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Shedding Light upon Macromolecular Behaviour: Luminescence Studies of Polymers

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SUMMARY: In this paper the use of two time-resolved luminescence techniques in the study of polymer behaviour is illustrated.

Time-resolved anisotropy measurements, TRAMS, have been used to study macromolecular mobilities both in solution and bulk phases. The first use of TRAMS involving phosphorescent labels in the study of synthetic polymers is reported and the potential of the technique for future applications in polymer science is discussed.

Time-resolved energy transfer has been used to study polymer compatibility and interdiffusion in blends of PS-PMMA. The data offer clear evidence of the fact that the local concentration of chain termini in phase-separated systems is enriched in the interphase regions compared to that in the two bulk phases of the blend.

Introduction

Luminescence spectroscopy is a powerful tool for polymer characterization. In some cases, where the chromophores of interest are intrinsic to the structure of the polymer, luminescence techniques may be used to interrogate the photophysical and/or photochemical behaviours of the system. In other instances, small amounts of a luminescent probe or label are incorporated into the macromolecular assembly in order to study its physical characteristics.

Luminescence studies provide information at the molecular level and can involve a variety of procedures ranging from relatively simple intensity and lifetime measurements to more sophisticated approaches involving energy transfer, excimer formation or anisotropy determinations. Examples of the application of luminescence spectroscopy in polymer science are to be found in a number of recent reviews [See, for example, references 1-3].

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As with any form of kinetic investigation, time-resolved methods can considerably extend the scope of the study compared to that afforded by steady-state measurements alone. In this article we illustrate the use of two time-resolved luminescence techniques, time-resolved anisotropy measurements (TRAMS), and time-resolved energy transfer (TRET) to study macromolecular mobility, both in solution and the solid phase, and phase separation in polymer blends, respectively.

TRAMS Studies of Polymer Mobility

The use of luminescence anisotropy in the study of polymer mobility has been described elsewhere. [See, for example, references 1-6]. Basically, the technique uses polarized radiation to preferentially excite those molecules whose transition vectors are aligned more or less parallel to the plane of polarization of the incident excitation. This photoselection procedure creates a degree of anisotropy of the emission from an otherwise randomly dispersed system of chromophores. Radiation emitted at the instant of absorption is polarized to a degree dictated by the intrinsic spectroscopic characteristics of the label/probe involved. As the time of sampling of luminescence increases (relative to the point of absorption) the observed emission becomes increasingly depolarized as a result of the effects of the micro-Brownian motion which serves to restore an isotropic distribution to the collection of chromophores photoselected at the moment of excitation. If the chromophore of interest is attached as a label at an appropriate position within the structure of a macromolecule, information regarding the motion of the polymer [subject to some restrictions/considerations] may be quantified in terms of the kinetics of the luminophore's reorientation.

For vertically polarized excitation, the anisotropy, r(t), of luminescence observed at some time, t, following excitation, is given by

$$r(t) = \frac{i_{vv}(t) - i_{vh}(t)}{i_{vv}(t) + 2i_{vh}(t)} = \frac{d(t)}{s(t)} \qquad (1)$$

where i_{vv} represents the intensity of luminescence sampled in a plane oriented parallel to that of the excitation and i_{vh} represents the component of intensity disposed perpendicularly to the vertically polarized incident radiation. The sum function, s(t), is comprised solely of luminescence information: it corresponds to the total luminescence decay. The anisotropy function, on the other hand, contains only information containing molecular reorientation. For a perfectly spherical rotor, the anisotropy decays by a first order rate law:

$$r(t) = r_o \exp(-t/\tau_c) \qquad (2)$$

where r_o is the intrinsic anisotropy (exhibited at t = 0, the instant of absorption) and τ_c is the correlation time associated with chromophore reorientation (the reciprocal of the rate constant characteristic of the loss of anisotropy).

The difference function, d(t), contains both luminescence and reorientation information. Consequently, comparison of the decay profiles of its two components, $i_{vv}(t)$ and $i_{vh}(t)$, affords a good visual impression of the relative importance of the molecular reorientational and electronic relaxation processes, as demonstrated in Figures 1(a) and 1(b).

