arrangement of domains, distribution in domain size, and the nature and extent of the interface. The details and predictions of this model are the subject of a paper currently in preparation.[35]

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Registry No. Styrene–isoprene copolymer, 25038-32-8; neutron, 12586-31-1.

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(39) It should be noted that the molecular weight dependence of domain size predicted by this theory is the same whether the domains are of isoprene or styrene; i.e., it is immaterial which part of the phase diagram is explored so long as the same domain morphology is obtained. This does not mean to say that the domains of polyisoprene and polystyrene will have the same size and separation for the same molecular weights; the differences are, however, negligibly small.

A Fluorescence Method To Determine the Solubility Parameters δ_H of Soluble Polymers at Infinite Dilution. Cyclization Dynamics of Polymers. 11

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ABSTRACT: A polystyrene sample was prepared containing pyrene groups spaced at regular intervals along the chain backbone. Fluorescence studies of this polymer in dilute solution showed both pyrene (I_M) and pyrene excimer (I_E) fluorescence. The ratio of these fluorescence intensities, I_E/I_M, varied sensitively with a change in solvent. One effect is due to solvent viscosity η_0. A plot of $\eta_0(I_E/I_M)$ against the Hildebrand solubility parameter δ_H gave two straight lines intersecting at $\delta_H = 9.1$. This is the δ_H value reported in the literature for polystyrene. A new technique based upon these observations for using fluorescence spectroscopy to determine δ_H for polymers is described.

Introduction

The solubility parameter concept based on regular solution theory has been used extensively in practical applications of polymers in various solvents and solvent mixtures. It has proven to be a valuable empirical tool in both laboratories and industries.

The solubility parameter, δ_H (units of $(\mathrm{cal/cm^3})^{1/2}$), for any compound is defined from Hildebrand–Scatchard solution theory as the square root of the cohesive energy density, which is itself defined as the ratio of the energy of vaporization, ΔE_v, to the molar volume, V_1, both referred to the same temperature (eq 1).

$$\delta_H \equiv (\Delta E_v/V_1)^{1/2} \qquad (1)$$

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The cohesive energy density of a high polymer cannot be obtained directly from vaporization experiments. From vapor pressure measurements on volatile compounds, Small[2] has assigned cohesive energy density terms for various molecular groups and used these to estimate cohesive energy density values for high polymers.

One widely used method to determine the solubility parameter of a polymer experimentally is to study the interaction of the polymer with a series of solvents and to assign to it the δ_H value of the liquid which proves to be the best solvent for the polymer. For example, the swelling of cross-linked or crystalline polymers may be examined in a variety of solvents.[3] One can assign to the polymer the δ_H value of the solvent that causes the greatest amount of swelling. Alternatively, for soluble polymers, one can determine the intrinsic viscosity $[\eta]$ in various solvents.[4] A plot of $[\eta]$ vs. the δ_H values of the solvents passes through a maximum, which is assigned to the δ_H value of the polymer.

Guillet and co-workers[5] pioneered a gas chromatographic method for determining the thermodynamic parameters for the interaction of small molecules with polymers. Partial molar heats of mixing, partial molar free energies of mixing, and the Flory–Huggins χ parameter were determined for a wide variety of solvents and polymers. From the χ parameters, a set of self-consistent solubility parameters was determined, using the expression

$$\chi = \frac{\bar{V}_1}{RT}(\delta_{H,1} - \delta_{H,2}) \qquad (2)$$

where $\bar{V}_1$ is the partial molar volume of the solvent and the subscripts 1 and 2 refer respectively to the small molecule and polymer. One should note that this method is applicable only above T_g of the polymer and gives δ_H values pertaining to the limit of zero solvent concentration ($\phi_2 \rightarrow 1.0$).

