Photochemistry in Polymer Solids. 11. The Effects of the Size of Reaction Groups and the Mode of Photoisomerization on Photochromic Reactions in Polycarbonate Film

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ABSTRACT: The trans to cis photoisomerization and cis to trans thermal isomerization of 9,9′-azophenanthrene and stilbene molecularly dispersed in polycarbonate films were measured in the wide temperature range, from liquid helium temperature to 373 K. The final cis fraction for 9,9′-azophenanthrene is similar to that for 1,1′-azonaphthalene. The final cis fraction for stilbene in a film at room temperature reaches photoequilibrium similar to the case of azobenzene, but at low temperatures the final cis fraction for stilbene becomes lower than that for azobenzene. These facts suggest that these azo compounds isomerize via an inversion mechanism that requires a smaller sweeping volume than the rotation mechanism for stilbene. The results of a simulation according to a kinetic model considering the influences of the free volume distribution and its local fluctuation on the reactivity were given in order to explain the non-first-order reaction profile of trans to cis photoisomerization of 9,9′-azophenanthrene and stilbene and their temperature dependences.

Introduction

The main feature of solid-state reactions different from reactions in solutions is the decrease in the freedom of molecular motion due to the restriction of mobility. As a result non-first-order progress of reactions that 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]

Photochemical and thermal isomerization of an azobenzene, and its derivatives bound in the main chain or attached to the side chain of polymers, has been reported by many investigators.[3-11] In our previous papers, trans to cis photoisomerization of azobenzene[12,14] and 1,1′-azonaphthalene[13,14] in polycarbonate film was studied over a very wide temperature range (4–423 K). The reaction proceeds with the same rate as in solution at the first stage and then deviates from the first-order kinetics. The final conversions of photoisomerization of both molecules in film decrease with decreasing temperature. These deviations and decrements of the final conversions should be due to restriction of the polymer chain mobility and heterogeneity of the free volume distribution at the reaction sites in polymer solids. The rates and extents of photoisomerization in polymer solids are supposed to be influenced much by the size of the isomerizing chromophore, since the larger local free volume should be needed for the isomerization of molecules with bulkier displacing group. The difference between the reactivities of azobenzene and 1,1′-azonaphthalene was discussed in our previous paper.[13,14]

In the present paper, the study in a very wide temperature range was extended to the photoisomerization of 9,9′-azophenanthrene, a bulkier reactant than 1,1′-azonaphthalene, in polycarbonate films, and to the photoisomerization of stilbene in polycarbonate, which requires a larger sweep volume for isomerization owing to its rotation mechanism. A kinetic model considering the influence of free volume distribution and fluctuation on the reactivity of the photoprobes was applied to the present cases, and a simulation is given in order to explain the non-first-order reaction profile of trans to cis photoisomerization in a polymer film and its dependence on temperature.

Experimental Section

Materials. 9,9′-Azophenanthrene (AZP) was synthesized from 9-phenanthrylamine by using a Bogoslovskii reaction (Figure 1).[15,16] The 9-phenanthrylamine was prepared from 9-phenanthrol by using a Bucherer reaction,[17] then 9-phenanthryl diazonium salt prepared by a diazotizing reaction from 9-phenanthrylamine was dissolved in diluted hydrochloric acid, and Cu(I) solution was added at 0 °C. The product was purified with column chromatography (hexane–silica gel) and was identified as 9,9′-azophenanthrene by NMR spectroscopy. The *cis*-9,9′-azophenanthrene produced by photoisomerization of *trans*-9,9′-azophenanthrene is not stable, owing to rapid thermal cis to trans isomerization. Therefore, the absorption spectrum of the cis isomer was determined from the spectrum of the pure trans isomer and that of a photoequilibrium mixture of cis and trans isomers obtained by the irradiation of the pure trans form with an isosbestic wavelength (340 nm) light at low temperature (−100 °C), together with the reaction curve of the trans isomer irradiated at the absorption maximum (407 nm). The UV absorption spectra of *trans*- and *cis*-9,9′-azophenanthrene are shown in Figure 2.

