Photochromic and Fluorescent Probe Studies in Glassy Polymer Matrices. 4. Effects of Physical Aging on Poly(methyl methacrylate) As Sensed by a Size Distribution of Photochromic Probes

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ABSTRACT: The effects of physical aging on poly(methyl methacrylate) (PMMA) have been investigated by observing the isomerization behavior of photochromic probes requiring various volumes to isomerize. Physical aging in PMMA decreases the isomerization ability of probes requiring larger volumes to isomerize more than the probes that require smaller volumes, similar to results found previously in polystyrene (PS). These results indicate that, upon physical aging, larger pockets of local free volume decrease in number more than the smaller pockets, causing the size distribution of local free volume to narrow upon aging. The degree of the decrease in a local free volume fraction was found to depend on the aging time and aging temperature. From the isomerization behavior of the larger probes, unannealed PMMA was also found to have a broader size distribution than unannealed PS. The fraction of local free volume large enough to allow diphenylstilbene to isomerize in PMMA is almost completely lost upon physical aging at 60 °C for 100 h, suggesting that through physical aging it may be possible to remove almost completely regions of local free volume exceeding certain sizes.

Introduction

Cooling a glass-forming liquid to a temperature below the glass transition temperature, T_g, results in nonlinear approaches toward equilibrium by measurable thermodynamic quantities such as specific volume[1-3] and enthalpy.[4-7] This slow approach toward equilibrium by a nonequilibrium glass has been termed physical aging.[8] In addition to volume and enthalpy, the aging process affects mechanical properties[9,10] and dielectric relaxation[11] of the material, as well as quantities studied with positron annihilation,[12] X-ray scattering,[13,14] permeation,[15,16] and molecular probe and label experiments (electron spin resonance,[17] fluorescent,[18,19] second-order nonlinear optical,[20-22] and photochromic[23-30]).

Various phenomenological models have been proposed to account for physical aging and more complex nonlinear kinetic behavior of polymer glasses after abrupt changes in temperature.[31-33] While different methods and assumptions were used to derive the governing equations of these models, an important result is that all require a distribution of relaxation times to produce quantitatively the nonlinear polymer responses. Molecular models based on size distributions of free volume and fluctuations therein have also been relatively successful in describing the effects of physical aging and other perturbations.[34-36] Even though results from all of these models begin to deviate from experimental data at temperatures not far below T_g, they do suggest that a distribution of relaxation times or free volume exists in polymer glasses.

Dilatometric measurements on poly(methyl methacrylate) (PMMA) have shown that specific volume decreases approximately linearly with the logarithm of aging time at temperatures below T_g, similar to polystyrene (PS).[2] A parameter described as the "volume relaxation rate" was defined as the normalized change in the specific volume as a function of the logarithm of aging time.[37] Resulting rates of volume recovery were found to increase as the temperature decreased below T_g and the "relaxation rate" reached a maximum at approximately 30 °C for PMMA. At all temperatures in the range between 0 and 90 °C, the relaxation rate of PS was found to be greater than that of PMMA.

Early studies found that excess enthalpy decreased approximately linearly with the logarithm of aging time for both PS[4] and PMMA[5] but with longer relaxation times than volume relaxation.[38,39] A method for calculating normalized heat capacities proposed by Hodge accounts for nonexponentiality with a Kohlrausch–Williams–Watts function[6]

$$Q(t) = \exp[-(t/\tau_0)^{\beta}] \qquad 1 \geq \beta \geq 0 \tag{1}$$

where Q is the relaxation function, t is the time, τ_0 is the characteristic relaxation time, and the exponent β characterizes the width of the relaxation time spectrum.[7] Hodge found that the best fits to heat capacity curves produced a value for β that was much smaller in PMMA than in PS. This analysis can be interpreted to suggest that with respect to enthalpy relaxation PMMA has a wider distribution of relaxation times than PS.

