A study of interpenetration using fluorescence quenching of chromophore-labelled polymers

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Fluorescence quenching was used to investigate the onset and extent of overlap and interpenetration in poly(vinyl methyl ether) (PVME) solutions using polystyrene with a dilute level of anthracene labelling (APS) as a probe. A low, constant concentration of APS was added to solutions varying in PVME concentration. The critical overlap concentration, c^*, was taken to be the PVME concentration at which quenching of the probe anthracene-labelled polymer molecules commenced. Variations in probe molecular weight and concentration produced no significant changes in c^* or in the rate of decrease in fluorescence intensity above c^*, lending credibility to the idea that the APS is simply probing the PVME system. The values of $c^*[\eta]$ from these experiments were found to lie in the range of 0.87–1.7 which agrees with the results from previous studies. The sensitivity of this method to small differences in solvent quality for PVME was also investigated.

(Keywords: interpenetration; c^*; fluorescence quenching; poly(vinyl methyl ether); polystyrene)

INTRODUCTION

The transition between the dilute and semidilute regimes in polymer solutions is characterized by c^*, the critical concentration at which polymer molecules begin to overlap and interpenetrate. Many basic solution properties exhibit changes at c^* including viscosity[1-4] and osmotic pressure[5,6]. In addition, many processes such as polymerization reactions[7,8] and crosslinking of resins[9,10] are influenced by the extent of interpenetration in a polymer system.

Many techniques which are sensitive to intermolecular interactions have been used to measure c^* including viscometry[1,3,11], osmometry[12-14], light scattering[15,16], diffusion measurements[17], stress compliance[18] and photophysical techniques[19-22]. Photophysical techniques such as fluorescence spectroscopy are particularly useful tools in this regard as they offer a non-destructive measurement capable of probing intermolecular interactions at the Ångström or nanometre level. Morawetz[21,22] has employed fluorescence spectroscopy in an energy transfer study in which fluorescent donor labels and fluorescent acceptor labels are placed on different chains. Significant energy transfer, as evidenced by a sharp increase in the ratio of acceptor to donor label fluorescence intensities, occurs only when there is substantial interaction of different polymer chains, as is the case in a semidilute solution. Morawetz performed his fluorescence measurements on solid samples made by freeze-drying solutions and pressing the polymer into pellets. Torkelson and Gilbert[20] have recently shown that, under certain conditions of labelling, energy transfer measurements made directly from polymer solutions also yield useful information on the onset and degree of interpenetration as polymer concentration in solutions is increased.

This paper discusses the use of a different fluorescence technique, fluorescence quenching, for measuring the onset and extent of interpenetration in polymer solutions. Fluorescence quenching involves the interaction of a fluorescent unit or chromophore with a second molecule or unit in which the quantum yield of the fluorescent chromophore is reduced whenever the two units come into close contact. Kirsh *et al.*[23] noted that the sensitivity of fluorescence quenching to intermolecular interactions could give information concerning c^*. They used a system containing poly(4-vinyl pyridine) (PVPY) copolymerized with either anthracene methyl methacrylate or pyridine residues in which the pyridine residues are capable of quenching anthracene fluorescence. When solution concentration was increased, they observed a substantial increase in quenching at a particular concentration which they denoted as c^*. Because their primary objective was to study diffusion in this system, they reported only a few comments concerning the determination of c^* by this method. In addition, since the system they used contained high levels of labelling, 26–50 mol% copolymerized quenching residues, their results may not represent the actual nature of interpenetration in an unlabelled PVPY system.

Recently, Halary, Monnerie and coworkers[24,25] have shown that anthracene fluorescence is very strongly quenched when an anthracene unit comes into close contact with the ether functions on poly(vinyl methyl ether) (PVME). They have used fluorescence quenching to study phase-separation in anthracene-labelled polystyrene (APS)/PVME blends. Other investigations[26,27] have used polystyrene as a probe in PVME solutions to study self-diffusion in polymer systems using light scattering techniques. The technique of Halary *et al.* is used in the present study which employs fluorescence quenching of APS by PVME for a variety of ASP/PVME/solvent systems. Under most of the conditions investigated, PS and PVME form a compatible system. A low, constant concentration of APS was used as a probe

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of PVME interpenetration in all solutions, and c^* of the PVME was determined by monitoring the anthracene-labelled fluorescence intensity as a function of PVME concentration. The effects of solvent and APS–molecular weight and concentration on the observed c^* and degree of interpenetration in PVME solutions are reported.

