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Pulsed Laser Spectroscopic Study of the Photoisomerization of Azo Labels at Three Different Locations on a Polystyrene Chain[†]

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ABSTRACT: Azobenzene chromophores have been incorporated as molecular labels at three specific sites on a polystyrene chain: the chain end, the chain center, or as the side group. Trans $\rightleftarrows$ cis photoisomerization kinetic behavior of azo labels has been studied both in dilute solution and in the glassy state at 20 °C, using nanosecond pulsed laser spectroscopy, which reduced the measurement time to only 2 s. In dilute solution, a small difference in the label's photoisomerization behavior has been observed at different sites of the chain; the end label can photoisomerize a little faster than the center label or the side label. A much greater difference is observed in the glassy state, especially between the end label and the center label, mainly due to the free volume differences in the vicinity of each label. Assuming that in the glassy state, only a certain fraction of the label can isomerize with the same rate as in dilute solution, only 8% of the center label is found to photoisomerize while about 45% of the chain end or the side group photoisomerizes at 20 °C. The experimental results are discussed in terms of the theoretical predictions based on the free volume size distribution theory of Robertson, which was applied to meet the photoisomerization requirement of the azobenzene label. This theory predicts that 23% of the azo label can isomerize at 20 °C. In view of the packing differences and the resulting free volume differences in the chain end vs. the chain center, the relationships between the theoretical value and the experimental values seem reasonable.

We recently utilized azobenzene chromophores as molecular labels in the main chains of amorphous polyurethanes and found that the photoisomerization of such azo labels is very sensitive to the volume changes taking place within the solid film.[1] While photoisomerization in dilute solution occurs by a single rate process, its initial portion in the solid films may be fitted by two separate rate processes. The first is as fast as in dilute solution and is followed by a slower one. The fractional amount of the fast process decreases with physical aging but increases with temperature, plasticization, or glassy deformation.[1b] We suggested that this fraction may be proportional to the number of regions where local free volumes are greater than a critical size necessary for the photoisomerization of the azobenzene group. The azo chromophores in our previous study were attached in the main chain of the amorphous polymers but their location was not specific. In this study, we have incorporated azo chromophores at three specific sites on a polystyrene chain, namely, the chain end, the chain center, or as the side group (see Chart I for their chemical structures). We hoped to observe the differences in the photoisomerization behavior in the glassy state, since the packing efficiency and thus the size distribution of free volumes are expected to depend upon the location of the group on the chain.[2] For example, the chain ends may be associated with more free volume than the center of the chain. The situation in the side group may depend upon the temperature of the glass matrix in relation to the characteristic relaxation temperature for the side-group motion.

With our previous experimental setup in which a xenon arc lamp was used as the irradiation source, the time scale of the photoisomerization measurement was in the hundred of seconds. During such time, free volume may be redistributed as well as decreased to some extent since it is well-known that densification proceeds faster in the initial stage than in the later stage of physical aging.[3] In order to obtain information on the matrix without such uncertainty, it is desirable to carry out time-resolved spectroscopy following short pulses of irradiation.

[†] This paper is dedicated in honor of Professor Herbert Morawetz.

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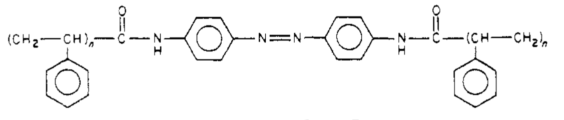
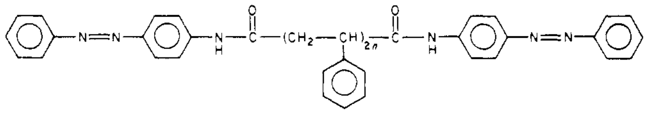
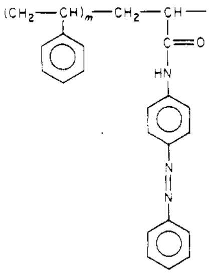
Chart I
Chemical Structures of Three Azo-Labeled Polystyrenes[a]



centered-labeled PS (C-PS)



end-labeled PS (E-PS)



side-labeled PS (S-PS)

[a] Where $n \simeq 80$; $m \simeq 26$.

Therefore, we employed 3-ns repetitively pulsed laser flashes as an irradiation source, followed by monitoring of the photoisomerization with a digital oscilloscope. In this manner, ten kinetic data points were obtained in 2 s.

