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Determination of Interpenetration of Polystyrene in Solution and Film by Energy-Transfer Techniques

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ABSTRACT: Energy-transfer techniques involving carbazole- and anthracene-labeled polystyrenes have been shown to be suitable for studying interpenetration of polystyrene in both good (toluene) and fair (ethyl acetate) solvents and for observing the correlation hole effect in polystyrene films. In solution, interpolymer energy transfer is negligible or limited until substantial polymer concentrations are reached. The critical concentration for chain overlap, c^*, can be determined by an increase or break in the plot of I_A/I_C as a function of concentration, where I_A/I_C is the ratio of fluorescence intensities of anthracene label to carbazole label. For polymers with nearly equivalent label content on a per repeat unit basis, the proportionality constant, A, relating c^* to $[\eta]^{-1}$ is observed to be molecular weight dependent. This can be accounted for by the molecular weight dependence of the density of repeat units of a polymer coil in solution. For a polystyrene solution with a bimodal molecular weight distribution, the coefficient A is smaller than for either of the monodisperse polystyrene solutions. At concentrations above c^*, I_A/I_C increases more rapidly for toluene solutions than for ethyl acetate solutions, suggesting that the tendency for interaction and thus interpenetration above c^* is greater in better solvents. In films cast from toluene and ethyl acetate solutions, I_A/I_C is nearly independent of solvent but is much smaller for higher molecular weight polymers; this is a manifestation of the correlation hole effect.

Introduction

Interpenetration or overlap of polymer coils in solution and in the bulk state has been the subject of many recent studies.[2-34] From a technological viewpoint, this interest can be related to the role interpenetration plays in a number of important processes including polymerization,[35,36] polymer adhesion or welding,[37,38] cross-linking of resins,[8,39] and dissolution processes such as those used in the development stages of photoresist production.[40] From a fundamental scientific viewpoint, this interest is justified by the roles played by polymer interpenetration in diffusion and sedimentation behavior,[41,42] in the concentration dependence of osmotic pressure,[26,43] and in modifying solution viscosity.[30,32,44,45]

The effect of polymer solution structure is particularly interesting in the interrelated effects it has on diffusional processes and polymerization phenomena. In a free radical polymerization, autoacceleration or the Trommsdorff effect[46] is associated with a sharp decline in the termination rate constant (the propagation rate constant is affected but to a lesser degree) which in turn is associated with a sharp decline in the rate of diffusion of the free radical on the terminal unit of the growing polymer chain. This sharp decline in the rate of diffusion has been ascribed to the development of entanglements between polymer chains which changes the mode of diffusion to a reptative one.[47,48] Interpenetration is of obvious importance in this phenomenon as polymers must interpenetrate to a signficant degree before polymer chain entanglements become important.[27] Khoklov et al.[49] have done work recently which suggests that the structure of polymer solutions also has an important effect on diffusion-controlled intermacromolecular reactions in systems with relatively low polymer concentrations which might be typical of termination reactions at low conversion of monomer in a polymerizing medium.

Many experimental methods have been used to study the onset and/or degree of interpenetration in polymer solutions including osmometry,[26,27,43] viscosity,[10,30,32] diffusion,[11,29] stress compliance,[12] small-angle neutron and X-ray scattering,[13,14] infrared and UV absorbance spectroscopy,[16,21,28] and photophysical techniques.[2,7,18-22,24,25] Caution must be used in interpreting the results of some of these techniques. For example, with UV absorbance spectroscopy an anomolous concentration dependence of the extinction coefficient which was originally interpreted as an indication of chain overlap[16] was later shown to be absent[21,28] in more critical absorbance experiments. Also, different groups using the same technique, photocross-linking, have reached different conclusions about the degree of interpenetration of polymer coils. Vollmert and Stutz[6,34] concluded from their photocross-linking study that the inner core of a polymer coil is not penetrated by other coils while an opposing view is provided by Braun,[8] Worsfeld,[33] and Reiser and Egerton[5] who conclude that a high degree of interpenetration is possible.

