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On Measuring the Distribution of Local Free Volume in Glassy Polymers by Photochromic and Fluorescence Techniques

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ABSTRACT: A general technique, based on photoisomerization of photochromic and fluorescent probe molecules having no net dipole moment, has been devised for measuring the distribution of local free volume in glassy polymers such as polystyrene. In this technique, the amount of probe photoisomerization in a glassy polymer relative to that in dilute solution in a nonviscous model solvent, where free volume is not a constraint to isomerization, is measured as a function of the volume required for photoisomerization of the probe. A total of eight probes were used with required isomerization volumes ranging from a low of 127 Å^3 for azobenzene to about 571 Å^3 for 4,4′-diphenylstilbene, the volume requirements calculated from the volume swept by the van der Waals area of a probe molecule during excited-state geometrical rearrangement. The median of the local free volume in unannealed polystyrene found by this method is about 260–280 Å^3, with over 90% larger than about 100–120 Å^3 and practically none larger than 400 Å^3. The size distribution of local free volume is sensitive to physical aging, with a greater reduction occurring in larger local free volume than smaller local free volume during sub-T_g annealing.

When an amorphous polymer is cooled from the melt through its glass transition, an accelerated increase in viscosity and elastic modulus occurs as the glass transition temperature, T_g, is approached. Near T_g the polymer molecules require times comparable with those of laboratory measurements to reach their equilibrium conformation and packing with respect to temperature. As the temperature is decreased below T_g, the molecules are trapped in a nonequilibrium state characterized thermodynamically by higher energy and volume relative to the equilibrium state at the same temperature. The excess volume is attributed to a difference in "free" volume between glassy and equilibrium states.

Although the translational and rotational molecular mobilities in the glass are much reduced with respect to the rubbery region just above T_g, polymer molecules may undergo further packing and conformational rearrangement. As a consequence, two of the measurable thermodynamic state functions, specific enthalpy and volume, are observed to decrease with annealing time at fixed temperature.[1-3] Associated with this enthalpy and volume recovery are changes in the physical and material properties of the polymer:[4-6] an increase in density, tensile and flexural yield stress, and elastic modulus; a decrease in impact strength, fracture energy, ultimate elongation, and creep rate; and a transition from ductile behavior to brittle fracture. On a molecular level, volume recovery in polymer glasses, or physical aging, has been hypothesized to occur by the disappearance and reduction in size of local free volume.[7] The concept that free volume in polymer glasses is composed of local free volume elements of different sizes has theoretical support.[8-13] However, little experimental evidence concerning the details of the distribution of local free volume is available at present.

Small-angle X-ray scattering (SAXS) revealed the apparent absence of structural density fluctuations in poly(methyl methacrylate) (PMMA) glass on a size scale larger than "several tens of angstroms".[14] Annealing of polystyrene glass slightly below T_g coincidentally with SAXS[15] caused a slow reduction of density fluctuations on a size scale reported as 8000 Å^3. Below 80° C, however, the density fluctuations remained constant even though bulk specific volume, measured by dilatometry, continued to decrease at temperatures as low as 61.3 °C. This small-scale homogenization was attributed to a change in the distribution of local free volume.[15,16]

Levita and Smith[17] investigated the diffusion of gases of different sizes in strained polystyrene film. They found that diffusion coefficents for xenon and CO_2 in a strained film decreased with time when the strain was held constant and that the diffusion coefficient for xenon decreased more rapidly than that of CO_2. They concluded that the larger xenon molecule needs larger free volume elements through which to diffuse than CO_2 and that, during the annealing with applied strain, the larger free volume elements decreased in size more rapidly than smaller ones. Another experiment[18] comparing the diffusion of xenon and argon in stretched polystyrene gave similar results.

Positron annihilation spectroscopy in amine-based, lightly cross-linked epoxy resins gave long-lived positron lifetime values[19] that corresponded to those in crystalline solids with structural defects less than 100 Å^3 in size.[20] The lifetime values decreased nearly 10% during the first 20 h of sub-T_g[21] annealing but decreased by less than 4% with continued annealing for 200 h. Changes in bulk specific volume were not measured. The decreasing lifetimes were attributed to a reduction in size of the "holes" which trap the positrons.[19] Another positron annihilation spectroscopy study in polystyrene glass[22] indicated "positronium micropore traps" of radius 5.43 Å. This is evidently a cubical radius because the lifetime of positrons was similar to that in crystalline cavities of sizes in the range 100–150 Å^3.

Photochromism of molecular probes is another technique which should be sensitive to the distribution of local free volume in polymer glasses. (Photochromism is the reversible change of a chemical between two (or more) species which have different absorbance spectra that can be induced in at least one direction by absorption of light.)[23] Photochromic molecular probes in polymer glasses were first used by Gardlund[24] who studied the thermal back reaction of colored forms of 6′-chloro-8′-nitro-1,3,3-trimethylindolinobenzopyrilospiran, finding it to obey first-order kinetics in methyl methacrylate solvent and a sum of two first-order rates in PMMA. Others have since studied thermal back reactions of photochromic probe or label molecules in polymer glasses.[25-35] These studies revealed that above T_g, the thermal back reactions obeyed a single first-order rate,[25-28] leading to the conclusion that the biphasic rates in glass were due to inhomogeneities in

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the density of the glass at a molecular level.[31] (An alternative hypothesis involving molecular association has been offered by Goldburt and Krongauz.[35]) While attempts have been made to model the dimensionless free volume distribution on the basis of biphasic thermal back reactions,[31] other work has shown that some photochromic molecule/polymer systems exhibit back reactions which are not biphasic but instead are a spectrum of single exponentials.[26] Thus, while some thermal back reactions appear to be sensitive to the distribution of local free volume, it is unlikely that a general method of analyzing thermal back reactions with regard to local free volume can be developed.

In contrast to the studies involving measurement of thermal back reactions, this work has emphasized the measurement of the photoinduced forward reaction of photochromic probe molecules in glassy polymers. This in itself is not novel, as Horie et al.[36] have measured the photoinduced back reaction of photochromic molecules in glassy polymers, and notable contributions concerning the measurement of photoinduced trans–cis reactions of photochromic molecules in glassy polymers have been made by Priest and Sifain[25] and Sung et al.[32,33,37,38] Priest and Sifain[25] found that 2,2′-azonaphthalene isomerized more in quenched polystyrene film than in film which had annealed 3 weeks at T_{g} −13° C. Furthermore, a smaller probe, 4-ethoxyazobenzene, isomerized more than the 2,2′-azonaphthalene probe. By incorporating azobenzene chromophores into the main chain of polyurethane, Sung et al.[32,33] have shown that the rate of photoisomerization decreases with annealing time (at T_{g} −10 °C) and that photostationary conversions of azobenzene-labeled polystyrene molecules were considerably lower in film than in dilute solution. These results also clearly demonstrate the sensitivity of photochromism to physical aging and the distribution of local free volume. However, a quantitative relationship between the photochromic phenomenon of probes needing different volumes to isomerize and the size distribution of local free volume and its changes during physical aging has been lacking.