We report in this paper the results of a study in which comparisons were made between the photoisomerization behavior of the azo label in the dilute solution and the glassy state at 20 °C. The results clearly show the difference in local mobility in the glassy state with respect to the position of the chain. The observed trends are discussed in view of Robertson's free volume size distribution theory.

Experimental Section

Syntheses of Azo-Labeled Polystyrenes. Side-labeled PS was made by free radical copolymerization from monomer mixtures (99 mol % styrene and 1 mol % of the comonomer containing the azo aromatic group). The comonomer was made by reacting recrystallized *p*-aminoazobenzene with distilled acryroyl chloride. Polymerization was carried out in dioxane solution with azobis(isobutyronitrile) initiator by heating for 2 h at 80 °C under a nitrogen atmosphere. End-labeled PS was made by first reacting dicarboxylic acid terminated polystyrene (M_w/M_n = 92 000/79 000) (a gift from Dr. Hsieh of Phillips) with thionyl chloride in benzene solution, followed by reaction with *p*-aminoazobenzene so as to label both ends of the chain with the azo group. Center-labeled PS was made by first reacting monocarboxylic acid terminated polystyrene (M_w/M_n = 42 000/40 000) (a gift from Dr. Hsieh of Phillips) with thionyl chloride in benzene solution for 8 h at 75 °C followed by the reaction with *p,p'*-diaminoazobenzene for 48 h at 75 °C. After the reaction, GPC analyses showed that the polymer is a mixture of the center label (as indicated by a molecular weight twice that of the starting PS) and the end label (labeled only on one end and having the same molecular weight as the starting PS). The center-labeled PS fraction was isolated by preparatory GPC (Waters System 506) using two preparatory columns (4 ft long × 2 1/2 in. diameter) designed for the pore sizes of 1.5×10^3 to 1.5×10^4 Å and 5×10^4 to 1.5×10^5 Å at the flow rate of 40 mL/min with 10% polymer solution in UV-grade THF.

Characterization of Labeled Polymers. T_g was measured with a differential scanning calorimeter (Perkin-Elmer DSC-II) at a heating rate of 10 °C/min. Molecular weight distribution has been determined by analytical GPC (Waters HPLC/GPC-244) using fine Ultra-Styragel columns at a flow rate of 2 mL/min from a dilute solution (UV-grade THF). Table I provides some characteristics of the labeled polymers.

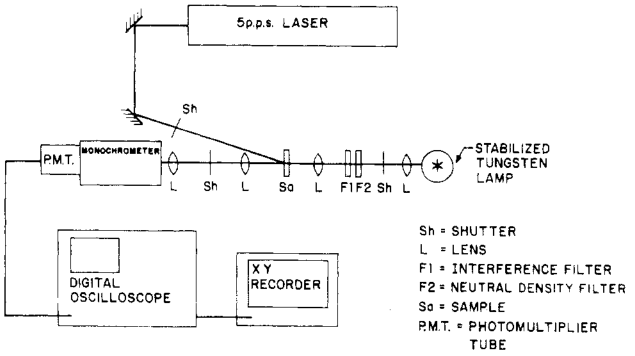


Figure 1. Schematic diagram used for the photoisomerization kinetic analyses.

Table I
Characteristics of Three Azo-Labeled Polystyrenes

sample desig	λ_{max} of azo residue, nm	azo residue, mol %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	T_g, °C
C-PS	390	0.12	84	80	1.05	103
E-PS	353	0.24	92	79	1.16	103
S-PS	353	<1.0	39	26	1.51	102

Photoisomerization Study with Nanosecond Pulsed Laser. Figure 1 shows the experimental setup for the photoisomerization kinetic analyses. A Quantel YG-441 Nd:YAG laser (351 nm 10 mJ, 3 ns, and operated at 5 pps) was used as an excitation source; the light was focused so that the excitation and analyzing beams overlapped at the cell holder. The analyzing light source used in the present work was a 45-W tungsten lamp with an Optronics 65 stabilized power supply. The analyzing light was collimated, passed through a neutral-density filter to reduce the intensity followed by an interference filter to pass only the light near the absorption maximum of the trans isomer (380 nm for the center label and 353 nm for the end label and the side) and focused onto the cell holder. The light collected after the cell holder was refocused onto the entrance slit of an ISA H-10 monochromator. The light intensity was measured with an IP 28 photomultiplier tube terminated into 10 kΩ. A Uniblitz 225 electronic shutter was used to prevent unnecessary irradiation of the sample. The transmitted light intensity before and after each pulse was recorded with a Biomation 4500 digital oscilloscope. Data from ten pulses were recorded on a 2-s sweep of the oscilloscope. For dilute benzene solution of azo-labeled polystyrenes, a constricted cell from Precision Cells was used with a small solution volume in order to reduce diffusion effects. For the glassy films, thin polymer films were cast onto quartz plates (1 in. × 1 in.) from filtered benzene solution (about 2% by weight). Kinetics were run with films after drying at 20 °C for 3 h and after 3 weeks.