Photophysical methods are well suited to the study of polymer overlap and interpenetration as polymers may be labeled (at very low ratios of labels to repeat units) with chromophores or moieties whose interactions can be observed by fluorescence quenching or energy transfer. Weill[24] and Kirsh et al.[2] were the first to apply the technique of fluorescence quenching. Weill found that quenching of diphenylanthracene by homo- and copolymers of (dimethylamino)styrene was sensitive to polymer overlap while Kirsh et al. showed that quenching of fluorescent chromophore-labeled polymers by quencher-labeled polymers did not take place appreciably until overlap occurred. Both the study by Weill and by Kirsh et al. demonstrate how well interactions of the type involved in polymerization phenomena such as propagation reactions (small molecules interacting with polymer chain segments as in Weill's study) and termination reactions (segments from different polymer chains interacting with each other as in Kirsh's study) are affected by polymer solution structure.

The photophysical technique which has received greater attention recently in studying interpenetration has been energy transfer between fluorescence donor and acceptor chromophores, where the donor and acceptor are on different polymer chains. Morawetz[19,25] has labeled polystyrene with either carbazole (donor) units or anthracene (acceptor) units. Energy transfer occurs between the two labels by a Förster mechanism in which transfer drops off

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with the inverse sixth power of distance between the labels. In the case of anthracene and carbazole, there is a 50% chance of energy transfer when the two units are separated by 26.3 Å.[50] Morawetz has evaluated the level of interpenetration in polymer solutions by making solutions of various concentrations, freeze-drying the solutions, and measuring the energy transfer from pellets pressed from the freeze-dried solutions. From this very important work, Morawetz has shown that energy transfer is extremely sensitive to interpenetration. He found a sharp increase in the level of energy transfer represented by the ratio of anthracene to carbazole fluorescence intensities, I_A/I_C, when the polymer concentration exceeded $1/[\eta]$.[19] He also found that I_A/I_C reached a plateau when the polymer concentration exceeded $3/[\eta]$. Morawetz concluded the critical concentration for polymer overlap, c^*, is $1/[\eta]$. This conclusion is consistent with theoretical arguments[3,10,32,51] which indicate that $c^* \sim [\eta]^{-1}$.

As with Morawetz's study,[19] energy transfer was used in the present study to investigate overlap and interpenetration in polymer solutions. However, instead of evaluating the energy transfer from freeze-dried pellets made from polymer solutions of various concentrations as Morawetz[19] did, energy transfer was measured directly from polymer solutions. As explained in the following section, these solution measurements yield information on the static property of chain overlap and are not seriously affected by dynamic effects such as diffusion of chromophores. Energy-transfer measurements were also made on polymer films which were solution cast. The results from the film studies not only serve as an upper bound on the concentration dependence of energy transfer but are also important in demonstrating the correlation hole effect,[51,52] in which, for distances less than the radius of the polymer coil, the interchain segment–segment correlation decreases with decreasing distance.

Measurement of Static Properties by Energy Transfer

That energy transfer between carbazyl and anthryl labels detects the static property of chain overlap or interpenetration and is not affected significantly by dynamic effects such as diffusion can be understood by the following argument. If r is the mean diffusion length of the chromophores, then $r = (2D\tau_{0D})^{1/2}$ where τ_{0D} is the excited-state fluorescence lifetime of the donor in the absence of acceptor, and $D = D_D + D_A$ where D_D and D_A are the donor and acceptor diffusion coefficients, respectively. Energy-transfer studies can be divided into three regimes depending on the values of r and R_0, the mean distance between a donor and an acceptor molecule for which there is a 50% probability of resonance energy transfer:[50] for $r > R_0$, a diffusion-controlled or Stern–Volmer regime; for $r \sim R_0$, an intermediate regime; and for $r < R_0$, an inductive-resonance or Förster regime. Thus, in order for diffusional processes to play an important role in the observed energy transfer, the labels on the polymer chains would need to diffuse distances at least comparable to R_0 during the donor fluorescence lifetime. Likewise, for static properties of interpeneration to dominate the observed energy transfer, the labels on the polymer chains would necessarily be required to diffuse less than R_0 during the donor fluorescence lifetime.