Stilbene was purchased from Tokyo Kasei Kogyo Co., Ltd, and was purified by recrystallization from ethanol solution.

Matrix polymer, bisphenol A type polycarbonate (PC), was obtained from Teijin Co. ($M_n = 2.5 \times 10^4$, $T_g = 145$ °C).

Cyclohexane, dichloromethane, and methylcyclohexane were spectrosol grade and used without further purification.

Sample Preparation. Polycarbonate films containing molecularly dispersed photoprobe (0.019 mol L^{-1} of 9,9′-azophenanthrene or 0.014 mol L^{-1} of stilbene) were prepared by using the solvent-cast method from dichloromethane and were evacuated at room temperature overnight and subsequently heated under vacuum for 12 h at 80 °C to eliminate the residual solvent.

Measurements of Photoisomerization. The sample films and solutions set in the Oxford DN-704 cryostat were irradiated by 407 nm (for 9,9′-azophenanthrene) or 355 nm (for stilbene) light from 150-W xenon lamp (Hamamatsu L-2195) with a combination of interference filter and color filter (KL-41 and UV-39 or UV-D2 and UV-29) for the measurements of trans to cis photoisomerization of the photoreactive probes. The change in intensity of a part of the transmitted light was monitored by a photomultiplier (Hamamatsu R-374) with a monochromator (JASCO CT-10) and recorded with an X–T recorder (Riken Denshi SP-H3C). For measurements below liquid nitrogen temperature, a continuous flow type liquid helium cryostat, Oxford CF-1204, was used.

Actinometry for the irradiation light was carried out by using a digital photometer (Ushio UTI-101), which was calibrated by using the potassium ferrioxalate/*o*-phenanthroline system.[18]

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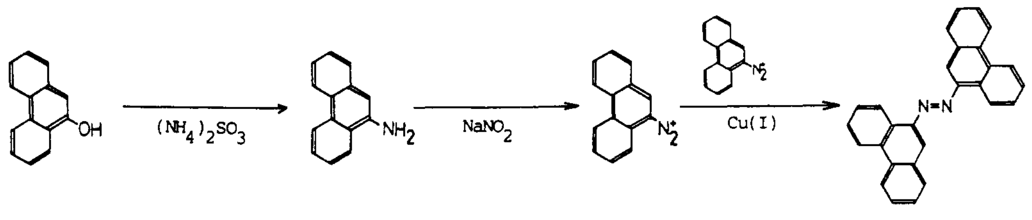

Figure 1. Preparation of 9,9′-azophenanthrene from 9-phenanthrol by Bucherer and Bogoslovskii reactions.

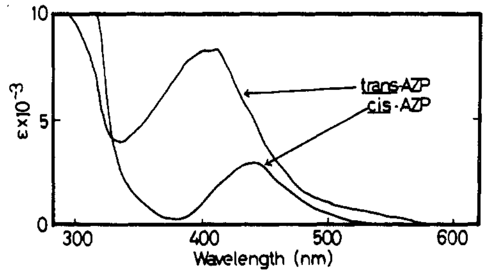

Figure 2. The UV absorption spectra of *trans*- and *cis*-9,9′-azophenanthrene in methylcyclohexane at 220 K.

Results and Discussion

Photoisomerization in Polycarbonate Film. When the trans isomer with initial concentration $[tr]_0$ is irradiated with continuous-wave light (407 nm for 9,9′-azophenanthrene and 355 nm for stilbene), the rate of the increase in cis isomer concentration at time t, $d[cis]_t/dt$, is given by eq 1, where A ($A = (2.3 \times 10^3)I_0\epsilon_{tr}\Phi_{tr\rightarrow cis}$) is an apparent