Results and Discussion

The kinetics of trans ⇄ cis photoisomerization of the azo labels in polystyrene were studied by irradiation with 3-ns flashes of 351-nm laser light and by analyzing the changes in the optical transmission at λ_{max} of the trans isomer about 20 ms after each flash. Figure 2 shows an example of the oscilloscope traces obtained for a kinetic study of the side-labeled polystyrene in benzene solution. The arrows indicate the time at which the laser irradiates the sample. It is noted that the optical transmission continuously increases at 353 nm because of the conversion of the trans to the cis isomer. From such an oscilloscope trace, the conversion of the trans isomer can be calculated, assuming that the optical absorption of the cis isomer is negligible at λ_{max}. Figure 3 shows the conversion of the trans isomer as a function of the number of laser flashes at 20 °C.

For dilute solutions of the labeled polystyrenes, the trans ⇄ cis photoisomerization occurs readily as shown in Figure

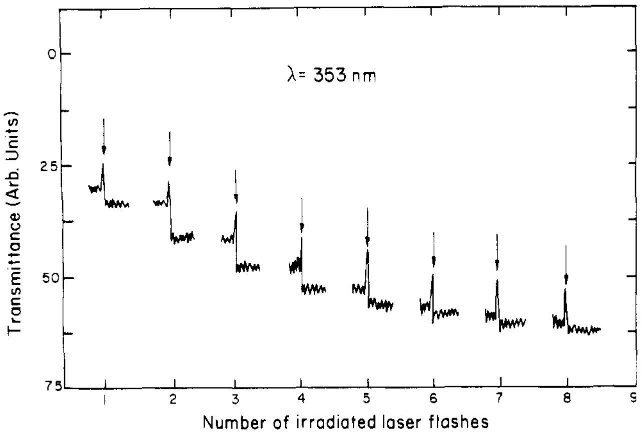


Figure 2. Oscilloscope tracing showing the changes in the transmittance at 353 nm as a function of 3-ns pulsed laser flash irradiation on a S-PS solution in benzene. Arrows represent the time at which the laser flashes irradiates the sample solution.

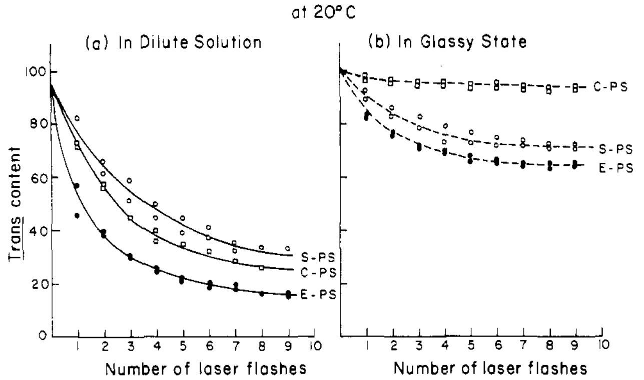


Figure 3. Course of trans ⇄ cis photoisomerization as indicated by the changes in the trans isomer concentration as a function of the number of the laser flashes at 20 °C (a) in dilute benzene solution and (b) in the glassy state. Dotted lines in (b) are predicted from eq 2.

3a. After about 10 laser flashes, all solutions reach apparent photostationary composition within the analyzed volume, with a trans content of approximately 33%, 26%, and 15% for the side label, the center label, and the end label, respectively. The trans content was estimated assuming negligible absorbance of the cis isomer at λ_{max} of the trans isomer. The trans content remains unchanged even after many more laser flashes as listed in Table II. For a reversible first-order reaction as in the trans ⇄ cis photoisomerization of azo labels, the trans content (A) after a number (5) of laser flashes is obtained after the integration of the reversible rate equation, assuming negligible thermal dark reaction, as shown in eq 1, where A_e is the

$$A = A_e + (1 - A_e)e^{-(k+k')t} \qquad (1)$$

trans content at the photostationary state and k and k' are the rate constants for the forward and the backward reaction, respectively. When $-\ln [(A - A_e)/(1 - A_e)]$ is plotted against t, the slope becomes $k + k'$. Such plots for all three labeled solutions are linear with the slope of 0.41 for the side label and the center label and about 0.52 for the end label (Table II). This means that even in dilute solution, the end label can photoisomerize a little faster than the center label or the side label. This trend of higher mobility at the chain end compared to the center or to the side group of the chain has been previously observed in dilute solution by other techniques such as fluorescence depolarization,[4] NMR studies,[5] and ESR spin label studies.[6] The limited mobility of the center label is not necessarily due to tying both ends of the label at least in dilute solution because the side label with only one end tied is similar in its mobility to the center label.

