the understanding of this effect, it has to be considered that the process under consideration is composed of a series of consecutive steps, as shown in Scheme I. After scissions of chemical bonds in the main chains have been accomplished (step (a)), disentanglement diffusion follows (steps (b) and (c)). If the fragments of the ruptured macromolecule are tight together by contact pairs, the latter must detach (step (b)) before the fragments can move freely (step (c)). It is inferred from our results that the rate of contact pair detachment (step (b)) is slower than the rate of the successive step (c). Thus, the rate of step (b) is determining the total rate of the disentanglement process. If the average distance between scissions is significantly smaller than that between sites of contact pairs (at $Z_s > Z_s$(crit)), $\tau_{1/2}$(LSI) is correlated to step (c). In this case, the disentanglement process cannot be influenced by contact pairs. On the other hand, if the average distance between scissions is much larger than that between sites of contact pairs, the influence of contact pairs on disentanglement is becoming important. For $Z_s < Z_s$(crit), the rate of contact pair detachment is only very slightly influenced by Z_s as is inferred from Figure 3. The rate of step (b) should, however, be influenced by the contact pair density which is expected to increase as the solvent quality is worsened. This assumption is substantiated by the finding that at $Z_s < Z_s$(crit) $\tau_{1/2}$(LSI) is increasing as the 1-propanol content approaches the cloud point (see Figure 3).

In conclusion, it might be pointed out that the concept of contact pair formation proves useful in order to understand phenomena referring to the influence of solvent quality on disentanglement diffusion.

The experimental technique applied during this work provides, on the other hand, a powerful tool for the detection of intramolecular contact pairs in macromolecules.

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Molecular Motion of Polymer Main Chains in the Solid State as Studied by Photoisomerization

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ABSTRACT: Molecular motion of polymer main chains in the solid state was investigated in an amorphous, single-phase polyurethane matrix, which has small concentrations of azobenzene residues as molecular probes built into the polymer main chain. Photochemical trans → cis isomerization of the azobenzene residue, which involves 2–3 kcal/mol of energy barrier, is found to proceed with equal ease in the rubbery state as in dilute solution, while below T_g the rate is somewhat slowed down. The relative quantum yield in the rubbery state is only 30% lower than that in the dilute solution, while at temperatures 20 °C below T_g, the quantum yield is lowered by a factor of 3. These results exclude a crankshaft motion in the rubbery state, but the hindered rotation in the glassy state may experience some additional restraints, although these restraints are not sufficient to suggest a doubling of the activation energy as would be required in a crackshaft motion. Composition of the photostationary states indicates that in the solid state a portion of the trans isomer is unable to isomerize to the cis form, probably due to the unfavorable environment. The extent of this difficulty increases with decreasing temperature of the solid matrix.

Local motions of polymer main chains in the solid state are extremely important because of their relation to many observable bulk properties such as toughness. Such motions have been studied in the solid state by a variety of techniques, such as dielectric dispersion,[1-3] NMR relaxation[1,4-6] including more recently ^{13}C NMR, fluorescence depolarization,[7-9] sound absorption,[10,11] and ESR of spin-labeled polymers.[12] More recently, excimer fluorescence,[13-16] which occurs due to the emission from a sandwich complex of an excited molecule with a second molecule in the ground state, has been utilized as a sensitive technique for studying hindered rotations with low activation energies.

UV and visible spectroscopy have also been utilized for the study of the hindered rotation, which is usually the mechanism for local motions in polymer chains. The spectroscopic method, by which rotation around a well-defined bond is followed kinetically, provides an additional advantage because one can follow precisely the progress of the isomerization process so as to obtain a dispersion of the rate constants rather than an average relaxation time. The azoaromatic group is such an example. It has been well known that the energy difference between the ground states of the trans and cis isomer is about 10 kcal/mol.[17] The stable trans form of an azoaromatic group may be photoisomerized to the cis form, reaching a photostationary state, and the reverse cis → trans isomerization occurs in the dark. In earlier work of Paik and Morawetz[18] and in more recent work by Eisenbach,[19] this technique was utilized in order to follow a hindered ro-

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tation, namely cis → trans thermal isomerization of azoaromatic chromophores as probes attached in small amounts to the side chains of the polymers. Their results indicated that the thermal cis → trans isomerization, which involves a relatively high activation energy ($\sim$20 kcal/mol), deviates strongly from first-order kinetics in the glassy matrix, while in the rubbery state, the kinetics proceeds with exactly the same rate constant as that in dilute solution. This result leads to the assumption that the rotation with a relatively high energy barrier does not take place in a single step. It involves many small oscillations of the internal angle of rotation. In this case, the so-called "crankshaft-like" motion suggested by Schatzki,[20] where simultaneous conformational transitions around two bonds take place, can be ruled out. However, when the energy barrier is small (in the order of 2–3 kcal/mol), which is the case with most hindered rotations, the rate of isomerization should depend on the rate of distortion of internal angles of rotation, and then the concept of crankshaft motion should become observable.

