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Photochromic and Fluorescent Probe Studies in Glassy Polymer Matrices. 3. Effects of Physical Aging and Molar Weight on the Size Distribution of Local Free Volume in Polystyrene

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ABSTRACT: Changes in the distribution of local free volume in polystyrene glass during physical aging were measured by using photochromic probe molecules requiring different amounts of volume to photoisomerize. The fraction of local free volume in the size range 130–180 Å^3 is constant as the polystyrene molar weight decreases to a critical value between 34 000 and 92 000. At lower molar weights the fraction of local free volume in the size range 130–280 Å^3 decreases with decreasing molar weight. Physical aging in polystyrene glass reduces or leaves unchanged the fraction of local free volume larger than each probe needs to isomerize. During physical aging the greatest loss of local free volume occurs in the size range larger than 280 Å^3, but the amount of loss varies with annealing temperature. The temperature of maximum rate of loss is 20–25 °C less than T_g for polystyrene of 3970 and 9050 molar weight. In polystyrene of 573 000 molar weight annealed 250 h at 30 °C, most of the loss of local free volume larger than 280 Å^3 occurs within the first 4 h.

Introduction

Physical aging, the loss of volume and enthalpy which occurs in glassy polymers and other amorphous solids cooled below their glass transition temperature T_g, has been extensively studied by a variety of measurement techniques. Dilatometry,[1–3] differential scanning calorimetry (DSC),[4–7] dielectric constant relaxation,[7,8] stress relaxation,[9,10] creep compliance,[3] and small-angle X-ray scattering (SAXS)[11] are some, but by no means all, of the methods and studies of physical aging appearing in the literature. As a result of these studies, various phenomenological models of physical aging in glassy polymers have been formulated which are capable of predicting the time-dependent behavior of polymer glasses with different thermal histories. These models, which have been reviewed by Tant and Wilkes[12] and discussed more recently by Matsuoka et al.,[8] are based on the concept that if δ represents the deviation from some equilibrium measurement value, then the rate of relaxation at a constant temperature is

$$-\mathrm{d}\delta/\mathrm{d}t = \delta/\tau \tag{1}$$

Matsuoka[8] observes that a limitation of this equation is that it applies strictly for small perturbations from equilibrium. For large perturbations a different time constant may apply so that, in general, τ can vary with δ. This has been observed experimentally. Marshall and Petrie[4] examined enthalpy recovery in polystyrene of various molar weights annealed at different temperatures below T_g. They analyzed their data according to eq 1, finding a relaxation time τ that varied exponentially with the inverse annealing temperature and exponentially with δ. The rate of enthalpy relaxation at a given temperature decreased as the molar weight increased to a value of about 50 000. For higher molar weight polystyrene, the rate of enthalpy recovery was independent of molar weight.

If the perturbations are sufficiently small that the magnitude of τ is unchanged, recovery may nevertheless be controlled by multiple rate constants $1/\tau_i$, such that the rate of relaxation at a constant temperature is given by

$$-\mathrm{d}\delta/\mathrm{d}t = \sum G_i\delta_i/\tau_i \tag{2}$$

where G_i is normalized so that $\sum G_i = 1$ and either $\delta = \sum\delta_i$ or $\delta = \sum G_i\delta_i$, depending on the phenomenological model used.[8] This implies the existence of a distribution of recovery times τ_i.

Jonscher[13] points out that eq 2 strictly applies to perturbation and subsequent return to equilibrium of assemblies of noninteracting systems. If a coupling potential $V_{i,i'}$ exists between displacements at two sites, i and i′, eq 2 must be changed to

$$-\mathrm{d}\delta/\mathrm{d}t = \sum G_i\delta_i/\tau_i + \sum\sum\delta_i\delta_{i'}V_{i,i'}$$

With a nonvanishing coupling potential summation term, an exponential solution is mathematically impossible, and Hill and Dissado[14] found that a hypergeometric function with three adjustable parameters fits creep relaxation in polystyrene above T_g, as opposed to a weighted series of exponential decays involving a distribution of recovery times.

By determining an enthalpy as the temperature in the glass decreases below T_g, sub-T_g enthalpy recovery in polystyrene has been modeled by using a series of small instantaneous temperature jumps followed by isothermal holds, with the enthalpy difference δ_H assumed to decrease with time (t) according to the nonexponential function

$$\delta_H(t) = \exp\{-(t/\tau_0)^\beta\} \tag{3}$$

where β determines the degree of nonexponentiality ($0 < \beta \leq 1$) and τ_0 is a characteristic recovery time.[6]

In contrast with the phenomenological models involving a distribution of recovery times, molecular-based models have been developed capable of simulating with fair accuracy physical aging and other behavior in well-characterized polymer glasses. These models either derive or assume some functional form for the size distribution of local free volume. Thus, Grest and Cohen[15] associate a local volume v with each flexible segment of a polymer molecule and assume that local free volume in glasses occurs in liquidlike cells of volume larger than some critical volume v_c. They derive an expression for $p(v)$, the probability distribution of local free volume v, as

$$p(v) = \exp[-(v - v_c)/v_f] \qquad \text{for} \quad v \geq v_c \tag{4}$$

with v_f being the mean local free volume.

Robertson et al.[16] in their stochastic model assume that the local free volume at equilibrium is distributed binomially with the two defining parameters determined from equating the mean and mean-square fluctuations with other variables related by an equation of state, an expression for the second derivative of the Helmholtz free energy with respect to the fraction of lattice sites occupied

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by polymer molecule segments, and an expression relating the specific volume of the glass to that of the equilibrium liquid at the same temperature. Robertson applied this stochastic model to determine how τ in eq 1 varied with volume recovery for polystyrene 5 °C below T_g.[17]

Curro et al.[18] in their diffusion model assume that the local free volume is distributed uniformly among equal-sized holes which diffuse in response to molecular motion. These molecular models have not been applied to volume recovery of polystyrene at temperatures more than a few degrees below T_g.

