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Spin-label studies of blends of immiscible polymers: 6. Phase morphology in blends of poly(methyl methacrylate) and poly(2-ethyl hexyl methacrylate)

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The correlation times, τ_R, for rotation in the slow-motion regime of nitroxide free radicals sited at chain-end positions on poly(methyl methacrylate) (PMMA) in the pure, unblended state and in a 1:1 (w/w) freeze-dried blend with unlabelled poly(2-ethyl hexyl methacrylate) (PEHMA) were determined by computer simulation of the slow-motion component of the composite electron spin resonance (e.s.r.) spectrum. Comparison of τ_R values indicates that the rubbery PEHMA apparently plasticizes the rotation of nitroxide-labelled PMMA chain ends which are expected to be located in the pure glassy PMMA phase. Although the spin-label studies seem to suggest that PMMA and PEHMA are partially miscible, dynamic mechanical thermal analysis (d.m.t.a.) and phase-contrast microscopy prove that PMMA–PEHMA blends comprise two separate phases which are essentially immiscible. The conclusions from the e.s.r., d.m.t.a. and phase-contrast microscopy experiments can be reconciled in terms of a wide-diffuse interphase between the bulk PMMA and PEHMA phases. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PMMA–PEHMA blends; phase morphology; spin-label study)

INTRODUCTION

The previous two papers in this series have reported spin-label studies on the immiscible pair poly(methyl methacrylate) (PMMA) and poly(2-ethyl hexyl methacrylate) (PEHMA)[1,2]. In these papers each component, in turn, was labelled at chain-end positions with a nitroxide free radical and the subsequent electron spin resonance (e.s.r.) spectra of the spin-labelled polymer, in both the pure state and in freeze-dried blends with the complementary unlabelled component, were recorded over a range of temperatures. With the glassy PMMA as the end-labelled component[1] in a blend with PEHMA, the spectra at low temperatures comprised a single broad-line (slow-motion) spectrum. As the temperature was increased, however, a second narrow-line (fast-motion) spectrum appeared and this component increased in intensity as the temperature increased. As in the case of an earlier study on the immiscible pair labelled poly-styrene (PS) and polyisoprene (PIP)[3–5], it was concluded that the fast-motion component in the e.s.r. spectra is attributable to labelled chain ends located in the interphase region of the blend where they experience increased motional freedom through a combination of plasticization by the rubbery component and a concentration of free volume. From these, and complementary studies in which the chain ends of the rubbery component (PEHMA) were labelled[2], it was further concluded that, in accord with the theoretical predictions

of Helfand[6–8], at thermodynamic equilibrium in a blend of two immiscible polymers there is an enrichment of chain ends within the interphase compared with the two bulk phases. Subsequent Monte Carlo calculations support these conclusions[9].

In our earlier papers it was shown that changes in the motionally-narrowed component of the e.s.r. spectra revealed information on the structure and composition of the interphase region. The corollary is that the slow-motion, broad-line component of the composite spectra reflects the behaviour, and hence the environment, of the labelled chain ends in the bulk phases of the blend. This proposition is explored in the present paper where the question is addressed as to whether, and to what extent, the rubbery PEHMA influences the dynamics of the chain ends of the glassy PMMA within the discrete domains of the latter. In other words, are the slowly-tumbling labelled PMMA chain ends in the blend in a pure PMMA environment? For this purpose the e.s.r. spectra of the pure end-labelled PMMA and the slow-motion component of the spectra of the 1:1 (w/w) freeze-dried blend of labelled PMMA with unlabelled PEHMA are compared and analysed over the same temperature range.

In the slow-motion regime the increasing mobility of the nitroxide label from the low temperature rigid limit is manifest by an inward shift of the extremes of the spectrum. Therefore, the simplest way to compare the relative mobilities of the PMMA chain ends in the pure and blended polymers is by measuring the respective extrema separations with temperature. A

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more quantitative estimate of the relative mobilities is available by calculating rotational correlation times, τ_R, by a more rigorous spectral analysis. Both approaches are discussed in this paper, and the e.s.r. results are complemented by data from differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.).

EXPERIMENTAL

Nitroxide end-labelled PMMA and unlabelled PEHMA were prepared by group transfer polymerization as described previously[1].