Based on the work of Malkin and Fischer,[17] who found that the photochemical trans → cis isomerization involves an energy barrier of 2–3 kcal/mol between the excited cis and trans species, Chen and Morawetz[21] studied the photochemical isomerization in the main chains of the polyamides. Their results show that in dilute polymer solutions, the rate is similar to that of the low molecular weight analogues. However, while the rates of the low molecular weight analogues were relatively insensitive to the concentration of the added polymer, the rate for the polymer main chain dropped very sharply with increasing concentration of the added polymer. In a glassy polymer film, containing 8% Me_2SO plasticizer, the rate is reduced by a factor of 2500 while it was reduced only by a factor of 5 for the small molecule. The photoisomerization behavior, as the polymeric solid undergoes the glassy–rubbery transition, was not directly available due to the high glass transition temperature of the polyamide matrix. At this temperature, the thermal dark reaction is fast enough to strongly interfere with the photoisomerization measurement.

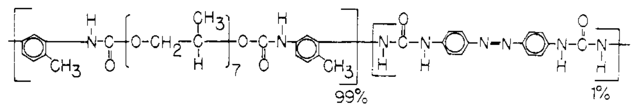
In this paper, we wish to report the results obtained with an amorphous, single-phase rubbery polyurethane as the polymeric solid matrix, which has small concentrations of azobenzene residues built into the polymer main chain. The polyurethane was synthesized by reacting toluene 2,4-diisocyanate, hydroxy-terminated poly(propylene oxide), and a small amount (1 mol %) of 4,4′-diaminoazobenzene. Since there was no chain extender added in the synthesis, the polyurethane matrix is a random copolymer with only one phase, rather than the two-phase system often encountered in segmented polyether polyurethanes. The observation of a single T_g at 8 °C was made with a differential scanning calorimeter. The temperature range of investigation was −20 to 30 °C, which covers both the glassy and rubbery states. In this temperature range, the thermal dark reaction is negligible, since the photoisomerization takes at the most 60 min to reach the photostationary state.

Experimental Section

Polymer Syntheses and Characterization. Toluene 2,4-diisocyanate obtained from Aldrich Chemical was vacuum distilled. Hydroxy-terminated poly(propylene oxide) (mol wt 400) was purchased from Polysciences, and 4,4′-diaminoazobenzene was obtained from Eastman Chemicals. Both of these were used as received. The solution polymerization was carried out in a dry glassware reactor under inert nitrogen atmosphere. First, to a solution of purified toluene 2,4-diisocyanate (0.10 mol) in 70 mL of dimethyl sulfoxide (Matheson Coleman and Bell, ACS Reagent Grade), a solution of 4,4′-diaminoazobenzene (0.001 mol) in 10 mL of dimethyl sulfoxide was added and allowed to react for 15 min at 100 °C. This was followed by the injection of poly(propylene oxide) (0.099 mol), and the polymerization proceeded for an additional 30 min at 100 °C. The ratio of NCO/(OH + NH_2) was carefully kept to be 1.0 to ensure the linearity of the polymer chain. The polymer was precipitated, washed, pressed into a thin film, and vacuum dried at 50 °C for 10 days. This polymer was a rubbery, yellow, transparent, relatively tough solid at room temperature and readily soluble in dimethylformamide. Characteristic absorption maxima of the trans isomer in thin films appeared at 379 nm. At this wavelength, the absorption of the cis isomer is negligible. Glass transition temperature was measured by using a Perkin-Elmer DSC-II at the heating rate of 20 °C/min. T_g was designated as the midpoint in the change of the slope in the DSC scan.

Chart I

Chemical Structure of the Polyurethane with a Small Amount of Azobenzene Residue



Photoisomerization Studies. Thin polymer films, about 10 μm in thickness, were cast directly on quartz from a 2.5% DMF solution of the polymer and dried at 70 °C for at least 3 days in a vacuum oven to ensure complete removal of the solvent. The films were stored at room temperature for 2 months in darkness until the irradiation setup was ready. Then the films were heated in darkness at 70 °C for a few hours to convert any amount of the cis isomer to trans isomer so as to start with 100% trans isomer before the kinetic study was undertaken. This treatment was repeated before carrying out the kinetic study at a different temperature. The initial optical density of the film was about 0.7. The incident light intensity, I_0, was determined to be 5.5 mW/cm^2. Kinetic studies were carried out in a Cary 14 spectrophotometer, which was modified so that samples could be alternately irradiated by a 450-W xeron osram lamp and analyzed in a direction perpendicular to the radiation direction. For further experimental details on this experiment, the reader may consult ref 18 and 21.