As measured by dilatometry, volume recovery in polystyrene undergoing physical aging at temperatures more than 20 °C below T_g appears to be linear with logarithmic time.[1,2,11] Recovery has a "plateau", an initial period of comparatively little volume recovery, changing to a constant decrease in volume with logarithmic time. This plateau period gets longer as the annealing temperature is lowered. At 60 °C the plateau lasts about half an hour; at 25 °C it lasts over 5 h.[1] The maximum rate of volume recovery for polystyrene annealed at least 100 h occurs in the 70–80 °C range for polystyrene with a glass transition near 100 °C. The rate of volume recovery (following the plateau period) decreases gradually with decreasing temperature.[1,2]

Roe and Curro[11] annealed polystyrene glass slightly below T_g while conducting SAXS measurements, finding a slow reduction in density fluctuations on a size scale reported as 8000 Å^3. Below 80 °C, however, the density fluctuations remained constant even though the bulk specific volume, measured by dilatometry, continued to decrease at lower temperatures. The density fluctuations at ambient temperature were smaller for slowly cooled 17 500 MW than for 233 000 MW polystyrene. Song and Roe[19] recently measured the change in density fluctuations over a volume range of 4–4000 Å^3 for commercial polystyrene undergoing a variety of bulk changes, including physical aging, using SAXS. They found that the density fluctuations in unannealed polystyrene were maximum at a volume of about 30 Å^3 and decreased steadily as the volume increased to 4000 Å^3.

Levita and Smith[20] found that the diffusion coefficients for xenon and CO_2 in a strained polystyrene 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 free volume elements in strained polystyrene decreased in size during annealing more rapidly than smaller ones.

Recently, a new measurement technique, involving photochromic probe molecules either as labels[21-24] or as independent molecules,[24-26] has been developed which is sensitive to changes in local free volume such as occur during physical aging or polymerization. Victor and Torkelson[26] calculated the extra volume needed by photochromic probe molecules to undergo trans–cis isomerization and found that probes needing more extra volume isomerized less in polystyrene relative to toluene solvent than probes with smaller extra volume requirements. They found that this correlation gave a measure of the cumulative size distribution of local free volume in polystyrene. We report here further results using photochromic probe molecules in an extensive series of single-temperature-jump annealing experiments with polystyrene of various molar weights, to investigate more precisely how physical aging changes the size distribution of local free volume in polystyrene.

Experimental Section

Polystyrene was narrow molar weight distribution from Pressure Chemical Co. (M_n = 3970, 8750, 9050, 13 000, 34 100, 92 600, 198 300, 573 000, 670 000) and Toyo Soda Co. (M_n = 6200). The molar weights (MW) indicated are those provided by the supplier. Photochromic molecular probes used were azobenzene and 4,4′-diphenylstilbene (Aldrich Chemical Co.); *m*-azotoluene, *p*-azotoluene, and 4,4′-dinitrostilbene (ICN Biomedicals, Inc. K&K Laboratories); stilbene (Eastman Kodak Chemicals); and 1,3-bis(1-pyrenyl)propane (Molecular Probes, Inc.). Toluene (Baker Chemical) was "Photorex" (UV quality). Film preparation has been described elsewhere.[26] Films averaged 0.02 cm in thickness, except for 34 100 MW polystyrene films which were 0.04 cm. Unannealed films which had been cast on 5 cm × 5 cm UV transmitting clear glass filters were kept at 120 °C, for 15–20 min in vacuum and then cooled rapidly (less than a minute) to ambient temperature, with photoisomerization carried out immediately after the films had cooled. Photoisomerizations were completed within several tens of minutes from the films being cooled. Films to be annealed were kept at 120 °C for 15–20 min in vacuum and then placed in a different vacuum oven in covered glass Petri dishes cooled rapidly to the lower annealing temperature. Following annealing, photoisomerizations were carried out as with the unannealed films.

A Photon Technology International arc lamp housing with a 150-W xenon lamp was used to irradiate films and solutions through a monochromator. For the azo probes the wavelength of irradiation had a bandwidth of 16 nm. For the stilbene the bandwidth was 12 nm. The extent of photoisomerization did not vary when the bandwidth was decreased. Measurements were made at ambient temperature, 23–27 °C. The fraction of cis isomer present at photoequilibrium was determined from the change in peak UV absorbance (measured digitally to one part in a thousand) with an IBM Instruments UV/VIS 9410 spectrophotometer. Both stilbene and, to a lesser extent, 4,4′-dinitrostilbene experienced a slow loss of absorbance at photoequilibrium upon continued irradiation. For stilbene, this is due to the cis isomer forming a closed-ring structure.[27] The technique for determining the extent of isomerization at photoequilibrium for stilbene is discussed later in this paper. For films containing 4,4′-dinitrostilbene, however, the slow (<0.0005 absorbance units/min) loss may be the result of local softening, the creation of hot spots in the polymer matrix near probe molecules. Absorbances corresponding to photoequilibrium without this slow loss can easily be found by prolonging the irradiation to determine the approximately constant rate of loss of absorbance and using as photoequilibrium the absorbance corresponding to the onset of the slow loss.

Results and Discussion

Films of polystyrene containing each photochromic probe (as the trans isomer) were annealed at a certain temperature for a fixed length of time. The films were then irradiated, isomerizing the probes to photoequilibrium. The fraction of cis isomer present at photoequilibrium, Y_{eq}, was determined from the following equation:

$$Y_{eq} = \frac{1 - A_{eq}/A_{trans}}{1 - \epsilon_{cis}/\epsilon_{trans}}$$

where A_{eq} is the absorbance at photoequilibrium at wavelength λ, A_{trans} is the initial (all trans isomer) absorbance at λ, and $\epsilon_{cis}/\epsilon_{trans}$ is the ratio of molar absorption coefficients of cis to trans isomer at λ. Table I gives the values of $\epsilon_{cis}/\epsilon_{trans}$ to Y_{eq} found in toluene, some of which have been previously reported.[26,28] The method of Fischer[29] was used to find $\epsilon_{cis}/\epsilon_{trans}$ for all the probes except stilbene, which was found by measuring ϵ_{cis} and ϵ_{trans} directly.

In films, the peak absorbance used to measure the cis-isomer content was red-shifted several nanometers from that in toluene, due to the higher index of refraction of polystyrene. To compensate, the irradiation wavelength used for films was several nanometers higher than that for toluene solutions. For films and solutions, Y_{eq} is equal to the extent of probe isomerization.