In this work we present for the first time a general method for determining quantitatively the size distribution of local free volume in a polymer glass, polystyrene. We adopt the hypothesis first formulated by Paik and Morawetz[26] and since expounded by others[32,33,37,38] that photoisomerization in the glassy state (relative to that in dilute solution) requires a minimum, critical size of local free volume in the vicinity of the chromophore and have devised a detailed method for determining the volume required for the photoisomerization of probe molecules. (An upper limit to the extra local free volume added by the presence of probe molecules is also determined.) We have employed a variety of photochromic probes, including a homologous series of azo chromophores and substituted stilbenes, each of which requires a different volume to undergo photoinduced trans–cis isomerization. This has resulted in the development of the first quantitative, experimental description of the distribution of local free volume in polystyrene which we present in this paper. As our method for the determination of the critical volume required for photoisomerization has not been previously reported and as photochromic techniques are not familiar to most polymer scientists, both will be described extensively.

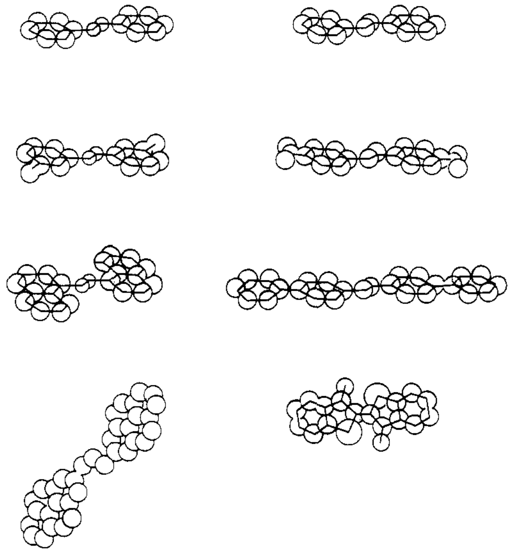

Figure 1. Molecular probes used. Clockwise from upper left: azobenzene, stilbene, 4,4′-dinitrostilbene, 4,4′-diphenylstilbene, thioindigo, 1,3-di(1-pyrenyl)propane, 1,1′-azonaphthalene, *m*-azotoluene.

Experimental Section

Polystyrene was atactic, narrow molar weight distribution ($M_{\mathrm{w}}/M_{\mathrm{n}} < 1.1$), from Pressure Chemicals, Inc. Prior to its use, the polymer was dissolved in ethyl acetate, filtered through standard laboratory filter paper (to remove dust), precipitated with methanol, and allowed to dry. The polystyrene was heated in vacuum (10^{-3} Torr) at a temperature of about 100 °C for several hours, to remove low molar weight residues or solvent which remained adsorbed. Several molar weights were used: 1790, 3570, 9050, 15 000, 92 600, 411 000, and 670 000. Polystyrene of 15 000 molar weight and lower formed cracked films, reducing subsequent measurement accuracy.

The molecular probes used were azobenzene (Aldrich Chemical Company, 99%), 4,4′-diphenylstilbene (Aldrich Chemical Company), stilbene (Eastman Kodak Chemicals, scintillation grade), 1,1′-azonaphthalene (ICN Pharmaceuticals, Life Sciences Group), 4,4′-dinitrostilbene (ICN Biomedicals, Inc., K & K Laboratories), *m*-azotoluene (ICN Biomedicals, Inc., K & K Laboratories), 1,3-di(1-pyrenyl)propane (Molecular Probes, Inc.), and thioindigo (custom synthesized by Molecular Probes, Inc.). All were used as received. Figure 1 shows the molecular probes used in this study, approximately to scale. Prior to their use in films, UV spectra and molar absorption coefficients were obtained using an IBM Instruments 9410 UV/visible spectrophotometer. A bandwidth resolution of 1 nm was used because it was found to give precise absorbance measurements with less unwanted irradiation of the samples than a 2-nm bandwidth. UV absorbances were measured digitally in the range 0.100–2.500 with a precision of about 0.1% in the upper part of this range. With matched cells carefully cleaned, accuracy was also about 0.1%. Solutions were prepared in foil-wrapped volumetric flasks and stored in a closed cabinet in the same dark room where measurements were taken. All absorbance measurements were made at ambient temperature which was recorded but varied seasonally from 23 to 28 °C.

The light used to irradiate films and solutions came from a Photon Technology International (PTI) arc lamp housing and dc power supply, attached to a variable slit width monochromator. The bandwidth used was 4 nm for stilbene and 4,4′-dinitrostilbene and 16 nm for 1,1′-azonaphthalene, azobenzene, *m*-azotoluene, thioindigo, and 4,4′-diphenylstilbene. The PTI arc lamp housing collects and focuses light from a water-cooled, 100-W mercury–xenon compact (high-pressure) arc lamp. (Use of a xenon lamp might give slightly different results because of its continuous UV emission spectrum and its flexibility to irradiate exactly at the wavelength of peak probe absorbance.) The lamp housing and monochromator are mounted on an optical rail. Light from the exit of the monochromator is collimated by a fused silica, $1^1/_2$-in.-diameter, 175-mm-focal length, planoconvex lens mounted on the optical rail 7 in. in front of the monochromator. On the basis of the photoisomerization of 1,1′-azonaphthalene in solution achieved in a few seconds, the light energy flux exceeded 1500 μW/cm^2 at 405 nm.

Fluorescence emission of thioindigo and 4,4′-diphenylstilbene was measured with a Spex Industries Fluorolog-2 DM1B spectrofluorimeter which automatically corrects for the radiometric response of detectors and optical components. Fluorescence emission was measured from the front surface of the sample, at a 22.5° angle to the exciting beam. Fluorescence emission of 1,3-di(1-pyrenyl)propane was measured with a Perkin-Elmer MPF-44A spectrofluorimeter from the front surface of the sample and was uncorrected.

Probe-in-polymer films were prepared by mixing 0.5 g of polystyrene with about 0.5 cm^3 of solutions containing about 0.2 g/L of probe chemical in spectrophotometric grade dichloromethane. Additional dichloromethane was added to give a pourable solution, roughly 10% by weight polymer, capable of covering a 5- × 5-cm glass UV filter. The resulting concentration of probe chemical in the film did not exceed the maximum found to give constant molar absorption coefficients in toluene, discussed in the Results and Discussion section. A sharp decrease in the molar absorption coefficient for thioindigo indicated that thioindigo agglomerated at concentrations exceeding 0.08 g/L in toluene, so concentrations in the film were kept an order of magnitude less than those of other probes. The solubility limit of 1,1′-azonaphthalene in toluene was found to be close to 5×10^{-4} g/cm^3 at ambient temperature.

Polymer solution was poured onto the center of a clean, 5- × 5-cm Corning (7058) clear glass UV filter transparent to wavelengths of 300 nm and higher. Unavoidable exposure to low intensity room light was kept to a minimum during polymer solution preparation and casting. Films were allowed to dry slowly, in a covered Petri dish, in the dark, for about 24 h. Films were then placed in a vacuum oven maintained at 60 °C for 48 h. Films were clear; however, stress cracks formed in the lower molar weight films. The films were heated to 10–20 °C above T_g in vacuum for several minutes and then removed from the oven and cooled rapidly in the dark. This drying procedure effectively removed all residual solvent from the films, as indicated by the lack of bubble formation within the rubbery films above their T_g, and in addition gave films a common thermal history. Some loss of *trans*-4,4′-diphenylstilbene in films occurred during the vacuum heating. For films with this probe, the vacuum heating was omitted. Films were stored in the dark, covered, until needed. Film thicknesses were measured with a Starrett Co. dial comparator and were less than 0.3 mm.

