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PHOTOCHEMISTRY IN POLYMER SOLIDS—10. PHOTOISOMERIZATION OF 1,1′-AZONAPHTHALENE IN A POLYCARBONATE FILM

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Abstract—The *trans*-to-*cis* photoisomerization and *cis*-to-*trans* thermal isomerization of 1,1′-azonaphthalene (AZN) molecularly dispersed in polycarbonate (PC) films were studied in the wide temperature range from liquid helium temperature to 340 K. The rate of the photoisomerization in PC film is equal to its rate in solution up to 84% conversion, beyond which it deviates from first-order kinetics. These deviations became more marked and the final conversions decreased with decreasing temperature. These results suggest that the reactivity of AZN is controlled not only by the average mobility of the reactants but also by the heterogeneity of the reaction sites in polymer solids because of the distribution of local free-volume. The results with the deviation from the first-order kinetics were compared with two kinds of kinetic models, i.e. stretched exponential and free-volume fluctuation models. The free-volume fluctuation model is supposed to describe the characteristics of photoisomerization of AZN in PC film.

INTRODUCTION

Photochemical and thermal isomerizations of an azobenzene, and its derivatives bound in the main chain or attached to the side chain of polymers, have been reported by many investigators [1–9]. In our previous paper [10], *trans*-to-*cis* photoisomerization of azobenzene at various temperatures (4–423 K), as well as *cis*-to-*trans* photo- and thermal backward isomerization, was reported for polycarbonate (PC) film. The reaction proceeds with the same rate as in solution up to 86% conversion at room temperature, and then deviates from first-order kinetics. The deviation becomes more marked as temperature decreases. The final conversion also decreases with decreasing temperature. These deviations and decreases of the final conversions could be due to the restriction of mobility in polymer solids and the heterogeneous distribution of free-volume at reaction sites. The rates and extents of photoisomerizations in polymer solids are supposed to be influenced greatly by the size of the isomerizing chromophore, since larger local free-volume would be needed for the isomerization of a bulkier molecule. Thus 1,1′-azonaphthalene (AZN), a bulkier reactant than azobenzene, is used as a photoprobe in the present paper, and its *trans*-to-*cis* photoisomerization in PC film is studied over a very wide temperature range (4–340 K).

A kinetic model considering the influence of free-volume distribution on the reactivity of AZN was applied to the present case, and simulation is presented to explain the non-first-order reaction profile of *trans*-to-*cis* photoisomerization and its dependence on temperature.

EXPERIMENTAL PROCEDURES

Materials

AZN was prepared as follows [11]. 4-Amino-1,1′-azonaphthalene was prepared by the azo-coupling of 1-naphthylamine with sodium nitrite, hydrochloric acid and sodium dicarbonate, and then transformed to AZN by adding hypophosphorous acid and sodium nitrite. The product was purified with column chromatography (silica-gel, eluent cyclohexane), and was identified as AZN by i.r. and NMR. The *cis*-AZN produced by photoisomerization of *trans*-AZN is not stable at room temperature because of thermal *cis*-to-*trans* isomerization. Therefore, the absorption spectrum of the *cis*-isomer was determined by extrapolating from the spectrum of a photoequilibrium mixture of *cis* and *trans* forms produced by the irradiation of the pure *trans* form with isosbestic wavelength (330 nm) light at low temperature (−80°C). The u.v. absorption spectra of *trans*- and *cis*-AZN are shown in Fig. 1. Matrix polymer, bisphenol-A type PC, was provided by Teijin Co. ($\bar{M}_n = 25{,}000$, $T_g = 145°C$). Dichloromethane, toluene, cyclohexane and methylcyclohexane were spectroscopically pure grade.

Sample preparation

PC films containing molecularly dispersed 0.015 mol l^{-1} AZN were prepared using the solvent-cast method from dichloromethane, and were evacuated at room temperature overnight, and subsequently heated in a vacuum for 12 hr at 80°C.

