Photochromic and Fluorescent Probe Studies in Glassy Polymer Matrices. 5. Effects of Physical Aging on Bisphenol-A Polycarbonate and Poly(vinyl acetate) As Sensed by a Size Distribution of Photochromic Probes

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ABSTRACT: Multiple photochromic probes requiring different volumes to isomerize were used to monitor the effects of physical aging on Bisphenol-A polycarbonate (PC) glass. PC was found to possess a local free volume distribution that is more broad than those of polystyrene (PS) and poly(methyl methacrylate) (PMMA). Contrary to aging results in PS and PMMA, physical aging of PC affected the isomerization abilities of the smaller probes as well as the larger probes, and all probes are affected nearly equally. Physical aging in dry and wet poly(vinyl acetate) (PVAc) showed that absorbed water increases the fraction of local free volume sampled by azobenzene as would be expected in a plasticized system. Additionally, it was found that a local free volume distribution is difficult to determine with the photochromic technique in polymers such as PVAc that have glass transition temperatures near the experimental temperature. At temperatures near T_g, the polymer has enough mobility to allow structural reorganization on the time scales required to reach the photostationary state, generally, 10-30 min. Therefore, the environments surrounding the probes change before the photostationary state is established, thereby making interpretation of the data difficult.

Introduction

Measurements of isothermal specific volume relaxation during physical aging have shown that the volume of Bisphenol-A polycarbonate (PC) relaxes approximately linearly with logarithmic time and that the aging rate varies with temperature as has been found in polystyrene (PS) and poly(methyl methacrylate) (PMMA).[1] The aging rate is defined as[1,2]

$$r = -\frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}\log t_a} \qquad (1)$$

where r is the volume relaxation rate, v is the specific volume, and t_a is the aging time. An independent dilatometric study by Bartos et al.[3] found similar aging rate values (r) at a given temperature as an earlier work by Greiner and Schwarzl[1] as well as nearly identical aging rate-temperature trends.

Bartos et al.[3] not only conducted bulk volume relaxation experiments on PC before and after cold drawing but also investigated the relaxation behavior on a molecular scale. Results from small-angle X-ray scattering and an electron spin resonance probe technique on isotropic PC (not drawn) were compared to the dilatometric changes during physical aging to determine how the magnitude of free volume and its distribution changed during relaxation. For the isotropic samples, the density fluctuations observed with X-ray scattering could not be correlated to the specific volume decreases observed during physical aging.[4] Similarly, no correlation was found between X-ray and dilatometric results in PC by Curro and Roe.[5]

Bartos et al.[3] found that physical aging decreased the rotational frequencies of an electron spin resonance (ESR) probe but that the frequencies were much higher than the polymer mechanical and dielectric frequencies. They interpreted the higher probe frequencies to mean that the probes were not affected directly by the polymer matrix mobility but indirectly through structural reorganization. This is equivalent to saying that the probes sense only the instantaneous local free volume, which decreases during physical aging.

Hodge[6] found that the nonexponentiality of the enthalpy relaxation of many glasses may be accounted for with a Kohlrausch-Williams-Watts function:

$$Q(t) = \exp[-(t/\tau_0)^{\beta}] \qquad 1 \geq \beta \geq 0 \qquad (2)$$

where Q is the relaxation function, t is time, τ_0 is the characteristic relaxation time, and the exponent β characterizes the width of the distribution of relaxation times.[7] The best fits to the enthalpy relaxation data produced a value of β for PC that was somewhat larger than that for PMMA and much smaller than that found for PS. Such results could be interpreted to mean that the widths of the distributions of relaxation times decrease in the following order: PMMA > PC ≫ PS.