Table II
Photoisomerization Parameters of Azo Labels in Dilute Solution and in the Glassy State at 20 °C

	in solution		in glassy state	
sample desig	A_e[a]	$k + k'$[b]	A_e^*[c]	α[d]
C-PS	0.26	0.41	0.94	0.08
E-PS	0.15	0.52	0.63	0.45
S-PS	0.33	0.41	0.70	0.44

[a] Trans content at the photostationary state, assuming negligible cis contribution at λ_{max} of the trans isomer. [b] Sum of the forward (trans → cis) and the backward (cis ← trans) reaction rate constants. [c] Trans content at the apparent photostationary state, which is equivalent to $(1 - \alpha) + \alpha A_e$ in eq 2. [d] The fraction of the azo label that can isomerize as fast as in dilute solution.

In comparison to the dilute solution, the photoisomerization in the glassy films at 20 °C is impeded as shown in Figure 3b. The glassy films used here were dried for 3 h at 20 °C after casting on a quartz plate. Most noteworthy from Figure 3b is that the center label finds it most difficult to isomerize, with 94% trans remaining after 10 laser flashes. The side label and the end label in the glassy film can isomerize more that the center label but not as much as in the dilute solution. The trans decays to 70% and 63% respectively, as shown in Table II. Since further laser flashes do not change the trans content in these films, we may refer to these values as corresponding to the apparent photostationary-state composition. The results in the glassy films were very reproducible either with the same films when different spots are studied or when the films were aged for 3 weeks at 20 °C and new spots are analyzed. Since the physical aging process at 20 °C (80 °C below T_g) is expected to be very slow,[7] it is not surprising that 3 weeks of aging at 20 °C did not change the photoisomerization behavior.

One plausible way to analyze the data in glassy films is by assuming that only a certain fraction (α) of the azo chromophore can isomerize with the same rate as in dilute solution[1] while the rest is unable to isomerize due to the lack of the free volume necessary for such a reaction during the time scale of this measurement. Then eq 2 can de-

$$A = (1 - \alpha) + \alpha\{A_e + (1 - A_e)e^{-(k+k')t}\} \qquad (2)$$

scribe the kinetic behavior of the photoisomerization occurring in the glassy films. From the asymptotic values of trans content (A_e^* of Table II), we can estimate α to be 0.08, 0.45, and 0.44 for the center label, the side label, and the end label, respectively (Table II). Using the values of $k + k'$ obtained from the dilute solution data, the predicted change in the trans content (A) as a function of the number of laser flashes (t) from eq 2 is plotted as a continuous curve for each sample shown in Figure 3b. It is seen that these curves fit the experimental data reasonably well.

This result implies that while about 45% of the label either at the chain end or at the side group of polystyrene can isomerize due to the availability of the free volume above a certain size, only 8% of the label in the center of the chain can isomerize in the glassy film at 20 °C under these aging conditions. The difference in mobility between the end label and the center label is much greater in the glassy films than in the dilute solutions. This large difference is probably due to the poor packing efficiency and the consequent local free volume associated with the chain ends. In addition, one may expect that the difficulty involved in the rotation of the chain center bond in the glassy state may also contribute to some extent for this difference. It is reasonable to predict that this difficulty is also influenced by the availability of the free volume. Our preliminary physical aging data at 90 °C seem to indicate that the fraction of photoisomerizable center label decreases sharply with aging time, suggesting that the availability of the local free volume is an important factor even in the chain center.

Using solid-state NMR techniques such as magic-angle ^{13}C NMR[8a] or pulse deuterium NMR,[8b,c] many researchers have obtained evidence for limited localized motions of the phenyl side group in glassy polystyrene. Spiess[8b] has also detected a motional heterogeneity from the line shapes and Sillescu[8e] attributes the β relaxation of polystyrene which is observed in the 20–30 °C range[9] as due to the rotation of some phenyl groups possessing less steric hindrance than the majority. Thus at 20 °C, which is within the β-transition range, some phenyls in polystyrene may flip, providing additional free volume for the neighboring azo side label to photoisomerize.