Gel permeation chromatography (PS standards, run in chloroform solution with toluene as the flow-rate marker) of the end-labelled PMMA sample indicated a molar mass (M_n) of $15\,300\,\mathrm{g\,mol^{-1}}$ and a dispersity index of 1.16. The unlabelled PEHMA sample had M_n of $38\,500\,\mathrm{g\,mol^{-1}}$ and a dispersity index of 1.29.

Blends were prepared by freeze-drying a 1% cosolution of the two polymers in benzene.

E.s.r. spectra were recorded with a Varian E-109 e.s.r. spectrometer equipped with a variable temperature accessory. Magnetic field strengths were determined using a Systron-Donner 3193 NMR digital gaussmeter.

D.s.c. experiments were performed using a Polymer Laboratories PL-DSC equipped with an autocool accessory and calibrated with indium. Each sample was heated from 223 to 423 K, held at 423 K for 3 min, cooled from 423 to 223 K, held at 223 K for 3 min and finally heated from 223 to 423 K. The heating and cooling rates in all cases were $10°C\,min^{-1}$.

D.m.t.a. measurements were performed on a Polymer Laboratories PL-DMTA Mark III. All samples were run in shear with the applied stress having a frequency of 1 Hz. Phase-contrast micrographs of both unblended components and of a freeze-dried blend of end-labelled PMMA and unlabelled PEHMA were recorded at room temperature after the sample had been annealed at ~423 K for 30 min.

The most rigorous method for determining rotational correlation times of a nitroxide in the slow-motion regime is by matching the observed e.s.r. spectrum with one simulated by computer by means of the well-known program developed by Freed[11]. The input parameters for this program include the principal components of both the hyperfine splitting A- and the g-tensors, a choice of unique axis for axially symmetric rotational diffusion (see *Figure 1*), a measure of the anisotropy of diffusion N, a diffusion model (Brownian, strong-jump or simple 'free' diffusion), the intrinsic linewidth and the correlation time τ_R. All of these parameters, except τ_R, are either measurable by experiment or may be estimated with
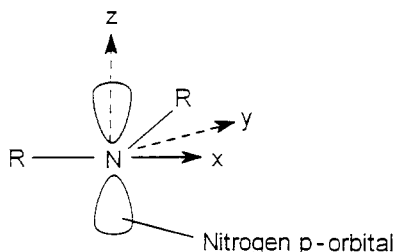
Table 1 Principal values for the g and A tensors for PMMA labelled at chain ends

	g	A (G)
x	2.0084	6.00
y	2.0064	5.51
z	2.0019	32.56
iso	2.0056	14.69

reasonable confidence so that the process of matching an experimental and a simulated spectrum mainly involves varying τ_R with minor adjustments of the other parameters, until a good fit is obtained.

The a_{iso} hyperfine coupling tensor was measured directly from the fast-motion spectrum obtained from a solution of end-labelled PMMA in chloroform, at room temperature, whilst A_{zz} was obtained from the rigid-limit spectrum. A_{xx} and A_{yy} were then calculated using the fact[11] that for similar nitroxide labels $A_{xx} - A_{yy} \approx 0.5\,G$. The g-tensors were derived in a similar fashion with $g_{xx} - g_{yy} \approx 2 \times 10^{-3}$. A charred dextrose standard ($g = 2.002592$)[12] was used to calibrate the spectra (*Table 1*).

The diffusion model for reorientation of the nitroxide was determined according to the method outlined by Kuznetsov and Ebert[13]. Analysis of the e.s.r. spectrum in this way indicated that Brownian diffusion was the preferred mode.

The value of the intrinsic linewidth, X, used in computer simulations of the e.s.r. spectra was taken from the published correlation which exists between X and τ_R[14,15]. The best match between simulated and experimental spectra was found when the preferred axis for rotation of the nitroxide was the y-axis (see *Figure 1*) and a threefold preference for rotation about this axis prevailed, i.e. the anisotropy of rotation, N, was three.

A series of e.s.r. spectra covering the entire slow-motion regime ($1 \times 10^{-6} \leq \tau_R \leq 4 \times 10^{-8}$ s) were simulated using the above input parameters along with the corresponding value of the intrinsic linewidth[14,15]. Since it proved impossible to simulate exactly the central features of all the observed spectra, the rotational correlation time τ_R corresponding to an experimental spectrum was estimated by measuring the extrema separation of the spectrum and comparing this with the simulated values. For the purposes of the present investigation where relative rather than absolute τ_R values were required, this procedure is satisfactory. A typical pair of observed and simulated spectra are shown in *Figure 2*; while the separations of the extrema in the observed and simulated spectra are an exact match, the inner features of the two spectra are not quite identical.