Positron annihilation studies have been performed in PC to determine an average free volume size and how it changes with physical aging.[8] No systematic change in the lifetime (τ_3) of the orthopositronium component was found during physical aging, but the orthopositronium intensity (I_3) decreased. The constant lifetimes and decreasing orthopositronium intensities were interpreted to mean that while the average size of the free volume remained constant, the concentration of free volume elements decreased during physical aging. Kobayashi et al.[9] found similar results in poly(vinyl acetate) (PVAc) and concluded that the decrease of free volume during physical aging is mainly due to the disappearance of "holes" and not the shrinkage of "holes".

Photochromic probe techniques have been used in PC to determine the temperature dependencies of molecular reaction rates (photoisomerization) in the solid state.[10] Through photoisomerization of azobenzene in PC, it was found that the conversion of the trans to the cis isomer increases as the temperature increases from 4 K to near 300 K. As the temperature increases above 300 K, a thermal cis to trans back-reaction begins to contribute

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significantly to the isomerization process and decreases the amount of cis isomer in the photostationary state. The fraction of probe able to isomerize to the cis conformer was also found to depend on the volume swept by the probe during isomerization. At 4 K, 17% of *trans*-azobenzene could still isomerize to the cis isomer while only 7% of azophenanthrene and 1% of stilbene could isomerize. Stilbene isomerized less than either of the azo probes because its rotation isomerization mechanism requires a significantly larger sweep volume than the planar inversion mechanisms of the azo probes. A rate analysis of the trans to cis isomerization led to the conclusion that three different molecular sites exist in a polymer glass. One site allows isomerization as freely as in low molecular weight solvent (liquid-like regions), a second allows isomerization at a rate controlled by the polymer mobility, and a third allows no isomerization at all.

In previous publications, we reported how a technique employing multiple photochromic probes that require different isomerization volumes was sensitive to various fractions of local free volume in PS and PMMA.[11] In both PS and PMMA the breadth of the local free volume distribution decreased upon physical aging with the larger fractions of local free volume decreasing more and at faster rates than the smaller fractions. This led to the conclusion that physical aging causes a narrowing of the distribution studied in these polymers. It was also found that PMMA possessed a broader overall local free volume distribution than PS for the volume range studied. In this paper, we report the results from similar studies in PC. It will be shown that while the distribution in PC is similar to PMMA in the smaller local free volume fractions, it is broader in the larger free volume regions. More aging occurs after 100 h at 85 °C than at 25 °C, which supports bulk volume relaxation findings that PC ages faster at 85 °C than at 25 °C.[1] However, in contrast to PS and PMMA, physical aging affects the isomerization abilities of all probes in PC, suggesting that the entire range of local free volume investigated is equally decreased by physical aging.

Additionally, the isomerization behavior of azobenzene in dry and wet PVAc has been investigated. Results show that a very small amount of water plasticizes PVAc and greatly increases the ability of azobenzene to isomerize. It will also be shown that the local free volume distribution is difficult to determine with this photochromic technique in polymers such as PVAc that have glass transition temperatures near the experimental temperature. In such systems, the relatively high polymer relaxation rates are comparable to the times required to reach the photostationary states, which allows significant polymer relaxation to occur during the photoisomerization experiment. Therefore, a photostationary state is not attainable on an experimentally useful time scale, and an unannealed local free volume distribution cannot be determined.

Experimental Section

Bisphenol-A polycarbonate (PC; nominal MW = 28 800; M_w/M_n = 1.66; Scientific Polymer Products, Inc.) and poly(vinyl acetate) (PVAc; nominal MW = 194 800; M_w/M_n = 4.08; Aldrich Chemical Co.) were used as received. Trans isomers of the photochromic molecules were used as received: azobenzene and 4,4′-diphenylstilbene (Aldrich); *p*-azotoluene and 4,4′-dinitrostilbene (ICN Biomedicals, Inc., K&K Laboratories); stilbene (Eastman Kodak Chemicals). The probe 4,4′-diphenylazobenzene was prepared according to the synthesis of azobenzene described by Fieser and Williamson.[12] The calculated isomerization volumes for each probe are listed in Table I.