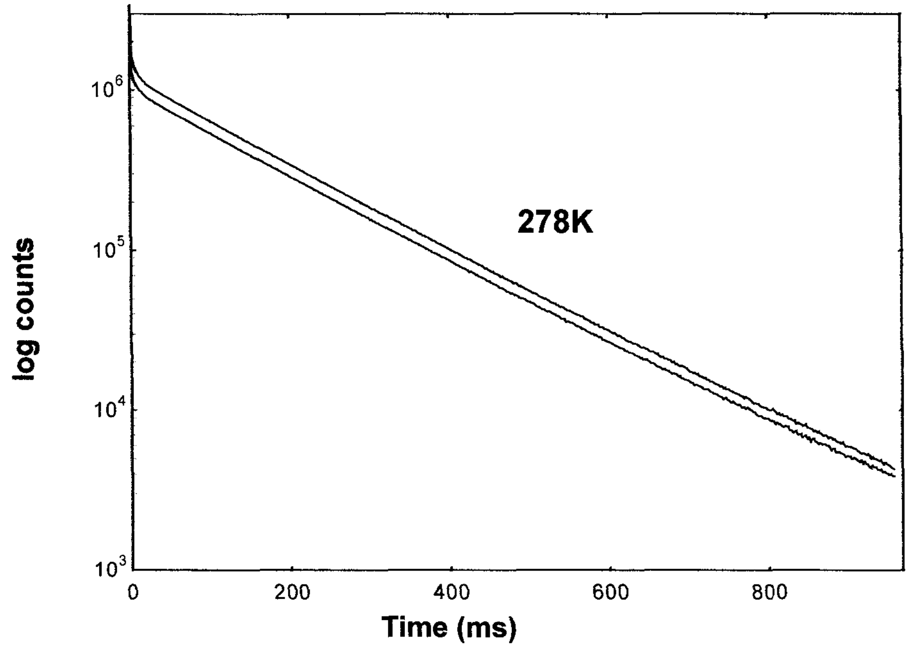


Fig. 1(a): Orthogonal components of phosphorescence from labelled PMA at 278K.

Figure 1(a) shows the orthogonally polarized components of the intensity of phosphorescence from a sample of poly(methyl acrylate), PMA, labelled with chlorovinylnaphthalene. At 278K, below the glass transition of the PMA matrix, the rate of segmental reorientation is negligible compared to that of the excited triplet state of the label. The decay curves converge slowly over the time-scale accessed, the rate of convergence being dictated by that of the electronic relaxation of the phosphor's excited state.

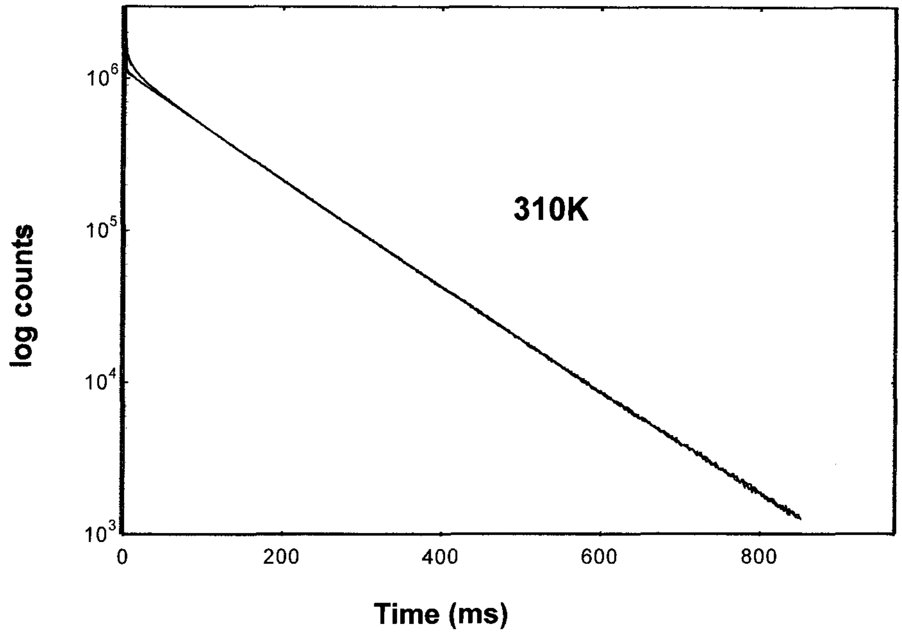


Fig. 1(b): Orthogonal components of phosphorescence from labelled PMA at 310K.