$$d[cis]_t/dt = A[tr]_t - B[cis]_t - K[cis]_t \qquad (1)$$

rate coefficient for trans to cis photoisomerization, B ($B = (2.3 \times 10^3)I_0\epsilon_{cis}\Phi_{cis\rightarrow tr}$) is an apparent rate coefficient for cis to trans photoisomerization, and K is a rate constant for cis to trans thermal isomerization. I_0 (einstein cm^{-2} s^{-1}) is the incident light intensity, ϵ (L mol^{-1} cm^{-1}) is the molar extinction coefficient at irradiation wavelength, Φ is the quantum yield for photoisomerization, and the subscripts tr and cis denote trans and cis isomers, respectively. The values of $[cis]_t$ and $[tr]_t$ were calculated from the optical density at time t, OD_t, by using eq 2, where $\epsilon_{cis}/\epsilon_{tr}$ is 0.120 for 9,9′-azophenanthrene at 407 nm

$$[cis]_t = \frac{1 - OD_t/OD_0}{1 - \epsilon_{cis}/\epsilon_{tr}}[tr]_0 \qquad (2)$$

and 0.060 for stilbene at 310 nm. When the photostationary state is attained, eq 3 holds for the final equilibrium concentration of the cis isomer, $[cis]_\infty$. The change

$$(A + B + K)[cis]_\infty = A[tr]_0 \qquad (3)$$

in $[cis]_t$ according to the first-order relationship can be given by

$$2.3 \log \frac{[cis]_\infty}{[cis]_\infty - [cis]_t} = \frac{[tr]_0}{[cis]_\infty}At = \frac{[tr]_0}{[tr]_0 - [cis]_\infty}(B + K)t \qquad (4)$$

The first-order plots according to eq 4 for trans to cis photoisomerization of the photoprobes at room temperature showed that the reaction proceeds with first-order kinetics in methylcyclohexane solution. In polycarbonate film the reaction proceeds initially with the same rate as in solution, but it deviates from first-order kinetics as were the cases for azobenzene[12] and 1,1′-azonaphthalene.[13,14]

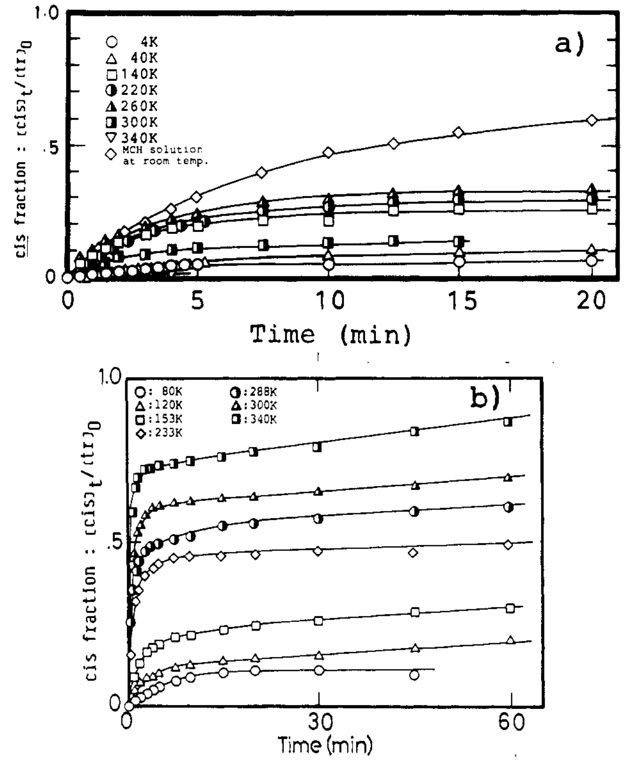

Figure 3. Change in the fraction, $[cis]_t/[tr]_0$, of *cis*-9,9′-azophenanthrene (a) and *cis*-stilbene (b) during trans to cis photoisomerization of 9,9′-azophenanthrene and stilbene in polycarbonate film at 4–340 K and in methylcyclohexane solution at room temperature.

Temperature Dependence for Trans to Cis Photoisomerization. The time courses of trans to cis photoisomerization of 9,9′-azophenanthrene and stilbene in polycarbonate films at various temperatures, from liquid helium temperature to 373 K, are shown in Figure 3. When the intensity of irradiation was constant, the initial rate of photoisomerization did not decrease as much with decreasing temperature, but the final conversion of trans to cis photoisomerization decreased markedly with decreasing temperature.