The instrumentation and techniques used to evaluate the isomerization characteristics of each probe in solution and polymer film have been reported previously.[11] Ethyl acetate (Aldrich, spectrophotometric grade) was chosen as the model solvent for PVAc because of the similarity of the solvent molecular structure to that of a PVAc repeat unit. Identifying a model solvent for PC is more difficult because of its complicated repeat structure and the lack of known athermal solvents; therefore, ethyl acetate was chosen as the model solvent for PC. The cis fractions at the photostationary state for azobenzene in ethyl acetate, toluene, and methyl isobutyrate were the same within experimental error for the band-passes used here. We found previously[11] that the cis fractions for all probes at the photostationary state were similar in both toluene and methyl isobutyrate. This indicates that for the systems considered here the photostationary state determined is largely independent of the model solvent chosen. Somewhat larger band-passes were used in this study than previously,[11] which resulted in a larger fraction of cis isomers in the photostationary state in both solvent and film (see Table II).

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

probe name	isom vol (Å^3)	probe name	isom vol (Å^3)
azobenzene	127	4,4′-dinitrostilbene	285
p-azotoluene	193	4,4′-diphenylazobenzene	356
stilbene	224	4,4′-diphenylstilbene	575

Table II
Molar Absorptivity Ratios ($\epsilon_{cis}/\epsilon_{trans}$ at the Wavelength Indicated) and Extents of Isomerization (Y_s) of Photochromic Probes in the Model Solvent for PVAc (Ethyl Acetate)

probe	$\epsilon_{cis}/\epsilon_{trans}$ (nm)	Y_s
azobenzene	0.05_2 (317)	0.19_1
p-azotoluene	0.02_5 (332)	0.21_5
stilbene	0.17_9 (307)	0.97_0
4,4′-dinitrostilbene	0.25_5 (355)	0.86_0
4,4′-diphenylazobenzene	0.25_7 (358)	0.52_7
4,4′-diphenylstilbene	0.29_5 (340)	0.48_5

PC and PVAc films were poured from dichloromethane as reported previously[11] with the following changes. Both PC and PVAc films were poured in a nitrogen-filled glovebox, allowed to dry for 8 h, and then dried for 3 days at 70 °C in a vacuum oven over desiccant. Additionally, PVAc films were heated to 120 °C for 3 h in vacuum before testing to remove any residual water that might plasticize the polymer. The thermal history was carefully erased by placing each film in a nitrogen-filled oven (without vacuum) for 30 min at 165 °C for PC (T_g = 147 °C) and 60 °C for PVAc (dry T_g = 39.5 °C) before each physical aging experiment. Erasing the thermal history in a nitrogen atmosphere was necessary for both polymers to keep the PVAc dry and to prevent the PC films from becoming cloudy. Cloudiness in the PC films was most likely due to degradation of the photochromic probes. Immediately after removal from the oven, the PC films were either quenched to room temperature for examining unannealed (quenched) films or placed into an oven at the aging temperature of choice. After 100 h of aging, the PC films were removed from the oven and quenched rapidly to room temperature, and the photoisomerization experiments were conducted. All photoisomerizations and absorbance measurements were performed at room temperature to ensure the same limited thermal back-reaction of the probes from test to test.

Dry PVAc films were removed from the oven, quenched to room temperature, and weighed, and then the photoisomerization experiments were conducted. After the photoisomerizations were concluded, the "dry" films were reweighed and found to have absorbed approximately 0.1 wt % water from the atmosphere in nearly 5 h in a partial nitrogen atmosphere (dry nitrogen was blown on the film during irradiation), which depressed the onset T_g by 1 °C to 38.5 °C. The temperature of the laboratory was 25 °C, and the relative humidity was less than 40%. Following a procedure by Bair et al.,[13] wet PVAc films were prepared by immersing the films into water until they had gained approximately 1 wt % water (after patting dry). The wet

