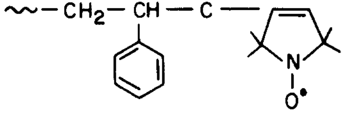
In the previous paper in this series[1] it was shown that in a blend of the immiscible polymer pair polystyrene (PS) and polyisoprene (PIP), in which the PS was terminally labelled with nitroxide groups, a proportion of the chain-end labels was plasticized by the PIP. This effect was manifest by the appearance of a motionally narrowed component in the electron spin resonance (e.s.r.) spectrum of the blend at a significantly lower temperature than occurred with the pure labelled PS. (See, for example, Figures 1 and 3 of ref. 1).

In this paper the significance of these observations is considered further. Since there is no evidence of macroscopic miscibility between PS and PIP[2] at 433 K it is most likely that the mobile chain-end labels (i.e. those with a motionally narrowed spectrum) are located in the interphase between the two polymers. We consider therefore whether these particular chain ends are located there on a purely statistical basis, i.e. whether the ratio of chain ends to inner segments of PS in the interphase is the same as in the bulk, and if not what factors, thermodynamic or other, are involved.

EXPERIMENTAL

The PIP ('Natsyn' 2200, 98% *cis*-1,4) was the same material (obtained from the Goodyear Chemical Company) as used previously[1,2].

The end-labelled PS, PS2 (M_n 50 150, M_w 58 600) with terminal nitroxide groups I



I

was prepared as described previously[1]. In the case of PS2 it was necessary to remove a small amount of high molecular weight polymer, presumably formed by coupling[1], by fractional precipitation.

The in-chain labelled PS (M_n 190 700, M_w 394 400) contained t-butyl nitroxide groups II in the *meta*-position

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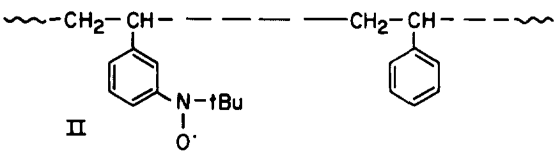
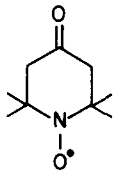
at random sites along the chain:


II

The preparation and characterization of this sample are described elsewhere[3,4].

The spin probe III, 2,2,6,6-tetramethyl-4-oxo-piperidine-1-oxyl (4-oxo-TEMPO, Aldrich) was used without purification.


III

All polymer blends were prepared by freeze drying benzene solutions as before[2]. For spin-probed samples, III was added to the benzene solution of the polymers to give a final concentration of ~170 ppm. In the spin-probe studies the PS was a g.p.c. standard (M_n 33 700, M_w 34 000) supplied by Polymer Laboratories Ltd.

For computer simulation studies the e.s.r. spectrometer (Varian E-109) was interfaced with an Apple II-Plus microcomputer which digitized and stored spectra as required[5]. For two spectra (such as in *Figures 3a* and *b*) simulated composite spectra are produced by the computer by combining the two spectra in known proportions. The proportions of the two spectra in an observed composite spectrum (such as in *Figure 4a*) are deduced when a good fit between observed and simulated spectra is obtained.

RESULTS AND DISCUSSION

Figures 1a to *d* show a series of e.s.r. spectra of the bulk PS2 and its 1:1 blend with PIP as the temperature is raised from 292 to 433 K. The spectrum of the blend shows, as before[1], a motionally narrowed component at ~420 K (*Figure 1c*) where the spectrum of the pure PS2 is still of the slow-motion type. At 433 K the differences between the spectra of the two samples are very marked, the 1:1 blend showing a strong, sharp narrow-line component, and the pure PS2 a gradual shift towards line-narrowing. On cooling from 433 K to room temperature, the spectra of the bulk PS2 are identical to those recorded during heating, i.e. the behaviour of the bulk PS2 is completely reversible. In the blend, by comparison, the spectral changes are not completely reversed on cooling; the motionally narrowed component persists and is clearly visible at temperatures where it was not detectable during the initial heat-up procedure. Thus, at room temperature after cooling from 433 K, the spectrum of the blend closely resembles the spectrum at 423 K in *Figure 1c*. The fifth pair of spectra (*Figure 1d*) was obtained by reheating to 343 K and emphasizes the contrasting behaviour of the pure PS2 and its blend — the former shows the usual slow-motion spectrum but the spectrum of the blend contains a very sharp fast-motion component. After storing the heat-treated blend under vacuum at room temperature for 1 week, the motionally narrowed component reappears on raising the temperature again to 343 K, though at a somewhat reduced intensity.