Physical aging in polymer glasses has also been investigated on a molecular-size scale. For example, restraints on probe mobility in glasses have been found with photochromic probes. Paik and Morawetz[24] examined the isomerization of azobenzene-labeled and 1,1′-azonaphthalene-labeled PMMA and found lower extents of isomerization in film than in dilute solution. They concluded that the free volume in the glassy film was unequally distributed, with a fraction of the volume too rigid to allow isomerization to occur. The rates of trans to cis photoisomerizations in polymer glasses have been modeled by the sum of two exponentials.[25,27] With this model, the first rate is interpreted to be equivalent to the single isomerization rate found in dilute solution while the second rate is much slower; this slower rate has been attributed to the lower mobility or free volume of the glass. Mita et

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al.[27] have proposed a kinetic model dependent on the free-volume distribution to account for the non-first-order photochromic reactions in film.

In previous publications, we reported how a size distribution of photochromic probes was sensitive to various fractions of local free volume in PS.[28,29] It was found that the overall size distribution observed decreased with aging time but that the amount of the decrease was dependent on both annealing time and temperature. The larger fractions of local free volume decreased more and at a faster rate than the smaller fractions, which led to the conclusion that a redistribution of free volume was occurring in PS during physical aging. In this paper, we report the results of physical aging at different annealing temperatures on the size distribution of probes in nearly monodisperse PMMA and compare the results with the findings in PS. These studies demonstrate that PMMA has a broader distribution of local free volume than PS. Although PMMA was found to physically age more slowly than PS, PMMA behaves similarly to PS in that larger pockets of free volume decrease at a faster rate than smaller pockets. It is also shown that in PMMA certain size ranges of local free volume can be nearly "annealed" out during physical aging. Additionally, a new and larger azo probe (4,4'-diphenylazobenzene; DPA) has been synthesized and added to the probe size distribution studies. The volume required for DPA to isomerize was calculated to be 356 Å^3. The addition of DPA to the set of photochromic probes provides detail in a size range missing in the "spectroscopic ruler" developed in the earlier PS studies.[28,29]

Experimental Section

Polystyrene (PS; nominal MW = 625 000; $M_w/M_n \leq 1.06$) and poly(methyl methacrylate) (PMMA; nominal MW = 265 000; $M_w/M_n \leq 1.15$) were used as received from Pressure Chemical. Trans isomers of the photochromic molecules were used as received: azobenzene (AZB) and 4,4'-diphenylstilbene (DPS; Aldrich); *p*-azotoluene (PAZT) and 4,4'-dinitrostilbene (DNS; ICN Biomedicals, Inc., K&K Laboratories); stilbene (SB; Eastman Kodak Chemicals). The probe 4,4'-diphenylazobenzene (DPA) was prepared by the method described by Fieser et al.[40] for the synthesis of azobenzene. The product was characterized by ^{1}H NMR and UV spectroscopy. The melting point was found to be 245–248 °C (lit.[41] mp 250 °C).

Photoisomerization of the probes in model solvent was carried out in spectrophotometric-grade toluene and methyl isobutyrate (Aldrich). Toluene was chosen as the model solvent for PS because the molecular structure is similar to a PS repeat unit and toluene is nearly an athermal solvent for PS as has been previously discussed.[29,42] Methyl isobutyrate was chosen as the model solvent for PMMA because it has the structure of a PMMA repeat unit; however, no information on its heat of mixing with PMMA is available. Polymer films were made by dissolving polymer in dichloromethane (Aldrich, spectrophotometric grade) to make approximately 7 wt % polymer solutions. These solutions, containing an appropriate amount of probe to give the film an absorbance of about 1 (never greater than 0.1 wt % probe in film), were poured onto 2 in. × 2 in. × 1/16 in. Q-grade quartz slides and allowed to dry at room temperature for 1 day (PS) to 1 week (PMMA). The films were then dried an additional 3 days in a vacuum oven at 80 °C.

The thermal history was carefully erased by placing each film in an oven (without vacuum) for 1 h at 120 °C for PS and 130 °C for PMMA. Immediately upon removal from the oven, the films were either quenched to room temperature for examining unannealed films or placed into an oven at the desired aging temperature. After films were aged 100 h at various aging temperatures, they were quenched rapidly to room temperature (all photoisomerizations were conducted and absorbance measurements were made at room temperature) and testing was completed in less than 40 min after the quench.