Another factor that may contribute to a higher mobility in the side-labeled polymer is the presence of some low molecular weight species, since this polymer has a broader molecular weight distribution. For the center- or end-labeled polymer, the molecular weight distribution is much sharper and without low molecular weight species.

Comparison with Theoretical Prediction. It is worthwhile to ask at this point whether our experimental results are in reasonable agreement with theoretical predictions. Cohen and Grest[10] recently extended the free volume model of the glass by distinguishing between solid-like cells and liquid-like cells. Liquid-like cells are those greater than some critical volume, and the solid-like cells are those smaller than the critical value. Only liquid-like cells are assumed to have mobility in the glass. According to their theory, the fraction of the liquid-like cells shows a sharp transition at T_g. If we assume a certain critical volume for the photoisomerization of the azobenzene label (see later part of this section for a rough estimate of such a critical volume), we may compare the predicted fraction of liquid-like cells based on their theory with our experimentally obtained estimate. Unfortunately, in their theory the fraction of the liquid-like cells is a complex function of the many parameters of each glass (eq 39 and 40 in ref 10), some of which are not well characterized for polystyrene. Therefore, we could not get a value on the basis of their theory.

Instead, we attempt to use Robertson's theory.[11] For convenience, he described the size distribution of the fractional free volume by a Γ function, as follows:

$$\xi(f) = \frac{\lambda}{\Gamma(\alpha)}(\lambda f)^{\alpha-1}e^{-\lambda f}$$

where $\xi(f)$ is the size distribution function, f is the fractional free volume, and α and λ are the characteristic material parameters given by

$$\alpha = \bar{f}^2(V/\Delta k)KT$$

and

$$\lambda = \bar{f}(V/\Delta k)KT$$

where $\bar{f}$ is a mean fractional free volume, $\Delta k = k_1 - k_g$; the difference in compressibility between liquid and glass, K is Boltzmann's constant, T is the temperature, and V is the volume of the relaxation environment.

Assuming that the smallest possible molecular rearrangement in the glassy state involves the simultaneous rotation about three parallel, noncollinear bonds, Robertson estimated the volume of the relaxation environment (V) to be the rearranging segment plus 12 nearest neighbors. For polystyrene, such a volume is equal to 4.32 nm^3.

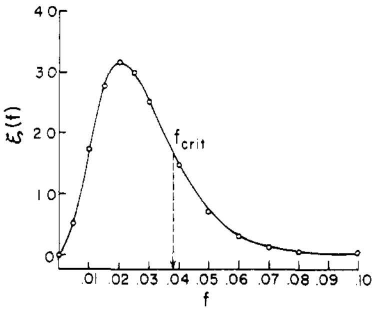


Figure 4. Size distribution function [$\xi(f)$] of the fractional free volume for polystyrene at 20 °C for the azobenzene relaxation environment based on Robertson's[10] theory.

For the volume of the relaxation environment in the vicinity of the azobenzene label regardless of its position in the chain, we will take the same approach as Robertson's. Then V would be 13 times the volume required for the motion of an azobenzene residue. Since the trans azobenzene is about 9 Å long, we may say as a rough estimate that the motion size for the photoisomerization of azobenzene assuming rotation as the mechanism is a sphere with a radius of 4.5 Å, which is 0.38 nm^3. Thus, $V = 13 \times 0.38 = 4.96$ nm^3.

For polystyrene, Goldbach and Rehage[12] obtained 2.5×10^{-10} Pa^{-1} for Δk near T_g. For $\bar{f}$ at T_g, we can use Plazek's value of 0.028.[13] Assuming that Δk and $\bar{k}$ do not change much at 20 °C, α and λ can be estimated by using 4.96 nm^3 for V. We find $\alpha = 3.84$ and $\lambda = 137.39$. The resulting free volume distribution function at 20 °C for polystyrene is shown in Figure 4.

From this figure, we are interested in finding the critical size of the fractional free volume (f_{crit}) above which the photoisomerization is possible

$$f_{crit} = (V_f)_{crit}/V$$

where $(V_f)_{crit}$ is the critical free volume per gram and V is the volume of polystyrene, approximately 0.961 cm^3/g. For a chain of polystyrene that has a molecular weight of 80 000 as in C-PS and E-PS, the weight of a chain is 1.33×10^{-19} g. For each chain, we need a relaxation volume of 4.96 nm^3 since we have at least one label per chain in C-PS and E-PS. Thus $(V_f)_{crit} = 4.96 \times 10^{-21}$ cm^3/1.33×10^{-19} g = 0.037 cm^3/g. By substituting these values of $(V_f)_{crit}$ and V into the above equation, one obtains $f_{crit} = 0.038$.