It is clear from these observations that on heating to ~430 K the blend is reorganized in such a way that more nitroxide labels end up in a region relatively rich in PIP. This could happen (i) if the volume of the interphase relative to that of the bulk PS increases on heating, or (ii) if heating allows the polymer chains to reorganize themselves so that a greater proportion of chain ends (nitroxide or otherwise) migrates to the interphase

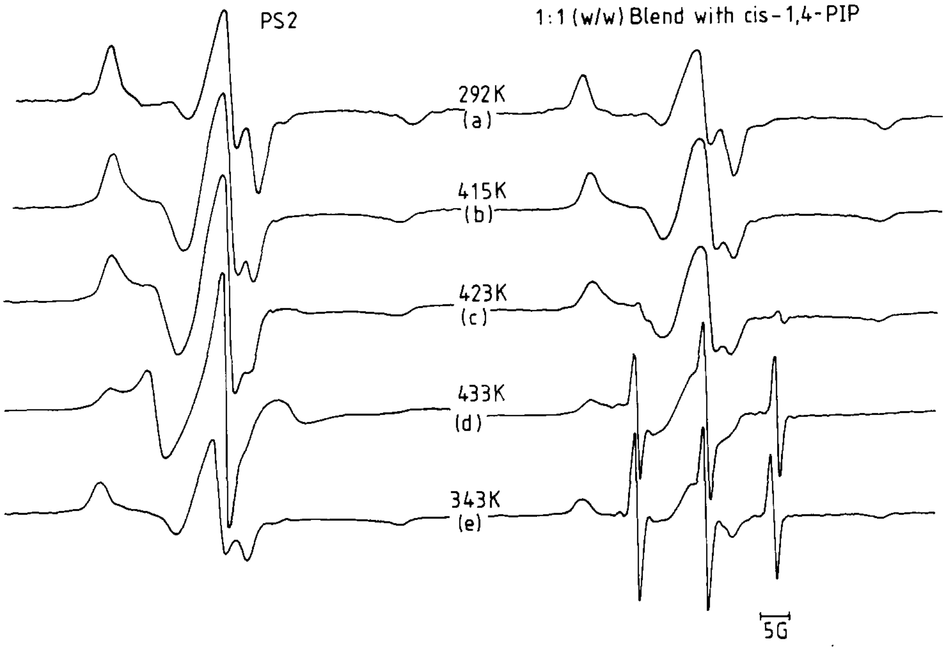


Figure 1 E.s.r. spectra of bulk end-labelled PS2 and its 1:1 (w/w) blend with *cis*-1,4-PIP: (a)–(d) temperature increased progressively from 292 K to 433 K; (e) samples heated to 433 K, cooled to room temperature then reheated to 343 K

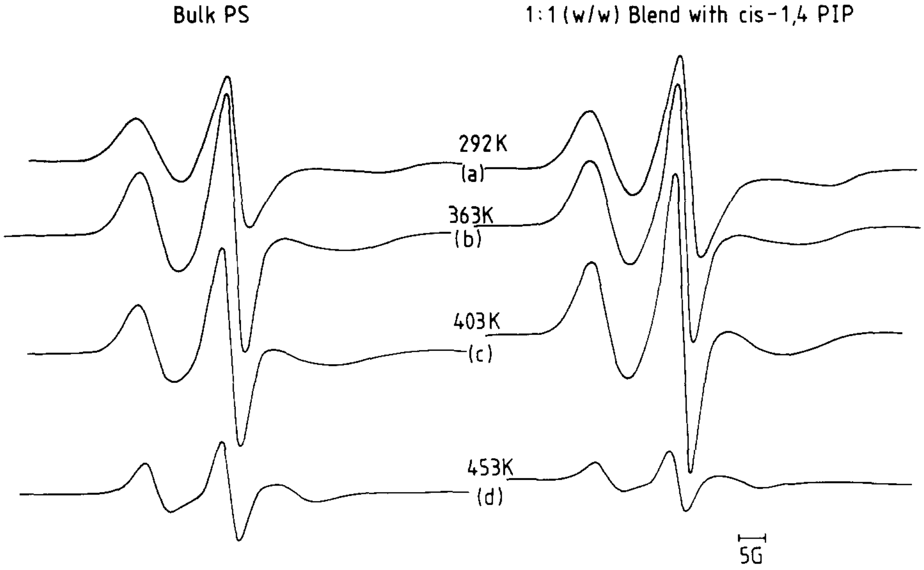


Figure 2 E.s.r. spectra of in-chain labelled PS (II) and its 1:1 (w/w) blend with *cis*-1,4-PIP: (a)–(d) temperature increased progressively from 292 to 453 K

(presumably displacing internal segments in the process).

