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Photochemistry in Polymer Solids. 9. Photoisomerization of Azobenzene in a Polycarbonate Film

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ABSTRACT: The photoinduced trans → cis and cis → trans and thermal cis → trans isomerizations of azobenzene molecularly dispersed in a polycarbonate film as well as in solution were measured in a very wide temperature range (4–423 K) under 360- or 440-nm light irradiation. The trans → cis photoisomerization in polycarbonate film at room temperature proceeds with the same rate as in solution up to 86% conversion and then deviates from the first-order kinetics. The deviation becomes more marked and the final conversion decreases with the decrease in temperature. The *trans*-azobenzene photoisomerizes up to 17% conversion at liquid helium temperature (4 K), and the rate at 4 K at mobile reaction sites is almost the same as that at room temperature and in solution. A kinetic model considering the influence of free volume distribution on the reactivity was proposed and simulations were given in order to explain the non-first-order reaction profile of trans → cis photoisomerization and its temperature dependence. The present results did not fit to stretched exponential plots. The anomalous matrix effect for the thermal backward cis → trans isomerization of azobenzene in the polymer film was also observed and attributed to the existence of residual strain in the *cis*-azobenzene film sample prepared by UV irradiation onto film.

Introduction

The main difference of solid-state reactions from reactions in solution is the difference in the freedom of molecular motion due to the restriction of mobility. As a result non-first-order progress of reactions which are expected to be unimolecular in solution is frequently observed in solid states due to the microscopically heterogeneous state of aggregation or the free volume distribution of the reaction media.[1,2] In our previous paper,[3a] the photoinduced decoloration of the merocyanine form of spirobenzopyran in polycarbonate film measured over a very wide temperature range (80–453 K) was shown to proceed exponentially for $T > T_g$ (423 K) but deviated from single-exponential type kinetics for $T < T_g$, which was probably due to the inhomogeneous distribution of free volume in the matrix polymer. However, in the case of photodecoloration of spiropyran the ambiguity of the reason for nonexponential-type kinetics might arise from the existence of various conformational isomers of the merocyanine form;[1] i.e., the different conformers may have diffusion-controlled rates of isomerization due to different rates of conformational transition. On the other hand, azobenzene has only one conformation for each isomer. Consequently, photoisomerization of azobenzene is a much better probe reaction than other reactions for the elucidation of effects of molecular motion and the microstructure of the matrix polymer on the reactivity in polymer solids. The outline of photochromic reactions of spirobenzopyran, azobenzene, and fulgide at 4 K in polymer films has already been reported.[3b]

Many studies have been done on the photochemical trans to cis isomerization[4-9] and thermal cis to trans backward isomerization[5,7,10,11] of an azobenzene chromophore bound in the backbone or attached to the side chain of polymers in film. While photoisomerization of an azobenzene residue in a polymer chain occurs by a single-rate process in dilute solution, its rate in solid films has been separated into two processes. The first is as fast as in dilute solution and is followed by a slower process. The fractional amount of the first process decreased with physical aging but increased with temperature, plasticization, or tensile deformation,[7] and this fraction was related to the amount of sites where local free volumes are greater than a critical size necessary for the photoisomerization of the azobenzene group.[8,9] In the case of thermal cis to trans isomerization of the photoisomerized azobenzene residue in the polymer side chain in a film, a deviation from first-order kinetics was also observed. In this case, however, the isomerization proceeds faster than in solution in the beginning and is followed by a process with the same rate as in solution. This anomalous fast process in the beginning of thermal backward isomerization was attributed by Paik and Morawetz[5] to trapping of some portion of cis isomer in a strained conformation, while Eisenbach[11] correlated it to the restrictions in the fluctuation of free volume.

The incorporation of molecularly dispersed chromophores, in polymer matrices is a useful method of studying the characteristics of reactions in polymer solids, and the measurement of temperature dependence of the photochemical process is very important since the reaction rates of photoexcited molecules reflecting the molecular motion of matrix polymer can be obtained in a very wide temperature range. The measurement of the distribution of local free volume in glassy polymers at room temperature has been reported recently by using photochromic and fluorescence probes.[12] In the present paper, photoinduced trans to cis isomerization under stationary-state irradiation of 360-nm light and thermal and photoinduced cis to trans isomerization of azobenzene molecularly dispersed in a polycarbonate film were measured over the temperature range from 4 K (liquid helium temperature) to 423 K, and non-first-order progress of trans to cis photoisomerization and its temperature dependence are correlated to a kinetic model considering the influence of the free volume distribution on the reactivity.

Experimental Section

Materials. *trans*-Azobenzene was purified by recrystallization from ethanol solution. A standard sample of bisphenol A type polycarbonate (PC) with $M_w = 33\,800$ and $M_w/M_n = 2.5$ was purchased from Scientific Polymer Product, Inc. Ethanol, dichloroethane, and ethyl acetate were spectrosol grade and used without further purification.