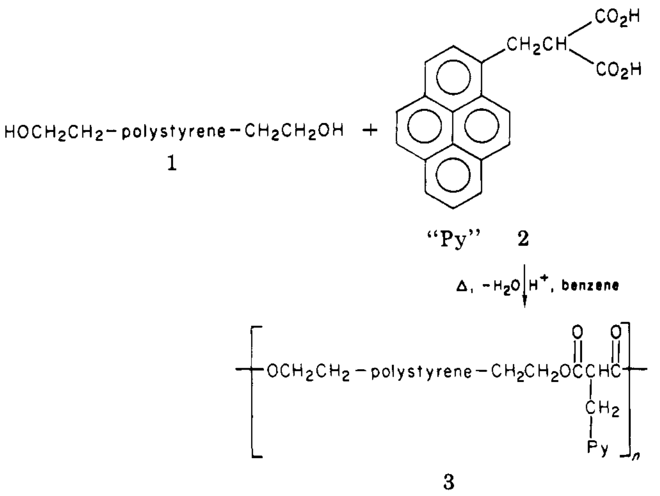
The present report describes a new method based upon excimer fluorescence of labeled polystyrene chains to determine the δ_H value of the polymer. Pyrene groups introduced into the polymer give both a blue pyrene fluorescence (I_M) and a green pyrene excimer fluorescence (I_E). Even after correction for solvent viscosity (η_0) differences, these values vary sensitively in different solvents. We show that a plot of $\eta_0(I_E/I_M)$ vs. δ_H for the various solvents tends to fall on two straight lines. Their intersection, the minimum in the $\eta_0(I_E/I_M)$ plot, corresponds to the value of δ_H for polystyrene determined independently. One of the interesting features of this method is that it gives the δ_H value of the polymer essentially in the limit of zero polymer concentration ($\phi_2 \rightarrow 0$).

Frank and his group at Stanford University have used a similar kind of analysis of excimer fluorescence intensity from poly(vinylnaphthalene) to examine its compatibility in solid films with other polymers.[6]

Experimental Section

Purification of Solvents. Most solvents, to begin with, were of analytical grade. They were purified and dried separately by the following procedures: Acetone and methyl ethyl ketone were refluxed for several hours over anhydrous potassium carbonate and then fractionally distilled. 1,4-Dioxane and tetrahydrofuran were refluxed and distilled over lithium aluminum hydride. Toluene, benzene, and ethylbenzene were dried over sodium metal strips and fractionally distilled. Dimethylformamide was dried when allowed to stand for a few days over molecular sieves. Ethyl acetate, butyl acetate, and ethyl benzoate were used as received. Cyclopentane and cyclohexane were stirred over sulfuric acid, under nitrogen, washed successively with water and aqueous sodium bicarbonate, dried over $CaSO_4$, and distilled from sodium metal. The solvents were examined for impurities in their UV absorption spectra and fluorescence spectra. No unexpected absorbance or fluorescence was observed.

Scheme I



Fluorescence Measurements. A series of solutions of polystyrene containing equally spaced pyrene groups with different molecular weight were prepared. Concentrations ranged from 7×10^{-7} to 4×10^{-6} mol/L of pyrene groups. The solutions in 13-mm-o.d. Pyrex tubes were rigorously degassed by five freeze–pump–thaw cycles and sealed under high vacuum ($<10^{-5}$ mmHg).

Fluorescence measurements were carried out on a Hitachi Perkin-Elmer MPF-44B spectrofluorimeter and were uncorrected. The excitation wavelength was 345 nm. The fluorescence spectra were scanned from 360 to 600 nm and the relative intensities of monomer (I_M) and excimer (I_E) fluorescence were measured by integrating the areas under the pyrene band and the excimer band, respectively.

Molecular Weight Measurements. Measurements by gel permeation chromatography (GPC) of the molecular weights of polystyrene samples containing pendant pyrene groups were made on a Varian Model 5020 liquid chromatograph. Both a variable-wavelength UV–visible detector (Varian UV-50) and a Waters differential refractometer, Model R401, were used in conjunction with DuPont bimodal columns. Polystyrene samples, purchased from Pressure Chemical Co., were used to calibrate the columns.

Polymer Preparation. Polymer 3 was prepared by refluxing a solution of bishydroxy-terminated polystyrene of $\bar{M}_n = 2800$, $\bar{M}_w/\bar{M}_n = 1.3$, with (1-pyrenemethyl)malonic acid in benzene in the presence of a trace of toluenesulfonic acid as a catalyst, with removal of water during the reaction. Details will be published elsewhere.[7] The product had a nominal molecular weight of 40 000, with a broad molecular weight distribution. Small amounts of this product were fractionated by using a 10^3-Å μ-Styragel column with the HPLC. These gave 3–10-mg portions of 3 having $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) values of 13 800 (1.70), 32 900 (1.24), and 52 200 (1.20).