RESULTS AND DISCUSSION

E.s.r. spectroscopy

Figures 3a–c show a series of spectra recorded in the range 240–340 K of (a) pure end-labelled PMMA, (b) 1:1 (w/w) freeze-dried blend of end-labelled PMMA and PEHMA and (c) the same blend after heating above 420 K, well above the glass transition temperature of PMMA (T_g of PMMA $\approx 385\,K$). The spectra are identical with those published previously[1] for the same system, showing, in particular, the appearance of the fast-motion component in the spectra of the blends. Of

Figure 1 Principal axis system for nitroxide free radical
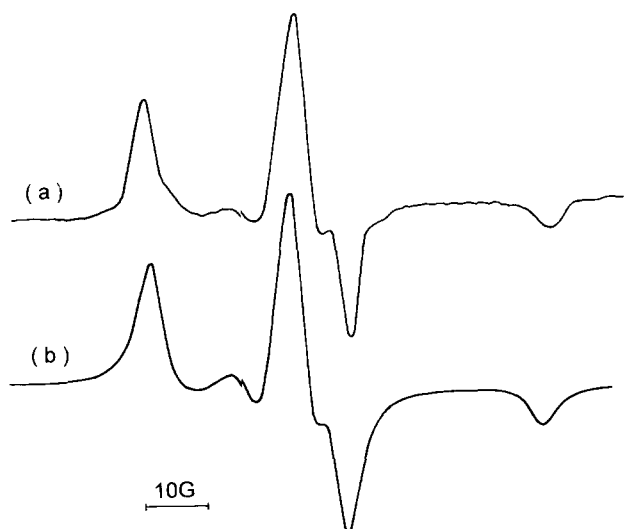
Figure 2 (a) E.s.r. spectrum of nitroxide end-labelled PMMA recorded at 264 K. (b) Simulated e.s.r. spectrum of a nitroxide radical possessing a correlation time of 4×10^{-7} s and an intrinsic linewidth of 3.0 G

more interest in the present context, however, is the slow-motion component, and in *Figure 3* the inward shift of the spectral extrema with increasing temperature is clearly discernible.

The separation between outermost spectral lines as a function of temperature is plotted in *Figure 4*, which reveals significant differences between the pure PMMA (*Figure 4a*) and the blend with PEHMA before and after
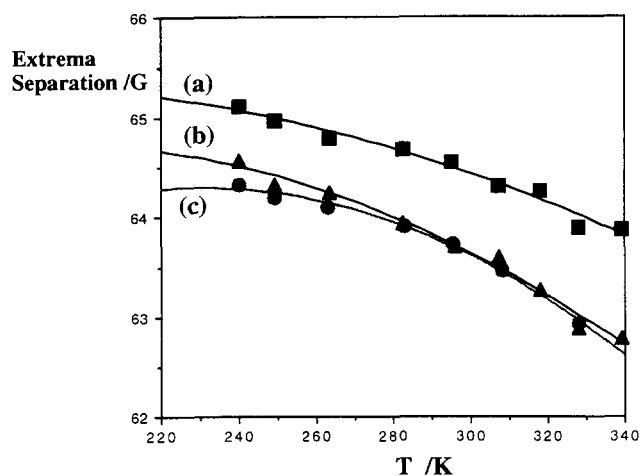

Figure 4 Plots of extrema separation of the slow-motion component of e.s.r. spectra in *Figure 3 versus* temperature