Carbazole has an excited-state lifetime of 16.1 ns in cyclohexane and 15.1 ns in ethanol.[53] As an approximation, it is reasonable to assume that the carbazole label has a 16-ns lifetime in the polymer solutions used in this study. If it is also assumed that the label on a polymer chain diffuses in a manner similar to the polymer chain itself (microBrownian motion effects will be small compared to polymer self-diffusion effects in increasing energy transfer between chains for concentrations below c^*), then the label diffusion coefficient can be approximated by the self-diffusion coefficient, D_s, of the polymer coil. Léger et al.[54] have measured the self-diffusion coefficient of polystyrene for four molecular weights of polystyrene in benzene. Given the similar viscosities of toluene and benzene, their data approximate well the self-diffusion coefficients of polystyrene in toluene, which is one of the two polymer–solvent systems used in this study. From the results of Léger et al., one can determine that in very dilute solutions $D_s \doteq 5 \times 10^{-7}$ cm^2/s for 100 000 MW PS and $D_s \doteq 1 \times 10^{-7}$ cm^2/s for 670 000 MW PS. (These are the two molecular weights of polystyrene for which measurements are reported in this study.) For concentrations around c^* (or apparent chain overlap), $D_s \doteq 2.5 \times 10^{-7}$ cm^2/s for 100 000 MW PS and $D_s \doteq 3.5 \times 10^{-8}$ cm^2/s for 670 000 MW PS. Thus, for the 100 000 MW PS system, $r = 17.9$ Å in very dilute solution and $r = 12.6$ Å around c^*; for 670 000 MW PS, $r = 8.0$ Å in very dilute solution and $r \doteq 4.7$ Å around c^*. For the carbazole–anthracene system, $R_0 = 26.3$ Å,[50] and a similar value is likely to obtain for the labeled polymers. Therefore, even in the most dilute case and for the lowest molecular weight polymer $r < 0.7R_0$; for concentrations of greatest interest, those being concentrations for which overlap is expected, $r < 0.5R_0$. At these small values of r, the energy transfer will be dominated by overlap and interpenetration, and consequently energy-transfer studies done in the solution state are sufficient for measuring static properties of polymer solutions.

Experimental Section

Spectrophotometric quality ethyl acetate and toluene were used as received from Aldrich. Nearly monodisperse 100 000 and 670 000 MW polystyrene (PS) samples were obtained from Pressure Chemical Co.

The labeled polystyrene was prepared as follows. Potassium carbazole (KCarb) was prepared as described by Gibson and Bailey[55] from an equimolar mixture of carbazole and KOH in xylene. Polystyrene was chloromethylated by using the technique of Jones.[56] The reaction involved adding 1 wt % $ZnCl_2$ to 10 wt % polystyrene in chloromethyl methyl ether and was run for 10 min at room temperature. The polystyrene was cleaned of excess $ZnCl_2$ by dissolving in dioxane and reprecipitating in water. The chloromethylated polystyrene was treated with KCarb by using the procedure of Gibson and Bailey.[51] The labeled polymer was cleaned of excess carbazole by repeated dioxane–water solution precipitation until the ratio of UV absorbance of carbazole (294 nm) to polystyrene (253.7 nm) remained constant. Anthracene-labeled PS was prepared by reacting chloromethylated PS with 9-anthracenemethanol and sodium hydride.[57] The anthryl-labeled PS was also cleaned by repeated solution precipitation to obtain a constant level of UV absorbance for the anthracene label (365 nm).

Absorbance measurements for characterizing label concentrations were made with an IBM UV–vis 9410 double-beam spectrophotometer. Label concentrations were found by using the following extinction coefficients of model compounds:[25] ϵ(9-benzylcarbazole) = 16070 cm^{-1} M^{-1} at 294 nm and ϵ(9-anthracenemethanol) = 8460 cm^{-1} M^{-1} at 365 nm in dioxane. Label concentrations were found to be 0.0925 and 0.0848 wt % for the anthracene- and carbazole-labeled 100K PS polymers, respectively, and 0.107 and 0.0858 wt % for the anthracene- and carbazole-labeled 670K PS polymers, respectively.

Solutions, containing an equimolar ratio of anthracene and carbazole labels, were mixed in 5- and 10-mL volumetrics and mechanically shaken for 24–48 h. Measurements were made on a Perkin-Elmer MPF-44A spectrophotometer with 6-nm slit widths or on a SPEX Fluorolog DM1B photon-counting spectrometer with slit widths of 2–3 nm. Excitation was done at 294 nm, and emission was measured at 365 and 410 nm for carbazole and anthracene, respectively. Front-face geometry was used for