Photoisomerization was carried out by irradiating films and solutions at the appropriate wavelength (see Table IV for the wavelengths used) with a Photon Technology International 150-W xenon arc lamp (equipped with a monochromator). The absorbance maximum of each probe was monitored with an IBM Instruments UV/vis 9410 spectrophotometer until a photostationary state was reached. A 12-nm bandwidth was used for stilbene while all other probes were irradiated with a 16-nm bandwidth. Stilbene probes are known to ring close to dihydrophenanthrenes and phenanthrenes during irradiation at appropriate wavelengths. Ring closure causes a loss of absorbance at wavelengths characteristic of the trans isomer. The interpretation of the extents of photoisomerization in the presence of ring closure has been discussed previously.[29]

Table I
Photochromic Probes Used and the Volumes Required for Each To Isomerize (ν)

probe name (abbrevn)	isomerzn vol, Å^3
azobenzene (AZB)	127
p-azotoluene (PAZT)	193
stilbene (SB)	224
4,4'-dinitrostilbene (DNS)	285
4,4'-diphenylazobenzene (DPA)	356
4,4'-diphenylstilbene (DPS)	575

Results and Discussion

The fraction of cis isomer present at the photostationary state (or the extent of isomerization at the photostationary state), Y, of all probes was found from the equation[28,29,42]

$$Y = \frac{1 - A/A_{trans}}{1 - \epsilon_{cis}/\epsilon_{trans}} \quad (2)$$

where A is the absorbance at the photostationary state at the chosen wavelength for measurement, λ, A_{trans} is the initial absorbance at λ before irradiation, and ϵ_{cis} and ϵ_{trans} are molar absorptivity coefficients at λ of the cis and trans isomers. If Y_S and Y_F are taken as the extents of isomerization at the photostionary state in model solvent and polymer film, respectively, then the fraction of local free volume in the film large enough for probe isomerization, ψ, can be defined by Y_F/Y_S. This interpretation of ψ assumes that the only difference in the ability of the probe to isomerize in solvent and film is a local free-volume restriction present in film but absent in solvent.

The method for calculating the volume required for isomerization (ν) has been discussed previously,[28,29,42] for all probes except DPA. In calculating the isomerization volume for the newly synthesized probe, DPA, we assumed that the isomerization mechanism was an inversion process that has been shown to be the major process for azobenzene[43-45] and has been justified for *p*-azotoluene.[28,29,42] Values of the local free volume required for isomerization for the probes (ν) are presented in Table I. It should be noted that free probes dispersed in a polymer contribute small amounts of free volume to the local environment, which have been estimated to be less than 30 Å^3 at T_g and even less in the glass.[28]

Figure 1 shows the normalized absorbance as a function of irradiation time for the new photochromic probe, 4,4'-diphenylazobenzene (DPA), in PMMA films of various aging treatments and in methyl isobutyrate. The extent of isomerization, Y, for all probes is calculated from plots such as in Figure 1. As is seen for DPA, more isomerization is possible in the model solvent than in polymer film for all probes. Figure 1 also demonstrates the effect of aging temperature on the photostationary state reached (or the extent of isomerization, Y). Unannealed film allows