heating above the T_g of PMMA (*Figures 4b* and *c*, respectively). Thus, at any specific temperature, the separation of the extrema of the blend is less than that of the pure polymer and as the temperature is increased the separation decreases more rapidly in the blend. The contrast between the pure polymer and the blend is even more marked after heat treatment of the latter. The slowly-tumbling labels in the blend are clearly in a more mobile environment than those in pure PMMA, and heat treatment of the blend further increases the motional freedom of these labels.
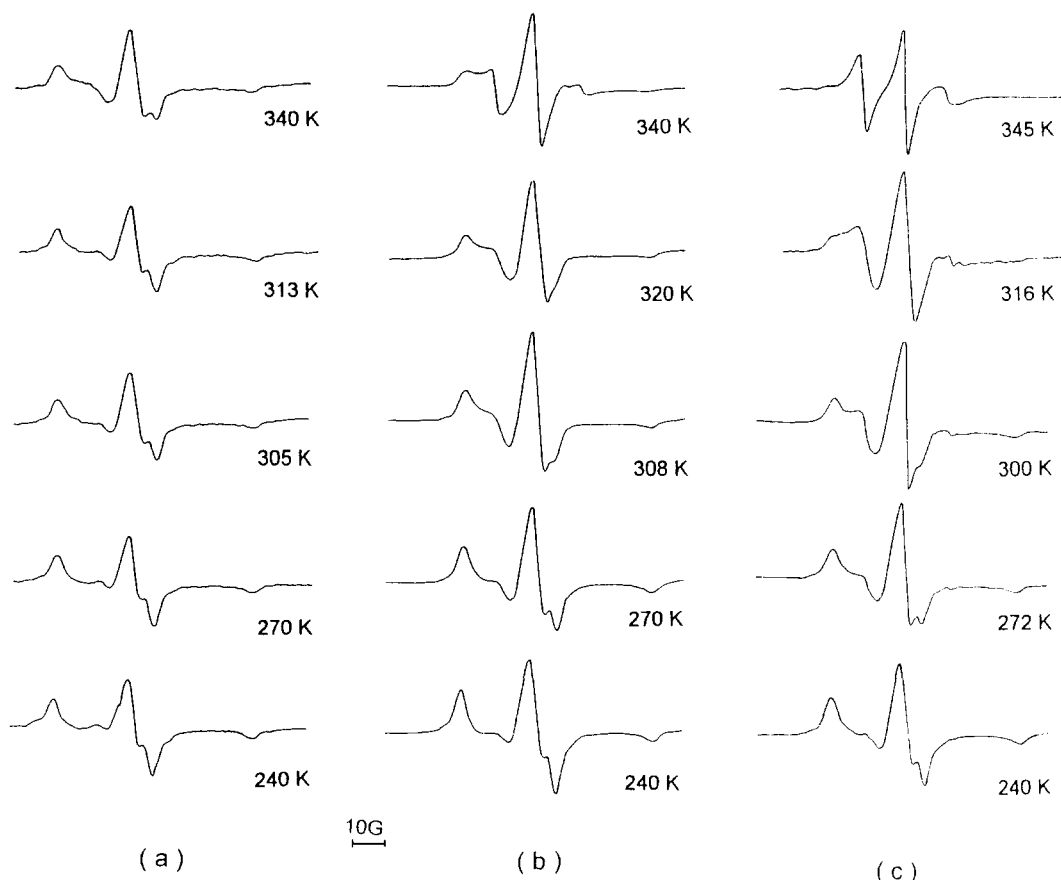
Figure 3 E.s.r. spectra of nitroxide end-labelled PMMA (a) in the pure, unblended state and in a 1:1 (w/w) freeze-dried blend with unlabelled PEHMA, (b) on initial heating and (c) on subsequent reheating
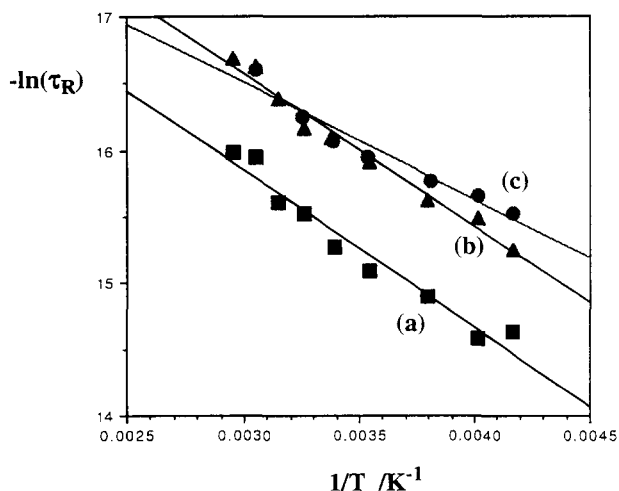
Figure 5 Arrhenius plots of correlation times for nitroxides responsible for the slow-motion component of e.s.r. spectra in *Figure 3*

Table 2 Activation energies (kJ mol^{-1}) for rotation of the nitroxide label on end-labelled PMMA

Pure PMMA	Blend with PEHMA on initial heating	Blend with PEHMA on reheating
11.3 ± 0.6	8.7 ± 0.4	7.4 ± 0.5

The distinctive behaviour of the PMMA–PEHMA blend compared with that of pure PMMA is also clearly visible in *Figure 5*, which shows Arrhenius plots of the correlation times τ_R calculated by spectral simulation as described in the Experimental section. The data points for the three systems—(a) pure end-labelled PMMA, (b) labelled PMMA–PEHMA (1:1) blend and (c) the blend after heating above 420 K—lie on three different, approximately linear curves. The activation energies derived from these plots are quoted in *Table 2*.