The temperature dependence of the equilibrium or the final cis fraction for 9,9′-azophenanthrene and stilbene as well as azobenzene[12,14] and 1,1′-azonaphthalene[13,14] is illustrated in Figure 4. Dashed lines in Figure 4 correspond to the results for azobenzene in ethanol (a) and 1,1′-azonaphthalene in toluene (b).

The decreases in the final cis conversions with increasing temperature above 280 K for 9,9′-azophenanthrene and above 340 K for stilbene are attributed to the occurrence of the cis to trans thermal isomerization.

Volume Required for Isomerization. The free volume that is required for trans to cis photoisomerization of photoprobes is the volume swept by the van der Waals area of the displacing group during photoisomerization. These sweep volumes of several photoreactive compounds were calculated by Victor and Torkelson[10] using the calculation method described by Bondi.[19] We also cal-

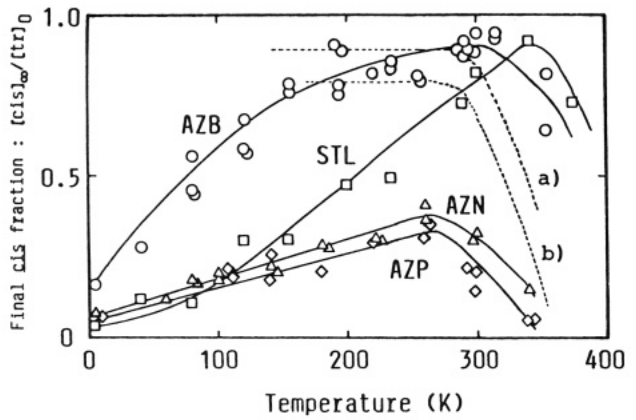

Figure 4. The final cis fraction, $[cis]_\infty/[tr]_0$, against temperature for trans to cis photoisomerization of azobenzene (○), 1,1′-azonaphthalene (△), 9,9′-azophenanthrene (◇), and stilbene (□) in polycarbonate film and in solution. Dashed lines correspond to that for azobenzene in ethanol (a) and for 1,1′-azonaphthalene in toluene (b).

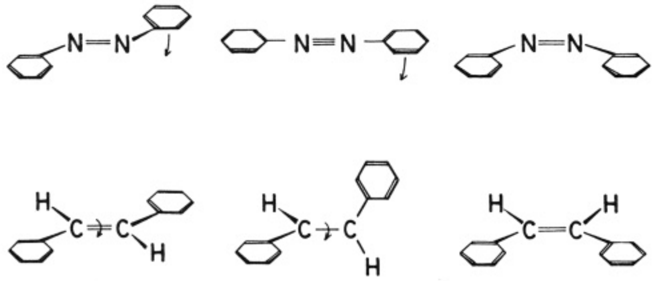

Figure 5. Isomerization mechanisms of azobenzene (upper) and stilbene (lower).

Table I
Sweep Volume for Molecular Motion (nm³)

mode	phenyl	1-naphthyl	9-phenanthryl
inversion	0.12	0.16	0.23
rotation	0.25	0.44	0.91

culated those for our probes with a similar method. For the inversion model applicable to the cases of azo compounds, an aromatic ring isomerizes by inversion in the CN=NC plane, with the narrower edge of the aromatic ring in the direction of motion, and is swept through a total angle of 120° (Figure 5, upper). On the other hand, stilbene cannot isomerize via inversion, owing to the hydrogen atom directly attached to a double-bonded carbon; therefore it isomerizes via a rotation model with an aromatic group rotating around an excited C–C bond for 180° (Figure 5, lower). Table I shows the calculated sweep volume for isomerization.