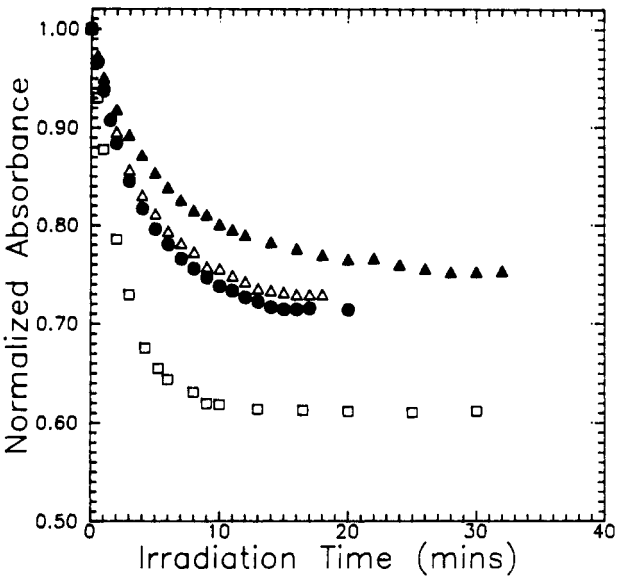

Figure 1. Normalized absorbance of 4,4′-diphenylazobenzene as a function of time of irradiation at a wavelength of 360 nm: (□) in methyl isobutyrate; (●) quenched PMMA film; (△) PMMA film aged at 25 °C for 100 h; (▲) PMMA film aged at 60 °C for 100 h. Errors are the size of the symbols or smaller. The cis fraction of DPA may be found by subtracting the value of the photostationary state (the plateaus) from 1 and dividing by 1 minus the molar absorptivity ratio at 360 nm.

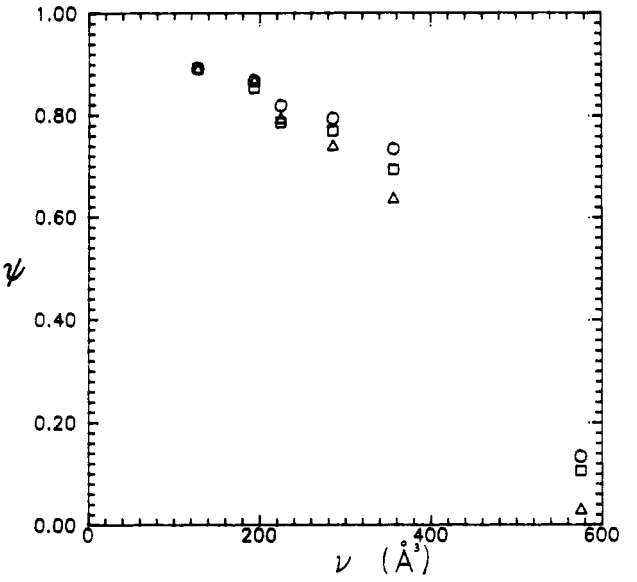

Figure 2. Cumulative distribution of local free volume in PMMA glass at 25 °C, measured by photochromic probes. Fraction of free volume larger than each probe needs for isomerization (ψ) as a function of the volume each probe needs to isomerize (ν): (○) unannealed PMMA film; (□) PMMA film aged at 25 °C for 100 h; (△) PMMA film aged at 60 °C for 100 h. Errors are the size of the symbols or smaller.

more isomerization than any other treatment in film, and aging 100 h at 25 °C allows more isomerization of DPA than aging 100 h at 60 °C. Thus, these results demonstrate that physical aging decreases the local free volume sensed by DPA, with the largest decrease in isomerization ability occurring after physical aging at 60 °C. It is interesting to note that this probe (as well as all probes used in this study except azobenzene) behaves qualitatively like the azobenzene labels in polyurethane studied by Lamarre and Sung,[25] with the fractional contribution of the initial fast rate (α in their work) decreasing with physical aging.

Figure 2 shows the effects of physical aging on the fraction of local free volume sites in PMMA that are large enough to allow probe isomerization (ψ) as a function of the volume needed for a probe to isomerize (ν). This plot represents a fractional local free volume size distribution in PMMA as detected by the size range of probes employed. This probe size distribution should not be interpreted as an absolute measure of the free-volume hole distribution. A literal interpretation of the volume required for isomerization as being equivalent to a hole or void in the polymer glass is incorrect for several reasons, most important being that it is incredibly unlikely that holes or voids with volumes exceeding 300 Å^3 would be found in consolidated polymer glasses. Instead, we prefer to interpret the local free volume probed as being related to local regions present in the glass that are of lower density or viscosity (such as those present in the model solvent), associated with density fluctuations occurring naturally in a polymer glass. This interpretation bears some relationship to the concepts (cooperatively rearranging regions) of Adam and Gibbs[46] and Robertson[35] in discussing relaxations in polymer glasses.