Table I
Extent of Isomerization of Photochromic Probes in Toluene at 25 °C

probe	wavelength, nm measd λ_m	irrad λ_i	$\epsilon_{cis}/\epsilon_{trans}$ at λ_m	Y_{eq}[a]
azobenzene	320	438	0.050	0.171 ± 0.001
p-azotoluene	336	438	0.032	0.202 ± 0.001
m-azotoluene	325	438	0.053	0.176 ± 0.001
stilbene	311	311	0.149	0.908 ± 0.001
dinitrostilbene	358	358	0.250	0.808 ± 0.001
diphenylstilbene	342	342		

[a] Photoequilibrium cis fraction.

Table II
Fraction of Local Free Volume Larger Than the Volume Photochromic Probes Need To Isomerize in Unannealed Polystyrene

probe	extra vol needed, Å^3	Y_{eq}(film)/Y_{eq}(toluene)[a] for polystyrene MW 573 000	34 100	9050	3970
azobenzene	127	0.892	0.860	0.845	0.830 ± 0.007
p-azotoluene	193	0.838	0.845	0.822	0.817 ± 0.005
m-azotoluene	202	0.820	0.783	0.778	0.805 ± 0.006
stilbene	224	0.812	0.775	0.772	0.805 ± 0.005
dinitrostilbene	285	0.717	0.718	0.719	0.736 ± 0.003
2,2′-azo-naphthalene	325	*b*			
dipyrenylpropane	439	0[26]			
diphenylstilbene	575				0[26]

[a] The ± error limits apply equally to the values in a given row. [b] A value of 0.58 can be calculated from the extent of isomerization of this probe in commercial-grade polystyrene reported by Priest and Sifain.[25]

The extent of isomerization at photoequilibrium in polystyrene film, divided by that in toluene solution, is equal to the fraction of local free volume larger than the extra volume needed for the probe to isomerize plus an additional amount due to the presence of the probe. This additional local free volume contributed by the probe molecule has been estimated[26] to be less than 30 Å^3 at T_g, and is even less in the glass.

The extra volumes needed for the probes to isomerize were calculated as described previously[26] by using the known ground-state geometries of the trans and cis isomers, assumed transitional state geometries, and a consistent set of van der Waals radii for the atoms comprising the probe molecules. The extra volume calculated is that swept out by the area of isomerizing segments normal to the direction of movement about their respective axes of rotation, less any volume occupied after the isomerization that was occupied at the same sites as before the isomerization. The resulting value, although precise, may be systematically high by a few percent because the isomerization may not be prevented if the cis isomer does not relax to its ground state; i.e., it could assume a slightly strained geometry. The azo probes were assumed to photoisomerize via a planar inversion pathway and stilbene probes via a rotational one.

Effect of Molar Weight. The fraction of local free volume larger than probes need to isomerize in 3970, 9050, 34 100, and 573 000 MW polystyrene films are given in Table II. The fractions of local free volume larger than azobenzene and 4,4′-dinitrostilbene need to isomerize in polystyrene of other molar weights were also found and are given in Table III, together with T_g and specific volume values calculated from a correlation for slowly cooled polystyrene found by Richardson and Savill.[30] The cumulative size distribution of local free volume as measured by photochromic probes for polystyrene of three molar weights is shown in Figure 1. The cumulative distribution is the fraction of local free volume larger than what a probe needs to isomerize versus the volume needed to isomerize. In this and other figures, the volume needed to isomerize has not been decreased by any additional local free volume contributed by the probe molecule itself. Figure 2 shows the fractions of local free volume larger than what 4,4-dinitrostilbene and azobenzene need to isomerize versus the degree of polymerization of polystyrene for the more extensive molar weight series. From these figures, it is

Table III
Effect of Polystyrene Molar Weight on the Fraction of Local Free Volume Larger Than What Photochromic Probes Need To Isomerize

molar wt, g/mol	T_g, °C[a]	glass specific vol, cm^3/g[a]	Y_{eq}(film)/Y_{eq}(toluene) azobenzene	dinitrostilbene
670 000	93	0.955	0.894 ± 0.007	
573 000	93	0.955	0.892	0.717 ± 0.003
92 600	93	0.955	0.896	0.721
34 100	90	0.955	0.860	0.718
15 100	86	0.955	0.855	
13 000	85	0.955		0.720
9 050	82	0.955	0.845	0.719
6 200	76	0.955	0.824	0.734
3 970	67	0.956	0.830	0.736

[a] T_g and specific volume values were calculated from the correlation of Richardson and Savill[30] for slowly cooled polystyrene.

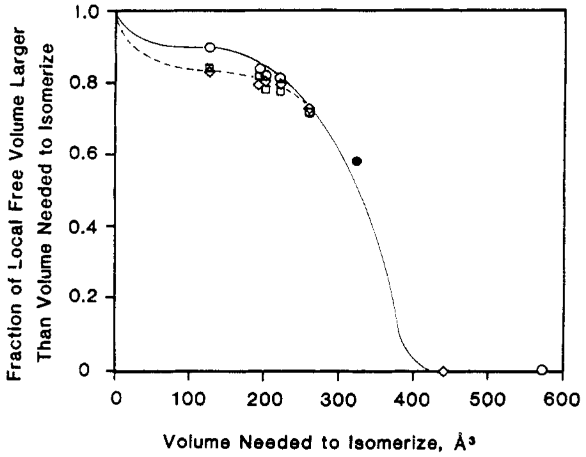

Figure 1. Cumulative distribution of local free volume larger than the volume needed to isomerize in polystyrene of different molar weights: (○) 573 000; (□) 9050; (◇) 3970 MW; (●) commercial polystyrene, Priest and Sifain.[25] Error limits are smaller than the size of the symbols.