The trend in these activation energies mirrors that observed for the inward shift of the spectral extrema in *Figure 4* and clearly illustrates the increase in the mobility of the slowly-tumbling nitroxide-labelled PMMA chain ends as a consequence of blending with PEHMA. Further, these activation energies show that this increase in mobility is enhanced after the blend has been heated above the T_g of PMMA.

The effects of PEHMA on the rate, and activation energy, of tumbling of the motionally-restricted chain-end labels of PMMA are not consistent with the view that these labels are located in a pure, bulk PMMA phase outside the range of influence of the PEHMA. On the contrary, it would appear that some mixing between the PMMA and PEHMA components occurs in regions of the sample remote from the interphase. Thus, there would appear to be a degree of miscibility between the two bulk polymers. To test this premise, d.s.c. and d.m.t.a. experiments, as described in the Experimental section, were performed.

D.s.c., d.m.t.a. and phase-contrast microscopy

Figure 6 illustrates the d.s.c. traces of a 1:1 (w/w) freeze-dried blend of end-labelled PMMA and unlabelled PEHMA on (a) initial heating and (b) subsequent reheating. These traces are typical of samples containing
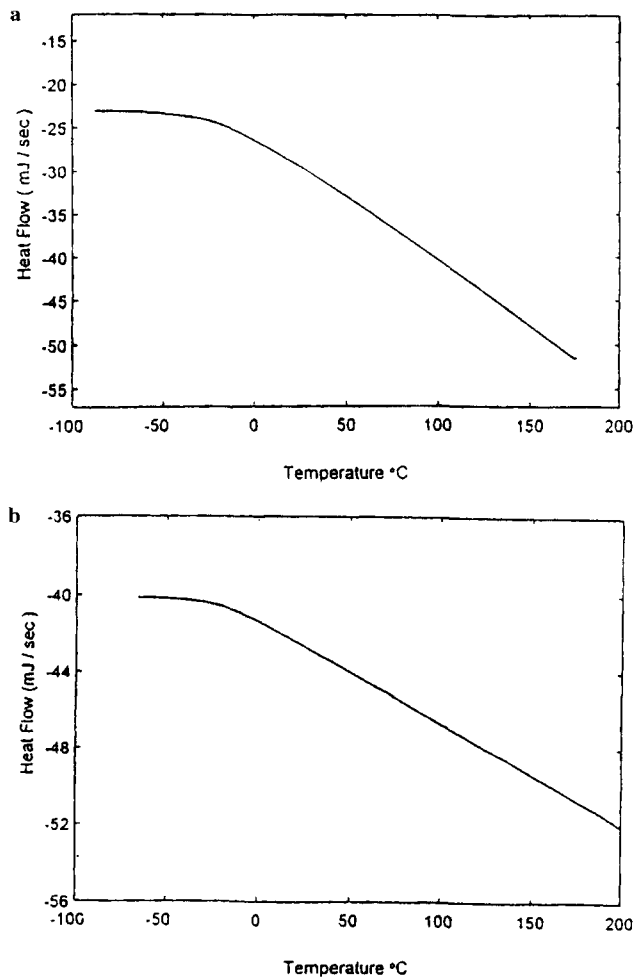
Figure 6 D.s.c. traces of a 1:1 (w/w) freeze-dried blend of end-labelled PMMA and unlabelled PEHMA on (a) initial heating and (b) subsequent reheating
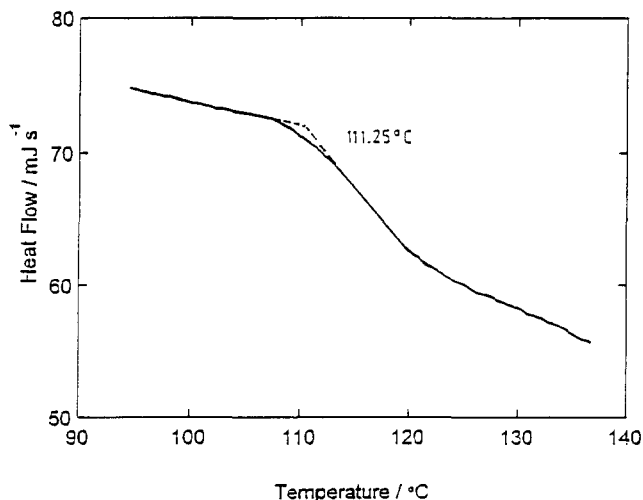
Figure 7 D.s.c. trace of unblended end-labelled PMMA

