Study of the Interpenetration of Monodisperse Polystyrene in Semidilute Solution by Fluorescence after Freeze-Drying[1]

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ABSTRACT: Polystyrene with a narrow molecular weight distribution was labeled with carbazole and anthracene. Benzene, dioxane, and cyclohexane solutions containing a mixture of the two labeled polystyrenes were rapidly frozen and the solvent was removed by sublimation. It was assumed that this procedure preserved the chain entanglement in the original solution. The ratio of the anthracene and carbazole emission intensity, I_A/I_C, observed in reflectance fluorescence spectra when pellets of the freeze-dried polymer were irradiated in the carbazole absorption band was compared with this ratio in films cast from the same polymer mixture, $(I_A/I_C)_f$, where the two polystyrene species could be assumed to be randomly mixed. Thus, $(I_A/I_C)/(I_A/I_C)_f$ was taken as linear in the fraction of interpenetrating polymer chains. The results showed that chain interpenetration is negligible for polymer solution concentrations, c, smaller than $1/[\eta]$, increases for $c > 1/[\eta]$, but seems to encounter a strong resistance to further interpenetration at $c \sim 3/[\eta]$. The extent of interpenetration *decreases* with decreasing solvent power of the medium, contrary to accepted theories. Our results seem to substantiate those of a computer simulation which suggests that in poor solvents polymers attract one another up to moderate chain interpenetration but repel one another at very small separations of their centers of mass. The interpretation of our data is consistent with that of small-angle light and neutron scattering which suggests long-range inhomogeneities in semidilute solutions.

Introduction

The Flory–Krigbaum theory of the thermodynamic properties of dilute solutions of flexible-chain polymers predicts that the interpenetration of the molecular coils is strongly resisted in good solvent media.[2] As the solution concentration, c, is increased, a point is eventually reached where the total space can no longer accommodate the swollen molecular coils without some chain entanglement. Beyond this "critical concentration", conventionally denoted by c^*, the dependence of thermodynamic and hydrodynamic properties of the system on polymer chain length and concentration changes in a striking manner because of the interpenetration of the molecular coils.[3,4] The question then arises what fraction of these molecular coils should be considered as mutually entangled in what is commonly referred to as the "semidilute region", i.e., when $c > c^*$.

Several attempts have been made to study this problem by spectroscopy. Destor et al.[5] claimed that a plot of optical density of solutions of poly(oxyethylene) and poly(vinyl acetate) against the polymer concentration exhibited a change of slope at c^*. However, a careful repetition of these experiments by Lee et al.[6] revealed no such break. Roots and Nyström[7] reported an upward curvature in plots of the ratio of excimer and monomer emission against polystyrene concentration in the region of c^*, but the work of Torkelson et al.[8] made such an effect appear improbable. Yet another approach was reported by Kirsh et al.,[9] who studied solutions containing two vinylpyridine copolymers, one containing fluorescent anthracene residues, and the other quaternary pyridinium residues which quench the anthracene fluorescence. They reported little quenching up to a critical polymer concentration and a quenching efficiency beyond this concentration which could be related to the quenching efficiency observed when the fluorophore and the quencher were carried by the same chain. Since they used copolymers with 26 and 50 mol % of quenching residues, the results cannot be considered typical of the interpenetration of similar polymer chains.

In a previous communication from this laboratory[10] we attempted the characterization of the extent of flexible-chain interpenetration as a function of solution concentration using the following approach: Two portions of poly(ethyl methacrylate) labeled by anthracene and carbazole, respectively, were dissolved in benzene and frozen within a fraction of a second. It was assumed that the extent of chain entanglement remained unchanged during the rapid freezing so that, after removal of the frozen benzene by sublimation, the material should retain a memory of the chain interpenetration that had existed in the original solution. Increasing chain entanglement was then expected to increase nonradiative energy transfer by the Förster mechanism,[11] leading to a decreasing ratio of emission intensity from the carbazole and anthracene, I_C/I_A, when the sample was irradiated in the carbazole absorption band. The data agreed with this expectation and the transition from a low to a high energy transfer efficiency seemed to correspond to solution concentrations in the range expected for c^*.

The use of a polydisperse sample in the previous study necessarily limited any interpretation of the data and we used, therefore, near-monodisperse polystyrene in the present investigation. The study of chain interpenetration as a function of solution concentration was expanded by the use of polymer with three molecular weights and three solvents ranging from a strongly solvating medium to the vicinity of the Θ point.