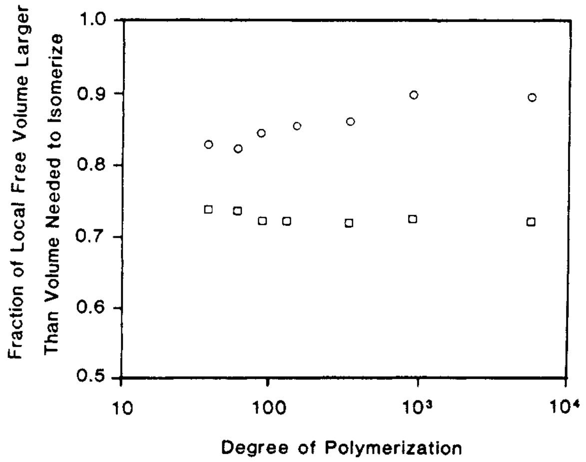

Figure 2. Fraction of local free volume larger than what probes need to isomerize versus degree of polymerization of polystyrene. (○) Azobenzene; (□) 4,4′-dinitrostilbene. Error limits are the size of the symbols.

apparent that the cumulative size distribution of local free volume is independent of polystyrene molar weight until the molar weight decreases to a critical value M_c in the 34 100–92 600 MW range. It is interesting to note that M_c corresponds to a molar weight range above which T_g becomes independent of molar weight.[4,30] As the molar weight decreases below M_c, the fraction of local free volume larger than what azobenzene needs to isomerize decreases, with little or no change in the fraction of local free volume larger than what 4,4′-dinitrostilbene needs to isomerize. Thus, for these low molar weight, unannealed polystyrenes, the fraction of local free volume in the size range of about 130–280 Å^3 decreases with decreasing molar weight.

A possible molecular basis for the change in the cumulative size distribution of local free volume is that polystyrene of molar weight lower than M_c could have greater density fluctuations in the rubbery state at a temperature of 120 °C (the temperature before cooling) than higher molar weight polystyrene, due either to the greater mobility of polymer molecule ends or to the relative lack of temporary molecular entanglements at lower molar weights. When the polymer is cooled below T_g, the density fluctuations are frozen-in, as demonstrated by the SAXS studies of Tanabe et al.[31] The hypothesized greater density fluctuations in lower molar weight polystyrene at 120 °C are preserved upon cooling below T_g, resulting in a smaller fraction of local free volume greater than what azobenzene needs to isomerize, as is apparent in Figure 2. The upper size limit of the open regions caused by these density fluctuations must be less than about 280 Å^3, the size of local free volume larger than what 4,4′-dinitrostilbene needs to isomerize, except in the lowest molar weight polystyrene for which a significant amount of local free volume is added that is larger than 280 Å^3.

Loutfy[32] measured the quantum yield of fluorescence for a malononitrile probe in polystyrene films of various molar weights, finding that the quantum yield increased steadily as the molar weight increased from a critical value of 10 000 to a value of 100 000. Loutfy attributed this result to a possible "change in bulk morphology" leading to restriction of the torsional relaxation of the probe at molar weights above 10 000. Fluorescence and isomerization are competing relaxation paths for some probe molecules (including stilbene[33]). The increase in local free volume with increasing molar weight we observe in the size range of about 130–280 Å^3 is thus *exactly opposite* to that which would be expected from Loutfy's results. However, Loutfy did not report the thermal history of the films, which may have been different from ours. It is also possible that Loutfy's malononitrile probe is sensing real differences in local free volume smaller than that capable of being measured by azobenzene, where we have no information.

In general, the values given in Table II agree with those few results reported previously,[26] using a mercury lamp to irradiate solutions and films containing the probes. However, the stilbene results reported previously, although numerically close to those in Table II, show a different trend with molar weight. Some of these previously reported results are probably not accurate because the UV filter glass on which those films were cast absorbed significant amounts of UV light less than 320 nm in wavelength. This could have led to a systematic error in the measurement of the extent of isomerization. Different UV filter plates, transparent to 220 nm and higher UV light, were used for films containing stilbene in the measurements reported here.

Table IV

Effect of Annealing 573 000 MW Polystyrene for 100 h on the Fraction of Local Free Volume Larger Than What Photochromic Probes Need To Isomerize

	Y_{eq}(film)/Y_{eq}(toluene) for films annealed at				
probe	unannealed	30 °C	50 °C	60 °C	70 °C
azobenzene	0.892	0.891	0.894	0.894	0.899 ± 0.007
p-azotoluene	0.838	0.837	0.818	0.817	0.832 ± 0.005
m-azotoluene	0.820	0.815	0.800	0.801	0.817 ± 0.006
stilbene	0.812	0.793	0.794	0.793	0.800 ± 0.005
dinitrostilbene	0.717	0.665	0.645	0.646	0.632 ± 0.003

Table V

Effect of Annealing 9050 MW Polystyrene for 100 h on the Fraction of Local Free Volume Larger Than What Photochromic Probes Need To Isomerize

	Y_{eq}(film)/Y_{eq}(toluene) for films annealed at				
probe	unannealed	30 °C	50 °C	60 °C	70 °C
azobenzene	0.845	cracks	0.853	0.805	0.836 ± 0.007
p-azotoluene	0.822	0.807	0.804	0.771	0.813 ± 0.005
m-azotoluene	0.778	0.778	0.780	0.773	0.781 ± 0.006
stilbene	0.772	0.765	0.762	0.768	0.765 ± 0.005
dinitrostilbene	0.719	0.687	0.631	0.631	0.641 ± 0.003

Distribution of Local Free Volume. While Figures 1 and 2 show cumulative distributions of local free volume *larger* than what the extra volume probes need to isomerize, Figure 3 shows the cumulative distribution of local free volume in unannealed 573 000 MW polystyrene *smaller* than the extra volume probes need to isomerize. (This is simply a plot of 1-normalized extent of photoisomerization versus the extra volume probes need to isomerize.) Also shown in Figure 3 is the size distribution of local free volume found by plotting the derivative of the cumulative size distribution of local free volume. The vertical scale of the size distribution was normalized to the scale of the cumulative distribution for comparison purposes. Assuming that the number of pockets of local free volume with volume v is practically infinite as v approaches zero, and zero as v approaches 500 Å^3 (discounting the apparently smaller, but less accurate, volume needed by the excimer probe to twist in the film), then the cumulative distribution of local free volume smaller than what a probe needs to isomerize has an infinite slope at 0 and a zero slope at about 500 Å^3.