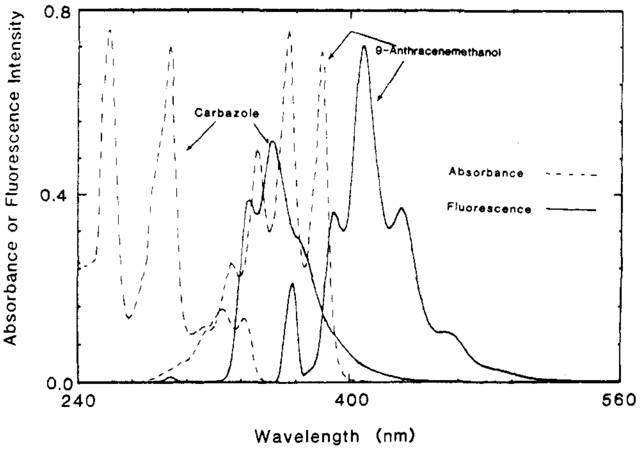

Figure 1. Absorbance and fluorescence spectra for dilute solutions of carbazole or 9-anthracenemethanol in ethyl acetate: carbazole concentration = 0.026 g/L; 9-anthracenemethanol concentration = 0.023 g/L.

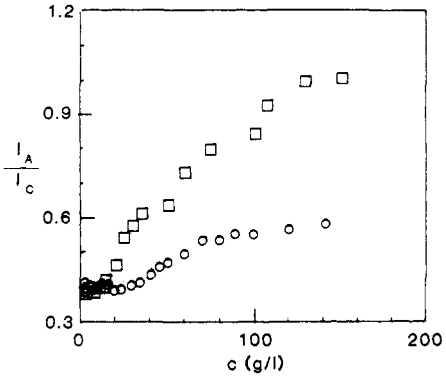

Figure 2. Linear concentration dependence of I_A/I_C for bimodal systems of 100 000 and 670 000 MW PS in ethyl acetate and in toluene: (○) ethyl acetate; (□) toluene.

all measurements. In order to remove oxygen from the solutions prior to fluorescence measurement, all solutions were nitrogenated by bubbling nitrogen through the cells for 10 min.

Films were cast from 10–15 wt % polymer solutions. Films were air dried for 24 h, followed by vacuum drying for 24–48 h at room temperature. Film thickness was 0.3–0.5 mm.

Intrinsic viscosities were obtained by using Ubbelohde No. 50 and 100 viscometers. Solvents were glass filtered to remove dust, and solutions were made to have a maximum concentration of 5–6 g/L in the viscometer.

Results and Discussion

Figure 1 shows the absorbance and fluorescence spectra for dilute solutions of 9-anthracenemethanol. There is very considerable overlap of the carbazole fluorescence and 9-anthracenemethanol absorbance spectra indicating that donor–acceptor characteristics of these chromophores are well matched. Furthermore, there is sufficient separation in the fluorescence spectra of the two chromophores to allow for easy characterization of energy transfer by measuring fluorescence intensities at specific wavelengths, one characteristic of carbazole fluorescence and one characteristic of anthracene fluorescence.

Figure 2 shows the linear concentration dependences of I_A/I_C for the bimodal system of 100 000 and 670 000 MW PS in ethyl acetate and in toluene. (Anthracene- and carbazole-labeled polymers are present in both the 100 000 and 670 000 MW polymers.) At low concentrations most of the fluorescence is due to the carbazole labels. The small amount of anthracene fluorescence is due to unavoidable direct excitation of the anthracene label at the chosen excitation wavelength. At higher concentrations associated with the semidilute solution regime, there is a significant increase in I_A/I_C indicative of interaction of different polymers.

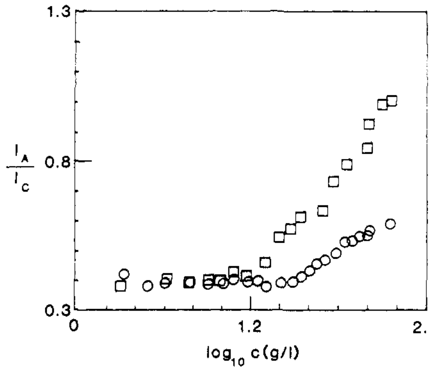

Figure 3. Logarithmic concentration dependence of I_A/I_C for bimodal systems of 100 000 and 670 000 MW PS in ethyl acetate and in toluene: (○) ethyl acetate; (□) toluene.