EXPERIMENTAL

Spectrophotometric grade methyl ethyl ketone (MEK), toluene (TOL) and butyl acetate (BA) were purchased from Aldrich as was the chloromethyl methyl ether and 9-anthracene methanol used in the labelling reactions. Nearly monodisperse polystyrene with molecular weights of 35000 and 90000 were purchased from Pressure Chemical. Polydisperse PVME ($M_w = 99000$ and $M_n = 46500$) was purchased from Scientific Polymer Products and cleaned by dissolution in toluene followed by precipitation in hot water. Anthracene labels were attached to the polystyrene samples by techniques described previously[20]. The anthracene content was determined using an IBM u.v.-vis 9410 double beam spectrophotometer and was found to be approximately one anthracene label per 970 styrene repeat units in the 35000 sample and one label per 1400 repeat units in the 90000 sample.

For a given set of data, the solution preparation and evaluation was as follows. Each solution for a particular trial contained the same concentration of APS, with different trials using either 0.40 ± 0.02, 0.20 ± 0.02 or $0.80 \pm 0.02\ g\ l^{-1}$. Varying amounts of PVME were added to the solutions for each trial. The solutions were shaken mechanically for 12–24 h and were nitrogenated for 10 min before taking steady-state fluorescence measurements with a Spex Fluorolog spectrophotometer. Each solution was irradiated at 365 nm, and the anthracene fluorescence for each solution was monitored at 415 nm. Front surface geometry was used for all measurements. Intrinsic viscosities were measured using an Ubbelohde no. 50 viscometer. Film measurements were taken in the same manner on films cast from solutions containing $0.4\ g\ l^{-1}$ APS and $5.0\ g\ l^{-1}$ PVME. Films were air dried for 24 h followed by vacuum drying for 24 h at room temperature.

RESULTS AND DISCUSSION

Data analysis

Fluorescence quenching was used to study six different polymer systems: 35000 APS plus PVME in MEK, TOL and BA, and 90000 APS plus PVME in MEK, TOL and BA. *Figure 1* shows the typical effect of fluorescence quenching in going from a dilute solution of PVME to a semidilute or concentrated solution of PVME. The dilute solution, consisting of $0.40\ g\ l^{-1}$ APS plus $2.16\ g\ l^{-1}$ PVME in TOL exhibits a fluorescence intensity which is nearly twice that of the more concentrated solution which consists of $0.40\ g\ l^{-1}$ APS plus $201.5\ g\ l^{-1}$ PVME in TOL. *Figure 1* clearly illustrates that quenching of APS by PVME is useful not only in studying the phase behaviour of polymer blends, as shown by Halary *et al.*[24,25] but that it is also sensitive to solution structure.

The data from this investigation are plotted as intensity of anthracene fluorescence *versus* logarithmic PVME concentration in *Figures 2–5*. For each set of data the

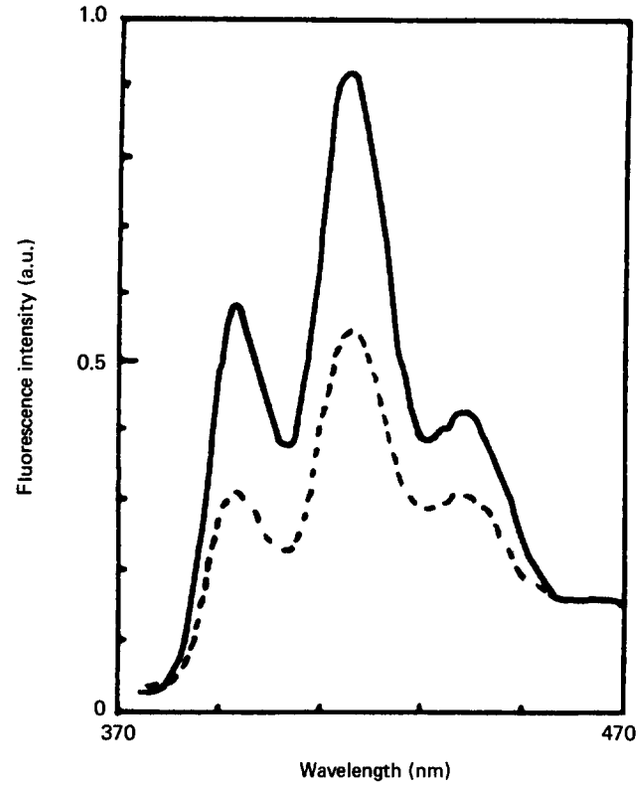

Figure 1 Effect of fluorescence quenching on the anthracene spectrum of $0.40\ g\ l^{-1}$ 90000 APS in TOL: ———, $2.18\ g\ l^{-1}$ PVME + $0.40\ g\ l^{-1}$ APS; – – –, $201.5\ g\ l^{-1}$ PVME + $0.40\ g\ l^{-1}$ APS