When we compare the final conversions for the photoisomerization of stilbene to those for azobenzene in polycarbonate films, the final conversions at room temperature are equal to the equilibrium value in both cases. But with decreasing temperature the final conversions for stilbene decrease much more markedly than those for azobenzene, and the final conversion for stilbene at the liquid helium temperature (4 K) was measured to be 1%, compared with 17% in the case of azobenzene. These differences are caused by the difference of sweep volume due to the different mechanisms of isomerization. Stilbene requires a larger free volume to isomerize, owing to the rotation of the phenyl group (0.25 nm³), than azobenzene, which isomerizes via inversion of the phenyl group (0.12 nm³).

As to the final conversions of photoisomerization for three azo compounds in polycarbonate films, those for 1,1′-azonaphthalene and 9,9′-azophenanthrene are similar to each other and less than half of that for azobenzene. We suggest that these differences are caused by not only the fact that the sweep volumes required for the inversion of larger aromatic rings are larger than that of phenyl ring but also the fact that half of the *trans*-1,1′-azonaphthalene and *trans*-9,9′-azophenanthrene rotamers need the rotation of one of their aromatic rings around a C–N bond for the completion of trans to cis photoisomerization due to intramolecular steric hindrance between two aromatic rings in the cis form (Figure 6).

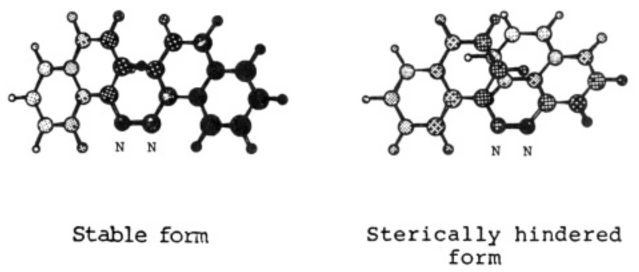

Figure 6. Stable (left) and sterically hindered (right) rotamers of *cis*-1,1′-azonaphthalene.

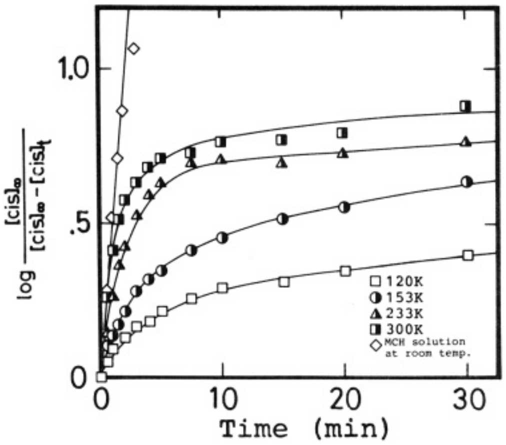

Figure 7. First-order plots for trans to cis photoisomerization of stilbene in polycarbonate film at various temperatures.

At the liquid helium temperature (4 K), the final conversion for the photoisomerization of 9,9′-azophenanthrene was measured to be 7% and that of stilbene was 1% in polycarbonate, compared with 17% in the case of azobenzene and 7% in the case of 1,1′-azonaphthalene. As the fluctuation of local free volume is suppressed at liquid helium temperature, the microenvironment for 7% of 9,9′-azophenanthrene molecules or that for 1% of stilbene is expected to have sufficient local free volume for photoisomerization to occur.

Comparison of the Results with a Kinetic Model. The example of first-order plots for trans to cis photoisomerization in polycarbonate films at typical temperatures are shown in Figure 7 for stilbene. The deviation from the straight lines in the first-order plots becomes more marked as the temperature decreases. Thus we compared the present results of the time courses of trans to cis photoisomerization of 9,9′-azophenanthrene and stilbene in polycarbonate with the free volume fluctuation model,[12-14] describing the heterogeneous progress of reactions in amorphous solids. In this model, the reaction sites in the polycarbonate film are divided into two parts by the critical free volume, V_c. In the first part, local free volume, V, around photoreactive probe molecules is larger than V_c, and the rate constant at this freely mobile site is equal to that in solution, k_0, and is independent of temperature since the rate constant of photoisomerization of these probe molecules in solution is not affected by tem-