The area above $f_{crit} = 0.038$ in Figure 4 has been measured to be about 23% of the total area. This means that 23% of the free volume sizes in the vicinity of azobenzene are above the critical size necessary for its isomerization, and thus photoisomerizable at 20 °C. Since many assumptions are made in the calculations, this value should be viewed only as an approximation.

Robertson's theory does not distinguish between free volumes associated with the chain ends and the chain center. The free volume is assumed to have a random distribution throughout the matrix. Thus the estimate of 23% would represent the case where azobenzene is either molecularly dispersed in a polystyrene matrix or randomly attached to the polystyrene which has the same molecular weight as our E-PS and C-PS polymers. Because of the possible aggregation of azobenzene compound when dispersed in a polystyrene matrix and the difficulty of preparing randomly labeled polystyrene, we do not have experimental data to compare directly with the theoretical estimate. However, it is of interest to compare this theoretical estimate with our data obtained with E-PS and C-PS. Our results showed that 8% of the center label and

45% of the end label, respectively, can photoisomerize in the glassy state at 20 °C. Assuming that these are the fractions of free volumes greater than the critical volume necessary for the photoisomerization, the theoretical estimate falls between these two values. Since the free volume sizes at the chain ends or the chain center are expected to be skewed toward larger or smaller than the overall average, respectively, the trends between the theoretical value and the experimental values seem reasonable.

Conclusions

In summary, we are able to probe different environments of the polymer chains (the chain end vs. the chain center vs. the side group) by site-specific azobenzene chromophore labeling on a polystyrene chain and by following the kinetics of trans ⇄ cis photoisomerization. We used nanosecond pulsed laser spectroscopy, which reduced the measurement time to only 2 s. Such a reduction in the measurement time is particularly desirable in studying the glassy state because of the nonequilibrium nature of the glass in general and specifically in this case because of the possible diffusion of free volume and its effect on the photoisomerization. Diffusion of free volume is now considered as the controlling factor in the volume recovery process.[14] In dilute solution at 20 °C, we observe a small difference in the label's photoisomerization behavior at different sites of the chain; the end label can photoisomerize a little faster than the center label or the side label. A much greater difference is observed in the glassy state, especially between the end label and the center label.

Assuming that only a certain fraction of the label can isomerize with the same rate as in dilute solution, only 8% of the center label is found to photoisomerize while about 45% of the chain end or the side group photoisomerizes in the glassy state at 20 °C.

Robertson's theory on the size distribution of the fractional free volume has been used to estimate the fraction of free volume greater than the critical size necessary for the azo group to isomerize photochemically in a polystyrene matrix at 20 °C. An approximate value of 23% was calculated, which corresponds to the case where the same amount of the azo label is either molecularly dispersed or randomly labeled. If we assume that the experimentally measured fraction of isomerizable label is equal to the fraction of the regions with free volume greater than the critical size for the azo group, then we expect that the theoretical value as an average will fall between the values for the center label and the end label. Indeed this is the case. At the chain ends, due to an inefficient chain packing, we may envision that the free volume sizes are skewed toward larger sizes than the overall averages, thus resulting in a higher percentage of isomerizable label (45%), while the chain center has free volume sizes skewed toward smaller sizes, resulting in a smaller percentage of isomerizable labels. The results obtained in this study clearly show the differences in the mobility with respect to the site of a chain both in dilute solution and in the glassy state. If one assumes that the availability of the free volume is the dominating factor for the photoisomerization of the azo label regardless of the label's position on a chain in the glassy state, then information may be obtained about the size distribution of free volume at different sites of the polymer chain provided that the azo label does not introduce significant perturbations in its vicinity. As discussed in our previous paper,[1b] this particular azo chromophore does not seem to introduce significant perturbations in the matrix. In this sense, it is tempting to call this type of labeling approach site-specific dilatometry.

It will be of interest to ask if a specific site on the chain ages with a different rate, as monitored by the azo labels. We are now working to answer such a question as well as investigating the temperature dependence of the photoisomerization behavior of the labels. Especially for the side label, it will be useful to know if the label's behavior is influenced by the β transition of the matrix.

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Registry No. S–PS, 90914-07-1.

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