Physical aging tests were carried out in a vacuum oven, under vacuum, with the temperature measured by a thermometer inside the oven. Temperature fluctuations at a given heater setting and in different areas of the oven amounted to ±1 °C, which can be considered the accuracy of the temperature measurement over a period longer than an hour.

Results and Discussion

In using any small-molecule light-sensitive probe, an upper concentration limit exists beyond which the probe molecules associate, or fail to act independently. Law and Loutfy[39] observed that malonitrile fluorescent probes agglomerated at concentrations exceeding 0.03 gmol/L, a limit which has been extended to other probes.[32] To see if the probes we used would agglomerate, we took UV absorbance spectra of each probe in toluene solution at various probe concentrations, normalized to the molar absorption coefficient at the wavelength of the principal absorbance peak. Except for thioindigo, no significant differences were found for probe concentrations as high as could give accurate peak absorbance measurements through a narrow path cuvette. Figure 2 shows that the molar absorption for thioindigo in toluene solution decreases significantly for concentrations greater than about 0.08 g/L (2.5×10^{-4} gmol/L). Table I gives the molar absorption coefficients found for the probes at the wavelength of the principal absorbance peak. Molar absorption coefficients in dichloromethane solutions used in film casting did not differ greatly from those found for toluene solutions. For probes in polystyrene films, molar absorption coefficients proved impossible to measure with accuracy comparable to solution values. Part of the inaccuracy came from variation in the film thickness and part from the (small) loss of probe during film drying.

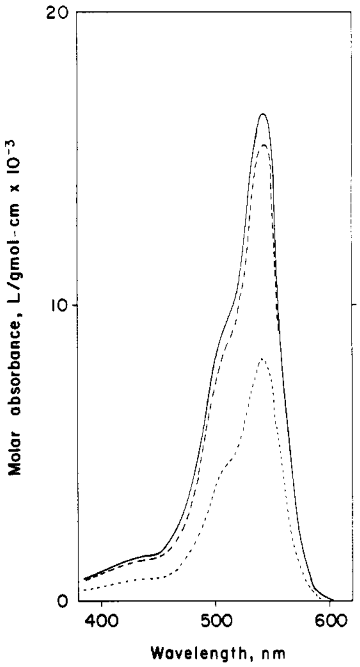

Figure 2. UV absorbance spectrum for *trans*-thioindigo in toluene: (—) 0.0029–0.0178 g/L, (- - -) 0.090 g/L, and (···) 0.208 g/L.

Table I
Molar Absorption Coefficients at Principal Absorbance Peaks for Molecular Probes in Toluene at Ambient Temperature

	molar absorption coeff at λ		
molecular probe (trans)	coeff, L/(gmol·cm)	λ, nm	highest concn, g/L
azobenzene	18700	320	0.0946
	468	450	0.504
m-azotoluene	20000	325	0.191
	522	445	0.191
1,1′-azonaphthalene	13300	402	0.297
	1790	480	0.503
stilbene	24800	311	0.154
4,4′-dinitrostilbene	28000	358	0.017
4,4′-diphenylstilbene	45100	342	0.100
thioindigo	16600	543	0.0178
1,3-di(1-pyrenyl)propane	69000	347.5	0.010

These measurements provided a conservative upper limit to probe concentration in polystyrene films which ensured the validity of Beer's law.[40] Also, the probe trans isomers initially present in the film had no net dipole moment, which obviated possible local ordering or clustering near polar molecular groups within the polymer. Thus, we feel assured that the probes in this study were distributed uniformly and isotropically within the polymer.

Fractional Isomerization. Azo Series. Three azo probes were used: azobenzene, *m*-azotoluene, and 1,1′-azonaphthalene. Polystyrene films and toluene solutions containing the trans isomers were irradiated to photoequilibrium. The cis isomer fraction Y was determined from spectrophotometric absorbance by

$$Y = \frac{1 - A/A_{\mathrm{dark}}}{1 - \epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}} \qquad (1)$$

where A_{dark} = peak initial absorbance with only trans

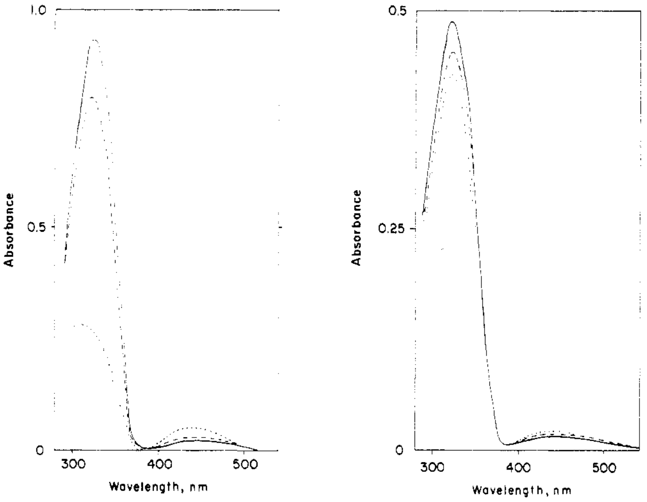

Figure 3. (A, left) UV absorbance spectrum of *m*-azotoluene in toluene (—) before irradiation. (- - -) after irradiation at 435 nm, and (···) after irradiation at 315 nm to photoequilibrium at ambient temperature. (B, right) UV absorbance spectrum of *m*-azotoluene in MW 411 000 polystyrene (—) before irradiation, (- - -) after 20 s of irradiation, and (···) after 2 min and longer irradiation at 435 nm at ambient temperature.

Table II
Ratio of $\epsilon_{cis}/\epsilon_{trans}$ Used To Determine Cis-Isomer Content of Probes in Toluene and in Polystyrene Films

probe	wavelength (λ, nm) of peak absorbance	$\epsilon_{cis}/\epsilon_{trans}$ at λ found	$\epsilon_{cis}/\epsilon_{trans}$ at λ lit.
azobenzene	320	0.050	0.052[68]
m-azotoluene	325	0.053	
1,1′-azonaphthalene	402		0.051[69]
stilbene	311		0.151[68]
4,4′-dinitrostilbene	358	0.245	0.456[70]
4,4′-diphenylstilbene	342	0.020	
thioindigo	543		0.074[45]

isomer present, at wavelength λ, A = absorbance at wavelength λ, and ϵ_{cis}, ϵ_{trans} = molar absorption coefficients of cis and trans isomers, respectively, at λ.

UV absorbance spectra for *m*-azotoluene in solution and in polystyrene film are shown in Figure 3. The $\epsilon_{cis}/\epsilon_{trans}$ ratios for azobenzene and *m*-azotoluene in eq 1 were found by using the method of Fischer.[41] Values of the $\epsilon_{cis}/\epsilon_{trans}$ ratios for the azo probes are given in Table II, together with those of the other probes used in this study.

Two ways of achieving photoequilibrium gave equivalent extents of photoisomerization. The first way was to irradiate at the wavelength of the smaller absorbance peak (435 nm for azobenzene and *m*-azotoluene) until the absorbance measured at the larger peak (320 nm for azobenzene; 325 nm for *m*-azotoluene) decreased to a value which did not change further with time. The second way was to irradiate briefly (about 1 min) at the wavelength of the larger absorbance peak until the absorbance decreased slightly more than in the first method. Then the wavelength of irradiation was changed to 435 nm so that further irradiation caused the absorbance to *increase* to a value which did not change further with time. The final absorbance achieved by either technique was the same and did not change upon further irradiation for hours.