Table II
Parameters for Photoisomerization by the Free Volume Fluctuation Model

	AZB	AZN	AZP	STL
isomerization mechanism	phenyl inversion	1-naphthyl inversion	9-phenanthryl inversion	phenyl rotation
sweep vol, nm^3	0.12	0.16	0.23	0.25
crit vol, nm^3	0.20	0.27	0.27	0.32
β, T^{-1}	8.0×10^{-5}	8.0×10^{-5}	9.3×10^{-5}	$(6.0–20) \times 10^{-5}$
C, J mol^{-1}	2.0×10^5	5.0×10^5	$(2.3–5.6) \times 10^5$	$(5.0–9.6) \times 10^5$

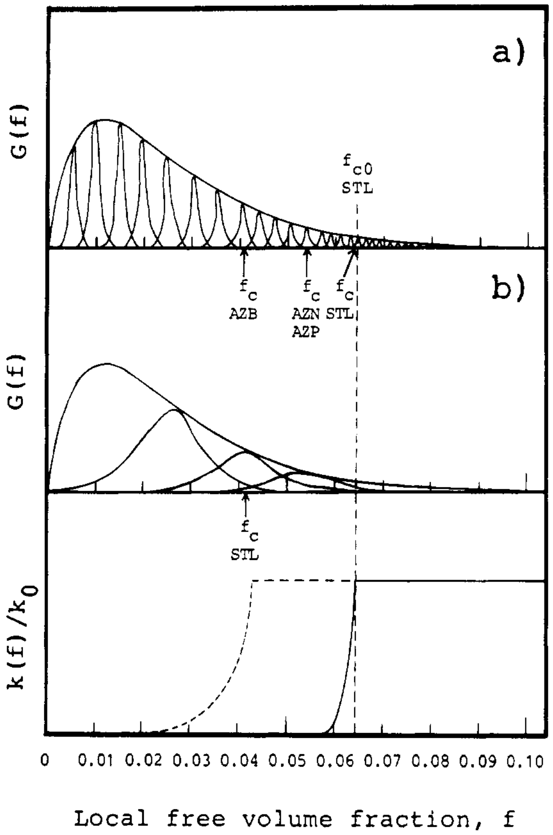

Figure 8. Schematic illustration of the fractional free volume distribution, $G(f)$, at 4 K (a) and at higher temperatures (b) and the reactivity, $k(f)/k_0$, according to the free volume fluctuation model. The solid line in the reactivity corresponds to 4 K (a) and the dashed line corresponds to a higher temperature (b) for stilbene.

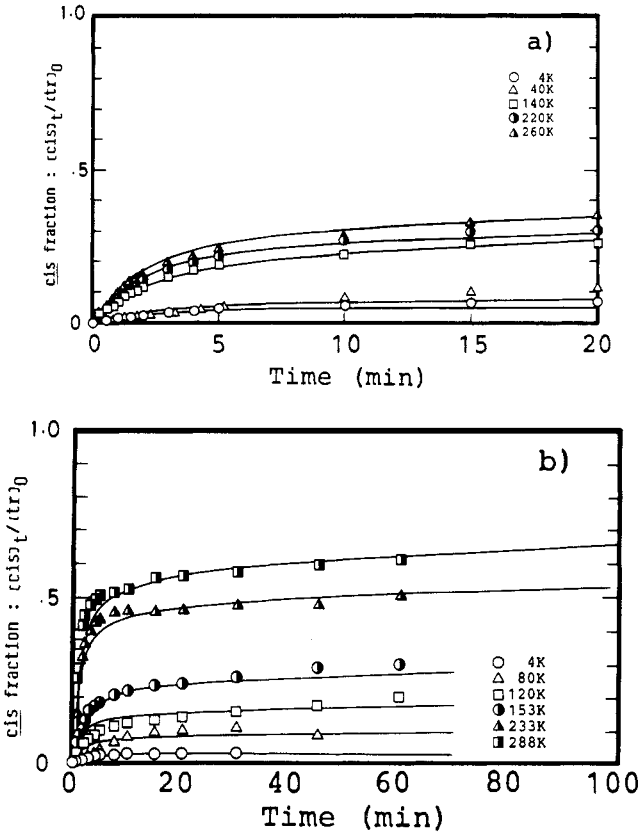

Figure 9. Results of a simulation according to the free volume fluctuation mode (eqs 5–10) (solid lines) for the photoisomerization of *trans*-9,9′-azophenanthrene (a) and stilbene (b) in polycarbonate film Symbols correspond to experimental values.