Table I
Determination by Energy-Transfer Measurements

MW polymer	solvent	c^*, g/L	$[\eta]^{-1}$, g/L	$c^*[\eta]$
100K PS	toluene	56 (38–74)	25.3_8	2.2
100K PS	ethyl acetate	76 (57–95)	35.0_4	2.2
670K PS	toluene	18 (13–25)	6.05	3.0
670K PS	ethyl acetate	35 (20–50)	11.9_1	2.9
670K PS/100K PS	toluene	17 (12–22)	10.5_0	1.6
670K PS/100K PS	ethyl acetate	33 (25.5–37)	17.6_4	1.9

That the increase in I_A/I_C was associated with intermolecular interactions and not with polymer concentration dependent quantum yields of the labels was checked by measuring the quantum yield of labeled polymer as a function of untagged polymer concentration. Slight increases in quantum yield were observed with increasing polymer concentration. However, these small changes are unable to account for the large, sudden increase in I_A/I_C observed with increasing concentration. From Figure 2 approximate values of c^* for the two solvent systems can be determined relatively easily by the sharp increases in I_A/I_C that occur at about 17 g/L in toluene and 33 g/L in ethyl acetate. Another view of the increases in I_A/I_C at c^* can be obtained from logarithmic concentration plots as in Figure 3. From Figure 2 (or Figure 3), c^* can be assigned by a break or discontinuity in the concentration dependence of I_A/I_C. At concentrations lower than c^*, I_A/I_C appears to be nearly independent of concentration for the ethyl acetate system while the toluene data suggest a slight increase in I_A/I_C with increasing concentration. (The differences in the ethyl acetate and toluene solutions are more easily observed in Figure 3 where the low-concentration data are spread out.) It should be noted that at infinite dilution, I_A/I_C is nearly the same in the toluene and ethyl acetate systems. At concentrations above c^*, I_A/I_C increases much more rapidly with increasing concentration for the toluene system than for the ethyl acetate system. These same general features of the linear concentration dependence of I_A/I_C were also present for the data taken on the monodisperse 100 000 and 670 000 MW PS solutions. However, the slight concentration dependence observed at low concentrations in the bimodal PS/toluene solutions was considerably greater in the 670 000 MW PS/toluene solution.

Values of c^* determined from the linear or logarithmic concentration plots are compared in Table I with $[\eta]^{-1}$ where $[\eta]$ is the intrinsic vicosity. It should be noted that measured intrinsic viscosities for the toluene solutions were in good agreement with data from the literature; an accepted value for the Mark–Houwink exponent for polystyrene in toluene is 0.75[58] while data from the solutions used in this study yield an exponent of 0.74. A Mark–Houwink equation for polystyrene/ethyl acetate was not found in the literature, but the data taken in this study suggest that the Mark–Houwink exponent is approximately 0.58–0.59. Thus, while toluene is a very good solvent for polystyrene, ethyl acetate is at most a fair solvent. This means that, for a given molecular weight of polystyrene, coil overlap should occur at lower concentrations in toluene solutions than in the ethyl acetate solutions, as the coils are expected to be more expanded in toluene than ethyl acetate.

Also listed in Table I are values of $c^*[\eta]$ which range from 1.6 to 3.0 for best estimates. Many theoretical and experimental results have been published which indicate that $c^* = A[\eta]^{-1}$ where A is a parameter that has taken on values of 0.77[32] to about 5.[12] Much of the theoretical or modeling work done on predicting values of A has centered on various strategies for putting spheres, which each contain one polymer coil and which each have a volume equal to the volume pervaded by the polymer coil in solution, into a close-packed arrangement. Depending on the strategy chosen, A can assume different values. (The relationship between $[\eta]^{-1}$ and c^* can be seen to arise from the relationship $[\eta] = \Phi(\overline{r^2})^{3/2}/M$ where $\overline{r^2}$ is the mean-square end-to-end distance of the polymer chain, M is its molecular weight, and Φ is approximately a universal constant.) Experimental results yield different values of A depending on the sensitivity of the technique to overlap. In any case, the results from this study yield values of A which fall within the range of values obtained in the previous theoretical and experimental studies.

An interesting feature of the A values obtained in the present study is that while A is independent or nearly independent of solvent at constant molecular weight, it is very much dependent on molecular weight. From the best estimates of c^*, $A \doteq 3.0$ for the 670 000 MW polystyrene which is in good agreement with predictions given by Jamieson et al.[29] and experimental determination of chain overlap by Ferry and others,[9] but A is considerably smaller for the 100 000 MW PS and smaller yet for the bimodal PS.