Sample Preparation. Bisphenol A polycarbonate film containing 0.006–0.02 mol/L of *trans*-azobenzene (8–40-μm thickness) was prepared with solvent-cast method onto a quartz plate from a 10% polycarbonate solution with *trans*-azobenzene in dichloroethane. The film was evacuated at room temperature for 2 h and then heated under vacuum at 100 °C for 4 h to eliminate the residual solvent. The concentration of *trans*-azobenzene was determined by ultraviolet absorption measurements ($\epsilon_{trans} = 2.04 \times 10^4$ M^{-1} cm^{-1}, $\epsilon_{cis} = 1.28 \times 10^3$ M^{-1} cm^{-1} at 320 nm).

Measurements of Photoisomerization and Thermal Isomerization. The sample film set in cryostat (Oxford DN 704) was irradiated by 360-nm light from a 150-W xenon lamp

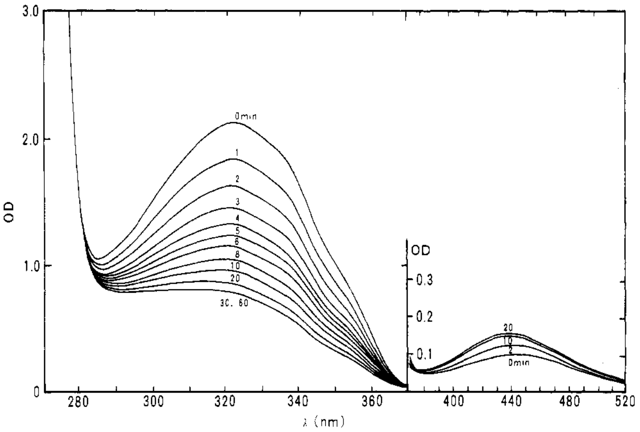

Figure 1. Change in UV spectra of *trans*-azobenzene in polycarbonate film during 360-nm light irradiation at room temperature.

(Hamamatsu L 2195) with a UVD36 color filter and a Pyrex glass filter for the measurements of trans to cis photoisomerization of azobenzene. A part of transmitted light through film was fed into a monochromater (JASCO CT 10), and the change in the intensity of the 320-nm light was monitored by a photomultiplier (Hamamatsu R 374) and recorded in a X–T recorder (Riken Denshi SP-H3C). For measurements at 4 and 40 K a continuous flow type liquid helium cryostat (Oxford CF 1204) was used. The 440-nm light from the 150-W xenon lamp with an interference filter (KL 44) and a color filter (UV 39) was utilized for the measurements of cis to trans backward photoisomerization of azobenzene in polycarbonate film photoirradiated in advance by a high-pressure mercury lamp. The thermal cis to trans isomerization of in-advance UV-irradiated azobenzene film as well as several photoisomerization experiments at room temperature was followed with an ultraviolet spectrophotometer (Shimazu MPS-5000). Reference experiments for trans to cis photoisomerization and thermal backward isomerization of azobenzene in dilute solution were carried out in ethanol, ethyl acetate, and dichloroethane. These polar solvents without aromatic rings were chosen in order to obtain the changes in azobenzene spectra at wavelengths not only above 280 nm but also below 280 nm. Actinometry for the irradiation light was carried out with an Ushio UIT-101 type photometer calibrated by the potassium ferrioxalate/*o*-phenanthroline system.[13]

Results and Discussion

Photoisomerization at Room Temperature. When *trans*-azobenzene with initial concentration $[t]_0$ is exposed to the irradiation of a continuous wave of 360-nm light, the rate of the change in *trans*-azobenzene concentration, $[t]$, approaching its equilibrium value, $[t]_\infty$, is composed of trans to cis and cis to trans photoisomerizations and thermal cis to trans isomerization as is given by eq 1, where

$$-\mathrm{d}[t]/\mathrm{d}t = 2.3 \times 10^3 I_0 \epsilon_t f_t \Phi_{t\rightarrow c}[t] - 2.3 \times 10^3 I_0 \epsilon_c f_c \Phi_{c\rightarrow t}[c] - K[c] = A[t] - B[c] - K[c] \quad (1)$$