PEHMA in that no glass-to-rubber transitions were detected. However, all the traces from these blends had a markedly sloping baseline. Pure, unblended PMMA analysed under the same conditions exhibited a well-defined T_g at $\sim$384 K (see *Figure 7*). It is interesting to
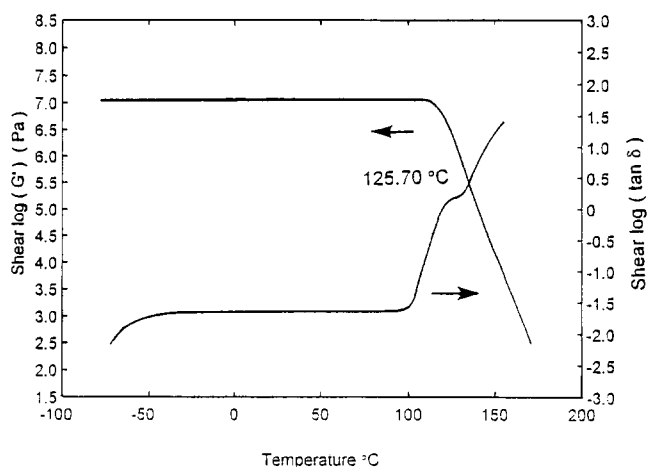
Figure 8 D.m.t.a. trace of unblended PMMA

Figure 10 D.m.t.a. trace of a 1:1 (w/w) freeze-dried blend of PMMA and PEHMA
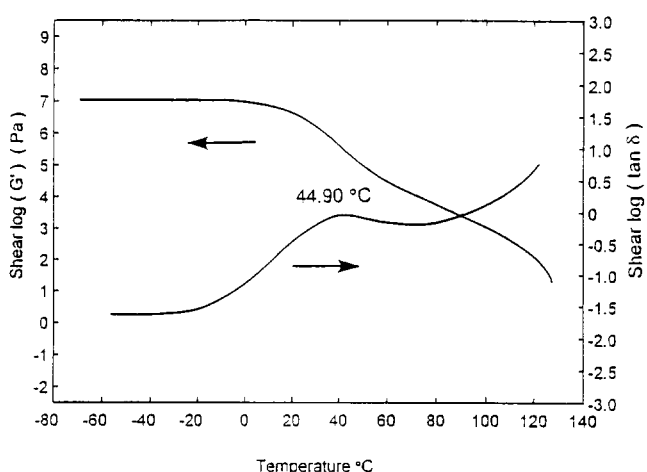

Figure 9 D.m.t.a. trace of unblended PEHMA

note that the only value which could be found in the literature for the T_g of PEHMA ($\sim$265 K) was determined from brittle point measurements[16,17]. Thus, while the d.s.c. experiment shows clearly that PEHMA interacts with, and affects the thermal properties of PMMA, it yields no information on the phase morphology of blends of the two polymers. The samples of these blends was therefore subjected to analysis by the more sensitive technique of d.m.t.a.