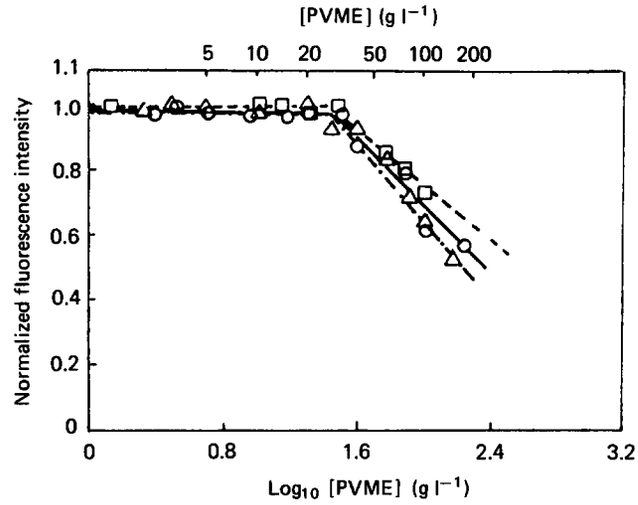

Figure 2 Normalized fluorescence intensity *versus* logarithmic PVME concentration for different concentrations of 35000 APS probe in MEK: □, 0.20; ○, 0.80; △, $0.40\ g\ l^{-1}$ APS

fluorescence intensities are normalized to the maximum fluorescence intensity for that set. The uncertainty in fluorescence intensity is ± 0.01. *Table 1* accounts for the uncertainty in the APS content for each sample by suggesting a range of PVME concentration in which c^* exists for each trial. The concentration of the films is taken to be the density of PVME, $1030\ g\ l^{-1}$.

The figures are interpreted as follows. Below c^* the polymer molecules in solution do not overlap or interact significantly with each other. Therefore, there is little opportunity for the ether group of a PVME chain to contact the anthracene group on an APS chain and quench the anthracene fluorescence. As a result, each set of data exhibits a relatively constant level of anthracene

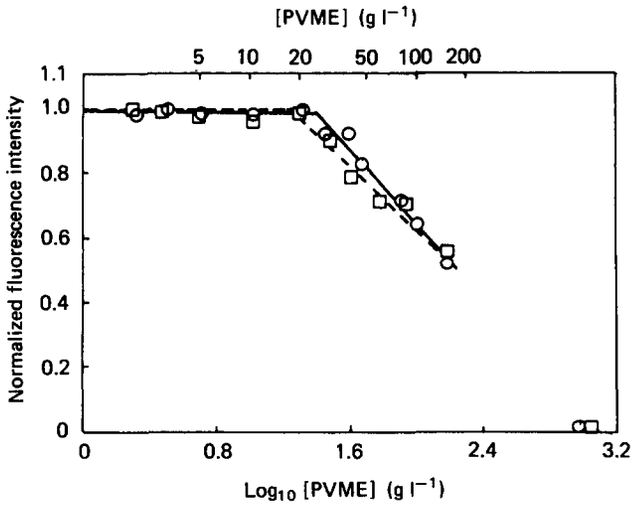

Figure 3 Normalized fluorescence intensity *versus* logarithmic PVME concentration for variation of molecular weight of APS probe in MEK: ○, 35000 APS+PVME in MEK; □, 90000 APS+PVME in MEK

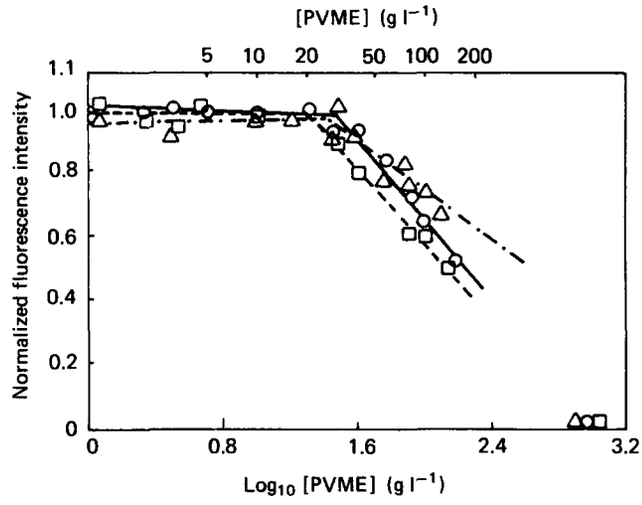

Figure 4 Normalized fluorescence intensity *versus* logarithmic PVME concentration for variation of solvent using 35000 APS probe: ○, in MEK; □, in TOL; △, in BA