Figure 2 shows that physical aging has little or no effect on the isomerization of probes requiring smaller volumes but drastically alters the distribution at larger ν. Aging has no noticeable effect on the extent of isomerization of azobenzene in PMMA film. Yu et al.[26] found similar results for 4-aminoazobenzene free probe in PS as did Victor and Torkelson[29] for azobenzene in PS. Aging reduces the photoisomerization ability of *p*-azotoluene, but the effect is rather small. The fraction of local free volume sensed by stilbene (SB) is decreased by physical aging, but there does not appear to be a significant difference between aging at 25 or 60 °C. This same result was found earlier for stilbene in PS.[42]

More dramatic changes were observed in the photoisomerization behavior of the three largest probes: DNS, DPA, and DPS. As may be seen in Figure 2, the amount of decrease in ψ for the three probes requiring the largest volumes to isomerize was dependent on annealing temperature. Overall, aging at 25 °C (100 h) decreases the extent of isomerization in the film less than aging at 60 °C (100 h). This result may be expected, for while the thermodynamic driving force to approach equilibrium is greater at 25 °C, the kinetics are much slower due to the decreased mobility. Decreased mobility with lower aging temperatures below T_g has also been observed with mobility-sensitive fluorescence probes.[19]

It is interesting to note that a significant amount of the local free volume allowing DPS to isomerize is lost upon aging 100 h at 60 °C. This result suggests that through physical aging it may be possible to remove almost completely the regions of local free volume exceeding certain sizes. This is consistent with the results of a recent study by one of us[20] involving second harmonic generation (SHG) probes in PMMA. In this recent study, the local microenvironment in PMMA films doped with 4-(dimethylamino)-4′-nitrostilbene (DANS) was studied by examining dopant orientation in samples physically aged before poling as a function of aging time and temperature. Films aged at 25 °C before corona poling showed decreased SHG intensities upon application of a corona field at 25 °C, due to decreased mobility and local free volume reducing rotational mobility of the dopant in the matrix. No SHG intensity could be observed in doped PMMA films aged for 100 h at 25 °C before poling, indicating that the regions of local free volume and mobility sufficiently large enough to allow mobility of DANS are removed by the aging process.

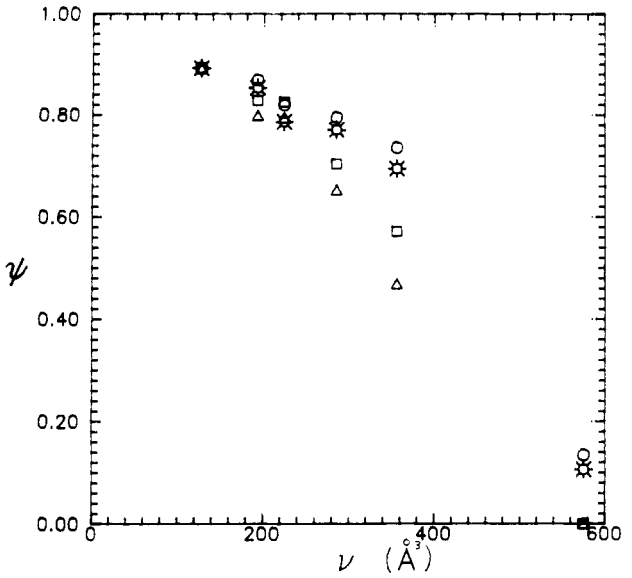

Figure 3. Comparison of distributions of local free volume in PMMA and PS films measured at 25 °C before and after aging for 100 h at 25 °C: (○) unaged PMMA; (✲) aged PMMA; (□) unaged PS; (△) aged PS. Errors are the size of the symbols or smaller.

Data in Figure 2 indicate that the distribution does not change uniformly during physical aging but instead narrows with a shift to smaller average size. Such a trend would agree with the suggestion of a redistribution of free volume put forth by Roe and Curro[13,14] to explain why the specific volume continued to decrease with aging below 96 °C for PMMA while the density fluctuations remained constant. The shifts in the distribution after aging are also in qualitative agreement with the theoretical findings of Robertson[35] that physical aging would shift a free-volume distribution to smaller free volumes.