In contrast, it can be seen {by reference to Figure 1(b)} that above the glass transition temperature of the matrix {e.g. at 310K}, the "parallel" and "perpendicular" components of phosphorescence intensity converge rapidly. This is a consequence of two effects induced by the glass transition:

(i) the temperature dependence of the excited state lifetime of the label exhibits a discontinuity at "Tg" (itself dependent upon the effective "test frequency" imposed by the label's excited state lifetime). Above Tg, enhanced triplet state decay will induce a more rapid collapse of d(t).

(ii) the onset of segmental motion, leading to decay of the anisotropy observed in the phosphorescence of the label, induces convergence within the decay curves, $i_{vv}(t)$ and $i_{vh}(t)$.

If the resultant anisotropy decay curves are analysed using a single-exponential decay model, according to equation (2), a temperature dependence of τ_c evolves which is shown, in Arrhenius form, in Figure 2.

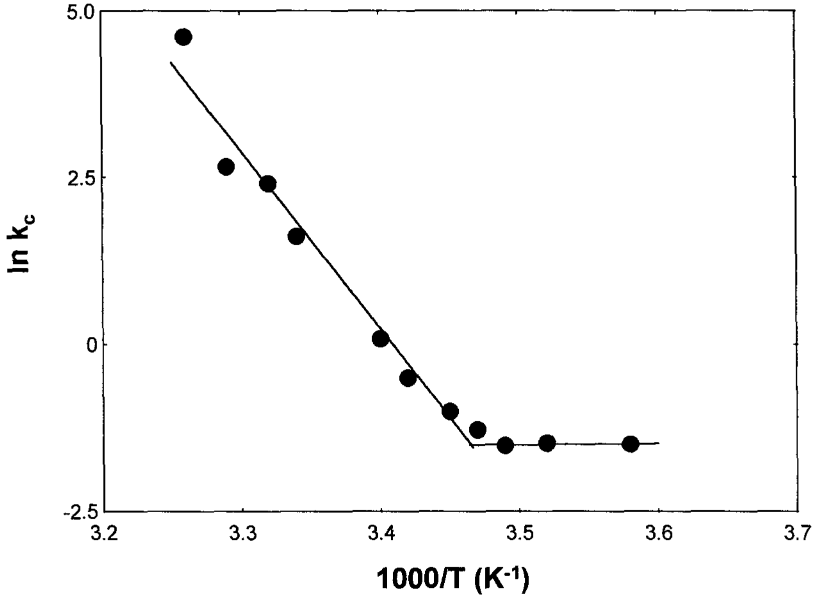


Fig. 2: Arrhenius representation of the temperature dependence of PMA segmental relaxation.

Two regions are evident.

(i) At temperatures below Tg, negligible segmental relaxation is apparent. This observation is in accord with the findings of (much) earlier *steady-state* phosphorescence anisotropy work from this group[7,8] using different phosphorescent labels.

(ii) Also in accord with our steady-state studies, it is apparent [Figure 2] that above Tg {determined as *ca.* 290K from the intersection point of the 2 linear regions shown in Figure (2)} segmental motion of the polymer is evinced in the decay of anisotropy of the phosphorescent label as characterized by τ_c. As is to be expected, the temperature dependence of τ_c is well described, over the limited temperature range accessed, by the Arrhenius function. The resultant activation energy of 230 kJ mol^{-1} is in excellent agreement with that averaged$^{9)}$ from dielectric and dynamic mechanical data for the α-relaxation of PMA. This is particularly gratifying, since the time resolved anisotropy measurements of phosphorescence (TRAMP) experiment is not trivial$^{10)}$: to our knowledge, apart from an earlier preliminary disclosure$^{11)}$, this is the first report of the successful application of this technique to the study of relaxations in synthetic polymer solids. This development offers exciting opportunities for studying the relaxation behaviour of individual polymer chains dispersed in complex media such as phase-separated blends, colloidal latices, inter-penetrating networks (IPNs) or gels.