Experimental Section

Solvents. Benzene and cyclohexane (Aldrich, spectrophotometric grade) were shaken with concentrated sulfuric acid and then with water, dilute NaOH, and again water. They were dried with P_2O_5 and distilled. Dioxane (Aldrich, spectrophotometric grade) was refluxed over metallic sodium and distilled under nitrogen. *N,N*-Dimethylformamide (Aldrich, spectrophotometric grade) was shaken with KOH pellets, stored overnight over $MgSO_4$, decanted, and distilled over $Ba(OH)_2$.

Reagents. Carbazole and 9-anthracenemethanol (Aldrich) recrystallized from methanol melted at 245 and 163 °C, respectively. Vinylbenzyl chloride (Dow Chemical Co.) was extracted with 0.5% KOH solution to remove *tert*-butylcatechol and nitromethane. It was dried over anhydrous K_2CO_3. Chloromethyl methyl ether (CME) (Pfalz and Bauer), stannic chloride (Aldrich), and "monodisperse" polystyrene (Polysciences) were used as received.

Polystyrene Labeling. Conventional polystyrene was used to define conditions for the attachment of carbazole and anthracene labels. A carbon tetrachloride solution containing 5% PS, 5 vol % CME, and 0.5 vol % $SnCl_4$ was allowed to react at 30 °C. To monitor the progress of the chloromethylation the

Table I
Characterization of Polystyrenes Used in This Study

		mol % label		[η], dL/g		
mol wt[a]	$\bar{M}_w/\bar{M}_n$[a]	carbazole	anthracene	benzene (25 °C)	dioxane (25 °C)	cyclohexane (50 °C)
1.00×10^5	1.06	0.22	0.19	0.47	0.41	0.28
1.85×10^5	1.06	0.19	0.20	0.74	0.67	0.43
4.10×10^5	1.06	0.20	0.18	1.31	1.16	0.68

[a] As specified by the supplier.

polymer from an aliquot of the solution was precipitated by a large excess of methanol, redissolved and reprecipitated to remove unreacted CME and $SnCl_4$, and vacuum-dried. To a solution of 0.2 g of polymer in 10 mL of dioxane was added 2 mL of a 25 wt % aqueous solution of trimethylamine. After 6 h at room temperature two drops of concentrated HNO_3 and 60 mL of water were added. Chloride was determined potentiometrically by titration with 0.001 N $AgNO_3$ using a chloride-sensitive electrode (Corning catalog no. 13-641-604) to locate the end point. Poly(vinylbenzyl chloride) was used as a standard. The extent of chloromethylation was linear in time, with 0.25% of the polystyrene residues reacting in 25 min. Potassium carbazolyl was reacted with the chloromethylated PS in DMF solution for 6 h at 30 °C.[12] The reaction of 9-anthracenemethoxide with the chloromethylated PS required 12 h at 70 °C. The label concentrations on the PS was determined by UV absorption.[13]

Sample Preparation. Solutions containing donor- and acceptor-labeled PS (with an equal concentration of the two labels) were rapidly frozen by immersion of a rotating round-bottom flask into liquid nitrogen. The solvent was sublimed at −5 to 0 °C at 10^{-3} Torr for 12 h and at room temperature for 24 h. The fluffy film was pressed under 5.3 kbar into partly transparent pellets. Films were cast on a Teflon plate from 15% solutions of mixtures of donor- and acceptor-labeled PS stirred for a few hours under a nitrogen atmosphere. The solvent was evaporated by a stream of nitrogen, and the films were further dried at 10^{-3} Torr at room temperature for 24 h.

Fluorescence Measurements. The same procedure as used in our previous study[10] was employed. The pellets or films were irradiated at 294 nm and eight reflectance spectra were recorded, rotating the sample by 45° between measurements. Results were expressed as I_A/I_C, the ratio of the emission intensity of the anthracene label at 415 nm and the carbazole label at 360 nm. The standard deviation of this ratio for any one sample was less than 5%.

Results

The characteristics of the three polystyrene samples used in this study are listed in Table I. The intrinsic viscosities in the three solvents were found to be in close agreement with those obtained from the Mark–Houwink parameters in the literature.[14-16]

It has been reported[17] that the freeze-drying of polymer solutions from solutions with a concentration below c^* leads to a collapse of each polymer molecule to a spherical globule if the polymer is below its glass transition temperature. Thus, the freeze-drying of donor- and acceptor-labeled PS from highly dilute solutions should contain separate globules containing donor or acceptor fluorophores, while freeze-drying from solutions with increasing concentrations above c^* was expected to contain an increasing fraction of interpenetrating chain molecules.

