

Photochemistry in polymer solids:

12. Effects of main-chain structures and formation of hydrogen bonds on photoisomerization of azobenzene in various polymer films

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(Received 3 December 1990; revised 16 November 1992)

The free-volume distribution in various polymers and the effect of hydrogen bonds on the free-volume distribution were examined by using a photoisomerization of azobenzene as a photosensitive probe. Poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) and phenoxy resin films containing molecularly dispersed azobenzene were irradiated over a wide temperature range (77–340 K). The final *cis* fraction for the *trans* to *cis* photoisomerization of azobenzene decreases with decreasing temperature in PMMA, and smaller fractions are produced than in polycarbonate at the same temperature. These differences are due to the fact that the local free-volume fluctuation of the methylene main chains of PMMA is smaller than that of the aromatic chains of polycarbonate. Since the side chains of PMMA compared to the main chains are larger than those of polycarbonate, the local free volume around the main chains is filled up by the side chains. Hence, the final *cis* fraction of azobenzene in PMMA is small. Furthermore, the final *cis* fraction in poly(vinyl alcohol) is smaller than that in PMMA. Since the hydrogen bonds among the polymer chains in poly(vinyl alcohol) restrict the local molecular motion at low temperatures, the azobenzene molecule is tightly seized by the matrix polymer chains and the free-volume fluctuation is restricted in poly(vinyl alcohol). The kinetic model considering the local fluctuation of the free volume was also applied to the results for PMMA, poly(vinyl alcohol) and phenoxy resin, and the parameters for the model in these polymers are discussed.

(Keywords: photoisomerization; free volume; azobenzene)

INTRODUCTION

The main feature of solid-state reactions that distinguishes them from reactions in solution is the decrease in the freedom of molecular motion due to the restriction of mobility. As a result, the non-first-order progress of reactions which are expected to be unimolecular in solution is frequently observed in the solid state due to the microscopically heterogeneous state of aggregation or the free-volume distribution of the reaction medium^{1,2}.

Photochemical and thermal isomerizations of azobenzene and its derivatives bound to the main chain or attached to the side chains of polymers have been reported by many investigators^{3–11}. In our previous papers, *trans* to *cis* photoisomerizations of azobenzene^{12,13}, 1,1'-azonaphthalene^{13,14}, 9,9'-azophenanthrene¹⁵ and stilbene¹⁵

in polycarbonate film were 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 first-order kinetics. The final conversions in photoisomerization of these probe molecules in the film decrease with decreasing temperature. These deviations and decrements in the final conversions may be due to the restriction of polymer chain mobility and the heterogeneity of the free-volume distribution at the reaction sites in the polymer solid. The rates and extents of photoisomerization in polymer solids are expected to be much influenced by the size of the isomerizing chromophore, since a larger local free volume is needed for the isomerization of molecules with bulkier aromatic groups. The difference between the reactivities of azobenzene, 1,1'-azonaphthalene and 9,9'-azophenanthrene has been discussed in previous papers^{13–15}.

In the present work, the study over a wide temperature range was extended to the photoisomerization of azobenzene in PMMA, poly(vinyl alcohol) and phenoxy

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resin films and the results were compared to the case in polycarbonate (PC). A kinetic model considering the influence of the free-volume distribution and fluctuation on the reactivity of the photo-probe was applied to the present cases, and a simulation is given in order to explain the non-first-order reaction profiles of *trans* to *cis* photoisomerizations in polymer films and their dependence on temperature.

EXPERIMENTAL

Materials

Azobenzene (AZB) was purchased from Tokyo Kasei Kogyo Co. Ltd, and was purified by recrystallization from ethanol. Poly(methyl methacrylate) (PMMA) was obtained from Mitsubishi Rayon Co. ($M_n = 2.1 \times 10^5$, $T_g = 110^\circ\text{C}$), phenoxy resin (aromatic polyhydroxyether, PhR) from Union Carbide Japan ($T_g = 102^\circ\text{C}$), and poly(vinyl alcohol) (PVA) from Wako Pure Chemical Ind. Ltd. Dichloromethane and hexafluoro-2-propanol were spectroscopic grade and used without further purification.