These blends were prepared by freeze drying a homogeneous solution of the two polymers. The literature on blends of other polymers reveals that freeze drying invariably produces a much finer, and generally metastable, dispersion of the components. Raising the temperature above the higher of the two glass transition temperatures (T_g) generally produces a coarser morphology. Thus, Jachowicz and Morawetz[6] studied blends of poly(ethyl methacrylate) and poly(methyl methacrylate) (PMMA) and observed that solvent-cast films exhibited much larger domains than blends prepared by freeze drying a homogeneous benzene solution of the two polymers. In the case of PMMA and poly(vinyl acetate) it is possible to prepare a homogeneous blend exhibiting a single T_g by freeze drying. However, phase separation occurs when this blend is heated above the T_g of PMMA[7]. Similarly, a high degree of molecular mixing of the incompatible pair of PS and PMMA has been achieved by freeze drying a cosolution in naphthalene[8,9].

It is evident from these examples that the changes brought about by heating a PS–PIP blend prepared by the freeze drying technique would almost certainly result in increased phase separation with a resulting decrease in the interphase volume. (Attempts to obtain direct evidence for such a change by means of electron microscopy were inconclusive.) The increase in number of labelled chain ends which are in a relatively more mobile state after heating, as evidenced by the changes in the e.s.r. spectra of the blend, must therefore be due to migration of labelled chain ends to the interphase under the influence of some thermodynamic driving force.

Such an effect could arise if the nitroxide groups had a greater affinity for PIP than for PS, or if at thermodynamic equilibrium the interphase was relatively rich in chain ends (of any structure) at the expense of internal segments. On this point it is interesting to compare the e.s.r. spectra of the in-chain *meta*-labelled PS (*Figure 2*) with those in *Figure 1*. Between ambient temperature and 450 K there is very little change in the spectra in *Figure 2* of either the bulk PS or the 1:1 PS/PIP blend; all are of the slow-motion type and at any temperature identical pairs of spectra are recorded. In both systems the behaviour in *Figure 2* is completely reversed on cooling. Thus, there is no evidence in *Figure 2* of plasticization of the nitroxide labels by PIP — the plasticization effect of PIP can only be detected by the e.s.r. experiment if the labels are at chain ends. Attempts to reach the temperature at which motional narrowing of the spectrum of the in-chain labelled polymer occurred were frustrated by the decay of the radicals. (Note the distinct loss of signal intensity in *Figure 2* at 453 K.)

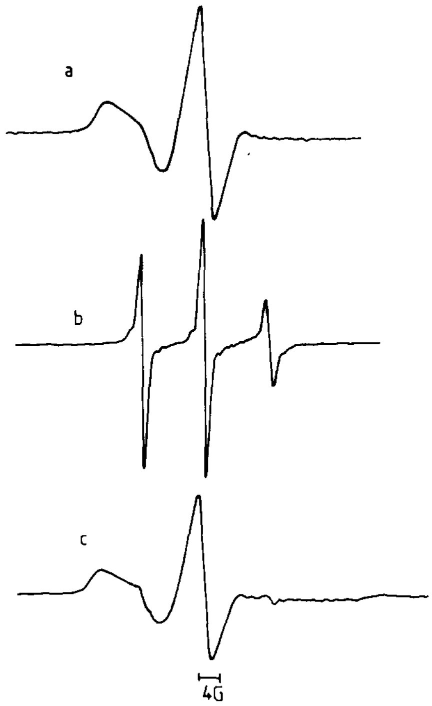


Figure 3 E.s.r. spectra at 293 K of polymer samples spin-probed with 4-oxo-TEMPO (III): (a) pure PS; (b) pure PIP; (c) 1:1 (w/w) blend of PS and PIP