Measurements of photoisomerization and thermal isomerization

The sample films and solutions set in the Oxford DN-704 cryostat were irradiated by 402 or 407 nm light from 500 W Xenon lamp (Ushio UXL-500D) with a combination of interference filter and colour filter (KL-40 and UV-37 or KL-41 and UV-39) for the measurements of *trans*-to-*cis* photoisomerization of AZN. The change in the intensity of part of 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

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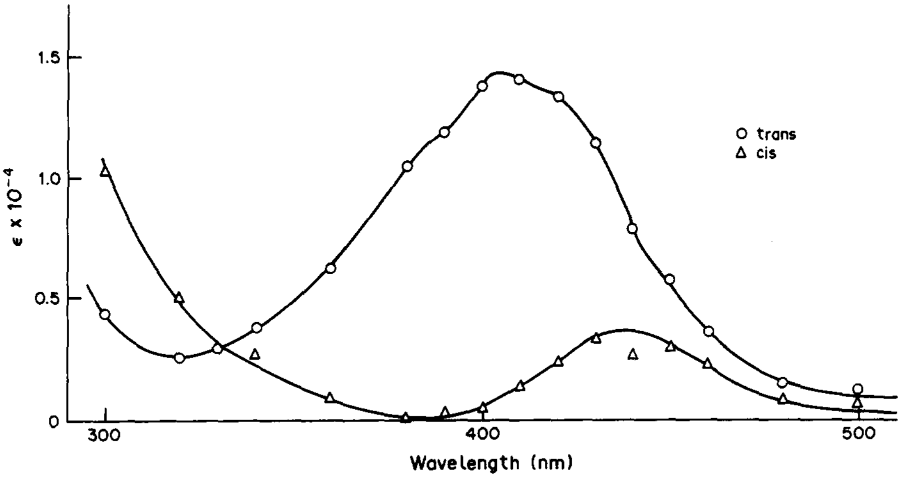

Fig. 1. The u.v. absorption spectra of *trans*- and *cis*-AZN in toluene solution at −80°C.

SP-H3C). For measurements at 4 and 60 K, the Oxford CF-1204, continuous flow type liquid helium cryostat, was used.

The thermal *cis*-to-*trans* backward isomerization of irradiated AZN solutions at various temperatures was followed with a u.v. spectrophotometer (JASCO UVIDEC-660).

Actinometry for the irradiation light was carried out with a digital photometer (Ushio UTI-101) calibrated with the potassium ferrioxalate/*o*-phenanthroline system [12].

RESULTS AND DISCUSSION

Thermal cis-to-trans isomerization

The thermal *cis*-to-*trans* backward isomerization of AZN samples equilibrated by 402 nm irradiation was followed in toluene at various temperatures.

The Arrhenius plots for the first-order rate constant for thermal *cis*-to-*trans* isomerization of AZN (Fig. 2) give an activation energy of 68 kJ mol^{-1}, which is similar to that of azobenzene (73.9 kJ mol^{-1}) [10]. The low activation energy compared with that of stilbene (168 kJ mol^{-1}) suggests that the thermal isomerization of AZN, as well as the case of azobenzene, proceeds via rehybridization or inversion mechanism, i.e. through a change in the hybrid orbital of the nitrogen atom from sp^2 to sp and then to sp^2 again.

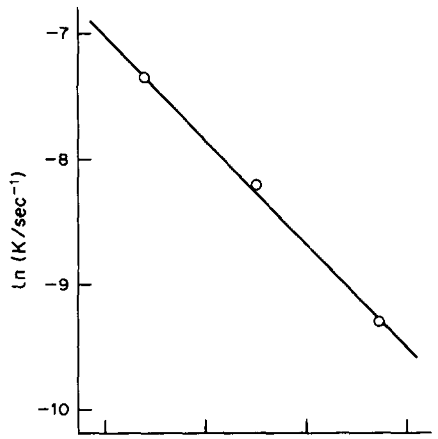

Fig. 2. Arrhenius plots for *cis*-to-*trans* thermal isomerization of AZN in toluene solution.