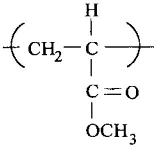
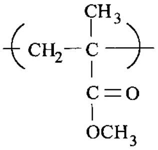
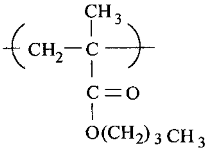
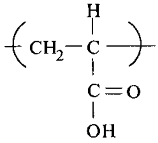
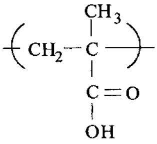
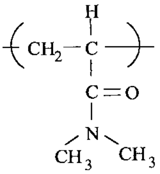
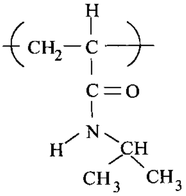
More conventionally, TRAMS has been employed using fluorescent labels to study macromolecular dynamics in dilute fluid solution. A selection of results from our laboratories is shown in Table 1.

The fluorescent label is the repeat unit derived from copolymerization of a small amount (0.5 mole %) of acenaphthylene, ACE, with the monomer of interest. The ACE label reports upon segmental motion of the polymer and, at the low macromolecular concentrations adopted in these systems (< 1wt %), intermolecular interactions are avoided.

As might be expected, the replacement of a proton with a methyl group as backbone substituent in comparing PMA with PMMA leads to a decrease in chain mobility as a result of the greater steric hindrance to rotation about main chain bonds. This influence is reflected in the bulk phase behaviour of these 2 systems, PMMA having a higher Tg than PMA. Increasing the bulk of the ester substituent also results in a reduction in the rate of intramolecular segmental motion (*cf.* PBMA *vs.* PMMA), a result which contradicts early dielectric relaxation data$^{12)}$. In the bulk polymers, on the other hand, the ester group adopts a role as "internal plasticizer" and, as a result of the dominance of intermolecular interactions, the Tg of PBMA is less than that of PMMA.

Similar influences of the bulk of substituents on the intramolecular dynamics of macromolecules are revealed through comparison [Table 1] of the relaxation data for PAA

Tab. 1: Intramolecular segmental relaxation data at 298K.

		solvent	τ_c/ns
poly(methyl acrylate) *(PMA)*	 $\left(CH_2-\overset{H}{\underset{\substack{C=O\\OCH_3}}{C}} \right)$	toluene	1.0
poly(methyl methacrylate) *(PMMA)*	 $\left(CH_2-\overset{CH_3}{\underset{\substack{C=O\\OCH_3}}{C}} \right)$	toluene	2.7
poly(butyl methacrylate) *(PBMA)*	 $\left(CH_2-\overset{CH_3}{\underset{\substack{C=O\\O(CH_2)_3CH_3}}{C}} \right)$	toluene	3.6
poly(acrylic acid) *(PAA)*	 $\left(CH_2-\overset{H}{\underset{\substack{C=O\\OH}}{C}} \right)$	methanol	1.3
poly(methacrylic acid) *(PMAA)*	 $\left(CH_2-\overset{CH_3}{\underset{\substack{C=O\\N/A}}{C}} \right)$	methanol	4.3
poly(dimethyl acrylamide) *(PDMAC)*	 $\left(CH_2-\overset{H}{\underset{\substack{C=O\\N(CH_3)_2}}{C}} \right)$	methanol	1.5
poly(N-isopropyl acrylamide) *(PNIPAM)*	 $\left(CH_2-\overset{H}{\underset{\substack{C=O\\NH-CH(CH_3)_2}}{C}} \right)$	methanol	1.9