I_0 (einstein cm^{-2} s^{-1}) is the incident light intensity, ϵ (L mol^{-1} cm^{-1}) is the molar extinction coefficient, $f_t = (1 - 10^{-\epsilon_t[t]_0 l})/(2.3\epsilon_t[t]_0 l)$, $f_c = (1 - 10^{-\epsilon_c[c]_0 l})/(2.3\epsilon_c[c]_0 l)$ are the correction factors for the absorption of light, $[c] = [t]_0 - [t]$ is concentration of *cis*-azobenzene, l (cm) is the film thickness, K is the rate constant for thermal cis → trans isomerization, subscripts t and c denote trans and cis isomers, respectively, and the product $I_0\epsilon f$ was summed over the wavelengths of incident light. Equation 1 holds for the case of $\epsilon_t[t]l < 0.4$ as an approximation resulting in the first-order kinetics and was ascertained to give the same results as the kinetics proposed by Zimmerman et al.[14,15] does for the present case. When the photostationary state is attained, we get

$$(A + B + K)[t]_\infty = (B + K)[t]_0 \quad (2)$$

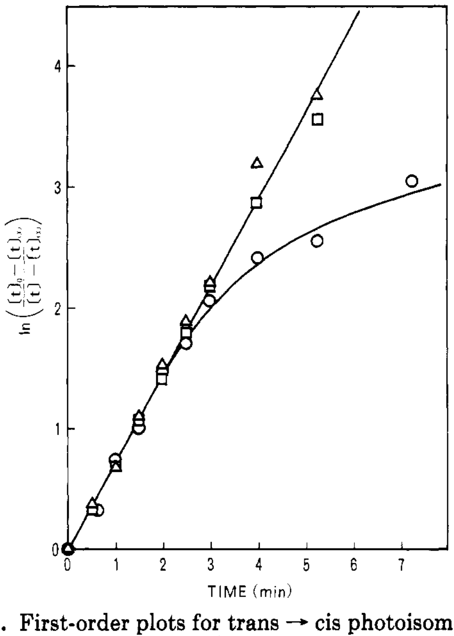

Figure 2. First-order plots for trans → cis photoisomerization of azobenzene in polycarbonate (○), in ethyl acetate (□), and in ethanol (△) at 288 K.

Table I
Quantum Yields for Trans to Cis and Cis to Trans Photoisomerizations of Azobenzene in a Polycarbonate Film as Well as in Solution

		$\Phi_{t\rightarrow c}$		$\Phi_{c\rightarrow t}$	
medium	temp, °C	$\pi\pi^*$[a]	$n\pi^*$[b]	$\pi\pi^*$[a]	$n\pi^*$[b]
polycarbonate	15	0.07	0.22	0.15	0.49
ethyl acetate	15	0.09	0.25	0.14	0.48
ethanol	15	0.12	0.15	0.23	0.55

[a] Ultraviolet light (360 nm) irradiation. [b] 440-nm light irradiation.

and hence the change in $[t]$ can be given by the following first-order relationship:

$$\ln\left(\frac{[t]_0 - [t]_\infty}{[t] - [t]_\infty}\right) = \frac{[t]_0}{[t]_0 - [t]_\infty}At = \frac{[t]_0}{[t]_\infty}(B + K)t \quad (3)$$

A typical change in the UV spectra of azobenzene during trans to cis photoisomerization by 360-nm light is shown in Figure 1, and the change in concentration of *trans*-azobenzene, $[t]$, was calculated from the absorbance at 320 nm by using $\epsilon_t = 2.04 \times 10^4$ M^{-1} cm^{-1} and $\epsilon_c = 1.28 \times 10^3$ M^{-1} cm^{-1}. The first-order plots according to eq 3 for trans → cis photoisomerization of azobenzene in polycarbonate at 25 °C are shown in Figure 2. The reaction proceeds in the first order in solution, but in polycarbonate film it proceeds with the same rate as in solution up to 86% conversion and then deviates from the first-order kinetics. This slowing down in rate is a characteristic phenomenon to the reaction in an amorphous solid below T_g. In contrast to the case of thermal decoloration of spirobenzopyran[16] where the rate in a polymer film is much slower than that in solution even at the beginning, the rate of photoisomerization of trans-azobenzene in polycarbonate film slows down only at its final stage of conversion at room temperature, which is far below T_g. This suggests that photoisomerization of trans-azobenzene is not controlled by a molecular motion step in a large portion of reaction sites even in the solid state below T_g owing to the rather small critical free volume necessary for the reaction to occur. The quantum yields for trans-to-cis and cis-to-trans isomerization were obtained by using eq 3. They are given in Table I.

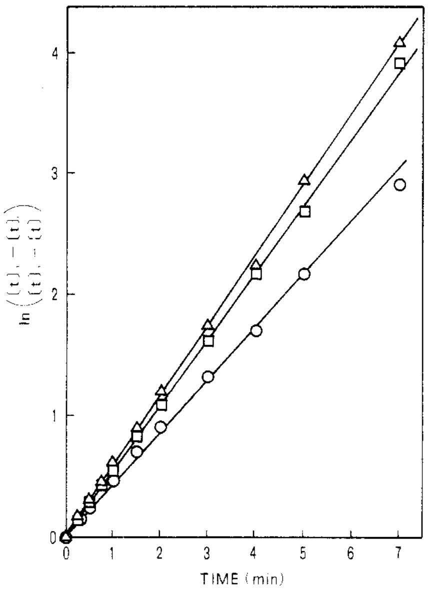

Figure 3. First-order plots for cis → trans photoisomerization of azobenzene in polycarbonate (○), in ethyl acetate (□), and in ethanol (△) at 288 K.