The thermal back reactions of both azobenzene and *m*-azotoluene in solutions and films were barely detectable: a butyl acetate solution of azobenzene, for example, took 3 days to recover from 95% to 60% cis isomer, at a temperature of 20 °C. The rate of thermal back reaction of 1,1′-azonaphthalene in solution and in films was much faster, causing absorbance values to change in seconds.

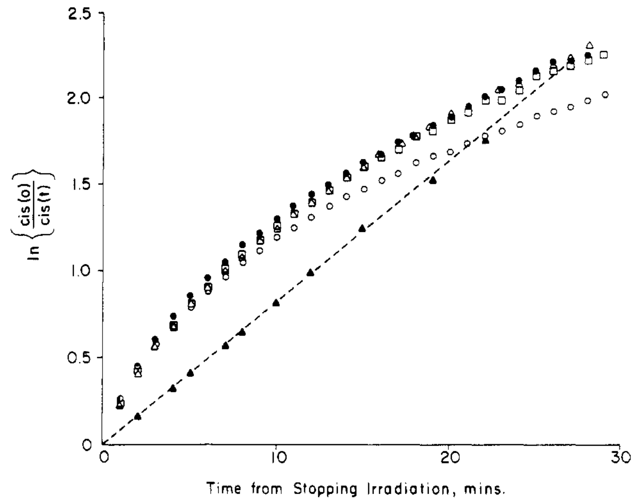

Figure 4. First-order thermal back reaction of *cis*-1,1′-azonaphthalene at ambient temperature. kt vs. t (time), according to cis (t) = cis (0) exp($-kt$): (○) MW 1790, (△) 3570, (□) 9050, and (●) 15 100 polystyrene and (▲) toluene.

Table III
Extent of Photoisomerization of Azo Probes in Unannealed Polystyrene and in Toluene at Ambient Temperature

probe substrate	irradn wavelength, nm	cis fraction at photoequilibrium	ratio cis in film to cis in soln at λ
		Azobenzene	
toluene	435	0.163 ± 0.001	
toluene	315	0.798	
polystyrene, MW 411 000	435	0.150 ± 0.001	0.92 ± 0.01
polystyrene, MW 92 600	435	0.147 ± 0.004	0.90 ± 0.02
polystyrene, MW 15 100	315	0.691	0.866 ± 0.002
		m-Azotoluene	
toluene	435	0.166 ± 0.001	
polystyrene, MW 411 000	435	0.144 ± 0.001	0.87 ± 0.01
		1,1′-Azonaphthalene	
toluene	405	0.796 (0.767–0.796)	
polystyrene, MW 92 600	405	0.646 (0.533–0.646)	0.812 ± 0.002

Figure 4 shows the change in cis fraction with time due to the thermal back reaction for 1,1′-azonaphthalene irradiated to photoequilibrium in toluene and in polystyrene films. The ordinate is given as the logarithm of the ratio of the cis fraction at photoequilibrium to that at time t after stopping the irradiation, which gives a straight line with slope equal to the rate constant for a first-order reaction. As has been noted for other azo probe/polymer systems,[25–28] the rate of thermal back reaction (the slope of the curves in Figure 4) is first-order in solution but, in film, decreases steadily from a value higher than that in solution to a lower one. The rate in polystyrene film cannot be fitted as the sum of two first-order rates, nor as a reaction of higher, or fractional, order. This relatively fast rate of thermal back reaction made reproducible measurements of extents of photoisomerization at photoequilibrium difficult for 1,1′-azonaphthalene.

The fractional isomerization of the azo probes achieved in toluene solutions and quenched (unannealed) polystyrene films at photoequilibrium are given in Table III. The values found for 1,1′-azonaphthalene are the maximum extents we obtained in our experiments, which we believe to be the same or very close to the extents of photoisomerization that would be found in the absence of any thermal back reaction. Higher ambient temperature, higher absorbance through the sample, and reduced bandwidth of light decreased the extent of photoisomerization. The ranges we observed are shown in parentheses next to the maximum extents.

The use of a 435-nm wavelength to photoisomerize solutions and films containing *m*-azotoluene and the spectrally similar azobenzene departs from the practice of other workers[26-28,32-34,37,38] who chose to irradiate azo chromophores with wavelengths close to the main absorbance peak (near 320 nm for azobenzene). The use of 435-nm light might seem counterproductive because only about 0.16 of the trans isomers photoisomerize, reducing the subsequent precision of the film/solution fractional isomerization ratio comparison. However, considerable experimental[42,43] and theoretical[44] evidence supports a purely inversion photoisomerization mechanism for the (n,π^*) transition at the higher wavelength, while an unknown amount of rotation about the N=N central bond occurs for the (π,π^*) transition at the lower wavelength.[44] The picture is less clear for 1,1′-azonaphthalene. Greater mixing of the electronic states for the (π,π^*) and (n,π^*) transitions occurs than in the other azo probes. Unfortunately, our mercury–xenon light source has a low output at wavelengths near the 490-nm wavelength of the 1,1′-azonaphthalene (n,π^*) transition, precluding a comparison with our findings based on excitation of the (π,π^*) transition at 402 nm.

From the results presented in Table III, it can be seen that the extent of photoisomerization of azo probes at photoequilibrium in polystyrene is always less than that in a toluene solution. This appears to be true for all trans–cis photoisomerizable probes in every polymer/model compound system described in the literature (except that Priest and Sifain[25] found that the polar probe 4-ethoxyazobenzene isomerized the same extent in polystyrene as in butylbenzene). This suggests that only a fraction of the probe molecules participate in the photoequilibrium in the polymer. This fraction is the ratio of the extent of isomerization in the polymer to that in a solution of model compound, shown in the last column of Table III. The simplest explanation why a probe molecule would fail to isomerize in a rigid polymer while doing so in a solution of a model compound of the polymer is that the extra volume the probe molecule needs to isomerize may not be present in the polymer on a time scale comparable with that of unimolecular photoisomerization. The ratio in Table III thus may be viewed as the fraction of local free volume in polystyrene larger than that needed by the azo probes to isomerize.

Within experimental measurement precision, both MW 411 000 and 92 600 polystyrene have the same fraction of local free volume larger than that needed by azobenzene to photoisomerize at 435 nm. The fraction is slightly less for *m*-azotoluene (confirmed by physical aging tests described later) which needs slightly more volume to photoisomerize than azobenzene. The 1,1′-azonaphthalene, which needs more volume to photoisomerize than either azobenzene or *m*-azotoluene, has the lowest ratio of fractional isomerization in film to that in solution.

Stilbene Series. Three stilbene-derived probes were used: stilbene, 4,4′-dinitrostilbene, and 4,4′-diphenylstilbene. Polystyrene films and toluene solutions containing the trans isomers were irradiated to photoequilibrium at wavelengths near the principal absorbance peak. The thermal back reactions for the stilbene-derived probes were negligibly slow at ambient temperature. For each probe the cis-isomer fraction was determined from spectrophotometric absorbance by eq 1.