According to Förster, the efficiency of nonradiative energy transfer is given by

$$\text{eff} = R_0^6/(r^6 + R_0^6) \tag{1}$$

where r is the spacing between the donor and acceptor and R_0, the characteristic distance corresponding to a 50% transfer efficiency, may be derived from the spectroscopic properties of the system. Using N-benzylcarbazole and 9-anthracenemethanol as analogues of the labels on the polystyrenes, we obtained $R_0 = 2.75$ nm, in close agreement with Berlman's value[18] of 2.875 nm for the energy transfer from N-methylcarbazole to 9-methylanthracene.

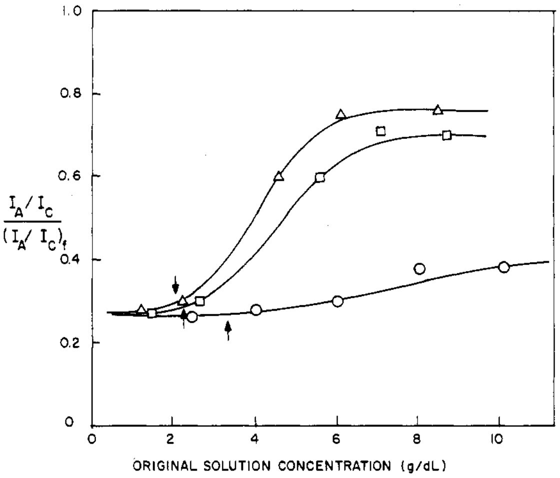

Figure 1. Dependence of the chain interpenetration on the concentration of polystyrene ($\bar{M} = 1.00 \times 10^5$) in benzene at 25 °C (△), dioxane at 25 °C (□), and cyclohexane at 50 °C (○).

The segregation of donor and acceptor fluorophores into separate globules reduces the extent of energy transfer as compared to a system in which the donor- and acceptor-labeled polystyrenes are randomly mixed. Such random mixing is obtained by the slow evaporation of solutions containing a mixture of the two polymeric species. We found that the $(I_A/I_C)_f$ ratio did not vary significantly when different solvents were used. The cast films containing PS with molecular weights of 1.00×10^5, 1.85×10^5, and 4.10×10^5 were characterized by $(I_A/I_C)_f$ of 8.52 ± 0.04, 8.10 ± 0.10, and 7.91 ± 0.05, respectively. If we denote by $(I_A/I_C)_0$ the I_A/I_C value obtained by the freeze-drying of solutions sufficiently dilute so that the polymer chains do not interpenetrate, then $[(I_A/I_C) - (I_A/I_C)_0]/[(I_A/I_C)_f - (I_A/I_C)_0]$ may be taken as the fraction of chains penetrating other molecular coils.

Plots of $(I_A/I_C)/(I_A/I_C)_f$ against the original polystyrene concentration in benzene and dioxane at 25 °C and in cyclohexane at 50 °C are shown for the three PS samples in Figures 1–3. Since the critical concentration c^* is generally taken as proportional to the inverse of the intrinsic viscosity (although different authors have proposed different proportionality constants[19]), the ratio of the solution concentration, c, to the critical concentration c^* is proportional to $c[\eta]$ and a plot of $(I_A/I_C)/(I_A/I_C)_f$ against $c[\eta]$ may be considered particularly meaningful. Such a plot for benzene and cyclohexane solutions is shown in Figure 4.

The following features of our results should be noted: (1) At high polymer dilutions freeze-drying leads to samples whose I_A/I_C is independent of the original solution concentration and independent of the solvent used. Figure 4 shows that this ratio decreases slightly with an increasing chain length of the polymer. This feature is easily understood: As the size of the globules into which the polymer molecules collapse is increased, a smaller fraction of their volume is within the characteristic energy transfer

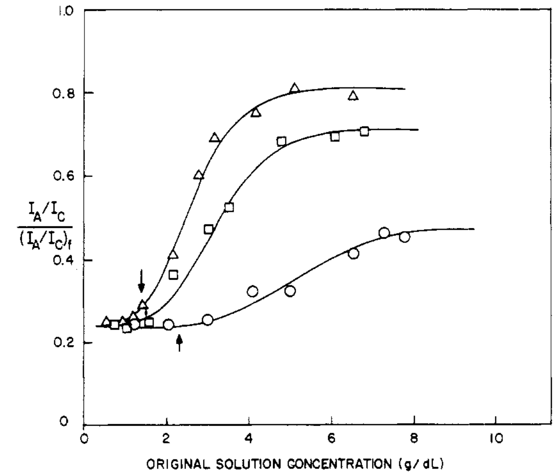

Figure 2. Dependence of the chain interpenetration on the concentration of polystyrene ($\bar{M} = 1.85 \times 10^5$) in benzene at 25 °C (△), dioxane at 25 °C (□), and cyclohexane at 50 °C (○).