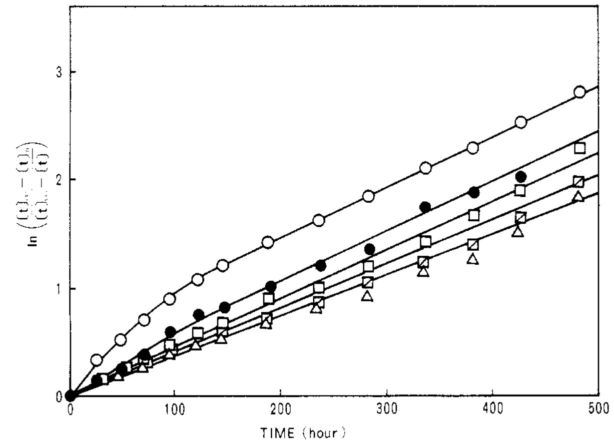

Figure 4. Thermal backward cis → trans isomerization of azobenzene at room temperature in polycarbonate films UV irradiated in advance onto the film (○) or UV irradiated during casting (●), as well as in ethyl acetate (□), ethanol (△), and dichloroethane (□) UV irradiated in advance.

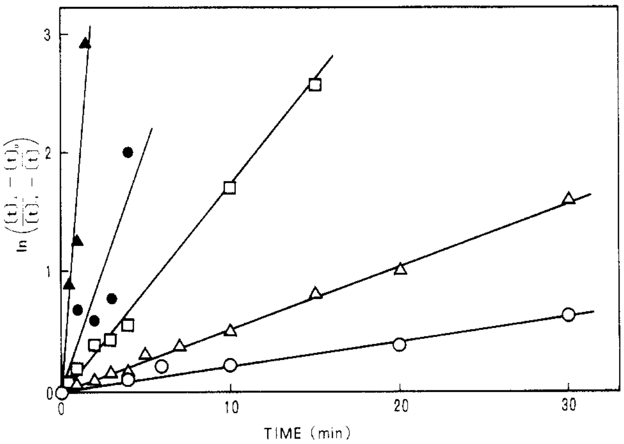

Figure 5. Temperature dependence of the first-order plots for thermal backward cis → trans isomerization of azobenzene in polycarbonate film UV irradiated in advance onto the film: (○) 70 °C, $K = 3.5 \times 10^{-4}$ s^{-1}; (△) 90 °C, $K = 8.7 \times 10^{-4}$ s^{-1}; (□) 110 °C, 3.1×10^{-3} s^{-1}; (●) 130 °C, 6.8×10^{-3} s^{-1}; (▲) 150 °C, 2.9×10^{-2} s^{-1}.

Similar experiments were carried out with visible light at 440 nm by starting from the cis-rich azobenzene sample prepared by UV irradiation of trans azobenzene in film at room temperature. The first-order plots for the cis to trans photoisomerization shown in Figure 3 give straight lines for both in solution and in polycarbonate film. In this case, $[t]_0$ corresponds to the initial cis-rich state and $[t]_\infty$ to the final trans-rich state. The difference in slopes is mainly due to the difference in the incident light intensities. The quantum yields for 440-nm irradiation are also given in Table I. The quantum yields both for 360-nm ($\pi\pi^*$) irradiation and 440-nm ($n\pi^*$) irradiation show no appreciable difference between the photoisomerization in polycarbonate film and its model reaction in ethyl acetate. These values in Table I are roughly consistent with those reported in several other solvents.[17]

Thermal Cis → Trans Isomerization in a Polymer Film. The thermal cis to trans isomerization of azobenzene samples equilibrated by UV irradiation (cis content about 90%) was followed at room temperature for 60 days. The first-order plots in Figure 4 show that the rate of thermal backward cis → trans isomerization of azobenzene in polycarbonate film prepared by UV irradiation on the film (○) is faster than the rates in solutions and it gradually approaches the same value as in solution. In this case also, $[t]_0$ corresponds to the initial equilibrium state and $[t]_\infty$ to the final trans-rich state. This anomalous matrix effect for the thermal backward reaction was also observed for aminoazobenzene residues bound to a poly(methyl methacrylate) matrix[5,10,11] and azonaphthalene in polystyrene,[12] as well as for thermal backward isomerization of dihydropyrene derivatives in poly(methyl methacrylate). Paik and Morawetz[5] attributed this anomalously fast matrix effect to the trapping of some of cis isomer in a strained conformation during UV irradiation below T_g, from which it could return more easily to the trans form than the relaxed cis species, while Eisenbach[11] correlated this anomaly to the restriction in the chain segmental relaxation processes and fluctuation of the free volume. In order to make this point clear, we prepared a cis-rich film by casting the solution containing azobenzene under UV light irradiation. The experiment with this sample (● in Figure 4) indicates the almost first-order progress of the thermal isomerization reaction, supporting the idea that the existence of residual strain in the *cis*-azobenzene film sample prepared by photoisomerization in a film would be the reason for this anomalous deviation from first-order kinetics in the polymer solids. The thermal cis to trans isomerization of the sample irradiated above T_g and then cooled through T_g during irradiation also showed no anomalously fast portion.[10]