Results

The structure of the polyurethane is represented in Chart I. Photoisomerization was carried out with the same film at different temperatures. It was found that the reaction is completely reversible. The photoisomerization kinetics which are applicable since the reverse thermal reaction is negligibly slow in the temperature range of our study, were analyzed based on the following equations[18]

$$I(\delta) \equiv \left(1 + \frac{D_\infty}{2} + \frac{{D_\infty}^2}{12}\right) \ln |\delta| - \left(\tfrac{1}{2} + \frac{D_\infty}{6}\right)\delta + \frac{\delta^2}{24}$$

$$I(\delta) = At + \text{constant, where } A = -I_0\phi_t\epsilon_t/y_\infty$$

Here D_∞ is the optical density in the photostationary state, $\delta \equiv D_\infty - D$ where D is the optical density at the time t, ϕ_t is the quantum efficiency for the trans → cis isomerization, ϵ_t is the molar extinction coefficient of the trans isomer, and y_∞ is the fraction of the chromophore in the cis form at the photostationary state.

In Figure 1, we have compared the course of photoisomerization, $I(\delta)$ versus t, for the dilute solution and the film at the same temperature of 27 °C. The concentration of the solution (0.1 g/100 cm^3) is dilute enough that we can neglect the interpenetration of the chains. The solid film at 27 °C is expected to be in the rubbery state since the measured T_g is 8 °C as assigned to the midpoint in the change of the slope in the DSC curve, which had the range of −2 to 18 °C for this polymer matrix. For more than 75% of the course of the reaction there is no difference in the

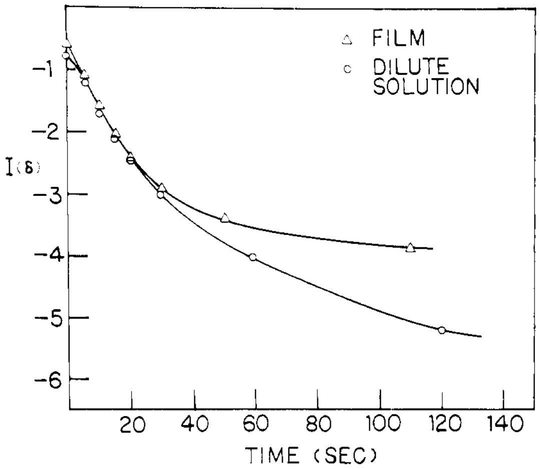


Figure 1. Course of the trans → cis photoisomerization of azobenzene residues in the main chain of polyurethane at 27 °C (○, dilute solution; △, film).

Table I
Photoisomerization of Azoaromatic Groups in the Main Chain of Polyurethane

nature of specimen	temp, °C	y_∞ (cis content)	rel rate,[a] s^{-1}
dilute soln	27	0.80	0.085
film	27	0.62	0.091
film	19	0.59	0.084
film	8	0.47	0.084
film	0	0.45	0.044
film	-10	0.39	0.040

[a] The error in the relative rate is ±0.004 s^{-1}.

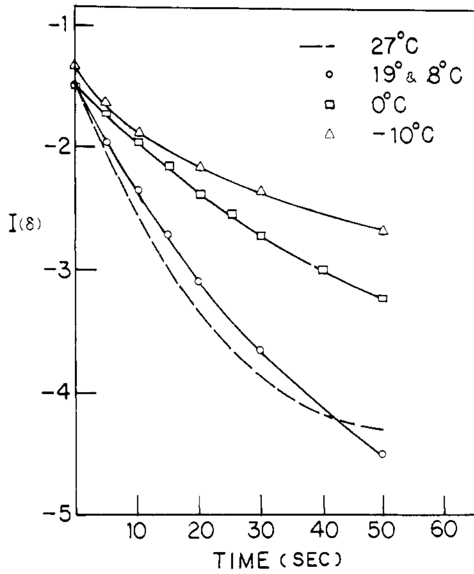


Figure 2. Course of trans → cis photoisomerization of azobenzene residues in the main chain of polyurethane in the solid state as a function of temperature (temperature covers rubbery, transition, and glassy states).