Photoisomerization of AZN in film

When *trans*-AZN, with initial concentration $[\mathrm{tr}]_0$, is irradiated continuously with 402 or 407 nm, the rate of increase in *cis*-AZN concentration at time t, $d[cis]_t/dt$, is given by:

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

where A ($A = 2.3 \times 10^3\ I_0\,\epsilon_{tr}\ \phi_{tr\to cis}$) is an apparent rate coefficient for *trans*-to-*cis* photoisomerization, B ($B = 2.3 \times 10^3\ I_0\ \epsilon_{cis}\ \Phi_{cis\to tr}$) 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} sec^{-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 $t(OD_t)$ using equation (2), where the value of 0.0809 was used for $\epsilon_{cis}/\epsilon_{tr}$ at 402 nm.

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

When the photostationary state is attained, equation (3) holds for the final equilibrium concentration of the *cis* isomer $[cis]_\infty$.

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

By using equation (3), equation (1) can be transformed to the first-order relationship:

$$2.3 \log \frac{[cis]_\infty}{[cis]_\infty - [cis]_t} = \frac{[tr]_0}{[cis]_\infty} At$$

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

The first-order plots according to equation (4) for *trans*-to-*cis* photoisomerization of AZN at room temperature are shown in Fig. 3. The reaction proceeds in accordance with first-order plots in toluene

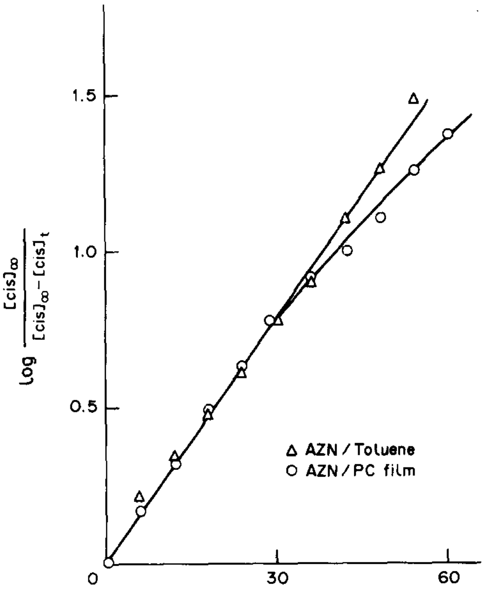

Fig. 3. The first-order plots for *trans*-to-*cis* photoisomerization of AZN in PC film and in toluene solution.

solution. In PC film, the reaction proceeds with the same rate as in solution up to 84% of the final conversion. Above that conversion, the reaction deviates from first-order kinetics and then reaction stops at 35% *cis* formation. The quantum yields for the photoisomerization of AZN calculated from the slope of the first-order plots are shown in Table 1.

In order to obtain the elementary rate constant for *trans*-to-*cis* photoisomerization, k_{iso}, the fluorescence lifetime, τ, at 470 nm for AZN under a picosecond pulse irradiation of high energy electron beam from LINAC [13] was measured with a streak camera (Hamamatsu C-1587) [14].

Figure 4 shows the semi-logarithmic plots for fluorescence decay of azonaphthalene in PC and PMMA films and in cyclohexane solution. The lifetime of the excited singlet state of AZN, τ, was found to be 1.4 ± 0.2 nsec from the slopes in Fig. 4 in all cases. As the photoisomerization of AZN is supposed to proceed from the excited singlet state, the rate constant for the photoisomerization, k_{iso}, was found to be $k_{iso} = 6.5 \times 10^7\,\mathrm{sec}^{-1}$ by using equation (5).

$$\Phi_{tr \to cis} = \frac{k_{iso}}{k_{iso} + k_f + k_d + k_{isc}} = \tau k_{iso} \qquad (5)$$

where k_f, k_d and k_{isc} are rate constants for fluorescence, deactivation and intersystem crossing, respectively.