Results

Synthesis. The method used to incorporate pyrene groups into polystyrene is outlined in Scheme I. Our intent was to develop a synthetic method for obtaining equally spaced pyrene groups. These polymers are required for another research project. Their synthesis will be described elsewhere.[7] The results reported here ought not to depend, except in detail, on the distribution of pyrene groups along the chain. The polymers 3 examined here have a pyrene group every 25–30 monomer units along the chain backbone.

Fluorescence Measurements. Samples of the polymer 3 at very low concentration (ca. 1–5 ppm by weight) were dissolved in a variety of solvents, degassed by several freeze–pump–thaw cycles, and sealed in Pyrex tubes. Typical fluorescence spectra are shown in Figure 1. These spectra are characterized by two bands, a structured blue emission (of intensity I_M) due to fluorescence of locally

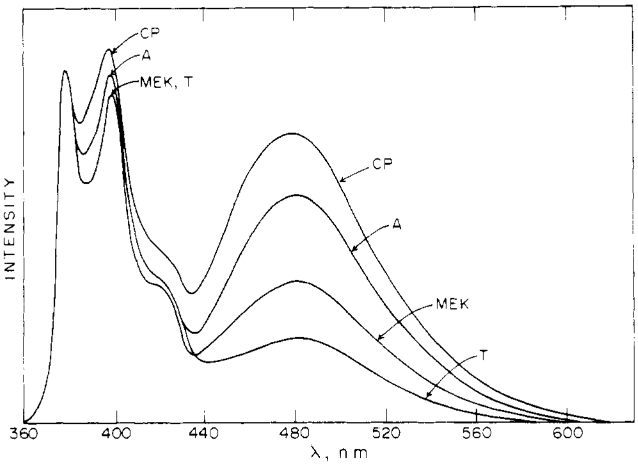


Figure 1. Fluorescence spectra of labeled polystyrenes **3** at ca. 4×10^{-6} M in pyrene groups in various solvents: CP, cyclopentane; A, acetone; MEK, methyl ethyl ketone; T, toluene. The spectra are normalized at the (0,0) band of the pyrene fluorescence.

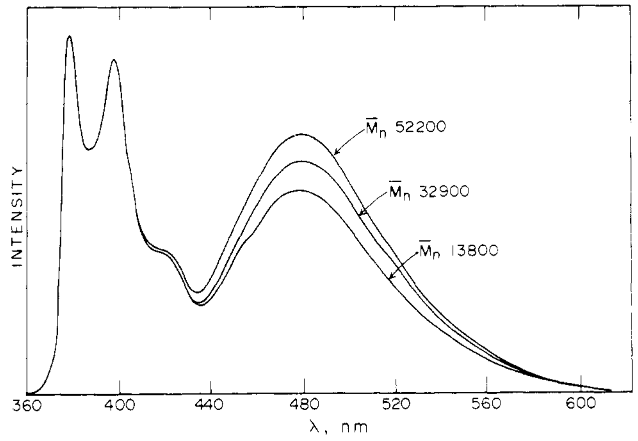


Figure 2. Fluorescence spectra of labeled polystyrenes **3** of different molecular weight in acetone solutions. Conditions as in Figure 1.

excited pyrene groups and a broad structureless green excimer emission (of intensity I_E). The ratio I_E/I_M is very sensitive to the solvent that **3** is dissolved in, with more excimer appearing in solvents that are poor solvents for polystyrene.

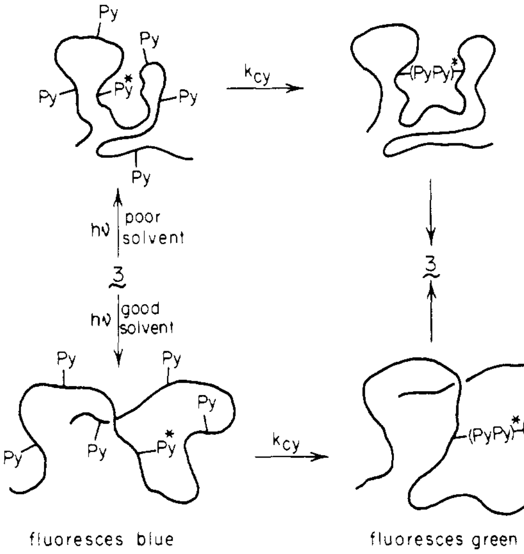
When fractionated samples of **3** are examined, the ratio I_E/I_M increases with chain length in *poor solvents* for polystyrene, Figure 2, but remains constant in *good solvents*.