It is apparent that the size distribution derived from the cumulative distribution in Figure 3 has two maxima: one at 0, the other between 350 and 500 Å^3. The exact shape, size, and location of the 350–500 Å^3 peak is uncertain without more data in the 280–500-Å^3 size range. Although unsymmetrical, the peaked part of the size distribution more closely resembles the binomial distribution used in molecular-based glass relaxation models[16] than the distribution in eq 4 derived by Grest and Cohen.[15]

We do not interpret the median in the size distribution at about 400 Å^3 as a defect or void in the glassy packing; rather, it is the size of a liquidlike region of viscosity comparable with toluene. Positronium lifetime values in polystyrene have been measured[34] which are comparable to those found in molecular crystals having defects 5.43 Å in cubical radius (160 Å^3). If the "positronium micropore traps" in polystyrene represent voids, then our higher median value supports an interpretation of the local free volume measured by photochromic probes being composed of mobile molecular segments as well as void space.

Effect of Physical Aging. The fraction of local free volume larger than what probes need to isomerize in 573 000, 9050, and 3970 MW polystyrene films annealed 100 h at various temperatures are given in Tables IV–VI. The fraction larger than the size 4,4′-dinitrostilbene needs

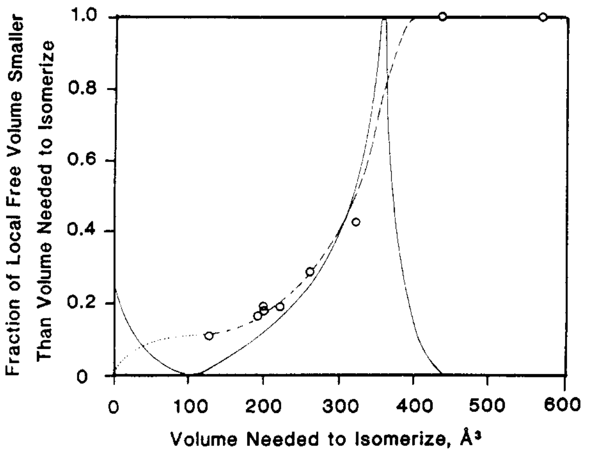

Figure 3. Cumulative distribution of local free volume smaller than the volume needed to isomerize in 573 000 MW polystyrene and distribution of local free volume: (---) cumulative distribution; (—) distribution. Vertical scale for the distribution was arbitrarily expanded. Error limits are the size of the symbols.

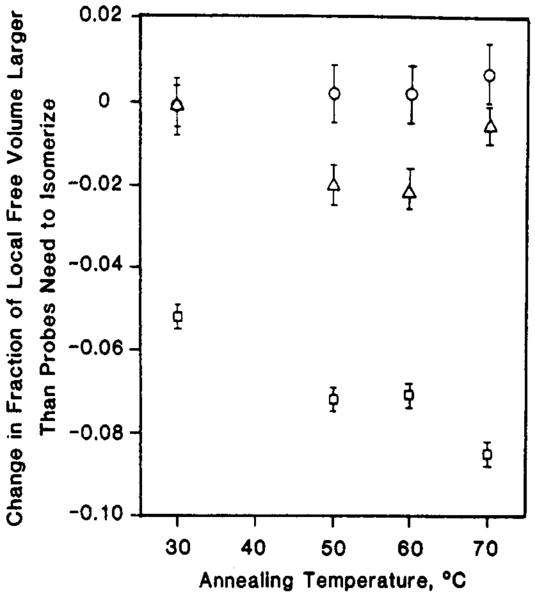

Figure 4. Difference between fraction of local free volume larger than what probes need to isomerize in 100-h annealed and unannealed 573 000 MW polystyrene. (○) Azobenzene; (△) *p*-azotoluene; (□) 4,4′-dinitrostilbene.

Table VI
Effect of Annealing 3970 MW Polystyrene for 100 h on the Fraction of Local Free Volume Larger Than What Photochromic Probes To Isomerize

	Y_{eq}(film)/Y_{eq}(toluene) for films annealed at			
probe	unannealed	30 °C	50 °C	60 °C
azobenzene	0.830	0.807	0.808	0.825 ± 0.007
p-azotoluene	0.817	0.780	0.754	0.781 ± 0.005
m-azotoluene	0.805	0.752	0.736	0.750 ± 0.006
stilbene	0.804	0.729	0.763[a]	0.717 ± 0.005
dinitrostilbene	0.736	0.686	0.624	0.675 ± 0.003

[a] Anomalously high, as discussed in the text.

to isomerize in 573 000 MW polystyrene annealed for various lengths of time at 60 °C is given in Table VII. The change in the fraction of local free volume larger than what azobenzene, *p*-azotoluene, and 4,4′-dinitrostilbene need to isomerize in polystyrene of 573 000, 9050, and 3970 MW annealed at various temperatures is shown in Figures 4, 6, and 7.

Table VII
Effect of Annealing 573 000 MW Polystyrene for Different Lengths of Time at 60 °C on the Fraction of Local Free Volume Larger Than What Dinitrostilbene Needs To Isomerize

annealing time, h	Y_{eq}(film)/Y_{eq}(toluene)
unannealed	0.717 ± 0.003
1	0.686
4	0.653, 0.647
23	0.649
26	0.643
30	0.646
97	0.646
216	0.630
250	0.635

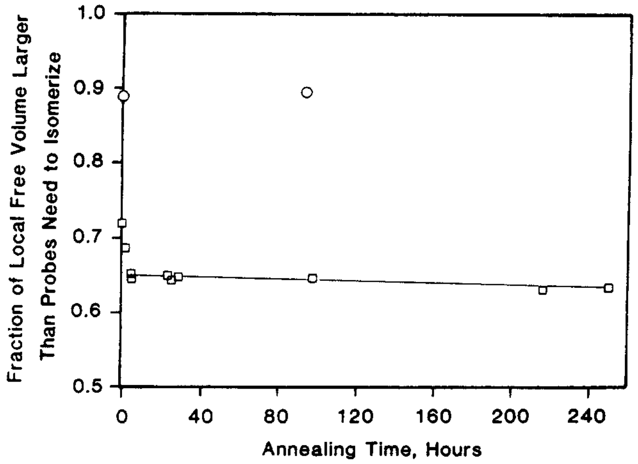

Figure 5. Effect of annealing 573 000 MW polystyrene at 60 °C on the fraction of local free volume larger than what the volume probes need to isomerize. (○) Azobenzene; (□) 4,4′-dinitrostilbene.