The temperature dependence of thermal cis → trans isomerization of azobenzene in polycarbonate shown in Figure 5 gives an activation energy of 17.6 kcal/mol, which is very small compared to that of stilbene (40 kcal/mol).[17] The difference can be explained by the rehybridization machanism[18] available to imines and azo compounds but not to olefins, consisting of the shift of the substituent attached to nitrogen from one side of the molecule through a linear transition state, the nitrogen atom adopting linear sp bonds, the π-bond remaining intact, and the electron pair occupying the perpendicular p-orbital in the transition state.

Temperature Dependence of Trans → Cis Photoisomerization in a Polymer Film. The trans to cis photoisomerization of azobenzene in polycarbonate film was measured over a very wide temperature range (4–400 K). Figure 6 shows that initial rate of photoisomerization does not decrease so much with decreasing temperature, but the final fraction of the trans form, $x_{t\infty} = [t]_\infty/[t]_0$,

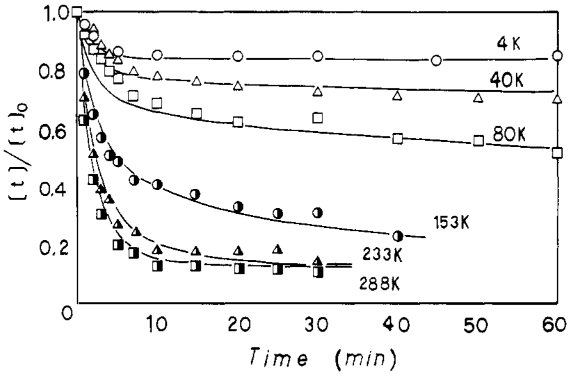

Figure 6. Change in the fraction of *trans*-azobenzene, $[t]/[t]_0$, during trans → cis photoisomerization of azobenzene in a polycarbonate film at temperatures indicated beside the curves. Symbols correspond to experimental values and solid curves are the results of simulation according to free volume fluctuation model (eq 5–11).

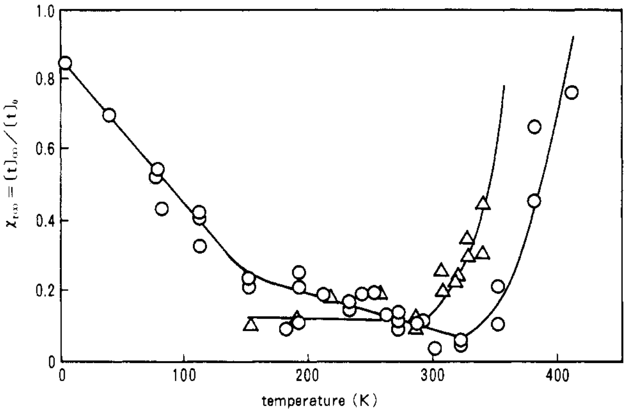

Figure 7. Final trans fraction, $x_{t\infty} = [t]_\infty/[t]_0$, against temperature for trans → cis photoisomerization of azobenzene in polycarbonate film (○) and in ethanol (△).

increases markedly with the decrease in temperature. The temperature dependence of equilibrium or limiting trans fractions, $x_{t\infty}$, is illustrated in Figure 7. In ethanol solution there is no substantial temperature dependence for equilibrium points. Since the influence of thermal backward reaction can be neglected below room temperature, this means that the ratio $\phi_{t\to c}/\phi_{c\to t}$ is independent of temperature caused by either equal or zero activation energies for both processes. But in polycarbonate film below room temperature, photoisomerization stops at a conversion smaller than the equilibrium value in solution and the limiting conversion decreases with decreasing temperature. The marked increase in $x_{t\infty}$ with increasing temperature above room temperature is due to the predominant occurrence of thermal cis → trans isomerization. The gradual change in slope in the limiting trans fraction at about 150 K may correspond to the γ-transition of matrix polycarbonate.[3] Small-scale rotational motions of polymer phenylene groups are also thought to be restricted at temperatures below T_γ, but nevertheless even at liquid helium temperature (4 K) *trans*-azobenzene photoisomerizes up to 17% conversion, and the rate at 4 K at the mobile reaction sites is almost same as that at room temperature and in solution as is shown in Figure 6.