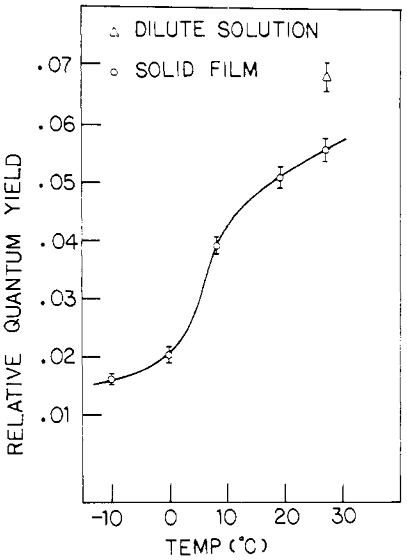


Figure 3. Relative quantum efficiency of trans → cis photoisomerization of azobenzene residues in the main chain of polyurethane as a function of temperature.

behavior of photoisomerization between the dilute solution and rubbery film. As the reaction approaches the photostationary state, a significant difference between the two samples is observed. This is mainly caused by the different compositions of the photostationary states: in the dilute solutions 80% of the azo groups are in the cis form, while in the rubbery solid 62% are in the cis form. This result suggests that while most of the trans azo species in the rubbery state experience the same local mobility as in dilute solution, small amounts of the trans species in the rubbery solid matrix may find themselves in an energetically unfavorable environment to isomerize to the cis form.

We then proceeded to study the effect of temperature on the course of photoisomerization. The temperature range was chosen to cover the transition region and the glassy state. Figure 2 illustrates the plot of $I(\delta)$ vs. t as a function of the temperature. The course of photoisomerization at or above T_g proceeds with almost the same rate; at 27 °C, the rate is only slightly greater than those at 19 or at 8 °C. In fact, the course of reaction at 19 or at 8 °C falls on the same line, as illustrated in Figure 2. These results are summarized in Table I. The relative rates are obtained by the initial slope from Figure 2. However, the cis isomer content at the photostationary state decreases with temperature steadily, as listed in the third column of Table I.

When the temperature is below T_g, the photoisomerization is slowed down as shown in Figure 2. At 0 °C, the relative rate is reduced by a factor of 2 compared with that at or above T_g. At -10 °C, the rate is about the same as that at 0 °C, as listed in Table I. Also, at the temperatures lower than T_g, the cis-isomer content at the photostationary state decreases steadily with temperature, which implies that increasing amounts of trans isomer find themselves in difficult environments to isomerize. Since the photoisomerization only involves 2-3 kcal/mol of activation energy, the reduced rate below T_g is a direct consequence of the difficulty imposed by the glassy matrix, rather than a simple response to the decrease in temperature.

The relative quantum yield, obtained by multiplying the relative rate and the fraction of the cis isomer at the photostationary state, is plotted as a function of temperature in Figure 3. Below T_g, the quantum yield is relatively small and independent of the temperature. At T_g, the quantum yield increases sharply and appears to level off at temperatures above T_g. When compared with the dilute solution at 27 °C, however, the quantum yield for the photoisomerization occurring in dilute solution is only 30% greater than the analogous process occurring in the film.

Discussion

Our results strongly indicate that, for the most part, trans → cis photoisomerization of azo chromophore built into the main chain of the polymer proceeds as easily in the rubbery state as in dilute solution, even though a small portion of the trans isomer experiences some difficulty in isomerizing to the cis form. We interpret this result as meaning that the "crankshaft-like" motion does not apply to the dynamic behavior of polymer chains in the rubbery state, since two correlated conformational transitions required for the crankshaft-like motion would have reduced the photoisomerization rate by a factor of 20–100. Rather, this type of hindered rotation in the rubbery state may involve a large number of small oscillations of the internal angle of rotations.

The results obtained in the glassy state definitely show the heterogeneity in the local environment of the matrix, in that some trans species can isomerize at a rate reduced by only a factor of 2, as compared in the rubbery matrix, but increasing portions of the trans isomers find themselves in unfavorable environments to isomerize, as evidenced by the steadily decreasing cis content of the photostationary state. We believe that the elegance of our technique is this capability to obtain information on the dispersion of the process rather than average relaxation times.

Smets[22] reported that a photoresponse, due to a similar isomerization in spirobenzopyran groups, which is built into the chain backbones of polyesters, showed a sharp increase as the matrix underwent the glass–rubber transition. Unfortunately, they did not show whether the photoisomerization in the rubbery state proceeded as fast as it did in the dilute solution. Our result is consistent with the general behavior observed by Smets. To the best of the author's knowledge, this work is the first to report that the hindered rotation of polymer main chains, which has a low-energy barrier, proceeds with similar ease in the rubbery state, as well as in the dilute solution. Another important observation made in our investigation is that, even in the glassy state, specifically at temperatures of 20 °C below T_g, the main chain motions of the polymer matrix are not frozen to the extent that was generally believed. By using another technique, namely by use of infrared spectroscopic bands, which had been unambiguously assigned to specific groups of the polycarbonate chain backbone, Yannas and Lunn[23,24] came to a similar conclusion. They have observed evidence of molecular motion at temperatures well below T_g. It would be interesting to extend our studies to see how the molecular mobility is affected at temperatures well below T_g. This work is in progress and will be reported in a later publication.

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