Figure 3 compares the distributions found in PS and PMMA after aging 100 h at 25 °C. Please note that the values of ψ plotted are the cis fractions found in film divided by the cis fractions found in toluene for PS or methyl isobutyrate for PMMA. (The isomerization found in toluene relative to that found in methyl isobutyrate is discussed later in this paper.) The fraction of local free volume large enough to allow azobenzene isomerization (ψ) is identical in the two polymers. However, in general, PMMA has a larger size distribution than PS before and after aging as seen by the larger values of ψ for most of the probes. The best evidence of this is the fact that no local free volume large enough for DPS isomerization is detected in aged or unaged PS while DPS isomerization does occur in PMMA. A broader distribution for PMMA is in qualitative agreement with the enthalpy exponents, β, found by Hodge,[6] which may be interpreted to indicate that PMMA has a broader distribution than PS.

Additionally, it may be seen from Figure 3 that aging at 25 °C narrows the distribution more in PS than in PMMA. The change in ψ with respect to the unannealed film for each probe in PS and PMMA at 25 °C may be seen in Table II where a negative sign indicates a decrease in ψ with aging. (The change in ψ for DPS in PS is zero because no DPS isomerization is observed even in unannealed PS glass.) If the aging rate of PS is greater than that in PMMA at 25 °C as suggested by the specific volume data from Greiner and Schwarzl,[2] then the mobility or free volume would be able to decrease faster in PS, resulting in a larger percentage decrease in ψ than would be found in PMMA.

Table II
Percentage Change Relative to the Unannealed Glass in the Local Free Volume Large Enough To Allow Isomerization (ψ) after Aging at 25 °C in PS and PMMA (Errors ±1%)

probe	ψ-PS	ψ-PMMA	probe	ψ-PS	ψ-PMMA
AZB	0	0	DNS	−7	−3
PAZT	−4	−1	DPA	−18	−6
SB	−4	−4	DPS	*a*	−21

[a] No DPS isomerization was detected in PS, unannealed or aged.

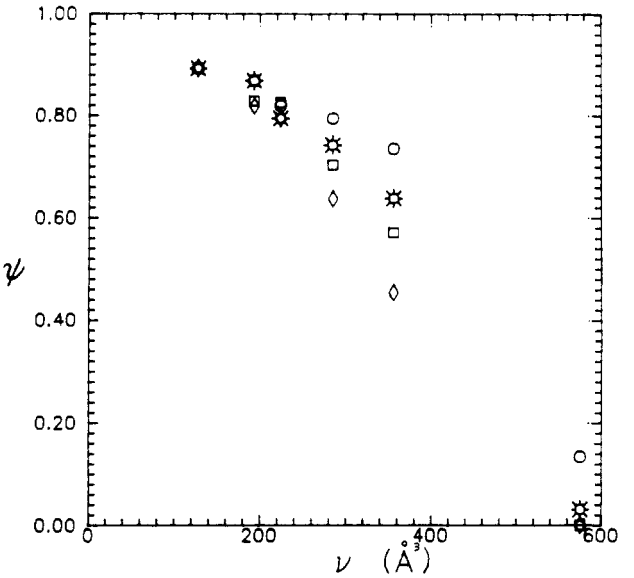

Figure 4. Size distributions of local free volume in PMMA and PS films measured at 25 °C before and after aging for 100 h at T_g − 50 °C: (○) unaged PMMA; (✲) aged PMMA; (□) unaged PS; (◇) aged PS. Errors are the size of the symbols or smaller.

Table III
Percentage Change Relative to the Unannealed Glass in the Local Free Volume Large Enough To Allow Isomerization (ψ) after Aging at T_g −50 °C in PS and PMMA (Errors ±1%)

probe	ψ-PS	ψ-PMMA	probe	ψ-PS	ψ-PMMA
AZB	0	0	DNS	−10	−7
PAZT	−3	0	DPA	−21	−13
SB	−4	−3	DPS	*a*	−77

[a] No DPS isomerization was detected in PS, unannealed or aged.