Discussion

Excimer formation requires an excited pyrene to encounter a second pyrene in an electronic state.[8] These form the excimer complex, which emits a green photon. Pyrene excimers are formed in a diffusion-controlled process. Consequently the extent of excimer formation, as measured by I_E/I_M, has a dynamic component that is sensitive to chain mobility and solvent viscosity (η_0). In addition, I_E/I_M has a configurational component.[9,10] Factors that increase the mean separation of pyrene groups lead to a decrease in I_E/I_M. Conversely factors that compress the polymer dimensions, resulting in a smaller mean separation of pyrene groups, lead to an increase in I_E/I_M. In this way I_E/I_M should be sensitive to the quality of the solvent in which the polymer is dissolved.

These factors are depicted in Scheme II. Light absorbed by pyrene groups excites a few pyrenes in the sample. Excimer formation involves cyclization of the polymer to bring the excited pyrene to within a few angstroms of another pyrene. The rate constant for this process can be called k_{cy}. I_E/I_M is proportional to k_{cy}, which in turn depends upon $1/\eta_0$. The magnitude of k_{cy} is also sensitive to the distance over which the pyrenes have to diffuse; hence, in a good solvent k_{cy} is smaller than in a poor solvent for the polymer.

Scheme II



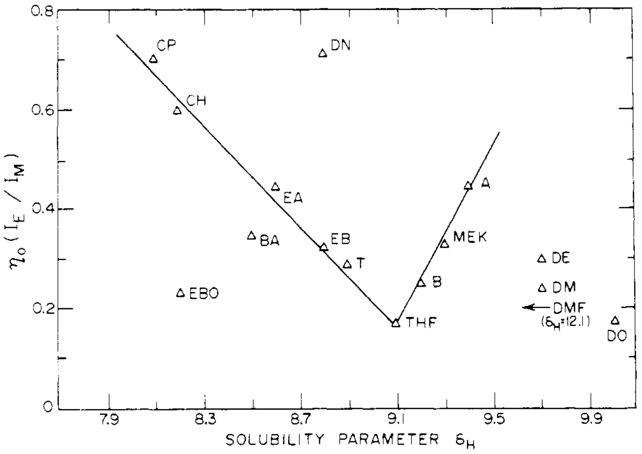


Figure 3. Plot of $\eta_0(I_E/I_M)$ for **3** ($\bar{M}_n = 32\,900$) vs. δ_H for various solvents: CP, cyclopentane; CH, cyclohexane; DN, Decalin (cis + trans); EBO, ethyl benzoate; BA, *n*-butyl acetate; EA, ethyl acetate; EB, ethylbenzene; T, toluene; THF, tetrahydrofuran; B, benzene; MEK, methyl ethyl ketone; A, acetone; DE, 1,2-dichloroethane; DM, dichloromethane; DO, 1,4-dioxane; DMF, *N,N*-dimethylformamide.

The product $\eta_0(I_E/I_M)$ for a given polymer should depend only upon chain dimensions. The Hildebrand δ_H value is a convenient measure of solvent quality. One expects the best solvent for a polymer to have a minimum value for $\delta_{H1} - \delta_{H2}$.

A plot of $\eta_0(I_E/I_M)$ vs. δ_H is shown in Figure 3 for the polystyrene sample **3** of $\bar{M}_n = 32\,900$. Most of the data can be fit to two straight lines which intersect at $\delta_H = 9.1$. This value corresponds to the average of several literature values for δ_H of polystyrene.[1a] In keeping with the model in Scheme II, the $\eta_0(I_E/I_M)$ value is a minimum in a solvent (here THF) whose δ_H value corresponds to that of the polymer.