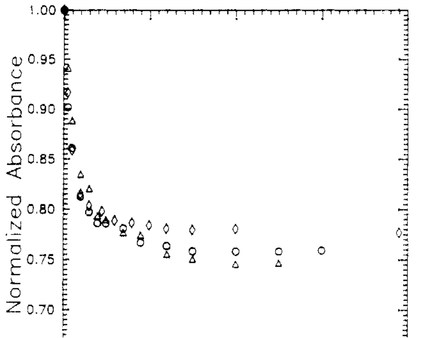

Figure 1. Normalized absorbance of 4,4′-diphenylazobenzene as a function of irradiation time at a wavelength of 360 nm: (△) quenched PC film; (○) PC film aged at 25 °C for 100 h; (◇) PC film aged at 85 °C for 100 h. Errors are the size of the symbols or smaller. The cis fraction of 4,4′-diphenylazobenzene is calculated with eq 3 in the text.

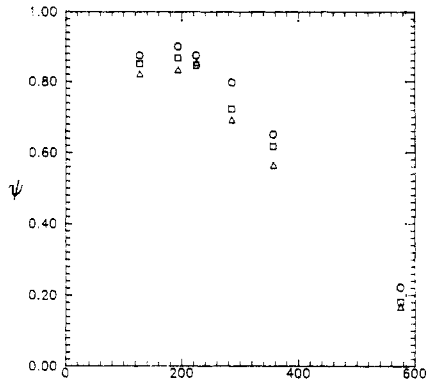

Figure 2. Cumulative local free volume distribution in PC glass measured at 25 °C with photochromic probes. Fraction of free volume larger than each probe needs for isomerization (ψ) as a function of the volume each probe needs to isomerize (ν): (○) unannealed PC film; (□) PC film aged at 25 °C for 100 h; (△) PC film aged at 85 °C for 100 h. Errors are the size of the symbols or smaller.

films were then placed into a 60 °C oven for 30 min to erase the thermal history, quenched to room temperature, and reweighed, and then the photochromic studies were performed. The wet films contained 0.5 wt % water before and after the photoisomerizations were performed. The onset T_g was depressed 4 °C from dry PVAc to 35.5 °C. Onset glass transition temperatures were determined on pieces of the test film in hermetically sealed DSC pans with a Perkin-Elmer DSC-2 differential scanning calorimeter.

Results and Discussion

The fraction of cis isomer present at the photostationary state Y (extent of isomerization) of all probes was found from the following equation:[11]

$$Y = \frac{1 - A/A_{\text{trans}}}{1 - \epsilon_{\text{cis}}/\epsilon_{\text{trans}}} \qquad (3)$$

where A is the absorbance at the photostationary state at the chosen wavelength for measurement, λ, A_{trans} is the absorbance the pure trans isomer 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 photostationary 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 or film is a local free volume restriction present in film but absent in solvent. The method for calculating probe isomerization volumes (ν) has been discussed previously[14] (see Table I for ν values).

Figure 1 shows the normalized absorbance as a function of irradiation time for 4,4′-diphenylazobenzene in PC films after various physical aging treatments. The extent of isomerization, Y, for all probes is calculated from such plots as Figure 1. Figure 1 demonstrates the effect of aging temperature on the photostationary state reached (or the extent of isomerization, Y). Unannealed film allows more isomerization than other treatments in film, and aging 100 h at 25 °C allows more isomerization of 4,4′-diphenylazobenzene than aging 100 h at 85 °C. Thus, physical aging decreases the local free volume sensed by 4,4′-diphenylazobenzene, with the most significant loss in isomerization ability occurring after aging at 85 °C.

Figure 2 shows the effects of physical aging on the fraction of local free volume sites in PC 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 distribution in PC as detected by the range of probes employed. This local free volume distribution should not be interpreted as an absolute measure of the free volume hole distribution. As mentioned previously,[11] we prefer to interpret the local free volume probed as being related to local regions in the glass of lower density or viscosity and hence of higher mobility (such as those present in the model solvent) associated with density fluctuations occurring naturally in a polymer glass.