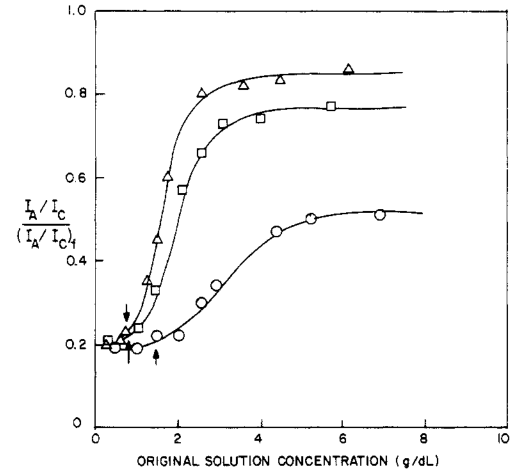

Figure 3. Dependence of the chain interpenetration on the concentration of polystyrene ($\bar{M} = 4.10 \times 10^5$) in benzene at 25 °C (△), dioxane at 25 °C (□), and cyclohexane at 50 °C (○).

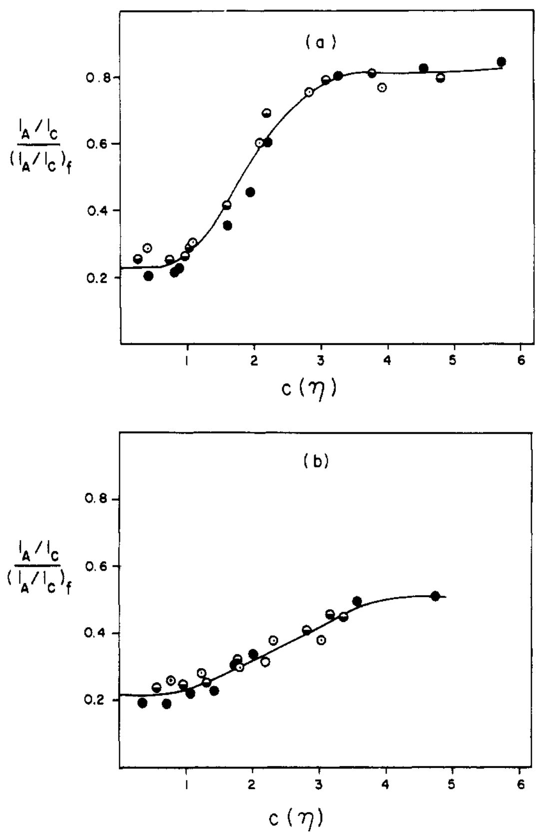

Figure 4. Dependence of the interpenetration of polystyrene chains on $c(\eta)$. (a) Solutions in benzene at 25 °C. (b) Solutions in cyclohexane at 50 °C. (○) $\bar{M} = 1.00 \times 10^5$; (◐) $\bar{M} = 1.85 \times 10^5$; (●) $\bar{M} = 4.10 \times 10^5$.

distance R_0 of donor- and acceptor-labeled globules in contact with one another. (2) I_A/I_C begins to rise for $c[\eta] \sim 1$. (3) The $(I_A/I_C)/(I_A/I_C)_f$ plots tend to level off near $c[\eta] \sim 3$,[20] suggesting that an increasing interpenetration of the molecular coils is encountering a considerable resistance at this point. (4) Contrary to expectation, all the data show that in the semidilute region, chain interpenetration is much more pronounced in the good solvent, benzene, that in solutions of cyclohaxane at 50 °C, close to the Θ temperature of 34.4 °C.[21] (5) For polystyrenes with a fourfold variation of molecular weight, the extent of chain interpenetration is a function of $c[\eta]$, i.e., c/c^*.

Discussion

It is not possible to prove rigorously that no change in the interpenetration of flexible molecular coils occurred during the rapid freezing of polymer solutions used in this study. Yet, the internal consistency of the data leaves little doubt that this assumption, on which all interpretations are based, is valid. We have also observed that in the range of polymer concentrations which yield freeze-dried samples with an increasing nonradiative energy transfer, these samples also exhibit a striking increase of cohesion indicative of chain entanglements.