Figure 4 shows the effect of aging in PMMA and PS at similar temperatures below T_g. PS was quenched from 120 °C (about T_g + 20 °C) and aged at 50 °C (about T_g − 50 °C). PMMA was quenched from 130 °C (about T_g + 20 °C) and aged at 60 °C (about T_g − 50 °C). By aging at the same distances below each phenomenological glass transition temperature, each polymer film is treated to similar undercooling and temperature gradients that occur immediately after a quench from above T_g. Hence, differences observed in polymer aging rate, mobility, and redistribution of free volume (or probe isomerization ability in the polymer glass) should be due more to inherent polymer properties rather than experimental treatments. As can be seen in Figure 4, aging under these conditions also results in a broader distribution for PMMA than for PS.

Subtle differences may be seen when comparing the distributions obtained by aging at T_g − 50 °C to those found after aging at 25 °C. Table III summarizes the percent decreases in ψ for all probes after aging at approximately T_g − 50 °C for both polymers. Aging at these conditions reduces ψ more in PS than in PMMA with respect to unannealed film, which agrees with the dilatometric data of Greiner and Schwarzl showing that

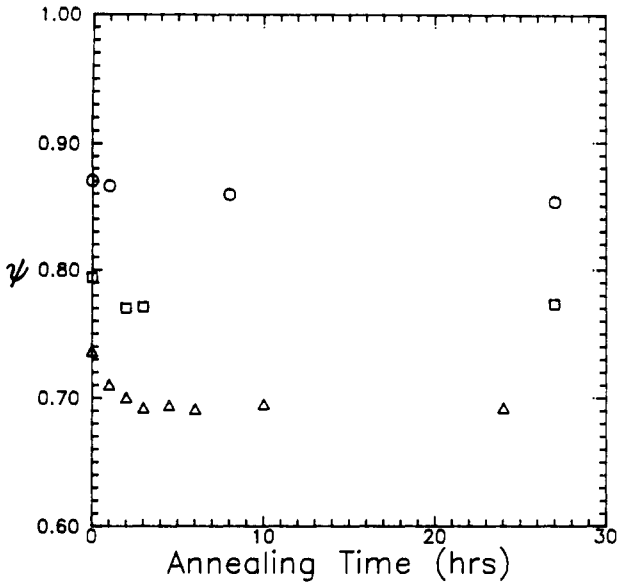

Figure 5. Fraction of free volume larger than probes need to isomerize (ψ) in PMMA film as a function of annealing time when aged at 25 °C: (○) *p*-azotoluene; (□) 4,4′-dinitrostilbene; (△) 4,4′-diphenylazobenzene. Errors are the size of the symbols or smaller.

the relaxation rate of PS is greater than the rate found for PMMA.[2] However, the percentage decreases in ψ for PS aged at 50 °C in Table III are on average only slightly larger than those caused by aging at 25 °C (Table II). In contrast, for the probes requiring larger isomerization volumes, aging PMMA at 60 °C dramatically reduces ψ compared to aging at 25 °C with an almost complete loss of the local free-volume fraction sensed by DPS after aging at 60 °C. Since specific volume data have shown that PS and PMMA cannot reach equilibrium in 100 h at these aging temperatures, this result indicates that different aging temperatures result in different aging rates for each polymer.

While the apparent aging rate of PS is only slightly faster at 50 °C than at 25 °C, the increase in aging temperature from 25 to 60 °C in PMMA produces a dramatic increase in the aging rate for some probes. A faster aging rate for PMMA at 60 °C compared to the apparent aging rate observed at 25 °C is in disagreement with the specific volume aging rate data found for PMMA by Greiner and Schwarzl[2] where the maximum aging rate occurred at 30 °C. This disagreement may be due to the fact that the PMMA used in the Greiner and Schwarzl study[2] was polydisperse. A more likely possibility is that the specific volume, being a bulk quantity, is subject to the total free volume in the system while these probes are sensing only certain fractions of free volume that we have shown to be unequally affected by aging. Changes in the fraction of local free volume much smaller than a probe needs to isomerize would not affect the isomerization ability of the probe during the aging experiment while they would still contribute to the changes occurring in the total free volume. Similarly, pockets of local free volume that remain larger than the isomerization volume of the probe during the physical aging experiment also would not affect the extent of isomerization of the probe.