Sample preparation

The films of PMMA, PVA and PhR containing molecularly dispersed AZB were prepared by the solvent cast method from dichloromethane (PMMA and PhR) or hexafluoro-2-propanol (PVA) solution and subsequently heated under vacuum for 12 h at 80°C to eliminate the residual solvent.

Measurements of photoisomerization

The sample films set in an Oxford DN-704 cryostat were irradiated with light of 360 nm wavelength from a 150 W xenon lamp (Hamamatsu L-2195) with a combination of colour filters (UV-D36A and Pyrex glass) for the measurement of *trans* to *cis* photoisomerization of AZB. The change in intensity of the transmitted light at the absorption maximum of AZB (317 nm) 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).

RESULTS AND DISCUSSION

Photoisomerization of azobenzene in polymer films

When the *trans* isomer with an initial concentration $[\text{tr}]_0$ is irradiated with continuous-wave light (360 nm), the change in the concentration $[\text{cis}]_t$ of *cis*-AZB at time t can be calculated from the optical density OD, using

$$[\text{cis}]_t = \frac{1 - \text{OD}_t / \text{OD}_0}{1 - \varepsilon_{\text{cis}} / \varepsilon_{\text{tr}}} [\text{tr}]_0 \quad (1)$$

where $\varepsilon_{\text{cis}} / \varepsilon_{\text{tr}}$ is 0.0591 for AZB at 317 nm.

The plots of *cis* fraction against time for AZB in PMMA, PVA and PhR films at various temperatures, from liquid nitrogen temperature to 300 K, are shown in Figure 1. Each plot shows that the final level of *trans* to *cis* photoisomerization decreases with decreasing temperature, but the initial rate of photoisomerization is not affected much by temperature.

Examples of semilogarithmic time-conversion plots for the *trans* to *cis* photoisomerization of AZB are shown in Figure 2 for PMMA films. The reaction at each temperature proceeds with first-order kinetics at the initial stage, then deviates from first-order kinetics