We are occasionally asked why we employed freeze-dried samples, rather than the solutions containing a mixture of donor- and acceptor-labeled polymers, for the study of the extent of chain entanglements by nonradiative energy transfer. There are two reasons for this choice: (1) Elimination of the solvent has led in our experiments to a concentration of the fluorescent labels by factors as large as 300. Thus, much smaller densities of the labels on the PS could be employed with a minimal perturbation of the polymer properties. (2) In the solid sample no diffusion of the labels is possible and energy transfer depends only on the static distribution of donors and acceptors. By contrast, the energy transfer in solution is affected by the motion of the labels during the lifetime of the excited state of the donor, and no reliable method exists by which the restrictions to such motions for solutions containing polymers with varying degrees of entanglement could be assessed.

The constancy of I_A/I_C when $c < 1/[\eta]$ confirms the general assumption that chain entanglements are negligible for $c < c^*$. However, two unexpected phenomena were discovered: (1) The extent of chain entanglement for any given polymer concentration, or for any given c/c^*, was found to increase with an increasing solvent power. This surprising result was confirmed by a recent study of Torkelson et al.,[22] who measured nonradiative energy transfer of labeled PS in solution. The result seems to indicate that in a poor solvent medium, chain entanglement is more hindered by the contraction of the molecular coils than it is assisted by the increasing attraction between chain segments. (2) The increase in chain entanglements encounters a large resistance at $c \sim 3/[\eta]$. It is particularly significant that this phenomenon was also observed in cyclohexane at 50 °C, fairly close to the Θ point at 34.4 °C.[21]

This result is particularly important because of its implications concerning the nature of polymer solutions in

Θ solvents. In formulating a theory of the second virial coefficient in solutions of flexible-chain molecules, Flory and Krigbaum[2] modeled the polymer as a spherically symmetrical cloud of disconnected chain segments. Thus, the excluded volume of the chain vanished if it vanished for the chain segment, and under these conditions the chains were considered to be "freely interpenetrating".[23] Yet, this conclusion seems to be invalidated if one takes account of the connectivity of the chain. Olaj and Pelinka carried out a computer simulation of two flexible chains approaching each other.[24] They found that when the separation R of their centers of mass was gradually decreased in a poor solvent medium, the pair distribution function $G(R)$ first increased for R values corresponding to small interpenetrations but later decreased to very small values for very small R. This result can be understood as follows: Relatively small chain interpenetrations are favored by the decreasing potential energy due to contacts between polymer segments, whereas for heavy interpenetration the interdependence of the conformations of the two chains decreases the statistical probability of such states and thus leads to an entropic resistance to increasing entanglement. Olaj and Pelinka showed that the binary cluster integral $\int[1 - G(R)](4\pi R^2)\,dR$ contains a negative and a positive term and that the vanishing excluded volume in Θ solvents is the result of a compensation between the chain attraction and repulsion over different ranges of R. Although the study of Olaj and Pelinka involved only relatively short chains of 50 segments, it may be expected that qualitatively similar results would be obtained with much longer chains.

We believe that our data provide powerful experimental support for the concept derived from the computer simulation referred to above. In fact, since the $(I_A/I_C)/(I_A/I_C)_f$ values at the point where this quantity becomes relatively insensitive to the original polymer concentration are much smaller in the neighborhood of the Θ point than in good solvents, we find that the resistance to heavy chain entanglements is particularly powerful in such solutions. Apparently, as the chains contract in media of decreasing solvent power, the interdependence of chain conformations leads to an increasing resistance to heavy chain interpenetration.

Our results are also of interest in a different context. Following de Gennes,[25] it has been assumed that semidilute solutions are microscopically uniform, characterized by a screening length ξ. Yet, studies of semidilute solutions have revealed an anomalously large light scattering at low angles[26] and recent small-angle neutron scattering data[27] have been interpreted by long-range inhomogeneities with an average correlation length comparable to the radius of gyration of the polymer coil. The conclusions of our investigation are in accord with these studies and are, in fact, identical with Dautzenberg's surmise[26b] that the excess light scattering indicates that "in the concentration range investigated *no* overlapping of the internal core of the molecules occurs".

The results of this study suggest that for a given polymer and solvent the volume fraction of the molecular coils which are interpenetrated in the semidilute region remains a constant function of c/c^* over a broad range of chain lengths. It would be desirable to find out if a similar result would be obtained by a computer simulation such as that carried out by Olaj and Pelinka.

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Registry No. Polystyrene, 9003-53-6.

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