At least a part of this molecular weight dependence is due to the method employed to detect interpenetration. In order for energy transfer to occur, the carbazole and anthracene units must be close to each other, within 26.3 Å for a 50% chance or greater of energy transfer.[50] In a good solvent, a higher molecular weight polymer occupies space less densely than a lower molecular weight polymer: $\rho \sim M^{1-3\nu}$ where ρ is the density of a single polymer chain ($\rho \sim M/R_G^3$ where R_G is the radius of gyration of the polymer) and ν is the exponent describing the molecular weight dependence of the radius of gyration of the polymer ($R_G \sim M^\nu$). At infinite dilution, $\nu = 0.5$ for a Θ solvent and 0.6 for a very good solvent. (Renormalization group theory calculations[59] have predicted $\nu = 0.588$ for a good solvent.) As concentration goes from infinite dilution to c^*, polymers in a good solvent contract in size and approach but do not yet reach their Gaussian dimensions. From neutron scattering data of ~110 000 MW PS in toluene solutions,[60] one can easily estimate that $\nu \doteq 0.51_8$ at c^* for the 100 000 MW PS in toluene solutions used in this study. Thus, regardless of the solvent quality, the density of a polymer coil in solution decreases with increasing molecular weight.

We estimate that at $2.2[\eta]^{-1}$, which is approximately c^* for the 100 000 MW PS systems, the density of a 670 000 MW PS coil is only about 35% the density of a 100 000 MW PS coil. Given that label contents on a per repeat unit basis are similar in the 100 000 and 670 000 MW PS systems, the density of anthracene or carbazole labels within the volume pervaded by a coil will be much lower in the 670 000 MW PS solutions than in the 100 000 MW PS solutions. As the likelihood of energy transfer from carbazole to anthracene labels depends only on the density of those labels, a somewhat greater packing of lower density polymer "spheres" of 670 000 MW PS must be achieved as compared to the packing of higher density polymer "spheres" before energy transfer is observed. This is consistent with the higher A value observed for the higher molecular weight polystyrene.

Of course, polymer molecules are not truly spherical in shape. Recent studies by Olaj[61] suggest that in dilute solution polymers have a shape like that of prolate ellipsoids (Θ solvent conditions) or oblate ellipsoids (athermal solvent conditions) and do not pervade a truly spherical volume until very high packing of polymer molecules. Thus, while the argument given above suffices to explain qualitatively the difference in A values obtained in the monodisperse systems, it is probably inadequate for developing a more quantitative explanation.

One feature of the experimental data that is not adequately treated even at a qualitative level by the argument above is the fact that the A value obtained for the bimodal system was lower than for either of the monodisperse systems. Some attention has been given in the literature to the differences in packing efficiencies that might be achieved between systems consisting of solutions of monodisperse polymer spheres and systems consisting of solutions of polydisperse spheres,[31] but this by itself is not able to explain the data. A better explanation may be given by the "blob" model,[51,62] in which a polymer coil may be visualized as a succession of blobs each of which consists of a length of the polymer coil of n_c repeats units. If $\langle r_n^2 \rangle$ is defined as the mean-square distance between two monomers n units apart along the backbone of the chain, then for $n > n_c$ all distances $\langle r_n^2 \rangle$ are swollen while for $n < n_c$ all distances $\langle r_n^2 \rangle$ are unperturbed.[51,62]. If the 100 000 and 670 000 MW PS chains are considered to consist of a series of blobs of ~20 000 MW (at ~20 000 MW or below, polystyrene molecules exhibit Θ behavior or near Θ behavior regardless of the solvent[63-65]), then Figure 4 illustrates the ways in which monodisperse and bimodally distributed polymers can interact with each other. In monodisperse polymer systems, significant interpenetration of chains occurs when all of the polymer spheres are in contact with other spheres in a close-packed manner. (This is sometimes called the "hard-sphere" model.) Steric effects prevent the moving in of one chain on another of the same size if close packing is not present. However, when the system is bimodal with one type of chain much smaller than the other, blobs from the smaller chain can move into the "holes" within the "sphere" of the larger polymer and interact with blobs of the larger polymer with only a relatively small steric effect present. Thus, considerable interpenetration of bimodal PS chains as monitored by interpolymer energy transfer may occur prior to close packing of the polymer "spheres". This means that while the simple model involving interaction of hard spheres has some validity for monodisperse polymer systems, modifications to that model including the relative ease with which smaller polymers may interact with larger polymers must be made for polydisperse systems.