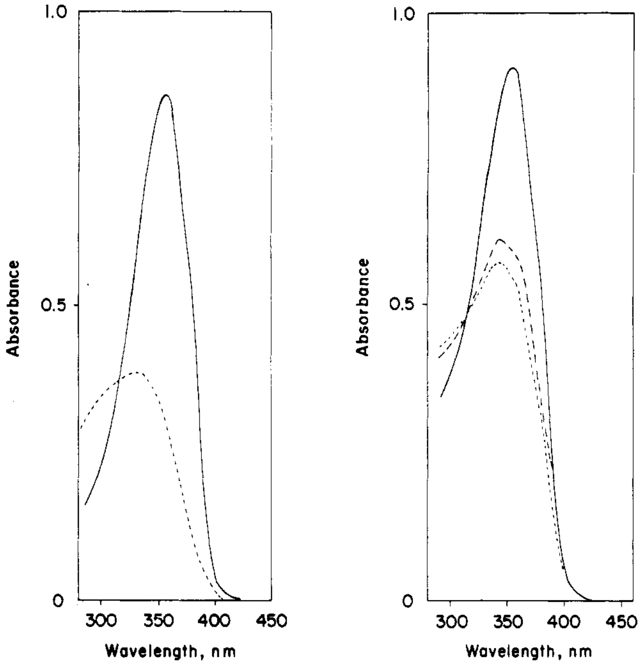

Figure 5. (A, left) UV absorbance spectrum of 4,4′-dinitrostilbene in toluene (—) before irradiation and (---) after irradiation at 364 nm to photoequilibrium at ambient temperature. (B, right) UV absorbance spectrum of 4,4′-dinitrostilbene in MW 411 000 polystyrene (—) before irradiation, (---) after 2 min of irradiation, and (···) after 20 min and longer irradiation at 364 nm at ambient temperature.

UV absorbance spectra for 4,4′-dinitrostilbene in toluene and in polystyrene film are shown in Figure 5. The $\epsilon_{cis}/\epsilon_{trans}$ ratio for 4,4′-diphenylstilbene was found by using the method of Blanc.[45] Values of the $\epsilon_{cis}/\epsilon_{trans}$ ratios for the stilbene-derived probes are given in Table II.

Determining the absorbance at photoequilibrium of stilbene was complicated by the relatively slow, irreversible loss of *cis*-stilbene via photo ring closure to phenanthrene in the presence of oxygen.[46,47] It was found experimentally that the *cis*-stilbene fraction at true photoequilibrium in O_2-free toluene was equal to that found in air-saturated toluene at the time when the loss of absorbance became constant over time. Based on the rate of loss of absorbance after reaching this pseudophotoequilibrium, less than 2% of the stilbene is lost in the time needed to attain pseudophotoequilibrium, at ambient temperature. The fraction of *cis*-stilbene in polystyrene measured at pseudophotoequilibrium was similarly assumed to be equal to that which would be found at photoequilibrium in an oxygen-free film. No loss of 4,4′-dinitrostilbene nor of 4,4′-diphenylstilbene similar to that of stilbene was found. However, *trans*-4,4′-diphenylstilbene appeared to be unstable at temperatures near 100 °C.

The fractional isomerization of the stilbene-based probes achieved in toluene solutions and quenched (unannealed) polystyrene films at photoequilibrium are given in Table IV. For 4,4′-diphenylstilbene in MW 15 100 polystyrene, an alternative technique was used for determining the ratio of the cis fraction at photoequilibrium in film to that in solution. Zimmerman[48] derived the rate of increase of the cis-isomer fraction Y of any cis–trans photoisomerizable probe in the absence of significant thermal back reaction:

$$dY/dt = W_0[(1 - 10^{-A})/A](\epsilon_x \Phi_x X - \epsilon_y \Phi_y Y) \qquad (2)$$

where W_0 = incident light energy flux at wavelength λ, A = absorbance at λ, ϵ_x, ϵ_y = trans- and cis-isomer molar

Table IV
Extent of Photoisomerization of Stilbene-Derived Probes in Unannealed Polystyrene and in Toluene at Ambient Temperature

probe substrate	irradn wavelength, nm	cis fraction at photoequilibrium	ratio cis in film to cis in soln at λ
		Stilbene	
toluene	314	0.898 (O_2-free)	
toluene	314	0.899 (air-saturated)	
polystyrene, MW 411 000	314	0.654	0.728
polystyrene, MW 3570	314	0.719	0.801
		4,4′-Dinitrostilbene	
toluene	364	0.852 ± 0.002	
polystyrene, MW 411 000	364	0.551 ± 0.001	0.647 ± 0.002
		4,4′-Diphenylstilbene	
toluene	315	0.963	
polystyrene, MW 9050	315	0	0
polystyrene, MW 15 100	365	(see text)	0

absorption coefficients at λ, X = trans-isomer fraction at time t, and Φ_x, Φ_y = quantum yield at λ for the trans → cis and cis → trans photoreactions, respectively. Initially, when the probe is nearly pure trans isomer, eq 2 simplifies to

$$dY/dt = W_0[(1 - 10^{-A})/A]\epsilon_x\Phi_x \qquad (3)$$

In a rigid polymer, if a fraction $1 - r$ of the probe molecules is blocked from photoisomerizing, the initial rate of trans → cis isomerization will be r [dY/dt(solution)]. This r is the same as the ratio of cis fraction at photoequilibrium in the film to that in solution. By measurement of the initial rate of photoisomerization in a rigid polymer and the initial rate found in solution, r can be determined. In the case of 4,4′-diphenylstilbene in MW 15 100 polystyrene, r was essentially zero: less than 0.02 cis-isomer fraction could be detected after irradiating at 365 nm for an hour; in toluene, almost 0.075 cis-isomer fraction was created in 5 s.

In one experiment, irradiation of two unannealed MW 411 000 polystyrene films containing 4,4′-dinitrostilbene, with one film having 6 times the probe concentration as the other, resulted in identical extents of photoisomerization, a further indication that the probe molecules were not agglomerated in the film.

From the results presented in Table IV, it can be seen that 4,4′-dinitrostilbene, which requires more volume to isomerize than stilbene, has the expected smaller r ratio. (An alternative explanation for this finding is that the higher energy light used to irradiate stilbene enabled a greater fraction of stilbene molecules to participate in isomerization than 4,4′-dinitrostilbene.) The MW 3570 polystyrene allows a greater fraction of stilbene to isomerize than MW 411 000 polystyrene. Loutfy, using molecular rotor fluorescence probes, has observed a trend of increasing emission intensity with increasing molar weight in polystyrene.[49,50] Our results qualitatively agree with this finding.

Thioindigo. Polystyrene films and toluene solutions containing *trans*-thioindigo were irradiated to photoequilibrium. The cis-isomer fraction Y was determined from spectrophotometric absorbance by eq 1. The UV spectrum of thioindigo is shown in Figure 2. The $\epsilon_{cis}/\epsilon_{trans}$ ratio in eq 1 was obtained from the literature, given in Table II.