Temperature dependence for trans-*to*-cis *photoisomerization*

The time courses of *trans*-to-*cis* photoisomerization of AZN in PC films at various temperatures, from liquid helium temperature to 260 K, are shown in Fig. 5. When the irradiation intensity is fixed ($I_0 = 5.6 \times 10^{-9}$ einstein sec^{-1} cm^{-2}), the initial rate of photoisomerization does not decrease much with decreasing temperature, but the final conversion of the *trans*-to-*cis* photoisomerization decreases markedly with decreasing temperature. The temperature dependences of equilibrium or final *cis* fraction are illustrated in Fig. 6, together with the results for *trans*-to-*cis* photoisomerization of azobenzene. Dashed lines in Fig. 6 correspond to the results for AZN in toluene(a) and azobenzene in ethanol (b).

Table 1. The final *cis*-fraction and quantum yields of AZN at room temperature

Medium	$[cis]_\infty$	$\Phi_{tr \to cis}$
PC	0.44	0.09
Toluene	0.79	0.12

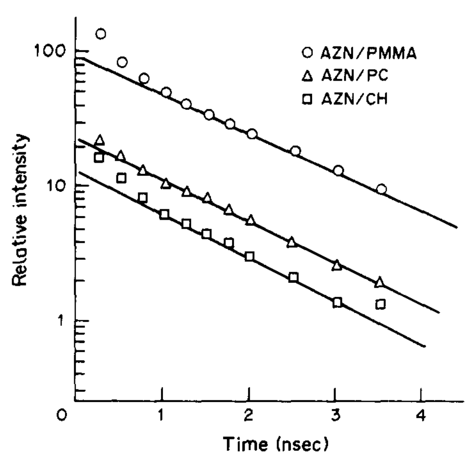

Fig. 4. Logarithmic plots for fluorescence decay of AZN in PMMA, in PC and in cyclohexane at 470 nm.

The decreases in final *cis*-conversions with increasing temperature above 280 K are attributed to the occurrence of the *cis*-to-*trans* thermal isomerization. There is no temperature dependence of final *cis* fraction for *trans*-to-*cis* photoisomerization of AZN below 280 K in toluene solution and the final conversion approaches 80%. The final conversions for AZN in PC are less than half of those for azobenzene in PC, and decrease with decreasing temperature. We believe that these differences are caused not only by the fact that the sweep volume for the inversion of the 1-naphthyl group (0.16 nm^3) is larger than that of phenyl group (0.12 nm^3), but also that half of the *trans*-AZN conformers need the rotation of a 1-napththyl group around the C–N bond (0.18 nm^3) for the *trans*-to-*cis* isomerization because of steric hindrance between naphthyl groups.

At liquid helium temperature (4 K), the final conversion for the photoisomerization of AZN was found to be 7% in PC, compared with 17% in the case of azobenzene. As the fluctuation of local free-volume is suppressed at liquid helium temperature, the micro-environment for 7% of AZN molecules is supposed to have sufficient local free-volume for photoisomerization to occur.

Comparison of the results with kinetic models

The first-order plots for *trans*-to-*cis* photoisomerization of AZN in PC films at various temperatures are shown in Fig. 7. The deviation from linearity in the first-order plots becomes more marked with decreasing temperature, as in the case of azobenzene.