and PMAA or PDMAC and PNIPAM. In contrast, when water is employed as a solvent for these polyacids or polyacrylamides, small changes in polymer structure, changing the hydrophobic-hydrophilic balance of the water-soluble polymer, can have a dramatic effect upon its conformational behaviour. For example, TRAMS have shown[2,3,13)] that neutralization of PAA is accompanied by a relatively modest conformational transition: the segmental mobility of the polyacid is characterized by a τ_c value of *ca.* 6 ns which drops to *ca.* 4 ns upon formation of the polysalt. In the case of PMAA, however, τ_c for the polyacid is more than 50 ns dropping to *ca.* 10 ns for the polysalt[5)]. In the acidic form of PMAA, hydrophobic intramolecular interactions between the backbone methyl groups lead to the creation of domains within the polymer coil which act as "anchor points" for the segments leading to an order of magnitude reduction in the polymer's segmental mobility compared to the acidic form of PAA. In the fully neutralized forms of the two polyelectrolytes, the methyl substituent exerts a much less restrictive influence upon chain mobility, the reduction in the rates of segmental motion of the PMAA polysalt relative to that of PAA being similar to that evident for the 2 polyacids in MeOH as solvent.

In the case of aqueous solutions of poly(alkyl acrylamides) subtle changes in structure (and consequent hydrophobic-hydrophilic balance) can result in marked differences in physical behaviour. For example, PNIPAM exhibits lower critical solution behaviour: the system phase separates upon heating at a characteristic temperature (the LCST) of *ca.* 32°C. PDMAC, on the other hand, does not show an LCST below the normal boiling point of water. Using TRAMS, we have shown[14)] that a dramatic conformational change occurs in PNIPAM as it is heated through its LCST, resulting in a marked loss in segmental mobility. These studies have provided corroborative evidence for earlier energy transfer studies in support of the mechanism proposed[15)] to explain the rapid thermoreversibility demonstrated by PNIPAM in its critical behaviour: at the LCST, individual chains collapse as a precursor to aggregation. Consequently, gross intermolecular entanglements which would impede rapid redispersal of the polymer, below its LCST, are not formed.

Time-resolved energy transfer (TRET) studies of miscibility in polymer blends

As its name implies, energy transfer, comprizes a process in which energy is exchanged between one species, the donor, D, and an acceptor molecule, A. The process, which can be represented as

$$D^* + A \rightarrow D^* + A \qquad (3)$$

can occur by various mechanisms. In "Förster transfer" interactions between D* and A occur through space at distances of up to 10 nm dependent, *inter alia*, upon the spectroscopic characters of D and A.

The distance dependence of the transfer efficiency within this mechanism can be used to advantage. In adopting the "spectroscopic ruler" approach developed by Stryer and Haughland16), Morawetz has pioneered the use of energy transfer measurements in studies of the interpenetration of polymer chains in blended systems. (See, for example, references 17-19). In this approach, one or both components of a binary blend can be labelled with fluorescent species which can act as a donor-acceptor pair. If D is attached to one component of the blend and A to the other, miscibility and macromolecular intermingling will encourage energy transfer. If on the other hand, D and A are labels for (different molecules of) a single component, energy transfer will be encouraged when phase separation occurs. Despite the popularity of the approach in steady-state experiments (e.g. references 17,18) and the adoption of time-resolved measurements in studies of colloid coalescence and coatings formed from latices20) there has been little use of TRET in studies of more conventional polymer blends. In this paper, we present some preliminary data demonstrating the use of TRET in studies of the immiscible system polystyrene (PS)-PMMA. In these studies we have used phenanthrene as donor and anthracene as acceptor.

Figure 3 shows the fluorescence decay of phenanthrene molecularly dispersed (10^{-6} M) in a 2-methyltetrahydrofuran glass at 77 K both in the absence and presence of anthracene (10^{-4} M). If Förster kinetics were rigorously obeyed the decay of the phenanthrene donor in the presence of acceptor would be given by

$$i_d(t) = i_o \exp[-t/\tau - 2\gamma(t/\tau)^{\frac{1}{2}}] \qquad (4)$$

where γ is a constant, containing, *inter alia*, information regarding the average distance between donor and acceptor. Equation 4 shows that the exponential decay exhibited by the phenanthrene in the absence of acceptor (*cf.* Figure 3) will become distorted at early times of analysis due to the influence of the "$t^{1/2}$" term. At longer times, when the influence of the "$t^{1/2}$" term becomes negligible, the quenched curve becomes exponential and parallel to that of the unquenched sample. For our current purposes we can simply concentrate upon the form of "distortion" of the quenched decay, as exemplified in Figure 3.