The initial shape of the distribution and changes in the shape after physical aging in PC are subtlely different from those observed in PS and PMMA with this technique.[11] Both 4,4′-dinitrostilbene and 4,4′-diphenylazobenzene show the dramatic decreases in their ability to isomerize after physical aging in PC as was found in PS and PMMA, and both probes indicate that PC ages more after 100 h at 85 °C than after 100 h at 25 °C. 4,4′-Diphenylstilbene also shows decreased isomerization after physical aging, with more aging occurring at 85 °C than at 25 °C. Since 4,4′-diphenylstilbene isomerizes in PC and not in PS under any conditions, the size distribution in PC is broader than in PS. 4,4′-Diphenylstilbene was also able to isomerize in quenched PMMA although to a lesser degree than in PC, and the extent of isomerization decreased to nearly zero after aging PMMA at $T_g - 50$ °C for 100 h. Aging PC at $T_g - 60$ °C (85 °C) for 100 h does not anneal out the local free volume of the size required by 4,4′-diphenylstilbene to isomerize. Therefore, PC possesses a higher fraction of larger local free volume (before or after aging) than either PS or PMMA. Stilbene isomerized less in aged PC than in an unannealed sample, but the extent of isomerization was independent of the aging temperature as was found in PS and PMMA.[11]

Physical aging affects the smaller fractions of free volume in PC to a much greater degree than in PS or PMMA. The isomerization abilities of azobenzene and *p*-azotoluene were not affected significantly by physical aging at any temperature in PS or PMMA.[11] In PC, however, both azobenzene and *p*-azotoluene isomerized less after physical aging at both temperatures studied. Therefore, while the small-scale mobility or local free volume in PS and PMMA was not affected by physical aging, these smaller fractions were observed by the probes to decrease after physical aging in PC.

The behavior of all of the photochromic probes indicates that more aging takes place in PC after 100 h of aging at

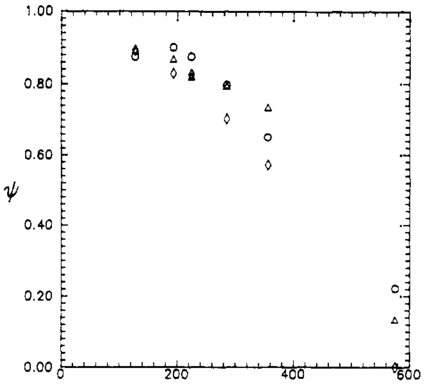

Figure 3. Comparison of unannealed local free volume distributions for (○) PC, (△) PMMA, and (◇) PS. Errors are the size of the symbols or smaller.

85 °C than for an equal aging time at 25 °C. This result agrees well with bulk volume aging studies performed on PC. Since the bulk volume of PC has been found to require months to reach equilibrium when aged at $T_g - 10$ °C, PC will not reach equilibrium on experimentally accessible time scales during aging at 85 °C ($T_g - 60$ °C) or 25 °C ($T_g - 120$ °C).[1,3] Consequently, for a given aging time, the largest effects of aging will be seen at the temperature that has the fastest aging rate, and dilatometric studies have shown that PC ages much faster at 85 °C than at 25 °C.[1,3] Similar to the photochromic studies, Bartos et al.[3] found that physical aging affects the rotational correlation times of ESR probes in PC, indicating that the local free volume surrounding the probes decreases during physical aging.

Figure 3 shows that the quenched PC size distribution is generally broader than those in PS and PMMA. Analysis of enthalpy relaxation behavior might suggest that PMMA has a slightly broader distribution than PC.[6] The photochromic results indicate the opposite, but the differences in the distributions are small at the smaller local free volumes. Enthalpy relaxation and the photochromic technique apparently have different sensitivities to the effects of physical aging. Muller and Wendorff[15] observed no enthalpy relaxation in PC after 19 days of physical aging at 45 °C with differential scanning calorimetry. The photochromic results presented here show that aging effects are detected after only 100 h of aging at 25 °C. Therefore, the photochromic technique appears to be more sensitive to physical aging than enthalpy techniques in this low temperature range.