Figure 5 shows the change in the fractional local free volume with respect to aging time for three different probes at 25 °C. Almost all of the decrease in the fraction of the local free volume larger than the value of v for PAZT takes place before the first 30 h of aging (the majority in the first 9 h) and in the first 3 h of aging for the DNS and DPA probes. Similar results were reported previously for photochromic probes in PS.[29] Thus, in both PMMA and PS most of the effects of aging to 100 h are present during the first few hours of aging.

Table IV
Molar Absorptivity Ratios ($\epsilon_{cis}/\epsilon_{trans}$ at the Wavelength Indicated) and Extents of Isomerization (Y_S) of Photochromic Probes in the Model Solvents for PS (Toluene) and PMMA (Methyl Isobutyrate)[47]

	toluene		methyl isobutyrate	
probe	$\epsilon_{cis}/\epsilon_{trans}$ (nm)	Y_S	$\epsilon_{cis}/\epsilon_{trans}$ (nm)	Y_S
AZB	0.05_8 (320)	0.17_2	0.05_4 (320)	0.17_5
PAZT	0.02_5 (336)	0.20_3	0.02_4 (332)	0.19_5
SB	0.18_3 (311)	0.95_6	0.17_3 (308)	0.96_2
DNS	0.25_0 (358)	0.88_1	0.24_8 (55)	0.87_8
DPA	0.28_9 (362)	0.50_2	0.25_1 (358)	0.51_9
DPS	0.29_7 (340)	0.44_8	0.29_9 (340)	0.45_9

As a result, although photochromic probes provide a powerful technique to investigate the effects of various treatments on a size distribution, other techniques, such as fluorescence, may have advantages over photochromic probes in certain areas. Employing a mobility-sensitive fluorescence probe to investigate short-time aging behavior has advantages because the test may be performed at the aging temperature and the initial aging behavior may be monitored continuously on the same film (which is not possible with photochromic probes). This demonstrates the necessity of employing a variety of probe techniques if the behavior of glassy polymers are to be explored in full with probe techniques.

As a final note, Table IV shows that the molar absorptivity ratios and the extents of isomerization of all probes at the photostationary state were similar in toluene and methyl isobutyrate, the model solvents for PS and PMMA, respectively. These results indicate that the choice of the model solvent for each polymer may not be as important as assumed in our initial work.[28,42] If the cis fractions of the probes at the photostationary state are relatively independent of the model solvent, it may be possible to investigate various systems where the identification of a model solvent is not simple, e.g., poly(vinyl acetate) and polycarbonate. Such studies are currently underway to determine the generality regarding the consistencies in the physical aging behavior observed in our studies of PMMA and PS.

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$$\beta = -\frac{1}{v}\frac{dv}{d \log t_a}$$

where β is the volume relaxation rate, v is the specific volume, and t_a is the aging time. This equation was applied in the region where the slope of the volume relaxation curves varied linearly with the logarithm of aging time. (It should be noted that the volume relaxation rate, β, is not the same β referred to in eq 1 in this manuscript.)
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(47) The values for the extents of isomerization (Y_S) for stilbene (SB) and 4,4′-dinitrostilbene (DNS) in toluene are somewhat higher than those reported earlier.[28,29,42] More than one person was involved in taking the data in this study, and the most likely cause for the differences in the data is the interpretation of where the photostationary states of the stilbene probes occur. However, the increases in the extents of isomerization are similar in solution and in film, resulting in little change in the values of ψ reported earlier[28,29,42] for the PS–toluene system.

Registry No. PMMA, 9011-14-7; AZB, 103-33-3; PAZT, 501-60-0; SB, 588-59-0; DNS, 2501-02-2; DPA, 5326-53-4; DPS, 2039-68-1.