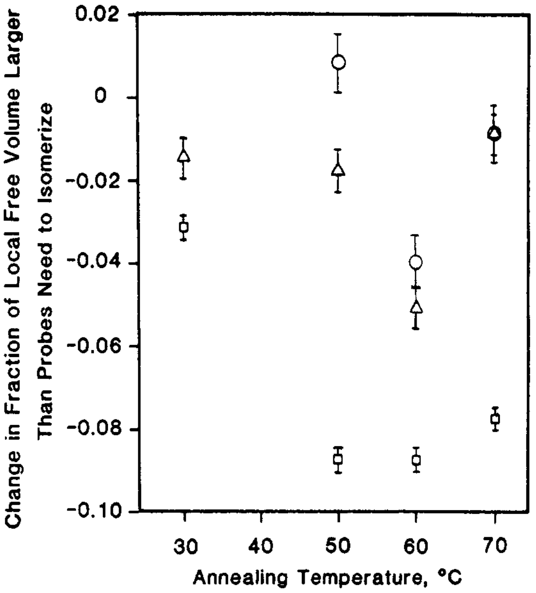

Figure 6. Difference between fraction of local free volume larger than what probes need to isomerize in 100-h annealed and unannealed 9050 MW polystyrene. (○) Azobenzene; (△) *p*-azotoluene; (□) 4,4′-dinitrostilbene.

For the 573 000 MW polystyrene, Figure 4 shows that physical aging in the temperature range 30–70 °C reduces or leaves unchanged the fraction of local free volume larger than the size each probe needs to isomerize, with a greater reduction found in films containing probes needing larger extra volume to isomerize, such as 4,4′-dinitrostilbene. Priest and Sifain[25] also found that the extent of isomerization of 2,2′-azonaphthalene, which we calculated as needing larger extra volume to isomerize than 4,4′-dinitrostilbene (Table II), decreased in polystyrene annealed

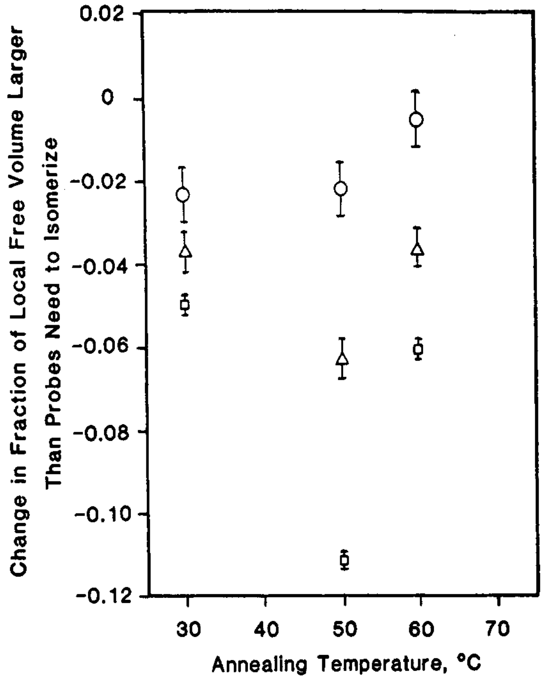

Figure 7. Difference between fraction of local free volume larger than what probes need to isomerize in 100-h annealed and unannealed 3970 MW polystyrene. (○) Azobenzene; (△) *p*-azotoluene; (□) 4,4′-dinitrostilbene.

at 80 °C (longer than a week) even more than 4,4′-dinitrostilbene. This is consistent with our finding that the fraction of larger local free volume decreases more than the fraction of smaller local free volume during physical aging.

Although direct comparison is difficult, our results qualitatively agree with the annealing study of Song and Roe[19] who found that density fluctuations decreased for volumes larger than about 40 Å^3 during annealing with greater decreases for larger volumes. In the range of annealing temperatures examined, the maximum reduction in the fraction of local free volume larger than what 4,4′-dinitrostilbene needs to isomerize occurs in films annealed at 70 °C. These results qualitatively agree with the increase in aging rate with increasing temperature found in DSC studies[4] and in dilatometric annealing studies.[1-3] We do find changes from annealing at ambient temperature, in contrast with Struik,[3] but in agreement with Greiner and Schwarzl[1] as well as Kovacs.[2]

Yu et al.[24] reported results of a physical aging study of polystyrene using a *p*-aminoazobenzene free probe as well as polystyrene with azobenzene labels attached as end groups, as side chains, and in the chain center. They irradiated their samples by flash photolysis and used a kinetic analysis to determine a fraction of fast-isomerizing azo species in the film which, in the case of the free probe, was similar to our fraction of local free volume larger than what azobenzene needs to isomerize. The azobenzene labels had smaller fast-isomerizing fractions in the film than the free probe. The fraction of fast-isomerizing azo probes and azo labels decreased during annealing of the films at three temperatures: 70, 80, and 90 °C. Although no definite temperature dependence was apparent for the rate of decrease of the fraction of fast-isomerizing free azo probe, the fraction of fast-isomerizing azo labels decreased faster at higher temperatures. The Robertson et al.[16] multiparameter free volume based volume recovery molecular model gave good agreement with the observed rates of decrease of the faster-isomerizing azo labels in films annealed at 80 and 90 °C.