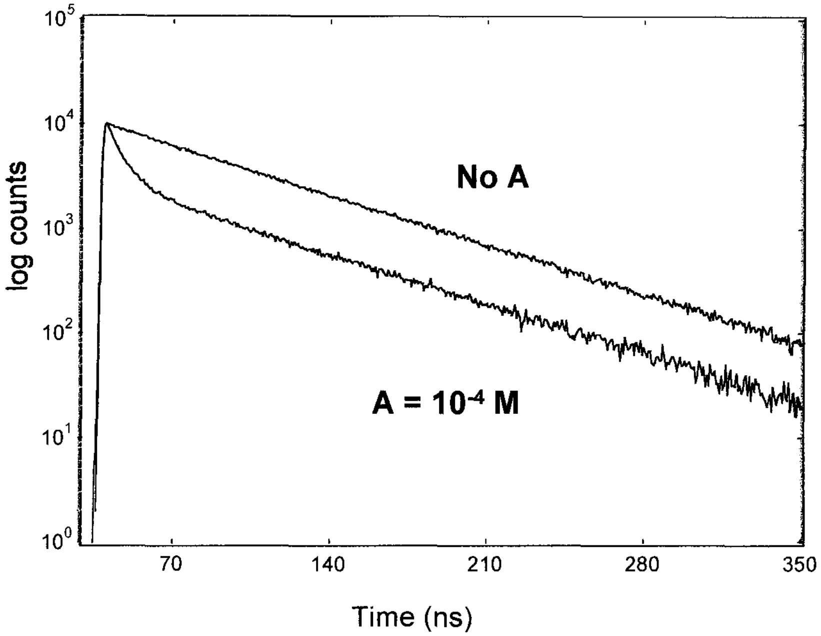


Fig. 3: Fluorescence decay curves for phenanthrene (10^{-6}M) in the presence (10^{-4}M) and abscence of anthracene in MeTHF at 77K.

In the present work, we have labelled both PMMA and PS with copolymerized arylmethyl methacrylate where aryl is phenanthryl **and** anthryl for each polymer. We have also labelled both polymers with terminally attached donor and acceptor labels. The objectives of this exercize are

(i) to demonstrate the potential of the TRET approach in probing polymer miscibility.

(ii) to assess the extent to which the term "totally immiscible" applies to the PS/PMMA system in the context of the TRET experiment.

(iii) to assess whether the labels, acting as a form of impurity, tend to aggregate in the interphase regions of the phase-separated blend.

(iv) to determine whether the TRET approach can provide useful information regarding the nature of the interphase regions of the blend.

Objectives (i)-(iii) are closely related. Any tendency of the labels to aggregate *of their own accord* within a phase-separated system would seriously impair the usefulness of the energy transfer approach. Similarly, the extent to which the blends appear to be totally immiscible again affects the degree to which we can gauge the potential of TRET in studying such systems.

We shall consider here, a brief collection of the results which we have accrued in these studies, as presented in Figure 4.

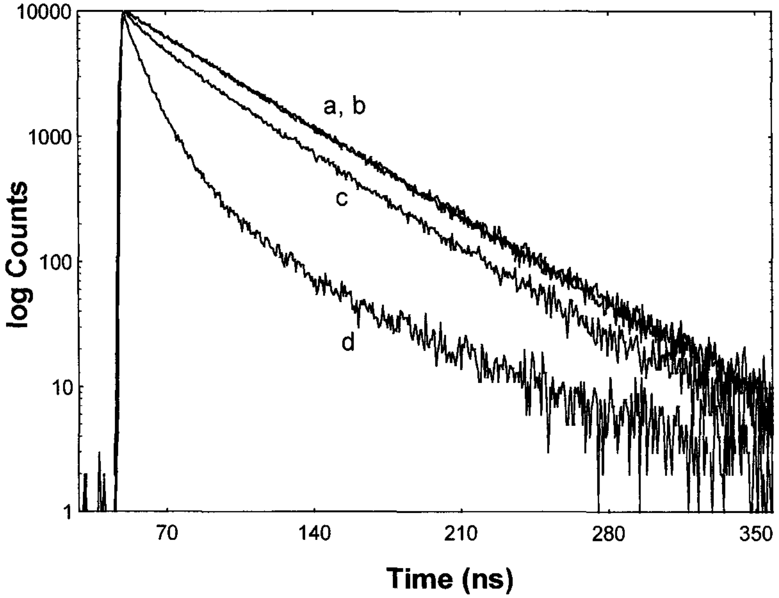


Fig. 4: Decays of phenanthrene fluorescence in various polymer blends.