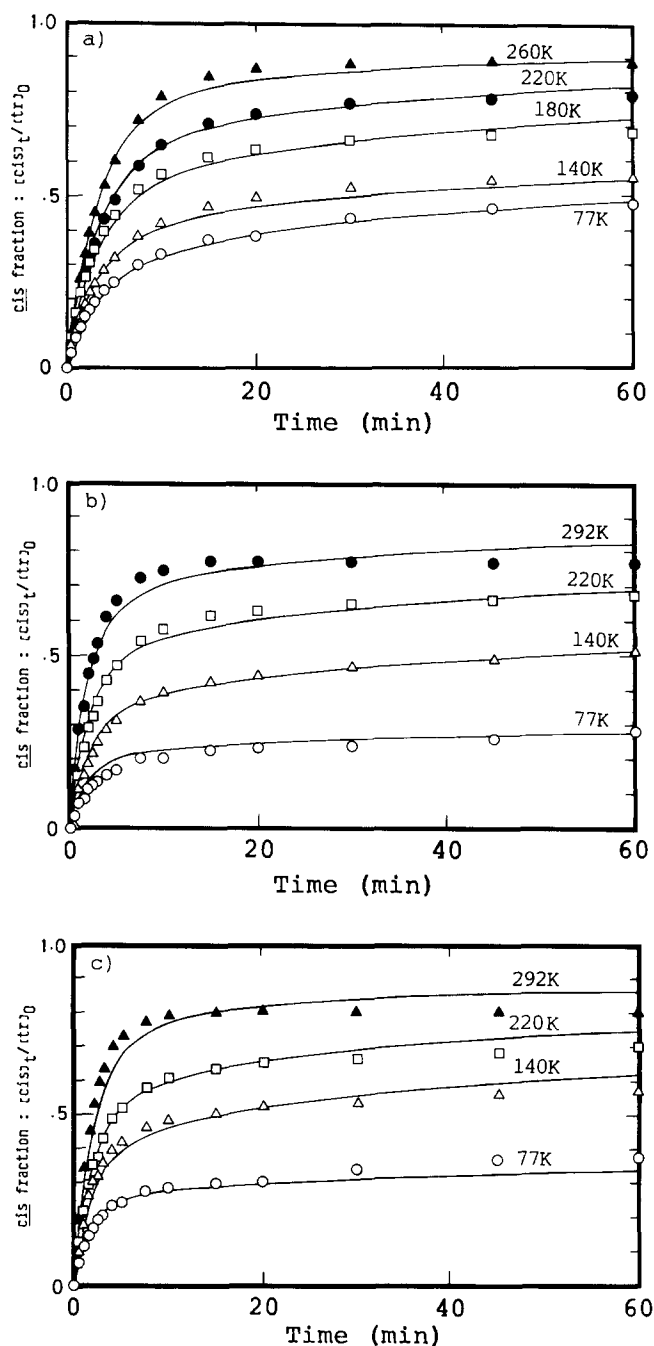


Figure 1 Change in the fraction $[\text{cis}]_t/[\text{tr}]_0$ of *cis*-azobenzene during *trans* to *cis* photoisomerization in (a) PMMA, (b) poly(vinyl alcohol) and (c) phenoxy resin films at various temperatures. Symbols correspond to experimental values and solid lines are the results of the simulation according to a free-volume fluctuation model

before the reaction reaches the final *cis* fraction. The Arrhenius plots (determined from the initial slopes of semilogarithmic plots such as Figure 2) for the *trans* to *cis* photoisomerization of AZB in various polymers (Figure 3) show a break in slope at 220 K, and fit in almost parallel lines both above and below the break. The apparent activation energy below 220 K was determined to be about $0.2 \text{ kcal mol}^{-1}$ ($1 \text{ cal} = 4.2 \text{ J}$). This value is comparable to the apparent activation energy for 4-dimethylamino-4'-nitroazobenzene at the same temperature in various polymers¹⁶. On the other hand, the slopes of the Arrhenius plots give an apparent activation energy of about $1.0 \text{ kcal mol}^{-1}$ above 220 K for all cases. These apparent activation energies for

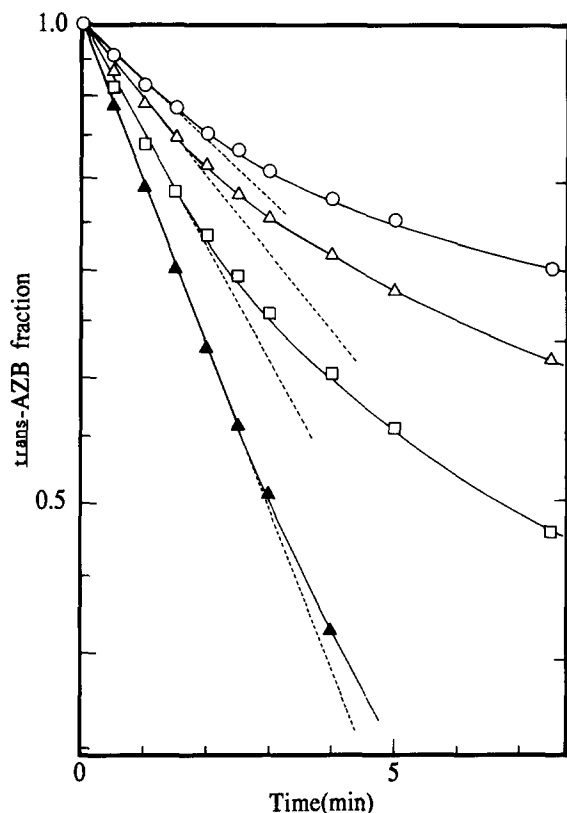


Figure 2 Typical semilogarithmic time-conversion plots for the *trans* to *cis* photoisomerization of azobenzene in PMMA films: (○) 77 K; (△) 140 K; (□) 220 K; (▲) 260 K