fluorescence for low PVME concentrations which correspond to the dilute solution regime. However, for each set of data, at some concentration between 17 g l^{-1} and 29 g l^{-1} PVME a decrease in anthracene fluorescence is observed. This concentration is interpreted as being c^*, the concentration at which overlap of different polymer chains first occurs. At this onset of interpretation the ether functions of PVME are able to contact and quench the anthracene units on APS so that a decrease in fluorescence intensity is seen. As the concentration of PVME is increased above c^*, the molecules in solution are packed even closer together, interpenetration increases, and the fluorescence intensity decreases by an even greater amount. This trend continues to the limiting case of the solid (film) state in which the anthracene fluorescence is almost completely quenched. This is in good agreement with Monnerie's work on compatible PVME–APS systems in the film state[24]. For each set of data the significant decrease in fluorescence intensity above c^* indicates that fluorescence spectroscopy is a useful method with which to study the onset of interpenetration because it is very sensitive to the onset of intermolecular interactions.

Effects of probe

For the concentrations and molecular weights of APS used in this study, the conclusion that APS serves essentially as a probe of PVME overlap and interpenetration is supported by the following. Only a small amount, 0.40 g l^{-1}, of APS probe was used for each data point in *Figures 3–5*. *Figure 2* shows the effect of varying APS concentration on the observed c^* and degree of interpenetration for the 35000 APS/PVME/MEK system. Three different trials using 0.20, 0.40 and 0.80 g l^{-1} APS, respectively, as probes for each solution were performed. The variation in probe concentration had virtually no effect on the determination of c^* between the different trials, as evidenced by the concentration at which fluorescence intensity begins to decrease in each trial. At most, there is only a very small effect of probe concentration on the rate of decrease in fluorescence intensity with increasing PVME concentration above c^*. Within experimental error, the rates of decrease for the 0.40 and 0.80 g l^{-1} runs are the same, with the rate of decrease for the 0.20 g l^{-1} run being only slightly smaller. The similar rates of decrease in fluorescence intensity above c^* indicate that the degrees of PVME interpenetration for a given PVME concentration are similar for these systems and are little affected by the concentration of APS used to probe the PVME systems.

In addition, *Figure 3* illustrates that the determination of c^* and degree of interpenetration above c^* for PVME is not significantly dependent on the molecular weight of the probe. As seen in *Figure 3* for the MEK system, both molecular weights show similar rates of decrease in fluorescence intensity above c^* indicating that the different molecular weight probes detect similar extents of

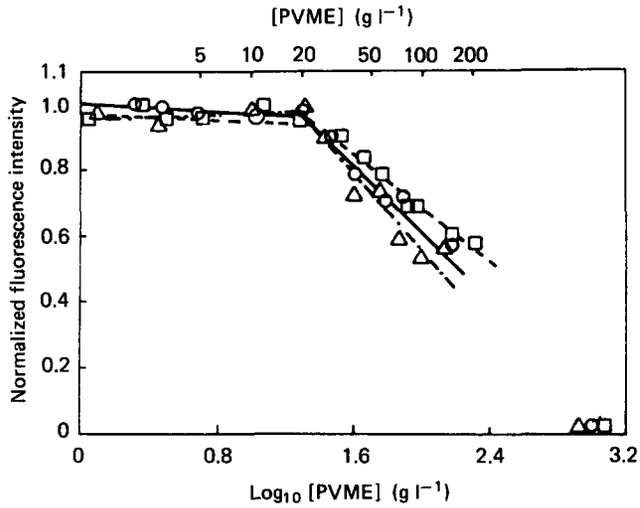

Figure 5 Normalized fluorescence intensity *versus* logarithmic PVME concentration for variation of solvent using 90000 APS probe: ○, in MEK; □, in TOL; △, in BA

Table 1 Values of c^*, $[\eta]$ and A for all trials

APS (M_w)	Solvent	c^* (g l^{-1})	$[\eta]$ (dl g^{-1})	A
35000	TOL	22 (18–25)	0.53	1.2
	MEK	28 (20–29)	0.52	1.4
	BA	29 (24–31)	0.59	1.7
90000	TOL	24 (20–27)	0.53	1.3
	MEK	17 (16–25)	0.52	0.87
	BA	18 (17–25)	0.59	1.1

interpenetration for a given concentration. Although there is some difference in the value of c^* determined from these different molecular weights, when viewed in light of the concentration range of PVME (1–200 g l^{-1}) over which the data were taken, this difference is not very significant compared with experimental error. Similar results were seen for variation of molecular weight in the TOL and BA systems.