Figure 5 shows the effect of annealing 573 000 MW polystyrene at 60 °C for various lengths of time on the fraction of local free volume larger than the size 4,4′-dinitrostilbene and azobenzene need to isomerize. Most of the decrease in the fraction of local free volume larger than what 4,4′-dinitrostilbene needs to isomerize from annealing at least 250 h at 60 °C occurs in the first few hours. The figure also shows that a similar decrease does not occur in the local free volume larger than what azobenzene needs to isomerize. A molecular mechanism consistent with this rapid initial redistribution of local free volume is one in which tightly packed polymer molecule segments relax into local free volume gradually, with numerous small relaxations. The small relaxations may create additional free volume but on a size scale smaller than what azobenzene needs to isomerize. This accounts for the plateau effect, the initial period in which little bulk volume change occurs in dilatometric measurements.[1] The density fluctuations apparently responsible for this initial rapid redistribution of local free volume arise in the rubbery state as deviations from the mean spacing between molecular segments. Contiguous regions are created with segments more tightly packed than at thermodynamic equilibrium and with segments more loosely packed. Even at the lower annealing temperature of the glass, some of these frozen-in density fluctuations contain segments that are more tightly packed than at thermodynamic equilibrium, so they spontaneously relax into spatially close regions of free volume, mostly in the 280–500-Å^3 size range.

A plateau effect has not been reported for physical aging studies using DSC, although a "sub-sub T_g" DSC study showed an enthalpy–time dependence consistent with an initial plateau.[35] Phenomenological models of physical aging using a distribution of recovery times τ_i for perturbations δ_i as in eq 1, based upon DSC measurements, cannot properly model this plateau effect and may systematically err over longer periods because they fail to account for expanding regions of local free volume, i.e, $\delta_i < 0$.

After the first few hours of annealing at 60 °C a slow loss of local free volume larger than the size 4,4′-dinitrostilbene needs to isomerize is apparent in Table VII. The rate of fractional loss amounts to about 7×10^{-5}/h and is an order of magnitude faster than the loss in bulk volume during a similar period, reported for polystyrene volume recovery at 60 °C,[1] implying that redistribution of local free volume to smaller sizes is much faster than the net loss of free volume during physical aging. Although the extent of isomerization of azobenzene did not decrease within the experimental error of our measurement, Yu et al.[24] reported a rate of decrease in the fraction of fast-isomerizing *p*-aminoazobenzene probe in polystyrene aged at 80 °C comparable with our value for 4,4′-dinitrostilbene.

Figure 6 shows that annealing 9050 MW polystyrene in the temperature range 30–70 °C causes a loss of some local free volume larger than what each probe needs to isomerize. The maximum loss is at 60 °C, about 20–25 °C less than T_g. The loss of local free volume in 9050 MW polystyrene annealed at 60 °C is greater for each probe than in 573 000 MW polystyrene, which may reflect a faster rate of physical aging taking place in 9050 MW polystyrene. Although dilatometric measurements of aging in low molar weight polystyrene have not been reported, DSC measurements[4] indicate that physical aging becomes faster at a given temperature as polystyrene molar weight decreases below 50 000. This faster aging may be due to fewer entanglements or to the greater concentration of polymer molecule ends in regions adjacent to local free volume of all sizes in the 9050 MW polystyrene. The ends may initiate relaxation into local free volume.

Annealing 3970 MW polystyrene in the temperature range 30–70 °C, as shown in Figure 7, gives results qualitatively similar to those for 9050 MW polystyrene, except that the temperature of maximum loss of local free volume greater than what 4,4′-dinitrostilbene needs to isomerize drops to 50 °C, about 20 °C less than T_g. The loss of local free volume larger than what all the probes need to isomerize in 3970 MW polystyrene annealed at 50 °C is greater than in the 9050 MW polystyrene annealed at 50 °C, which agrees with the idea that the higher concentration of polymer ends in 3970 MW polystyrene helps to initiate or propagate relaxation into local free volume.

Experimental Variability. The experimental variability for isomerizations carried out in solution was comparable with the error limits of measurement shown in Table I. In films, greater variability in measurements was found, entailing up to five replications to ensure accuracy. Much of the extra variability occurred in lower molar weight films.

Polystyrene films less than 92 000 MW cracked when rapidly cooled from above T_g to any temperature below about 65 °C. Cracks caused the base-line UV absorbance to increase making absorbance measurements less precise. Films with a base-line absorbance higher than 0.2 generally could not be used because the procedure to match the reference and sample base line became unreliable. Cracked films also had small regions separated from the quartz plate which gave colorful Moire patterns. These were occasionally large enough to cause anomalously high sample absorbances in the wavelength region used to match the sample base-line UV absorbance with that of the reference. In addition, these patterns tended to change during photoisomerization, causing uncertainty in the measurement of the UV absorbance.

Replicate independent aging tests given in Table VII show that variability of the 4,4′-dinitrostilbene results is greater in annealed films by about ±0.002. This is because the rate of film cooling from above T_g to the annealing temperature could not be controlled with precision. Hot films were waved about in uncovered petri dishes until the temperature felt sufficiently lowered to place the film in the annealing oven. Thus, although temperature equilibration was achieved in a minute, the distribution of local free volume still may have varied slightly with the cooling rate.

In unannealed 9050 MW film, the azobenzene and *p*-azotoluene isomerization varied slightly with the amount of time taken to complete the isomerization. When photoequilibrium was reached within 25 min, the fraction of local free volume larger than what the probes need to isomerize was as given in Tables II, III, and V. When photoequilibrium took 40 min or longer, the extent of isomerization was significantly less, although not as low as that in a film annealed 100 h at ambient temperature (30 °C).

Stilbene proved to be a difficult probe to use in films. It was found experimentally that in air-saturated toluene solutions, continued irradiation led to a relatively slow, constant loss of stilbene absorbance (due to cis-isomer closure catalyzed by oxygen[27]), the onset of which occurred at an absorbance equivalent to that attained at true photoequilibrium in deoxygenated toluene. This was assumed to apply as well in films: the absorbance that would be achieved at photoequilibrium in an oxygen-free film is the same as the absorbance attained at the onset of the constant loss of absorbance with time upon continued irradiation. However, applying this criterion appears to result in a systematically high (by about 0.02) normalized extent of isomerization of stilbene in the film, most apparent in the lower molar weight polystyrenes where the normalized extent of isomerization of stilbene found after one annealing test (Table VI) exceeded that of *m*-azotoluene. This may be because a significant portion of *cis*-stilbene molecules formed in the film are in strained conformations, due to the rigidity of the confining matrix, which enhances stilbene ring closure. With continued irradiation, loss of absorbance would appear to become constant with time, but nevertheless be biased toward higher extents of isomerization. Local softening, such as that experienced in films containing 4,4′-dinitrostilbene, may also contribute to this bias.