Table V
Extent of Photoisomerization of Thioindigo in Unannealed Polystyrene and in Toluene at Ambient Temperature

probe substrate	irradn wavelength, nm	cis fraction at photoequilibrium	ratio cis in film to cis in soln at λ
toluene	546	0.623 ± 0.001	
polystyrene, MW 3570	547	0.282 ± 0.003	0.453 ± 0.005
polystyrene, MW 670 000	547	0.255 ± 0.001	0.409 ± 0.002

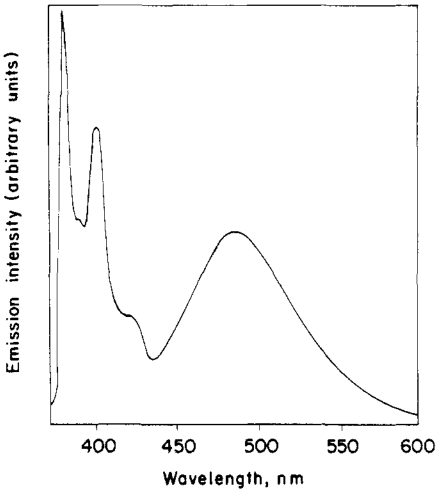

Figure 6. Fluorescence emission spectrum (corrected) of 1,3-di(1-pyrenyl)propane in air-saturated toluene at 23 °C.

The thermal back reaction of thioindigo is negligibly slow at ambient temperature. *trans*-Thioindigo absorbs room light readily, making light contamination difficult to avoid. Solutions and films were irradiated initially at the *cis*-thioindigo peak absorbance wavelength of 470 nm, which was found by experiment to give a photoequilibrium with just 0.018 cis/(cis + trans) thioindigo. The initial absorbances were then corrected to obtain the *all-trans*-thioindigo absorbance.

The fractional isomerizations of thioindigo achieved in toluene solution and quenched (unannealed) MW 3570 and MW 670 000 polystyrene film at photoequilibrium are given in Table V. Significantly more thioindigo photoisomerized in the MW 3570 polystyrene than in the MW 670 000 polystyrene.

1,3-Di(1-pyrenyl)propane. Excimer emission of 1,3-di(1-pyrenyl)propane has been extensively studied as a fluorescent probe of "microviscosity".[51-53] In this study we carried out experiments to see if excimers could form in polystyrene film. When a pyrene group absorbs a photon of a certain wavelength, it enters a long-lived (370 ns for 2-ethylpyrene[53]) excited electronic state which can interact with another pyrene group to form an excimer. This excimer is comprised of one pyrene stacked like a pancake atop the other. The excimer eventually emits a characteristic longer wavelength photon or simply loses its energy by radiationless decay and reverts to the ground state of two unassociated pyrene groups. Oxygen quenches the excited state of pyrene.[51] If a pyrene group is blocked from rotating about the central propane to form the excimer, the excimer/monomer fluorescence emission intensity ratio will be zero. Figure 6 shows the fluorescence emission spectrum of 1,3-di(1-pyrenyl)propane in toluene at ambient temperature. The excimer emission in Figure 6 has a broad peak at about 485 nm, and the monomer emission has two

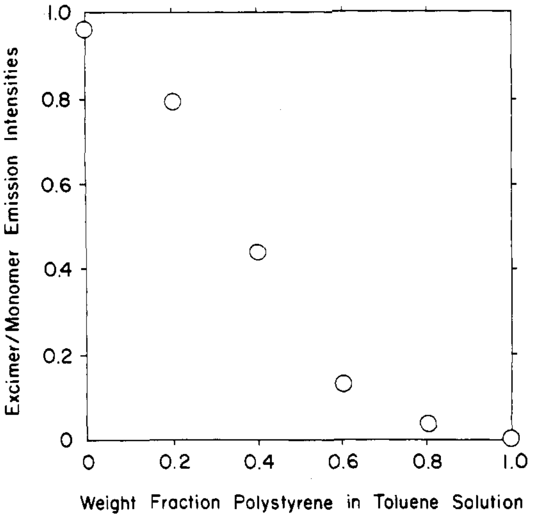

Figure 7. Ratio of excimer to monomer emission intensities of 1,3-di(1-pyrenyl)propane in solutions of MW 1790 polystyrene in toluene.

narrow peaks at 379 and 399 nm. Monomer emission intensity was measured at 388 nm, a flat area between the two monomer emission peaks, with excimer emission intensity measured at 485 nm. Monomer and excimer emission had no significant overlap at either of these wavelengths. The excitation wavelength was 347.5 nm. Measurements with solutions of different probe concentration showed that the excimer/monomer emission intensity ratio decreased with decreasing concentration to a constant value, due to intermolecular excimer formation and energy migration at the higher concentrations. At around 0.01 g/L, probe intermolecular excimer formation was negligible, and this concentration was used in all the subsequent solutions. Solutions of probe in toluene and MW 1790 polystyrene were prepared with approximately the same concentration of probe. A film of the probe in MW 1790 polystyrene was cast from a solution in dichloromethane. The results are shown in Figure 7. No excimer forms in the film.

Volume Required for Isomerization. A probe molecule has an associated van der Waals volume which represents volume occupied by the molecule, impenetrable for other molecules at ordinary temperatures. This volume can be calculated using van der Waals radii tabulated by Bondi[54] and Kitaigorodsky[55] together with intramolecular bonded atom spacings found by X-ray crystallography of molecular crystals or by gas electron diffraction. The calculation method is described by Bondi.[54] Recently, the van der Waals radii tabulated by Bondi were refined to enable the prediction of sterically allowed conformations of protein molecules.[56] We have used these recent values in our calculations. The van der Waals volumes for the probes used in this study are given in Table VI.

The extra volume needed by a probe molecule to isomerize is the volume swept by the van der Waals area. For azobenzene, the trans isomer is nearly planar with the phenyl rings twisted about their axes by 11° from the plane made by the N=N—C.[57] A phenyl untwists 11° and isomerizes by inversion in the N=N—C plane, with the narrower phenyl edge in the direction of motion. During inversion the phenyl is swept through a total angle of 114° (64° in *trans*-azobenzene plus 50° like *cis*-stilbene)[58] and twists 30° to assume the equilibrium conformation of the cis isomer. The volume required for isomerization consists of two components: phenyl ring twist and the volume swept by the area comprised of the product of the phenyl thickness and length. We assume that these are additive; in reality there is probably some overlap. The swept volume is the product of the area and the length of the path of the centroid of the area. Of the 127 Å^3 needed to isomerize, most (101 Å^3) is swept volume. For phenyl ring twist, it is important only to calculate *extra* volume: if a phenyl ring rotates about an axis in its plane, part of its radius (the phenyl ring thickness) needs no new volume. Thus, a cylindrical core of diameter equal to the thickness of the phenyl must be subtracted from the volume of a round-ended cylinder of diameter equal to the width of the phenyl ring. This volume is multiplied by the fraction of 180° the phenyl twists, to give the extra volume for phenyl ring twist. Bond lengths from a gas electron diffraction study[58] were used in calculating the extra volume needed by azobenzene to isomerize, given in Table VI.