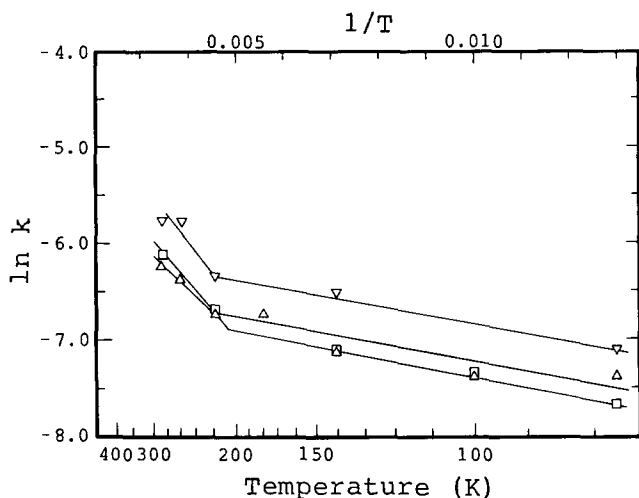


Figure 3 Arrhenius plots of the initial apparent rates based on the semilogarithmic time-conversion plots for the *trans* to *cis* photoisomerization of azobenzene in: (△) PMMA; (□) poly(vinyl alcohol); (▽) phenoxy resin

photoisomerization are thought to be due to the temperature dependence of the final *cis* conversion, which means that the increase in the fraction of restricted reaction sites in the polymer at low temperatures is reflected by the existence of an apparent activation energy.

The first-order plots according to equation (2) for the photoisomerization of AZB as described in a previous paper¹² are shown in Figure 4 for the PMMA film.

$$2.3 \log \left(\frac{[cis]_{\infty}}{[cis]_{\infty} - [cis]_t} \right) = \frac{[tr]_0}{[cis]_{\infty}} At = \frac{[tr]_0}{[tr]_0 - [cis]_{\infty}} (B + K)t \quad (2)$$

$A = 2.3 \times 10^3 I_0 \epsilon_{tr} \Phi_{tr \rightarrow cis}$ and is an apparent rate coefficient for the *trans* to *cis* photoisomerization, $B = 2.3 \times 10^3 I_0 \epsilon_{cis} \Phi_{cis \rightarrow tr}$ and is an apparent rate coefficient for the *cis* to *trans* photoisomerization, and K is a rate constant for the *cis* to *trans* thermal isomerization. I_0 (einstein $\text{cm}^{-2} \text{s}^{-1}$) is the incident light intensity, ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$) is the molar extinction coefficient at the irradiation wavelength, Φ is the quantum yield for photoisomerization, and the subscripts tr and cis denote the *trans* and *cis* isomers, respectively.

In these first-order plots, only the AZB molecules which could isomerize were considered to be reactant, and the molecules which were substantially at immobilized sites were excluded from the calculation. The first-order plots show that deviation from the straight lines becomes more marked with decreasing temperature, as was the case for PC films. In the other polymers, i.e. PVA and PhR, a similar deviation also occurred.

Comparison of the simple semilogarithmic plots with the first-order plots according to equation (2) suggests that the reaction sites in polymers are divided into two parts: at one part, the photo-probe can isomerize freely in accordance with a first-order rate; and at the other part, the mobility of the photo-probe is restricted and controlled by matrices. We will discuss this point in the next section.

The equilibrium, or final, *cis* fractions of AZB in PMMA, PhR, PVA and PC^{12,13} are plotted against temperature in Figure 5.

The decrease in the final *cis* conversions with increasing temperature above 300 K is attributed to the occurrence of the *cis* to *trans* thermal isomerization. The final *cis* conversions in PMMA are a little smaller than those in polycarbonate regardless of the similar densities (in g cm^{-3}) of these polymers (PMMA 1.19¹⁷⁻²⁰, PC