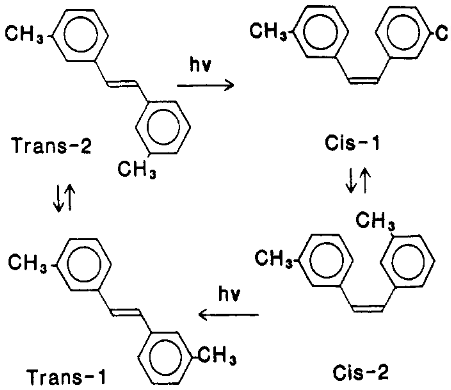

Figure 8. Isomerization pathway of *m*-azotoluene. (Note: The double bond represents a double bond between two nitrogen atoms.)

Despite these sources of experimental variability, we note that few other measurement techniques, with the exception of DSC,[4] SAXS,[11] and dilatometry,[30] can even be used with low molar weight, brittle polymer glasses.

Revision of Extra Volume Calculated for Probes. After publishing our first results using photochromic molecular probes, another probe, *p*-azotoluene, was obtained and photoisomerized in films and solution. The extra volume calculated for this probe to isomerize from trans to cis (193 Å^3) is that of azobenzene plus an additional amount from the cross-sectional area of a methyl group, replacing a hydrogen at the end of the phenyl. It became apparent, however, that the extent of photoisomerization of *p*-azotoluene in polystyrene divided by that in toluene (the normalized extent of photoisomerization) was higher than that of *m*-azotoluene for which the extra volume needed to isomerize had been calculated and reported[26] as 166 Å^3. We believe this anomaly is due to *m*-azotoluene forming conformers (isoenergetic rotational isomers) which were not accounted for in the original calculation of extra volume needed to isomerize. Figure 8 shows the conformers of *m*-azotoluene, analogous with the diarylethylenes.[36] Referring to Figure 8, the extra volume needed to isomerize that we reported was for trans-2 to become cis-1. However, cis-1 cannot reversibly isomerize unless the *m*-phenyl rotates about the axis joining it to the nitrogen so that it becomes cis-2. Similarly, trans-1 cannot isomerize to cis-1 without a rotation of the *m*-phenyl to form trans-2. Thus, instead of the *m*-phenyl rotating by 41° (trans-2 → cis-1), it must rotate by 161° (trans-1 ↔ cis-1). The revised extra volume for *m*-azotoluene to isomerize given in Table II is greater than that of *p*-azotoluene but less than that of stilbene.

The probe 2,2′-azonaphthalene used by Priest and Sifain[25] also forms rotational isomers analogous with the diarylethylenes. The extra volume we calculated and reported for this probe did not include the naphthyl rotation between isoenergetic rotational isomers. Like *m*-azotoluene, instead of the 2-naphthyl rotating by 41° during trans–cis isomerization, it actually must rotate by 161°. The revised extra volume for 2,2′-azonaphthalene to photoisomerize given in Table II is now greater than that of 4,4′-dinitrostilbene, and the normalized extent of isomerization reported by Priest and Sifain fits the correlation of the other probes in Figure 1.

Only one stable conformer of *trans*-1,1′-dinaphthylethylene exists.[36] We had previously calculated the extra volume needed to isomerize 1,1′-azonaphthalene, the azo analogue of 1,1′-dinapthylethylene, on the basis of one trans conformer photoisomerizing to one cis conformer, so that no revision in the extra volume needed for 1,1′-azonaphthalene to isomerize is needed.

We found that the presence of oxygen dramatically reduced the extent of isomerization of thioindigo in solution. Gorner and Schulte-Frohlinde[37] had reported this earlier and postulated a mechanism of isomerization of thioindigo via a planar triplet electronic excited state in thermal equilibrium with a twisted triplet state. The relaxation time (150–200 ns)[37] is thousands of times longer than that of stilbene. The pathway of the isomerization need not be similar to that of stilbene with its twisted singlet intermediate excited state, as we had previously assumed in calculating the extra volume needed for thioindigo to isomerize. Without knowing the path followed by thioindigo in rotating from trans to cis, a new value of the extra volume needed by thioindigo to isomerize cannot be calculated.

A correction was found for the 4,4′-dinitrostilbene value previously reported[26] for which the extra volume needed by the NO_2 group to twist with the phenyl ring had been neglected. However, the phenyl group twists 137° in the course of the isomerization and if the NO_2 failed to turn with the phenyl it would present a larger surface area, which would increase the extra volume needed to isomerize even more. The revised value is 23 Å^3 larger. Trivial corrections were also made in the values calculated for the other stilbene probes.

Summary

A probe technique, based upon photochromic and fluorescent molecules with known isomerization pathways, was used to measure the cumulative distribution of local free volume in glassy polystyrene of different molar weights and to measure how physical aging at various temperatures changes the distribution. Lower molar weight polystyrene was found to have a smaller fraction of local free volume in the 130–280-Å^3 size range. Annealing high molar weight polystyrene in the temperature range 30–70 °C caused a redistribution in local free volume involving a greater loss of local free volume larger than 280 Å^3 than of local free volume larger than 130 Å^3. Most of the redistribution occurred in the first few hours of a 250-h annealing period, consistent with a molecular mechanism involving tightly packed molecules relaxing into spatially close, loosely packed regions. A maximum loss of local free volume larger than what all probes need to isomerize occurred in lower molar weight polystyrene annealed at temperatures 20–25 °C below T_g.

We are investigating other glassy polymers to determine the effect of chemical composition on the distribution of local free volume and to measure how mobile pendant groups affect the redistribution of local free volume during physical aging. A related study involving fluorescent probes is also being carried out to investigate the distribution of local free volume in viscous solutions.

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Registry No. Polystyrene, 9003-53-6; azobenzene, 103-33-3; 4,4′-diphenylstilbene, 2039-68-1; *m*-azotoluene, 588-04-5; *p*-azotoluene, 501-60-0; 4,4′-dinitrostilbene, 2501-02-2; stilbene, 588-59-0; 1,3-bis(1-pyrenyl)propane, 61549-24-4.

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