In order to determine the effect of solvent on the level of interpenetration of polystyrene at $c > c^*$, two approaches may be taken. One is to simply inspect Figures

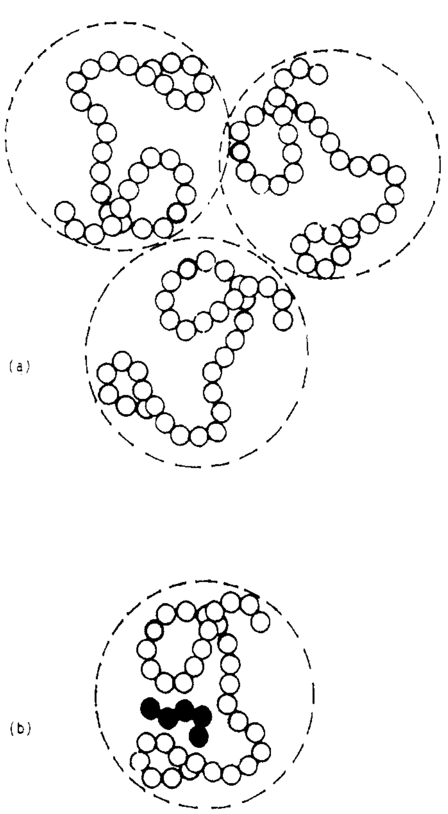

Figure 4. (a) Representation of interaction of monodisperse polymers as hard spheres. (b) Representation of interpenetration of a high molecular weight polymer by a low molecular weight polymer.

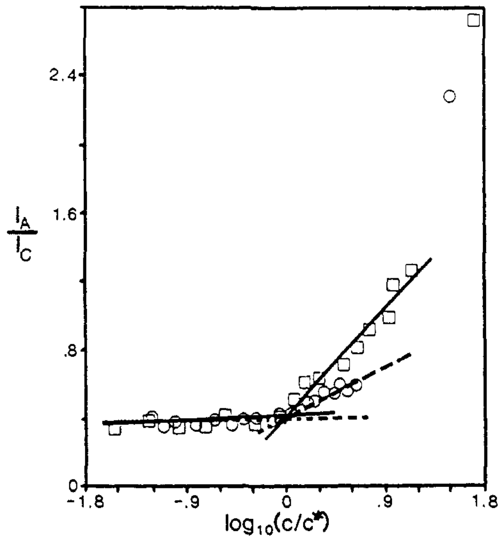

Figure 5. Logarithmic concentration dependence of I_A/I_C for bimodal systems of 100 000 and 670 000 MW PS in ethyl acetate and in toluene with concentration scaled to c^*: (○) ethyl acetate; (□) toluene.

2 and 3 in which I_A/I_C is plotted as a function of linear or logarithmic concentration; a second approach given in Figure 5 involves scaling the concentration with respect to c^*. From both approaches, it is obvious that I_A/I_C increases more rapidly at concentrations slightly above c^* for toluene solutions than for ethyl acetate solutions. This effect was observed for both monodisperse polymer systems as well. This apparently greater interaction of labels in toluene solutions suggests that greater interpenetration occurs in better solvents for concentrations slightly above c^*. It is interesting to note that qualitatively the same solvent effect was observed by Morawetz[19] with his energy-transfer studies on freeze-dried systems.

Table II
I_A/I_C of Solution-Cast Films

MW polymer	solvent	I_A/I_C	MW polymer	solvent	I_A/I_C
100K PS	toluene	8.58	100K PS	ethyl acetate	1.91
100K PS	ethyl acetate	8.25	670K PS/100K PS	toluene	2.29
670K PS	toluene	2.09	670K PS/100K PS	ethyl acetate	2.71