The ψ value of 4,4′-diphenylstilbene in PC is nearly twice that in quenched PMMA. Therefore, while the smaller and medium probe size ranges contribute most to the PMMA and PS distribution, PC maintains a considerable fraction of larger local free volume even after physical aging. It was suggested previously[11] that physical aging in PS and PMMA narrows the free volume distribution with a shift to smaller average size. In contrast, the entire local free volume distribution investigated in PC decreases during physical aging which indicates that there is a loss of local free volume at all probe sizes. The photochromic results in PC suggest that while there is a loss in local free volume, the average size remains constant, which agrees with conclusions drawn from positron annihilation data.[8,9]

During initial attempts to construct a similar size distribution with the photochromic technique in PVAc, it was found that the photoisomerization results presented uncertainties of up to ±14% in ψ for azobenzene and 4,4′-dinitrostilbene. A major contributor to these large margins of error was the variable amounts of water in the PVAc, resulting in plasticization. Plasticization depresses the T_g of a polymer and results in a higher mobility than the unplasticized sample at any given temperature.[16] This higher mobility allows more isomerization of the photochromic probes and produces a higher value of ψ for plasticized films than for dry films. Using the data in Figure 4 and eq 3, it may be seen that, for the isomerization conditions used in this study, 30 min of irradiation in dry PVAc results in 14.4% conversion of *trans*-azobenzene to *cis*-azobenzene while 16.6% of the cis conformer is produced in the wet PVAc. We have reported recently[17] that 30 min of exposure to 70% relative humidity at 26 °C can result in nearly 1 wt % water uptake by a PVAc film which depresses T_g by 5 °C and greatly increases the local mobility surrounding molecular fluorescence probes. Therefore, great care must be taken to control the water content of hydrophilic polymers if test results are to be interpretable.

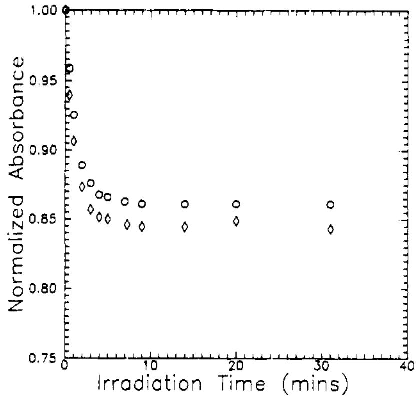

Figure 4. Normalized absorbance of azobenzene in PVAc as a function of irradiation time at 320 nm: (○) dry PVAc; (◇) PVAc containing 0.5 wt % water. Errors are the size of the symbols or smaller.

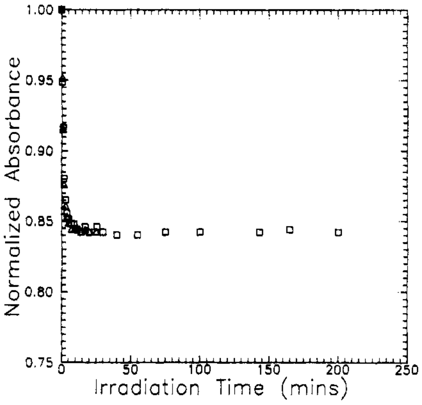

Figure 5. Normalized absorbance of azobenzene in PC as a function of irradiation time at 320 nm: (△) 30 min of total irradiation; (□) 200 min of total irradiation. Errors are the size of the symbols or smaller.