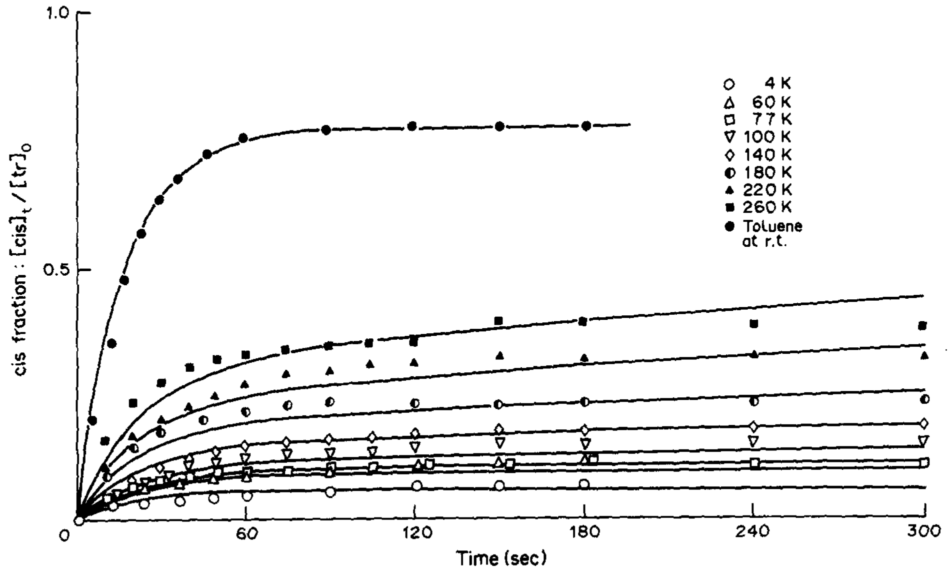

Fig. 5. Change in the fraction of *cis*-AZN, $[cis]_t/[tr]_0$, during *trans*-to-*cis* photoisomerization of AZN in PC film at 4–260 K. Symbols correspond to experimental values and solid lines are the results of simulation according to the free-volume fluctuation model [equations (8–13)].

The slope for *trans*-to-*cis* photoisomerization in mobile sites at 4 K is almost the same as that at room temperature. This tendency is the same as in the case of azobenzene and shows that $\Phi_{tr\rightarrow cis}/\Phi_{cis\rightarrow tr}$ is independent of temperature for photoisomerization in freely mobile environments as in solution.

Thus we compare the present results of the time-courses of *trans*-to-*cis* photoisomerization of AZN in polycarbonate with two kinds of kinetic models, i.e. the stretched exponential model [15, 16] and the free-volume fluctuation model [10], both describing the heterogeneous progress of reactions in amorphous solids.

Stretched exponential model

The curve fitting to the stretched exponential plots of $\ln\{\ln([tr]_0/[tr]_t)\}$ against in t according to equations (6) and (7) for photoisomerization of AZN did not give straight lines over the whole time range (Fig. 8).

$$[tr]_t = [tr]_0 \exp(-kt^{\alpha}) \tag{6}$$

$$\ln\{\ln([tr]_0/[tr]_t)\} = \alpha \ln t + \ln k. \tag{7}$$

This effect could be due to the existence of hardly isomerizing molecules which show a substantial limiting conversion within the experimental time scale, caused by the distribution of local free-volume.

Free-volume fluctuation model

In the free-volume fluctuation model [10], the reaction sites in PC film are divided into two groups by the critical free-volume, V_c. In the first group, AZN molecules have larger local free-volume, V,