Table VI
van der Waals Volume of Photochromic Probes and Extra Volume Needed To Isomerize

	trans, Å^3	extra to isomerize, Å^3
azobenzene	144	127
m-azotoluene	170	166
1,1′-azonaphthalene	216	200
4-ethoxyazobenzene		127
2,2′-azonaphthalene	216	230
stilbene	151	222
4,4′-dinitrostilbene	187	262
4,4′-diphenylstilbene	270	571
thioindigo	197	212
1,3-di(1-pyrenyl)propane		439

trans-Stilbene is also nearly planar with each phenyl initially twisted by 5° about its axis which form a 53° angle with the axis of the central C=C.[59] Upon excitation, one of the central carbons twists 90° to the geometry of the (π,π^*) excited state. The double bond character disappears, allowing rotational diffusion about a single C–C bond.[60,61] To attain the excited-state geometry, the phenyl twists about 85° to keep its narrow edge parallel with the direction of rotational motion. Following rotation by 180°, the newly formed cis isomer relaxes from the excited state, with the phenyl twisting another 47° in order to assume the equilibrium conformation of the cis isomer. Extra twist volume from the symmetrically opposite phenyl group has not been added, under the premise that blocking this twist would not prevent the isomerization. The extra volume derived from this isomerization pathway is given in Table VI. Of the 222 Å^3 needed to isomerize, 138 Å^3 is swept volume.

The extra volumes needed for the other azo- and stilbene-derived probes were calculated similarly to that of azobenzene and stilbene and are given in Table VI. Stilbene has the least uncertainty with regard to ground-state conformations of both trans and cis isomers. The accuracy of the values is as good as that of the bond lengths and angles, the van der Waals radii, the assumption made regarding nonoverlap of twist and swept volumes, and the extent of phenyl ring twist to a strained cis isomer. We guess our values are not more than 5% higher than the actual ones.

Thioindigo is different from stilbene in that the central carbon is bound in a heterocyclic ring with less than a 120° bond angle (102° from X-ray diffraction).[62] The isomerization of thioindigo is similar to that of stilbene, in that the central double bond character disappears upon excitation and rotation to the 90° twisted (assumed singlet) excited electronic state. Although *cis*-thioindigo is probably not coplanar, based on its UV absorbance peak blue shift, no measurements of its bond angles have been made. The calculated extra volume needed to isomerize for

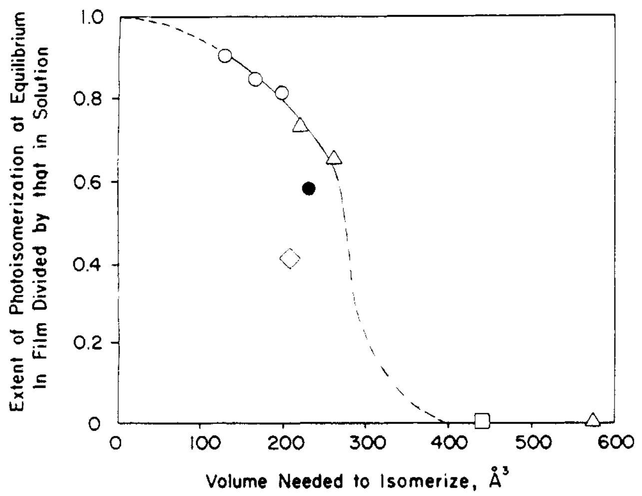

Figure 8. Cumulative distribution of local free volume in unannealed polystyrene glass at 25 °C, measured by photochromic and fluorescent probes: (○) azo probes, (△) stilbene probes, (□) excimer probe, (◇) thioindigo, (●) 2,2′-azonaphthalene (isomerization data of Priest and Sifain).

Table VII
Effect of Physical Aging on the Distribution and Cumulative Distribution of Local Free Volume in Polystyrene

	fraction of free volume larger than required to isomerize			
thermal history	azobenzene	*m*-azotoluene	stilbene	4,4′-dinitrostilbene
quenched	0.92	0.87	0.728	0.646
24 h at 84 °C	0.90	0.87		
4 days at 60 °C				0.607
5 days at 60 °C		0.87		
14 days at 60 °C	0.89	0.84		
10 days at 52 °C			0.729	

	fraction of local free volume in the size range		
size range	quenched	4 days at 60 °C	14 days at 60 °C
<127 Å³	0.08		0.11
127–166 Å³	0.05		0.04
166–262 Å³	0.22	0.26	
262–439 Å³	0.646	0.607	

thioindigo in Table VI is based on bond lengths and angles found 30 years ago.[62] These values show that the long axis of rotation through the C=C nearly bisects the phenyl ring. Any out-of-plane component to the rotation of thioindigo would increase the amount of volume needed to isomerize by many tens of cubic angstroms from the calculated value given in Table VI.

The extra volume for the excimer fluorescence probe 1,3-di(1-pyrenyl)propane was calculated assuming a ground-state and excimer geometry similar to that of 1,1′-di(2-naphthyl) diethyl ether.[63] This involves an 80°, combined total, twist of the pyrenyl groups about their axes, and a 110°, total, rotation of pyrenyl groups, edge foremost, about the C–C propane bond.

The ratio of extent of photoisomerization of the probes in polystyrene film to that in toluene is shown as a function of the extra volume needed by the probes to photoisomerize in Figure 8. The data of Priest and Sifain[25] are included in comparison. (Priest and Sifain determined only relative isomerizations; we calculated the volumes required for isomerization of their probes.) The curve in Figure 8 is the cumulative distribution of local free volume in polystyrene displaced to larger volumes by an amount equal to the extra free volume contributed by the isomerizing half of each probe molecule.

In perturbing the local environment by their very presence, probe molecules may add a certain amount of local free volume. The extra amount of local free volume added by the isomerizing half of a probe molecule can be estimated by considering the entire probe molecule to be the equivalent of *two* polymer molecule chain ends, although the central double bond rigidity in probe molecules probably makes such an estimate too large. Many workers (e.g., Bueche[64]) have used the relation between T_g and polymer molar weight to determine the extra free volume of chain ends in glasses. By use of Richardson's dilatometric measurements of specific volume of polystyrene with various molar weights,[65] each polystyrene chain end contributes about 28 Å³ of local free volume more than the average local free volume per repeat unit. Thus, the isomerizing half of a probe molecule adds, on average, less than 30 Å³ of extra local free volume. (A commonly cited value of 80 Å³ per chain end[64] is too high. It is based on early measurements by Fox and Flory[66] on polystyrenes of low molar weight. Rudin[67] used updated Mark–Houwink parameters to redetermine Fox and Flory's molar weights and found a smaller T_g vs. inverse molar weight slope which leads to a value of about 20 Å³ for extra local free volume of a chain end.) We are thus convinced that the curve in Figure 8 is close to being the true distribution of local free volume in polystyrene.

Thioindigo seems to require an anomalously small amount of local free volume to isomerize. This is probably due to displacement of the axis of rotation during the isomerization, not accounted for in calculating the volume needed to isomerize.

From Figure 8 it can be seen that more than 90% of the local free volume in polystryene is greater than 120–130 Å³, none of it is greater than about 400 Å³, and half the local free volume is greater than 260–280 Å³. Positron annihilation spectroscopy, a technique which is limited to obtaining a single value for the size of local free volume and which relies on equating lifetime values in amorphous solids with those in crystalline ones, has been used to obtain a mean value[22] of 160 Å³. This and our median value of 260–280 Å³ (less a possible 30 Å³ of extra local free volume attributable to the isomerizing half of a probe molecule) qualitatively agree with an "amorphous defect" of size comparable with that of a polystyrene repeat unit, about 180 Å³ from the specific volume of the quenched glass.[65]

This work shows that a clear relationship exists between the fractional isomerization in polystyrene relative to that in solution and the volume required for isomerization of photochromic probes having no net dipole moment. The molecular probes used in this study not only allowed a straightforward computation of the extra volume required for isomerization but, as the probes had no net dipole moment, accurately sampled a local environment minimally perturbed by their presence. Use of polar probes, probes with odd shapes, or probes which undergo excited-state chemistry with the possible production of catalytic species might give different results.