This effect is seemingly in conflict with the notion that polymers will reduce their interactions in better solvents but could be expected on the basis of the notion that even at c^* polymers are swollen more in a good solvent than in a fair solvent. However, the degree of swelling present at c^* is often misunderstood. While it is true that polystyrene molecules at infinite dilution have much greater excluded volume in toluene than in ethyl acetate, the differences is much smaller at $c \sim c^*$. A common measure of excluded volume is ν where $R_G \sim M^\nu$ with R_G being the radius of gyration and M being the molecular weight of the polymer. ν can be related to a, the Mark–Houwink exponent, according to the relation $\nu = (a + 1)/3$. Thus, from values of a reported above, at infinite dilution $\nu \doteq 0.58_3$ for PS in toluene while $\nu \doteq 0.52_9$ for PS in ethyl acetate. This indicates a significant difference in excluded volume and thus "swelling" of the coil size. However, as polymer concentration is increased, coils lose excluded volume and contract until at bulk concentration $\nu = 0.500$. From the measurements made recently by King et al.[60] on the concentration dependence of R_G of polystyrene in toluene, it can be estimated that for 100 000 MW PS $\nu = 0.51_8$ at c^*. No data are available concerning the concentration dependence of R_G for polystyrene in ethyl acetate, but it is likely that $0.50 < \nu < 0.51$ for 100 000 MW PS at c^* in ethyl acetate. The slight difference in ν at c^* for the two solvent systems would suggest that effects due to thermodynamic solvent quality would be present but relatively small at $c \geqslant c^*$. In fact, the effects observed in this study are substantial at $c \geqslant c^*$. Further work is being undertaken at present to understand more fully the role played by thermodynamic solvent quality and to determine how even small differences in excluded volume affect interpenetration.

Data below c^* are apparently in conflict with the concept, first put forward by Flory[66,67] and now quite generally accepted, that polymer molecules in a good solvent repel each other so as to be impenetrable in dilute solution or at least to minimize their interactions with each other in order to maximize their interactions with solvent. As noted earlier in Figures 2 and 3, below c^* the values of I_A/I_C for ethyl acetate solutions are nearly independent of concentration while the data for toluene solutions exhibit a small measureable increase in I_A/I_C with increasing concentration. The increase in I_A/I_C with increasing concentration was observed to be greatest in the 670 000 MW PS/toluene solution. Flory's theory predicts that polymer spheres become even more impenetrable in dilute solution as molecular weight increases. Recently, Flory's theory has been disputed by Khalatur and Khoklov[68] who claim that monodisperse polymer spheres with excluded volume are not mutually impenetrable. While it appears that the present data support Khalatur and Khoklov's ideas and are in conflict with Flory's prediction, further work is being undertaken in order to provide definitive conclusions.

A final point of interest concerns the values of I_A/I_C obtained from solution-cast films. Table II lists the film values as a function of polymer molecular weight and solvent. It is evident that for films the casting solvent plays little role in the observed energy transfer but that molecular weight plays a very important role. The values of I_A/I_C increase in the following order: 670 000 MW PS $\lesssim$ bimodal PS < 100 000 MW PS. Most striking is the fact that I_A/I_C is approximately 4 times greater in the 100 000 MW PS than in the 670 000 MW PS film. As indicated in the experimental section, the label contents of the two polymers are nearly identical, with the 100 000 MW PS having slightly greater labeling. If the polymer films were to have a totally random distribution of labels, I_A/I_C would be similar in the 100 000 and 670 000 MW PS systems, with a slightly higher value occurring for 100 000 MW PS. Instead, a factor of 4 difference is observed which can be explained qualitatively by the correlation hole effect.

The correlation hole is the depletion of interpolymer segment–segment correlations over a distance on the order of R_G of the polymer chain.[51,52] As the energy transfer in this system is strictly interpolymer and as R_0 is considerably less than R_G ($R_G \sim$ 90–100 Å for 100 000 MW PS[60] and about 230–260 Å for 670 000 MW PS while R_0 = 26.3 Å[50]), the only way that energy transfer can take place is if an anthracene label from one polymer interacts with a carbazole label from a second polymer over a distance considerably less than R_G. Thus, energy transfer between carbazole and anthracene labels can serve as a sensitive measure of the correlation hole. de Gennes[51] indicates that, besides having a width comparable to R_G, the correlation hole has an average depth which scales with $M^{-3/2}$. The observation of much reduced interpolymer label–label energy transfer in the higher molecular weight polymer is consistent with de Gennes' prediction. Further work relating energy transfer to the correlation hole effect in labeled polymer films is in progress; in particular, studies allowing quantitative determination of the correlation hole effect by transient energy-transfer studies[69] are under way.

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