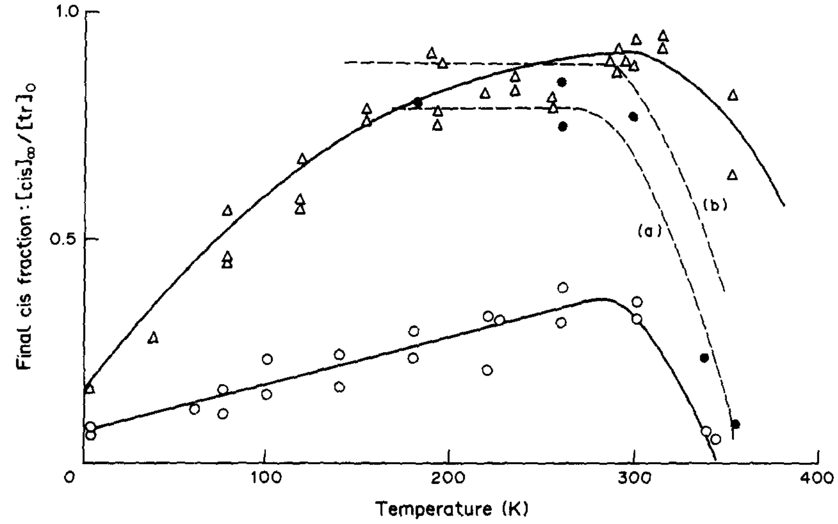

Fig. 6. The final *cis* fraction $[cis]_\infty/[tr]_0$, against temperature for *trans*-to-*cis* photoisomerization of AZN (○) and azobenzene (△) in PC film and in solution [dashed line (a) and ● for AZN dashed line (b) for azobenzene].

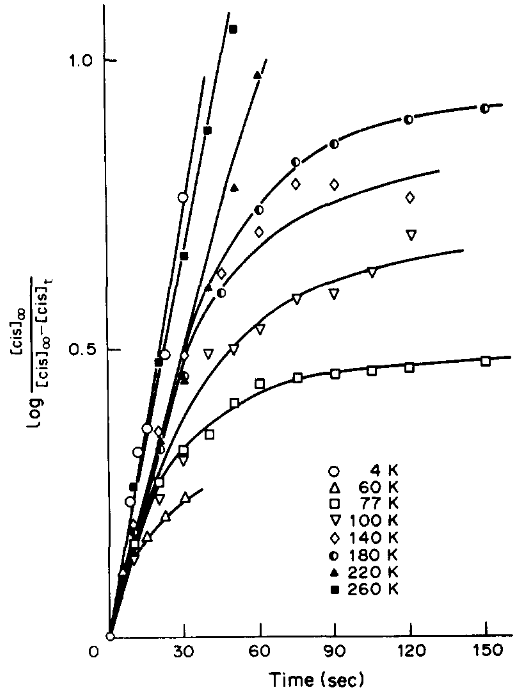

Fig. 7. First-order plots for *trans*-to-*cis* photoisomerization of AZN in PC film at 4–260 K.

than V_c around them. The rate constant at this freely mobile site is equal to that in solution, k_0, and is independent of temperature since the photoisomerization of AZN molecules is not affected by the matrix polymer. In the second group, where V is smaller than V_c, the mobility of micro-environment controls the rate with an activation energy, ΔE_a, which 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 equations (8) and (9).

$$k(f) = k_0 \exp(-\Delta E_a)/k_B T) \qquad (8)$$

$$\Delta E_a = \begin{cases} 0 & \text{for } f > f_c \\ C(f_c - f) & \text{for } f < f_c \end{cases} \qquad (9)$$

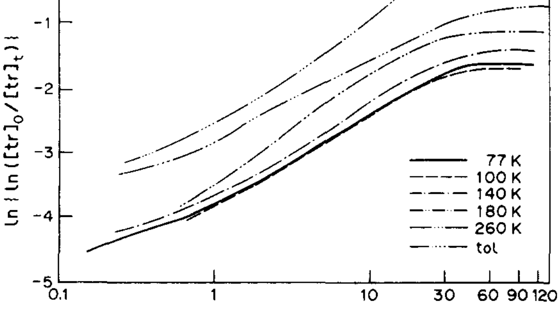

Fig. 8. Stretched exponential plots for photoisomerization of AZN in PC film.

where V_0 is the volume of the relaxation environment at room temperature, 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 given by equation (10) because of the local fluctuation of free-volume caused by the local molecular relaxation within the time scale of the excited state lifetime, where f_{c0} was found to be 0.0445 from $[cis]_\infty$ at 4 K where local fluctuation of free-volume can be negligible.

$$f_c = f_{c0} - \beta T \qquad (10)$$

The distribution of fractional local free-volume, G(f), was given by γ-distribution as equation (11) according to Robertson [17].

$$G(f) = \frac{\lambda}{\Gamma(\alpha)} (\lambda f)^{\alpha - 1} e^{-\lambda f} \qquad (11)$$