Figure 4 shows [curve (a)] the decay of fluorescence from donor-labelled PS, diluted with unlabelled PS, in a 50:50 wt%, phase-separated blend with unlabelled PMMA. Also shown [curve (b)] is the decay of fluorescence exhibited by an identical concentration of donor-labelled PS contained in a similar blend with PMMA in which 20 wt% of the PMMA molecules are labelled with acceptor. The fluorescence decay curves are, within experimental error, superimposable and exponential: no energy transfer is discernible. Clearly, the donor and acceptor labels can not "communicate with one another" in such a phase-separated blend.

This is significant. It implies that

(a) within the limits of resolution of distance afforded by this approach and the chosen donor/acceptor pair, polymer immiscibility is complete within this system. [The critical transfer distance, R_o, for this donor-acceptor combination is *ca.* 2 nm[21)]]

(b) the fluorescent labels [PhMMA and AMMA] do not exert a significant perturbing influence upon the phase separation behaviour of the system in the sense that they do not appear to congregate within the interphase regions of the blend. This is an important observation in terms of the TRET technique and has obvious significance for the conclusions to be drawn from observations upon blends incorporating terminally-labelled polymers, as discussed below.

In contrast [curve (c)] the decay of fluorescence from a phenanthryl donor attached to an internal segment of PMMA becomes non-exponential when the PMMA is incorporated into a 50:50 wt% PMMA/PS blend which contains a proportion [20 wt% of total PS] of acceptor labelled PS. The occurrence of energy transfer which is obviously implicated by the distortions induced in the decay of the donor's emission, can only be rationalized by concluding that the donor-acceptor pairs are located at closer proximities than encountered in the blend [curve (b)] in which the two labels are bound to internal segments of the macromolecular constituents. This, in turn, leads to the conclusion that the acceptor-labelled chain termini of the PS component are concentrated within the interphase regions of the blend and thereby enjoy an increased probability of engaging in transfer interactions with the donor species dispersed throughout the phase separated PMMA domains.

The effects of congregation of chain termini within the interphases become even more apparent [curve (d)] when both polymer components, PMMA and PS, bear terminally-bound chromophores. The fluorescence decay curve of the phenanthryl donor is markedly non-exponential: aggregation of chain termini within the interphase produces a high local concentration of both donor and acceptor, resulting in significant extents of transfer of energy.

Theoretical studies of Helfand et al.[22,23)] predicted that, compared to the bulk phases of an equilibrated, phase-separated blend of two immiscible polymers, enrichment of chain ends occurs within the interphase. The current spectroscopic studies support this premise. To our knowledge, this is the first instance in which this has been established by the use of energy transfer experiments. Previously, Cameron *et al.* [references 24, 25 and references therein] using innovative ESR measurements of polymer mobility, reached the same conclusion.

With any labelling experiment, there is always the worry that the label will distort the behaviour of the system it is designed to interrogate. Given the results of the current study [which indicate that the labels do not *per se* display a marked tendency to congregate within the interphase] and differences in the nature of the labels involved in our fluorescence experiments and the ESR studies of Cameron *et al.*[24,25)] upon different immiscible blends, the experimental data constitute a convincing demonstration of the applicability of Helfand's theoretical predictions.

Conclusions

1. Time-resolved anisotropy measurements are powerful means of measuring macromolecular dynamics. The use of phosphorescent labels allows the relaxation behaviour of polymers in the bulk state to be studied and "opens the door" to investigations of individual macromolecular species within polymer blends, colloidal latices, IPNs etc.
2. Time-resolved energy transfer measurements have confirmed the "totally immiscible" nature of PS-PMMA blends and have demonstrated the tendency of terminal segments of polymer chains to congregate in the interphase regions of phase-separated blends.

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