This occurrence of photoisomerization even at 4 K can be explained only by considering the existence of free-volume distribution on the polymer matrix, where 17% of azobenzene would be surrounded by a local free volume larger than its critical volume necessary for the isomerization to occur. The rehybridization mechanism mentioned above will also explain the small critical volume needed for the photoisomerization to occur compared to that for olefin isomerization. The van der Waals volume of *trans*-azobenzene and the extra volume needed to isomerize were calculated recently by Victor and Torkelson.[12]

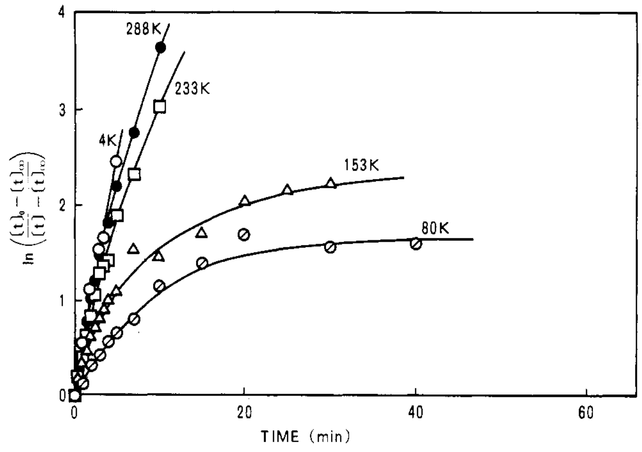

Figure 8. First-order plots of trans → cis photoisomerization of azobenzene in polycarbonate film at temperatures indicated beside the curves.

The first-order plots for trans to cis photoisomerization of azobenzene in polycarbonate at typical temperatures are shown in Figure 8. The deviation from the straight lines in the first-order plots becomes more marked with decreasing temperature, but at 4 K the slope for *trans*-azobenzene in the mobile sites is ascertained to be almost the same as that at room temperature. This is reasonable if we accept the fact that $\phi_{t\to c}/\phi_{c\to t}$ is independent of temperature for photoisomerization of azobenzene in freely mobile environments as in solution. Thus, in order to analyze these reaction profiles more closely, the reaction sites in polymer solid below T_g would be divided into two parts. The first part is a mobile part where the rate is equal to the rate in solution, which is independent of temperature. The second is the part where the rate is controlled by the mobility of microenvironment, including the part where the reaction does not take place at all.

We present now a model based on the ideas, that the critical fractional free volume, f_c, between freely mobile and diffusion-controlled sites decreases with increasing temperature due to local fluctuation of free volume caused by local molecular motion of the matrix polymer and that the reaction in diffusion-controlled sites proceeds with an activation energy proportional to $f_0 - f$, where f is local fractional free volume. The size distribution function, $G(f)$, in solid state was assumed to be frozen and constant irrespective of temperature during the time scale of measurements. The extent of reaction, $R(t)$, in polymer solids can be given generally be eq 4 as an integration of uncoupled individual first-order reaction with rate coefficient, $k(t)$, and weight distribution, $G(f)$, as functions of reaction site.

$$R(t) = \int_0^\infty G(f) \exp[-k(f)t]\, \mathrm{d}f \qquad (4)$$

In the present case, the local fractional free volume, f, serves as a parameter characterizing the reaction site, and the fraction of *trans*-azobenzene at time t, $[t]/[t]_0$, in given by eq 5

$$[t]/[t]_0 = \int_0^\infty G(f)\left\{\frac{A}{A+B} \exp[-k(f)t] + \frac{B}{A+B}\right\} \mathrm{d}f \quad (5)$$

where A and B are apparent rate coefficients for trans → cis and cis → trans photoisomerization in solution as defined in eq 1, respectively.

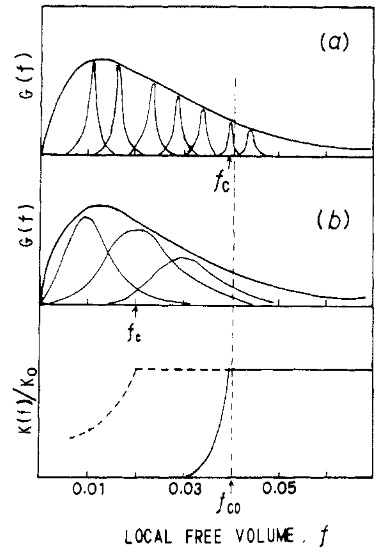

Figure 9. Schematic illustration of fractional free volume distribution, $G(f)$, at 4 K (a) and at higher temperature (b) and reactivity, $k(f)/k_0$, according to free volume fluctuation model. Solid line in reactivity corresponds to 4 K (a); dashed line corresponds to a higher temperature (b).