Figure 8 shows the d.m.t.a. trace of an unblended PMMA sample which exhibits a peak in $\tan\delta$ and a step in the log of the modulus *versus* temperature plot (each characteristic of a glass transition) at $\sim$399 K, a temperature approximately 15 K higher than the T_g observed in the corresponding d.s.c. measurements. The discrepancy can be attributed to the intrinsically higher frequency of the d.m.t.a. experiment compared with the d.s.c. technique. The d.m.t.a. trace of pure, unblended PEHMA (*Figure 9*) exhibits a T_g at $\sim$318 K, a temperature well above the reported[16] figure of 265 K. The d.m.t.a. trace of 1:1 (w/w) freeze-dried blend of end-labelled PMMA and unlabelled PEHMA (*Figure 10*) exhibits two glass transition temperatures at $\sim$318 K and $\sim$394 K. These temperatures are very close to the observed T_gs of the respective unblended components, suggesting that the two polymers are
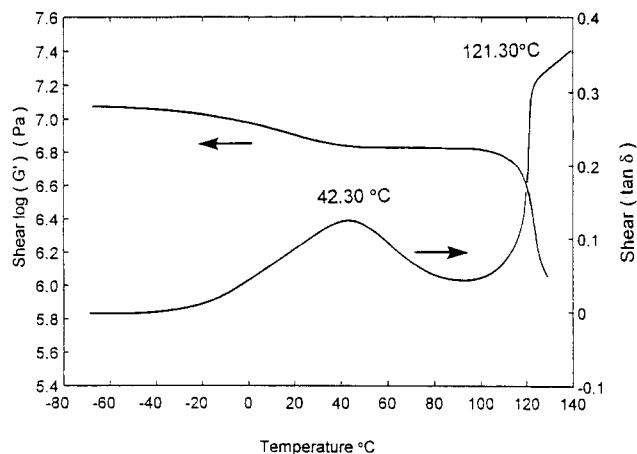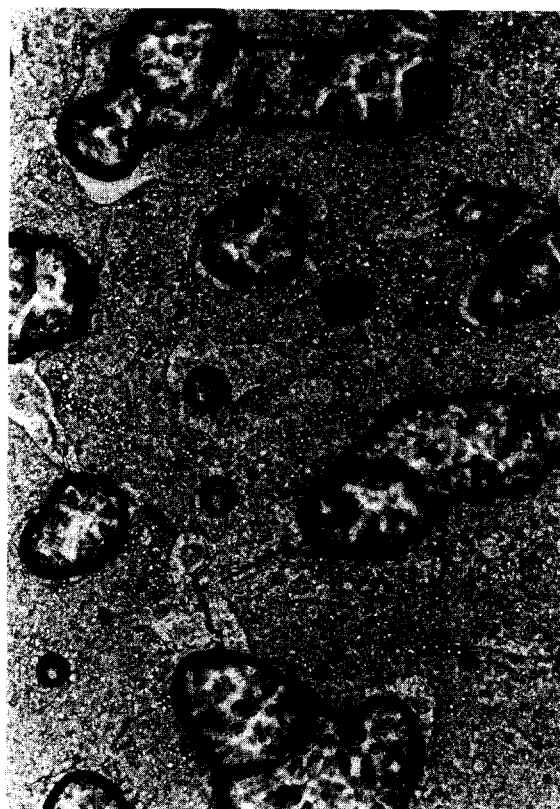

Figure 11 Phase-contrast micrograph of a 1:1 (w/w) freeze-dried blend of PMMA and PEHMA recorded at 298 K after annealing at 420 K for 30 min

almost completely immiscible since any significant degree of miscibility would have resulted in a shift of the T_gs of both component polymers. In the extreme case of complete miscibility, only one T_g would have been observed at a temperature between the T_gs of the components.

Figure 11 shows the phase-contrast micrograph of a 1:1 (w/w) freeze-dried blend of PMMA and PEHMA recorded at 298 K after the sample had been annealed at 420 K for 30 min. This micrograph clearly shows that two distinct phases are present, the boundaries of which are depicted by solid black lines.

CONCLUSIONS

The results presented here and in our previous papers on the PMMA–PEHMA system[1,2] are incompatible with either total miscibility of the component or with total immiscibility and minimal interaction of the separate phases. Apart from the d.s.c. results, which are rather uninformative, all the experiments point to a well-developed two-phase morphology. The d.m.t.a. experiments, in particular, indicate that the two phases are essentially pure PMMA and pure PEHMA. The spin-label experiment, however, shows clearly that slowly-tumbling labels, which one might expect to be in an environment of pure PMMA, are in fact plasticized to some extent by the rubbery PEHMA.

These data can be reconciled on the basis that the interphase is both relatively thick and diffuse. PMMA labelled chain ends near the centre (and towards the PEHMA side) of the interphase region experience maximum plasticization by the combined influences of the rubbery PEHMA and the accumu-lated free volume[1,2]. Such chain-end labels are characterized by spectra of the motionally-narrowed type. Those labels nearer the PMMA fringe of the interphase tumble much less freely; they contribute to the slow-motion compo-nent of the e.s.r. spectrum, but are somewhat more mobile than labels located in the interior of the PMMA phase. The overall effect is to decrease the measured correlation time of the labels in the slow-motion regime compared with that of labels in unblended PMMA.

ACKNOWLEDGEMENTS

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