One of the interesting features of the data is that the presence not only of the pyrene groups but also of the two ester groups appearing every 25–30 monomer units along the chain seems to have little affect on the solubility pa-

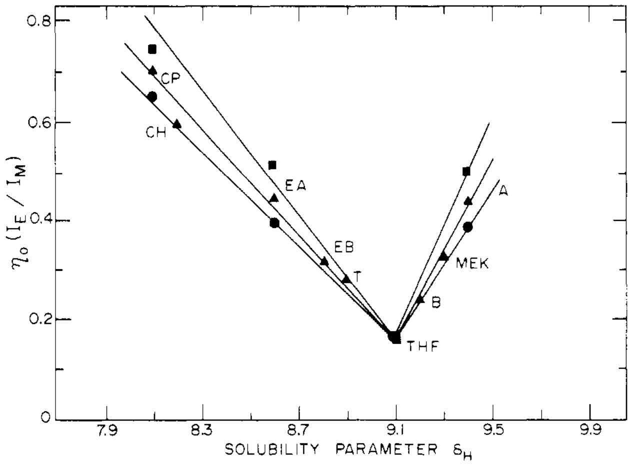


Figure 4. Plot of $\eta_0(I_E/I_M)$ vs. δ_H for samples of **3** of different molecular weight: (■) $\bar{M}_n$ = 52 200; (▲) $\bar{M}_n$ = 32 900; (●) $\bar{M}_n$ = 13 800.

rameter of the polymer. This can be checked in future experiments by using longer polystyrene (PS) oligomers in the synthesis of **3** or by incorporating pyrene into PS via nonpolar linkages.

Several solvents give $\eta_0(I_E/I_M)$ values inconsistent with their δ_H values. These include dimethylformamide (DMF), ethyl benzoate, CH_2Cl_2, and 1,4-dioxane. Such deviations are well documented in the polymer literature.[11] They arise from a variety of sources, most ultimately reflecting differences between molecular interactions and bulk properties (e.g., ΔE_v) of the solvents. For example, 1,4-dioxane is locally dipolar and DMF must undergo specific donor–acceptor interactions with PS. In many instances, δ_H solvent values are not determined from experimental values of ΔE_v. They are estimated from the boiling point of the solvent. These values may be in error and complicate the analysis we present. For example, Decalin is often assigned a δ_H value above 8 whereas $\eta_0(I_E/I_M)$ is more typical of **3** in other alkane solvents.

Molecular weight plays an interesting role in determining the sensitivity of the $\eta_0(I_E/I_M)$ ratio of a polymer to solvent quality. In poor solvents (e.g., cyclopentane, Figure 2) a strong sensitivity is seen, whereas in good solvents, this sensitivity is lost. Figure 4 shows that for a selected group of solvents, the intersecting bilinear dependence of $\eta_0(I_E/I_M)$ upon δ_H is maintained for fractionated samples. The slopes differ, and the sample of highest molecular weight has the steepest slope.

One anticipates that I_E/I_M should be chain-length dependent since excimer formation can occur between pyrenes that are nonadjacent along the chain contour. A longer chain length means that an excited pyrene has more pyrenes with which it can form excimer. As the chain length increases, the effective concentration of pyrenes within the coil increases.

Both the effective concentration and the rate of excimer formation between pairs of pyrenes fall off approximately as $N^{-3\nu}$, where N is the degree of polymerization of the polymer segment connecting the two pyrenes.[9,10,12] The exponent ν takes the value $^1/_2$ in a Θ solvent and $^3/_5$ in a very good solvent. Since I_E/I_M represents a sum over all possible excimer pairs in a polymer chain, the largest contributor will be from pairs adjacent along the chain contour, with pairs more remotely separated each contributing lesser amounts. For pairs of pyrenes far enough apart, their cyclization rate will be so slow that their contribution to I_E/I_M will be negligible. One predicts that in a given solvent, I_E/I_M will approach a maximum value with an increase in chain length.

This effect has been observed by Cuniberti and Perico in poly(vinyl acetate) polymers containing a small amount of pyrene chromophores, presumably randomly distributed along the chain.[13] It is also observed in computer simulations of polymer cyclization in the interior of a chain where cyclization at many sites is summed.[14]

The curious aspect of the data in Figure 4 is that I_E/I_M is independent of chain length in THF. Two factors may operate here. First, the chains are swollen. The mean separation of pyrenes is large, and the effective pyrene concentration within the coil is small. Second, this effective concentration and the pairwise k_{cy} value decrease more rapidly in THF than in poorer solvents: ν approaches its maximum value. The consequence of these effects is that longer chains, in spite of their larger number of pyrene groups, make much smaller contributions to I_E/I_M than they do in poorer solvents. The additional contributions to I_E/I_M from pyrenes remote along the chain contour must be smaller than the experimental error in the I_E/I_M measurement.

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Registry No. Polystyrene, 9003-53-6.

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