Finally, APS and PVME have been reported to form a compatible, or miscible system in TOL[26–29], and are expected to behave similarly in MEK and BA. This idea is supported by two observations which indicate that APS and PVME do not phase separate in the three solvents. The first observation is that films cast from the three solvents were optically clear. This is in contrast to the cloudy films cast from trichloroethane (TCE) which is known to form an incompatible system for APS and PVME[28,29]. The second is that films cast from TOL, MEK and BA showed negligible fluorescence at 415 nm while films cast from TCE showed significant fluorescence at this wavelength (and also exhibited an anthracene spectrum over the 370–570 nm range). These results indicate that for films cast from TOL, MEK and BA, APS and PVME are in intimate contact with no significant regions of phase separation. In films prepared from an incompatible solvent such as TCE, phase separation occurs and anthracene fluorescence is not completely quenched.

Effects of solvent

Figures 4 and *5* show the effect of solvent on the observed interpenetration of PVME for the three solvents employed. There were only small differences observed in c^* and the rates of decrease in fluorescence intensity above c^*. As seen in *Table 1*, the intrinsic viscosities of PVME in MEK and TOL are similar and both are slightly less than the value obtained in BA. Intrinsic viscosity is an indication of solvent quality, as a larger intrinsic viscosity is an indication of a more expanded polymer coil, with polymer coils being expanded to a greater degree in better solvents. Thus, the intrinsic viscosity data indicate that MEK and TOL are of similar solvent quality for PVME, while BA is a slightly better solvent. Therefore, it is reasonable that there was no significant difference in the observed c^* or rate of decrease in fluorescence intensity above c^* for MEK and TOL. This is due to similar degrees of overlap and interpenetration at a given concentration being expected in either solvent as a result of PVME coils having similar dimensions at a given concentration for each solvent.

It was expected that in BA, the better solvent, differences in c^* and the rate of decrease in fluorescence intensity above c^* would be observed with regard to MEK and TOL due to the differing degree of polymer–polymer interpenetration found in a better solvent. However, significant differences were not observed, and it is possible that, for this type of an investigation, a larger variation in solvent quality is needed to observe such differences.

Relationship between c^* and $[\eta]$

There has been much theoretical and experimental evidence suggesting that $c^* = A/[\eta]$ with the constant A being reported in the range of 0.77–5.0[2,30]. As seen in *Table 1*, values of A from this investigation range from 0.87–1.7, which agrees with these earlier works. There are several possible reasons why the values for A are at the lower end of this range. The lower values of A found in this investigation may be due in part to the nature of fluorescence quenching used. For example, in the energy transfer work done by Torkelson *et al.*[20], the observed values of A ranged from 1.9–3.0. However, their measurements were made from systems in which polymer chains were dilutely labelled with either anthracene or carbazole with close proximity between the two labels being necessary for energy transfer to occur. In these fluorescence-quenching trials dilutely labelled APS was used but theoretically any ether function on a PVME chain is capable of quenching anthracene fluorescence. Therefore, it is possible that for equivalent levels of interpenetration, the type of fluorescence quenching used in this investigation is affected to a greater degree by low levels of interpenetration than the energy transfer technique used in Torkelson's studies. As a result, this technique may detect c^* at a lower concentration than would the energy transfer technique if used on this system.

Another explanation for these results may follow along the lines recently suggested by Torkelson *et al.*[20] This explanation was put forth to account for their observation that a bimodal 670 000 and 100 000 PS system exhibited a lower A value than either of the monodisperse 100 000 or 670 000 systems. They suggested that, for monodisperse polymer coils viewed as spheres, significant interpenetration occurs only when the polymer coils in solution achieve a close-packed configuration. Interpenetration before this point is prevented by steric effects. However, in a bimodal or polydisperse system, it is conceivable that a smaller chain may interaction with a segment of a larger chain before this close-packed configuration is reached. This would lead to interpenetration at a lowerconcentration than the monodisperse system, and hence lower values for c^* and A. In this fluorescence quenching investigation, although nearly monodisperse APS was used, the APS detected interpenetration of a polydisperse PVME solution. The polydisperse PVME system, which contains some chains that may be significantly larger or smaller than the APS probe, should allow for detection of interactions between PVME and APS at lower concentrations than would be the case if both the PVME and APS systems were monodisperse and of equal size. This could contribute to the relatively low values of A observed in this study.

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