The experiments on the partition of the nitroxide spin probe III between PIP and PS indicate that the probe is not preferentially solvated by PIP. At room temperature the e.s.r. spectra of the probe in PIP and PS are of the motionally narrowed and slow-motion type respectively (*Figures 3a* and *b*) and the spectrum of the blend (*Figure 3c*) is a composite of these two, apparently with the

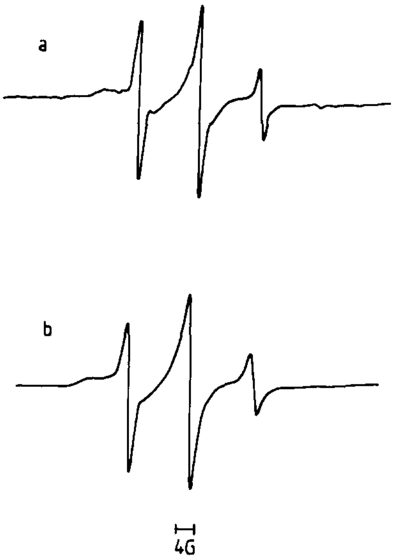


Figure 4 (a) Observed spectrum at 293 K of spin-probed 1:1 blend of PS and PIP after annealing at 378 K for 30 min then cooling to room temperature; (b) simulated spectrum containing fast-tumbling: slow-tumbling radicals in the ratio 1:2.3

slow-motion spectrum predominating. *Figure 3c* is somewhat misleading, however, because the spin probe evaporates preferentially from the PIP phase during sample preparation since PIP is well above T_g during this process while PS is well below its T_g. Annealing the spin-probed blend at 378 K to allow the probe to redistribute itself produced the room temperature spectrum in *Figure 4a*. Superficially this spectrum appears to have a predominating fast-motion component. However, the intensity of the e.s.r. signal is inversely proportional to the square of the linewidth and hence a relatively small proportion of fast tumbling radicals with narrow lines can easily mask the main slow-motion component of a composite spectrum. In fact the simulated spectrum in *Figure 4b*, which is a reasonable match to the observed spectrum in *Figure 4a*, comprises a ratio of fast-tumbling to slow-tumbling radicals of ~1:2.3. We never succeeded in finding conditions that produced a composite spectrum of the 1:1 blend in which the fast-tumbling probes, i.e. those in the PIP phase, were in the majority. Thus, these experiments produced no evidence that the nitroxide group is preferentially solvated by PIP. Indeed, if anything the probe appears to be slightly preferentially solvated by PS.

Calculation of solubility parameters[10] of the probe and the chain-end label gave 10.42 and 9.83 $\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ respectively*. The literature gives 9.32 and 8.16 $\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ for the solubility parameters of PS and PIP respectively[11], and hence both probe and label would be expected to interact preferentially with PS. This is in line with the results from the partition experiments above.

These observations, plus the interfacial tension values reported previously[2], force us to the conclusion that the nitroxide labels in the blends containing end-labelled PS find their way to the interphase not because of their particular chemical structure but simply because they are sited at chain ends. It follows that, in the absence of any specific physico-chemical interaction, any chain end has a stronger tendency than an inner segment to be located in the interphase. This conclusion is wholly in accord with Helfand's theoretically based predictions[12–14]. In brief, because chain ends have fewer constraints on their mobility than in-chain segments, the entropy of mixing at the interphase is maximized if chain ends concentrate in this region at the expense of other segments. This is the origin of the thermodynamic influence driving chain ends to the interfacial region. The results described here appear to be the first experimental demonstration of this effect. Helfand's theory is general in application and we are currently seeking confirmation of our results from studies of other pairs of immiscible polymers having widely different T_gs. The interphase should be enriched with chain ends of both components of the blend and hence if the polymer of lower T_g is end-labelled those labels within the interphase should have a lower mobility than the others; in theory, the spectrum of such labels within the interphase should be distinguishable from the fast-motion spectrum of the others. If successful, such an experiment would provide very strong support for the conclusions drawn in this paper, but there are major experimental difficulties. Because of the linewidth–intensity relationship (see above) it is relatively easy to detect 2–3% of rapidly tumbling radicals in an otherwise slow-motion spectrum, but in the reverse situation a small proportion of slow-moving radicals is very difficult to detect.

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* The molar group attraction for =N–O was taken as 400 by comparison with the structurally related ONO and $-NO_2$ groups which were assigned a value of 440 by Small[9]