perature. In the other part, where V is smaller than V_c, the mobility of microenvironment controls the rate with an activation energy, ΔE_a, that is proportional to $V_c - V$. The rate constant for the individual reaction site, $k(f)$, which depends on fractional local free volume, f ($f = V/V_0$), is given by eqs 5 and 6, where V_0 is the volume of the

$$k(f) = k_0 \exp(-\Delta E_a/k_B T) \qquad (5)$$

$$\begin{aligned}\Delta E_a &= 0 \quad \text{for } f > f_c \\ &= C(f_c - f) \quad \text{for } f < f_c \qquad (6)\end{aligned}$$

relaxation environment at room temperature,[20] C is a parameter characterizing the rigidity of the matrix, and $f_c = V_c/V_0$ is a critical free volume fraction. The value of f_c was assumed to depend on temperature as is given by eq 7 due to the local fluctuation of free volume caused by

$$f_c = f_{c0} - \beta T \qquad (7)$$

the local molecular relaxation within the time scale of the excited-state lifetime, where f_{c0} was determined to be 0.0544 for 9,9′-azophenanthrene and 0.0646 for stilbene from $[cis]_\infty$ at 4 K, where local fluctuation of free volume can be ignored.

The distribution of fractional local free volume, $G(f)$, was given by a Γ-distribution as eq 8 according to Robertson.[20]

$$G(f) = \frac{\lambda}{\Gamma(\alpha)}(\lambda f)^{\alpha-1} e^{-\lambda f} \qquad (8)$$

The parameters α and λ are determined by

$$\alpha = \bar{f}^2 V_0/(\Delta\kappa k_B T), \qquad \lambda = \bar{f} V_0/(\Delta\kappa k_B T) \qquad (9)$$

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, and T is temperature. The values of $\bar{f} = 0.025$, $\Delta\kappa = 4.2 \times 10^{-10}$ Pa^{-1},[21] and $V_0 = 4.96$ nm^3 were used for the calculation. The schematic illustrations of the distribution function, $G(f)$, and relative reactivity, $k(f)/k_0$, are shown in Figure 8. At as low a temperature as liquid helium temperature, the fluctuation width of the local free volume around the photoprobe molecule is very narrow (Figure 8a). But it broadens with increasing temperature, and the lower limit for a freely mobile photoisomerization site, f_c, becomes smaller according to eq 7 as is shown in Figure 8b.

In the solid state, the reaction at each site proceeds individually, so the extent of reaction can be expressed by the integration of each first-order reactions, as is given by

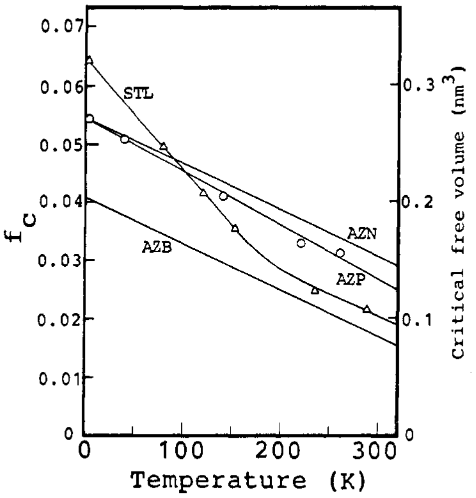

Figure 10. Temperature dependence of the values of the critical free volume fraction, f_c.