Physical Aging. The glass transition temperature of polystyrene with several hundred or more repeat units (MW 17 500 or higher) is about 93 °C when measured by dilatometry.[65] Physical aging in polystyrene is reported to occur throughout a temperature range extending from T_g down to about 50 °C.[4] We photoisomerized several different probes in polystyrene film to see how the fraction of local free volume larger than the probes needed to isomerize in polystyrene changed after annealing at different temperatures. The results are given in the upper part of Table VII.

Films containing azobenzene and *m*-azotoluene gave no significant reductions in the extent of isomerization at photoequilibrium after prolonged annealing at 85 °C. After 14 days at 60 °C, however, both experienced a slight, but significant, reduction in the cis fraction at photoequilibrium. The slight differences in cis fraction at photoequilibrium between films containing azobenzene and *m*-azotoluene are maintained during a similar thermal history, confirming the slightly smaller extent of fractional photoisomerization of *m*-azotoluene.

Films containing stilbene gave no significant difference in cis fraction at photoequilibrium aged 10 days at 52 °C or heated above T_g to 110 °C and quenched. This is because the 52 °C temperature is close to the lower temperature limit for physical aging in polystyrene. In contrast, films containing 4,4′-dinitrostilbene aged 4 days at 60 °C gave a significant reduction in the cis fraction at photoequilibrium.

The distribution of local free volume in polystyrene is given in the lower part of Table VII, together with the changes seen during the annealing experiments. Physical aging at 60 °C reduces the fraction of local free volume larger than 262 $Å^3$, the volume needed by 4,4′-dinitrostilbene to isomerize, but increases the fraction of local free volume between 166 $Å^3$, the volume needed by *m*-azotoluene to isomerize, and 262 $Å^3$. Thus, our study, involving probes having different size requirements for isomerization, demonstrates that physical aging reduces larger local free volume more than smaller local free volume.

Summary

A generally applicable technique for obtaining a quantitative measurement of the cumulative size distribution of local free volume in polymer glasses has been found and applied for a specific case, polystyrene. The technique is based upon the lesser extent of photoisomerization of nonpolar and fluorescent probes in a glass than in a dilute solution. In unannealed polystyrene, over 90% of the local free volume is larger than 120–130 $Å^3$, while practically none is larger than 400 $Å^3$. Physical aging was found to reduce larger local free volume more than smaller local free volume.

We are extending this work to different polymer systems to see how the chemical composition of a polymer affects the distribution of local free volume in the glass. We are also using fluorescent probes to study the distribution of local free volume at a nansecond time scale in viscous solution. Dilatometry is being carried out to compare the effect of physical aging on bulk free volume with that on the distribution of local free volume in polymer glasses. Also, photochromic probes other than those discussed in this work are being investigated.

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Registry No. Polystyrene, 9003-53-6; azobenzene, 103-33-3; 4,4′-diphenylstilbene, 2039-68-1; stilbene, 588-59-0; 1,1′-azonaphthalene, 487-10-5; 4,4′-dinitrostilbene, 2501-02-2; *m*-azotoluene, 588-04-5; 1,3-di(1-pyrenyl)propane, 61549-24-4; thioindigo, 522-75-8.

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Molecular Weight and Concentration Dependences of the Terminal Relaxation Time and Viscosity of Entangled Polymer Solutions†

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ABSTRACT: A new model is presented for entangled polymer solutions which accounts for the observed molecular weight and concentration dependences of the zero-shear viscosity η_0 and the terminal relaxation time τ_d. Our development, based upon the coupling model of relaxation, quantitatively describes how relaxation of a primitive mode is modified by coupling through entanglements to its environment. The primitive mode is represented by a Rouse chain of Gaussian submolecules, each of root mean square length σ equal to the entanglement distance and each characterized by an entanglement friction coefficient f_0. By extending the analyses developed previously for polymer melts, the model predicts that $\eta_0 \propto f^* M^{2/(1-n)} \phi^{\gamma} [\phi^{\alpha(1-\nu)}]^{2/(1-n)}$ where ϕ is the polymer volume fraction. Here n is the coupling parameter describing the terminal relaxation and γ, α, and ν are given by $G_N{}^0 \propto \phi^{\gamma}$, $M_e \propto \phi^{-\alpha}$, and $\sigma \propto \phi^{-\nu\alpha}$. Numerical examples are shown to agree with experiment; e.g., for $n = 0.41$, $\gamma = 2$, $\alpha = 1$, $\nu = 0.6$, $\eta_0 \propto f^* M^{3.4} \phi^{3.4}$. Comparison of the present results is also made to the reptation and scaling theory predictions.

I. Introduction

An understanding of the dynamics of the polymer chain in entangled systems includes not only a description of how the viscoelastic behavior in the terminal zone depends upon molecular weight but also how it depends upon the polymer concentration in entangled solutions. From experimental data, the picture which emerges[1-5] for the entangled polymer system is that the viscosity can be factored into a temperature- and concentration-dependent friction factor $\zeta(T,\phi)$ and a molecular weight dependent structural (topology) factor $g(M,\phi)$. The structure factor follows a power law dependence in both molecular weight, M, and concentration (volume fraction, ϕ), i.e.,

$$\eta_0 = \zeta(T,\phi) g(M,\phi) \propto \zeta(T,\phi) M^x \phi^y \tag{1}$$

The exponents x and y are generally reported to be approximately the same and have values between 3.4 and 3.7. The temperature and concentration dependencies of the friction factor are often considered[1] to be due to free volume changes and data are normally represented in an "isorelative (or fractional) free volume" state. This allows the dependence of ζ on $\zeta(T,\phi) = \zeta(T - T_g)$ to be separated from the topological effects due to M and ϕ. While x and y appear to be approximately the same for small molecule solvents ($x \approx 3.4$, $y \approx 3.4$), there have been recent reports[6] which indicate that in certain systems, for which the solvent molecular weight is near the polymer entanglement molecular weight, $y \cong 3.0$.

Furthermore, the plateau modulus, $G_N{}^0$, of the polymer system, while being independent of the molecular weight, is reported as scaling with the concentration as

$$G_N{}^0 \propto \phi^{\gamma} \tag{2}$$

where γ is reported to be approximately[7-10] 2.0–2.3. On the other hand, the terminal relaxation time, τ_d, is reported[9,11] to scale as

$$\tau_d \; \alpha \; \zeta(T,\phi) M^x \phi^z \tag{3}$$

where x is approximately 3.4–3.7, and now the value of z is approximately 1.4.

In this paper we present a new model for entangled polymer systems which accounts for the observed molecular weight and concentration dependences of η_0 and τ_d in entangled polymer systems. Our development is based upon a recently developed coupling model of relaxation.[12,13] The model describes how relaxation of a primitive mode is modified by coupling to its environment. In the application to entangled polymer systems, the primitive mode is approximately represented by a Rouse chain. The Rouse chain is coupled to its environment through entanglements. The coupling model allows such effects to be incorporated

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