The parameters α and λ are determined by

$$\alpha = \bar{f}^2 V_0/(\Delta\kappa k_B T), \quad \lambda = \bar{f} V_0/(\Delta\kappa k_B T) \qquad (12)$$

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 $\bar{f} = 0.025$, $\Delta\kappa = 4.2 \times 10^{-10}\,\text{Pa}^{-1}$ [18] and $V_0 = 4.96\,\text{nm}^3$ were used for the calculation. The schematic illustration of the distribution function, G(f) and relative reactivity, $k(f)/k_0$, (Fig. 9) is reproduced from our previous paper [10]. At a low temperature such as liquid helium temperature, the fluctuation width of the local free-volume around an AZN molecule is very narrow [Fig. 9(a)]. It broadens with increasing temperature, and the lower limit for a freely mobile photoisomerization site, f_c, becomes smaller according to equation (10) as shown in Fig. 9(b).

In the solid state, the reaction at each site proceeds separately, so the extent of reaction can be expressed by the integration of each first-order reaction, as given by equation (13).

$$[tr]_t/[tr]_0 = \int_0^\infty G(f) \left[\frac{A}{A+B} \exp[-k(f)t] + \frac{B}{A+B} \right] df \qquad (13)$$

where A and B are the apparent rate coefficients for *trans*-to-*cis* and *cis*-to-*trans* photoisomerization in solution as determined for equation (1). The results of the calculation according to the free-volume fluctuation model with the values of $C = 5.0 \times 10^5\,\text{J mol}^{-1}$ and $\beta = 8.0 \times 10^{-5}\,\text{K}^{-1}$ are shown as solid lines in Fig. 5. It shows good fit with experimental results. The value of β is the same as for azobenzene, which is reasonable since the temperature dependence of the fluctuation of local free-volume is a function of the matrix polymer. The parameter C determining the activation energy for photoisomerization at the sites of restricted mobility is larger than for azobenzene ($2.0 \times 10^5\,\text{J mol}^{-1}$) [10] and seems to depend on the size of the chromophore molecule. Thus, it could be supposed that the free-volume fluctuation model can describe the characteristics of *trans*-to-*cis* photoisomerization of AZN in polymer films.

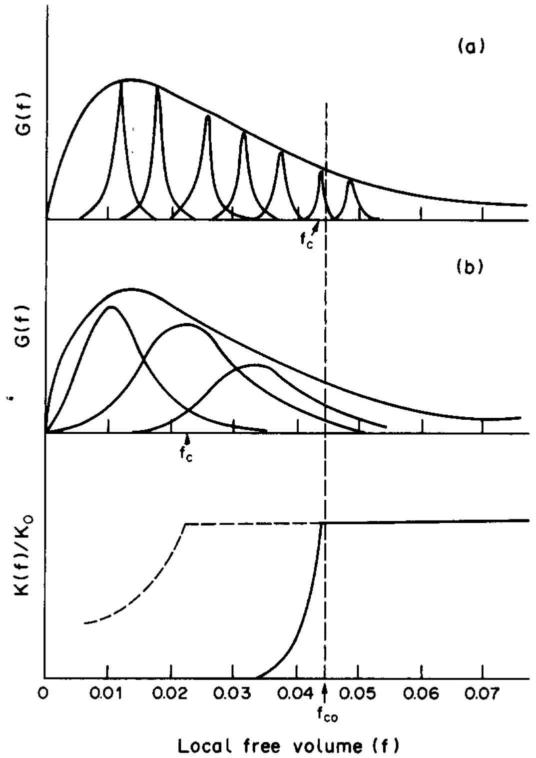

Fig. 9. Schematic illustration of fractional free-volume distribution, G(f), at 4 K (a), at higher temperature (b), and reactivity, $k(f)/k_0$, according to the free-volume fluctuation model. Solid line in reactivity corresponds to 4 K (a), dashed line corresponds to a higher temperature (b).

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