The $G(f)$ was assumed to be a Λ function of fractional free volume, f, according to Robertson.[19]

$$G(f) = \frac{\lambda}{\Lambda(\alpha)}(\lambda f)^{\alpha-1}e^{-\lambda f} \qquad (6)$$

where α and λ are the characteristic material parameters given by

$$\alpha = \bar{f}^2 V_0/(\Delta\kappa k_B T) \qquad (7)$$

and

$$\lambda = \bar{f} V_0/(\Delta\kappa k_B T) \qquad (8)$$

where $\bar{f}$ is a mean fractional free volume, $\Delta\kappa$ is the difference in compressibility between liquid and glass, k_B is Boltzmann's constant, T is temperature, and V_0 is the volume of the relaxation environment at room temperature. The values[8,20] of V_0 = 4.96 nm^3, $\bar{f}$ = 0.025, and $\Delta\kappa$ = 4.2 × 10^{-10} Pa^{-1} were used for the calculation.

The rate coefficient, $k(f)$, and its activation energy, ΔE, can be given by

$$k(f) = k_0 \exp[-\Delta E/k_B T] \qquad (9)$$

and

$$\Delta E = c(f_c - f) \quad \text{for } f < f_c$$
$$= 0 \quad \text{for } f > f_c \qquad (10)$$

with

$$f_c = f_{c0} - \beta T \qquad (11)$$

where $k_{k0} = A + B$ is a sum of the apparent rate coefficients for photoisomerization in solution, C is a parameter characterizing the rigidity of the matrix, and f_{c0} is the value of f_c in the absence of local fluctuation and was determined to be 0.0405 from $x_{t\infty}$ at 4 K.

The schematic illustration of the distribution function, $G(f)$, and reactivity, $k(f)/k_0$, according to eq 6–11 are given in Figure 9. The fluctuation width of local free volume around each azobenzene molecule shown in Figure 9a is very narrow at 4 K but it broadens with increasing temperature (Figure 9b). Hence, the volume of relaxation environment around azobenzene increases, and the lower limit f_c for freely mobile photoisomerization becomes smaller with increasing temperature owing to the rapid density fluctuation during the lifetime due to the activated local molecular motion of the matrix polymer. Fractional critical free volume, f_c, and reactivity, $k(f)/k_0$, at 4 K and those at higher temperatures are also shown in Figure 9 by solid lines and dashed lines, respectively. The calculated time-course curves with the values of C = 2.0 × 10^5 J/mol and β = 8.0 × 10^{-5} K^{-1} show good fitting with experimental results as illustrated in Figure 6. The value of ΔE_a for the site $f = f_c - 0.005$ is estimated to be 1.0 kJ/mol. The value of fluctuation of fractional critical free volume at 288 K, βT = 0.023, is compared with the square root of the variance for the free volume distribution, $\langle (f - \bar{f})^2 \rangle^{1/2}$ = 0.018, calculated according to Robertson.[19] Thus, we suppose that the free volume fluctuation model would describe the characteristics of photoisomerization of *trans*-azobenzene in polymer films.

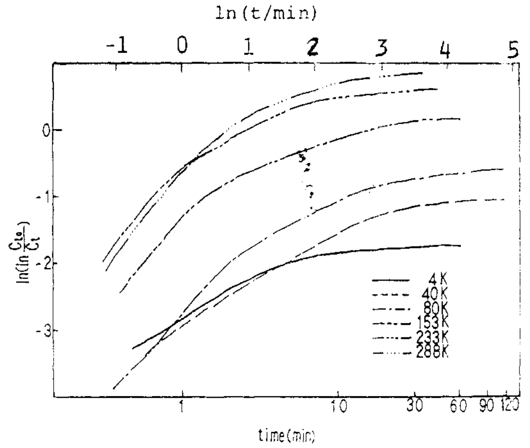

Figure 10. Stretched exponential plots (eq 13) for photoisomerization of *trans*-azobenzene in a polycarbonate film.

The curve fitting of the results to the stretched exponential[21,22] (eq 12 and 13) failed to give straight lines for

$$[t] = [t]_0 \exp(-kt^{\gamma}) \qquad (12)$$

$$\ln\{\ln([t]_0/[t])\} = \gamma \ln t + \ln k \qquad (13)$$

the $\ln\{\ln([t]_0/[t])\}$ against $\ln t$ (Figure 10). This would be due to the existence of substantical limiting conversion of photoisomerization of *trans*-azobenzene in polymer films having the distribution of free volume, which a model fit to the stretched exponential may have to include a serial relaxation process.