eq 10, where A and B are the apparent rate coefficients

$$[\mathrm{tr}]_t/[\mathrm{tr}]_0 = \int_0^{\infty} G(f)\left[\frac{A}{A+B}\exp\{-k(f)t\} + \frac{B}{A+B}\right] \mathrm{d}f \tag{10}$$

for trans to cis and cis to trans photoisomerization in solution as determined for eq 1. The results of the calculation according to the free volume fluctuation model are shown as solid lines in Figure 9. Reaction profiles at various temperatures of 9,9′-azophenanthrene and stilbene could not be described with uniform parameters β and C. Thus we tried to fit the calculation separately to experimental results at each temperature. The values of C used for the simulation are (2.3–5.7) × 10^5 J mol^{-1} for 9,9′-azophenanthrene and (5.0–9.6) × 10^5 J mol^{-1} for stilbene, and the values of β used for the simulation are 9.3 × 10^{-5} K^{-1} for 9,9′-azophenanthrene and (6.0–20) × 10^{-5} K^{-1} for stilbene. This shows good fitting with experimental results. The parameters for the probes used in these simulations are summarized in Table II. The critical volume for photoisomerization becomes larger with increasing sweep volume of the photoprobes. The critical free volume fractions, f_c, for 9,9′-azophenanthrene and stilbene at each temperature as well as for azobenzene[12,14] and 1,1′-azonaphthalene[13,14] are shown in Figure 10. Constant values of β for azo compounds give straight lines in Figure 10. Temperature dependences for these three azo compounds fit in almost parallel lines but that for stilbene breaks at 170 K, corresponding to the γ-transition temperature, T_γ, of polycarbonate. This suggests that, owing to its rotation mechanism, a photoisomerization of stilbene reflects markedly the change in local molecular motion at lower temperatures, but above T_γ, the effect of the fluctuation of local free volume of the polycarbonate matrix prevails and the temperature dependence of f_c becomes similar to those for azo compounds.

In conclusion, the time–conversion curves and their temperature dependences for trans to cis photoisomerization of azo compounds and stilbene in polycarbonate films were studied over the temperature range 4–373 K and correlated to the kinetic model, considering the free volume distribution and its local fluctuation.

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References and Notes

(1) Smets, G. *Adv. Polym. Sci.* **1983**, *50*, 17.
(2) Horie, K.; Mita, I. *Adv. Polym. Sci.* **1989**, *88*, 77.
(3) Paik, C. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171.
(4) Eisenbach, C. D. *Makromol. Chem.* **1978**, *179*, 2489.
(5) Paik Sung, C. S.; Lamarre, L.; Tse, M. K. *Macromolecules* **1979**, *12*, 666.
(6) Eisenbach, C. D. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 680.
(7) Sung, C. S. P.; Lamarre, L.; Chung, K. H. *Macromolecules* **1981**, *14*, 1839.
(8) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729.
(9) Sung, C. S. P.; Gould, I. R.; Turro, N. J. *Macromolecules* **1984**, *17*, 1447.
(10) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241.
(11) Yu, W. C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355.
(12) Mita, I.; Horie, K.; Hirao, K. *Macromolecules* **1989**, *22*, 558.
(13) Naito, T.; Horie, K.; Mita, I. *Eur. Polym. J.* **1990**, *26*, 1295.
(14) Mita, I.; Naito, T.; Horie, K. *J. Photopolym. Sci. Technol.* **1988**, *1*, 303.
(15) Bogoslovskii, B. M. *J. Gen. Chem. USSR* **1946**, *16*, 193.
(16) Freeman, D. C., Jr.; White, C. E. *J. Org. Chem.* **1956**, *21*, 379.
(17) Fieser, L. F.; Jacobsen, R. P.; Price, C. C. *J. Am. Chem. Soc.* **1936**, *58*, 2163.
(18) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 119.
(19) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(20) Robertson, R. E. *J. Polym. Sci., Polym. Symp.* **1978**, *63*, 173.
(21) Wendorff, J. H.; Fischer, E. W. *Kolloid Z. Z. Polym.* **1973**, *251*, 876.

Registry No. AZP, 131956-59-7; (bisphenol A)(PC) (copolymer, 25037-45-0; (bisphenol A)(PC) (SRU), 24936-68-3; stilbene, 588-59-0.