Even after controlling the water content of the PVAc, we found the value of ψ still varied up to ±6% for azobenzene. This poor reproducibility is related to the difficulty in accurately determining the photostationary state in the film. From the results in Figure 4, it might appear that the photostationary state of azobenzene had been reached after 30 min of irradiation. Indeed, Figure 5 shows that azobenzene reaches a photostationary state after 30 min of irradiation in PC, and no further change is observed for irradiation times as long as 200 min. Similarly, for the irradiation conditions used here and in previous studies,[11] all probes were found to reach a photostationary state in 40 min or less of irradiation time in PS, PMMA, and PC, with no further trans to cis conversion detected for

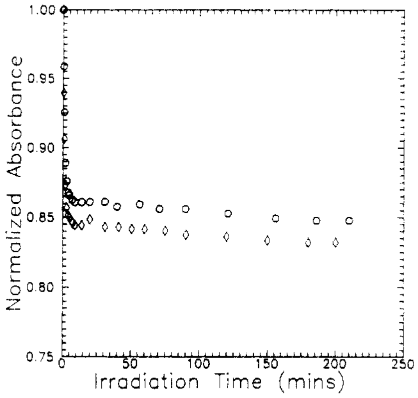

Figure 6. Normalized absorbance of azobenzene in PVAc as a function of irradiation time at 320 nm: (○) dry PVAc; (◇) PVAc containing 0.5 wt % water. Errors are the size of the symbols or smaller. Note how the system appears to be at the photostationary state in Figure 4 but actually continues to decrease upon further irradiation.

longer irradiation times (≤200 min). Therefore, determining the cis fraction in the photostationary state is unambiguous in these polymers where the photoisomerization test temperature of 25 °C ranges from $T_g - 80$ °C (PS and PMMA) to $T_g - 120$ °C (PC).

Figure 6 shows the normalized absorbance of azobenzene at 320 nm as a function of irradiation time for dry and plasticized PVAc (0.5 wt % H_2O) out to approximately 200 min of irradiation. In contrast to results in PC, azobenzene absorbance in PVAc continues to decrease slowly and does not reach a photostationary state even after 200 min of irradiation. After 210 min of irradiation in dry PVAc, 16.1% *trans*-azobenzene isomerized to the cis conformer, giving a ψ value of 0.84_5 (increased from the 30-min value of 0.75_7). In wet PVAc, azobenzene isomerized 17.7%, yielding $\psi = 0.92_8$, which is larger than the 30-min value of 0.86_2.

The photostationary state is not reached in these PVAc samples over the time scales investigated because the photoisomerization temperature, T_e, is near the sample T_g. Dry PVAc has a T_g of 39.5 °C, and a wet sample with 0.5 wt % water has a T_g of 35.5 °C; therefore, the photoisomerization was carried out at $T_g - 14.5$ °C for the dry PVAc and $T_g - 10.5$ °C for the wet sample, which are much closer to T_g than the tests performed in PS, PMMA, or PC. As the value of $T_g - T_e$ becomes sufficiently small, the fraction of the polymer relaxation time scales short enough to affect the extent of isomerization increases. (It should be noted that if the photoisomerization were carried out for hundreds of hours in PS, PMMA, or PC, slightly more isomerization would be likely to occur.) If the polymer relaxation time scales are short enough to allow polymer structural change during the irradiation/isomerization process, the position of the photostationary state will be affected. Analyzing the PVAc data with the model of Horie et al.[10] would show that the fraction of rigid environments (those not allowing isomerization) is relatively small near T_g.

In the case of PVAc, the plasticization effect of water is the more important contributor to varying degrees of isomerization in a film, but the relatively large polymer mobility associated with a small value of $T_g - T_e$ does not allow the system to reach a photostationary state even after 3.5 h of irradiation in a dry film. Any technique that requires time scales comparable to the polymer relaxation times cannot be used to measure the local free volume distribution of the quenched state because many changes occur in relatively short times. Therefore, caution should be used in employing techniques that require large acquisition times (e.g., this photochromic technique or positron annihilation[8]) to examine the quenched states of polymers at temperatures near T_g.

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