In conclusion, photoinduced and thermal isomerizations of azobenzene in polycarbonate film were studied over the temperature range 4–423 K, and the deviation from first-order kinetics and its temperature dependence were correlated to kinetic models considering the influence of free volume distribution on the reactivity.

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Registry No. *trans*-Azobenzene, 17082-12-1; *cis*-azobenzene, 1080-16-6; ethyl acetate, 141-78-6; ethanol, 64-17-5; dichloroethane, 1300-21-6.

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Methyl Methacrylate Polymerization Photoinitiated by Pyrene in the Presence of Triethylamine

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ABSTRACT: The polymerization of methyl methacrylate photosensitized by pyrene and anthracene in the presence of triethylamine has been investigated. Under all conditions employed, anthracene polymerization efficiencies were very low. On the other hand, pyrene is an efficient sensitizer in the presence of triethylamine. The efficiency observed is larger in polar solvents. From the fact that pyrene consumption is prevented by methyl methacrylate and the lack of pyrenyl groups incorporated into the polymer, it is proposed that the active free radicals are produced as a consequence of the interaction of the monomer with the pyrene–triethylamine complex and/or the PyH$^\bullet$ radical.

Introduction

The photopolymerization of vinyl monomers using a photoinitiator and triethylamine as co-initiator has received the attention of many research groups,[1,2] but most of the studies have been carried out using carbonyl compounds as sensitizers.[3–6] For these systems the photoinitiation mechanism is well established, and it proceeds through a charge-transfer complex that decomposes giving free radicals that can initiate the polymerization.[3,5–8] On the other hand, sensitization by aromatic hydrocarbons has been much less studied.[9,10] In particular Kubota and Ogiwara[10] have studied the polymerization of acrylonitrile and methyl methacrylate photoinitiated by aromatic hydrocarbon–amine mixtures. With regard to methyl methacrylate, these authors reported that phenanthrene and naphthalene were efficient photoinitiators in the presence of triethylamine (TEA). However, anthracene was almost completely ineffective. A mechanism was proposed in which radicals are produced from an aromatic–TEA charge-transfer complex. In the present work, we have carried out an analysis of the effect of the solvent polarity and TEA concentration on the photoinitiation efficiency. From these data and an analysis of the effect of the monomer concentration on the sensitizer bleaching rate, further insight is obtained on the initiation mechanism.

Experimental Section

The polycyclic aromatic hydrocarbons (PAH) employed, pyrene (Py) and anthracene (An) (Fluka), were purified by recrystallization from ethanol. Triethylamine (TEA) and methyl methacrylate (MMA) were vacuum distilled prior to their use.

Photopolymerization rates, in arbitrary units (millimeters of contraction/minute) were measured in Pyrex dilatometers under nitrogen at room temperature (20 ± 2 °C). The samples were irradiated with light from a medium-pressure mercury lamp. When An was employed, a glass filter was used to isolate the 366-nm band. Di-*tert*-butyl peroxide and azobis(isobutyronitrile) (AIBN) were employed as reference photoinitiators for Py and An, respectively. Matched solutions of the aromatic polycyclic and the reference compounds were irradiated under identical conditions. TEA addition to the reference initiators did not produce any significant change in the polymerization rates. Low absorbances (below 0.4) were employed to avoid the generation of an inhomogeneous free radical distribution.[11]

Polymer molecular weights were determined viscosimetrically in benzene at 30 °C, $\log \mathrm{MW} = 1.31 \times \log (\eta/5.2 \times 10^{-5})$ with η in g/100 mL.[12]

Quenching experiments of PAH by TEA were carried out in a Perkin-Elmer LS-5 spectrofluorimeter by measuring the fluorescence yield as a function of the TEA concentration. Bleaching experiments were carried out by irradiation of the samples as described for the photopolymerization. The bleaching was evaluated from the change in its near-UV absorption in a Shimadzu-160 spectrophotometer. Carbon tetrachloride was employed as reference.[13] The position and the fine structure of the UV absorption band of pyrene are not altered by the amine addition. Similarly, they were not modified after irradiation of the samples.

Results and Discussion

Polymerization rates photoinitiated by Py were measured as a function of TEA concentration with acetonitrile or benzene as solvent. The results obtained are given in Table I. These data show that Py is a poor initiator both in benzene and in acetonitrile. These results can be explained in terms of the low quenching rate constant ($k_q = 4 \times 10^6$ M^{-1} s^{-1}) reported for the excited singlet pyrene deactivation by MMA.[15] TEA addition notably increases the photopolymerization rate. The effect obtained is more relevant when acetonitrile is employed as solvent. Figure 1 shows that the polymerization rate photoinitiated by Py and TEA changes almost linearly with the percentage of acetonitrile in the solvent mixture. This increase can be

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