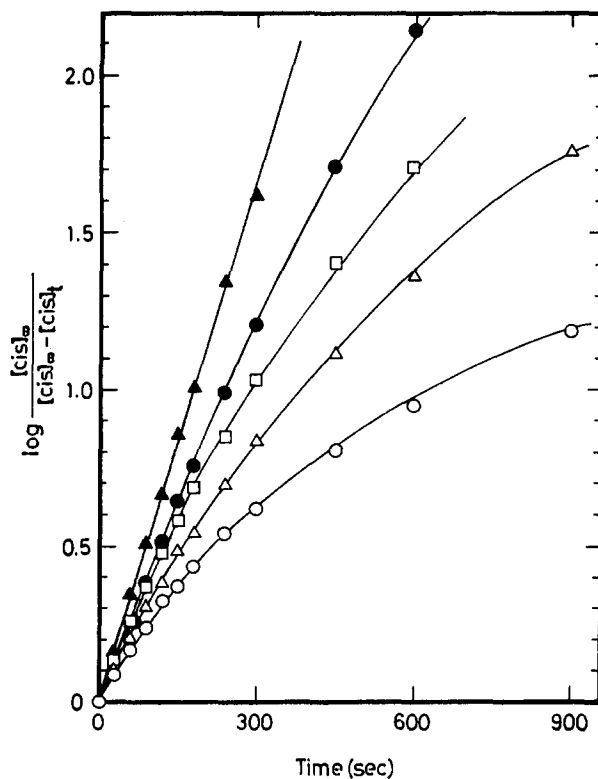


Figure 4 First-order plots based on equation (2) for the *trans* to *cis* photoisomerization of azobenzene in PMMA film at: (○) 77 K; (△) 140 K; (□) 180 K; (●) 260 K; (▲) 288 K

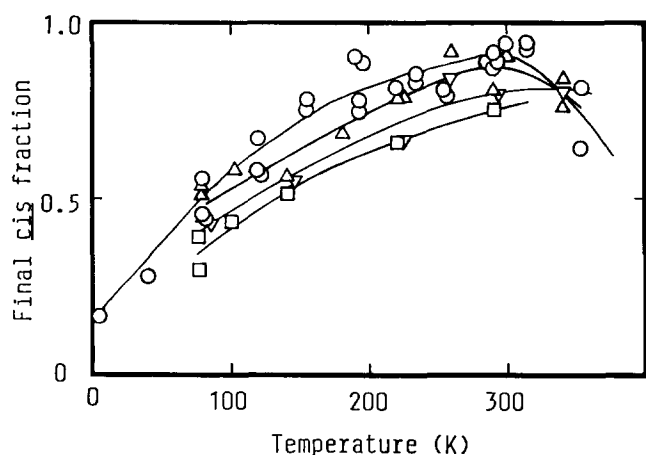


Figure 5 The final *cis* fraction $[cis]_{\infty}/[tr]_0$ against temperature for the *trans* to *cis* photoisomerization of azobenzene in: (○) polycarbonate; (△) PMMA; (□) poly(vinyl alcohol); (▽) phenoxy resin

1.20^{17,18,21}). This is because the fraction of the van der Waals occupied volume for PMMA, found to be 0.67 by using the atomic increment method²², is larger than that for polycarbonate (0.63). Also, the distribution of local free volume in PMMA with its flexible methylene main chains is thought to be narrower than that in PC with its bulky aromatic chains. The effects of the formation of hydrogen bonds among the matrix main chains are also shown in *Figure 5*. In the case of PC and PhR, although the main chains of both polymers consist of the bisphenol A structure in their repeating units, the final *cis* fractions in PhR, which has hydroxy groups in its main chain, are smaller than those in PC. In the case of PMMA and PVA, the result is similar. This suggests that the restriction of chain mobility due to hydrogen-bond formation among the main chains suppresses the extent of photoisomerization in polymer solids.

Comparison of the results with a kinetic model

In previous papers¹²⁻¹⁵ the free-volume fluctuation model was proposed in order to explain the heterogeneous progress of reaction and its temperature dependence in polymer solids. The model was fitted to the results from the conversion-time plots of *trans* to *cis* photoisomerization of azo compounds in PC. The model is extended here to be fitted to other polymers, i.e. PMMA, PhR and PVA.

In this model, the reaction sites in polymer films are divided into two parts by the critical free volume V_c . In the first part, the local free volume V around the photoreactive probe molecule 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 for photoisomerization of these probe molecules in solution is not affected by temperature. In the other part, where V is smaller than V_c , the mobility in the microenvironment controls the rate with an activation energy ΔE_a proportional to $V_c - V$. The rate constant $k(f)$ for an individual reaction site, which depends on the fractional local free volume $f = V/V_0$, is given by

$$k(f) = k_0 \exp(-\Delta E_a/k_B T) \quad (3)$$

$$\Delta E_a = \begin{cases} 0 & \text{for } f > f_c \\ C(f_c - f) & \text{for } f < f_c \end{cases} \quad (4)$$

where V_0 is the volume of the relaxation environment at

room temperature²³, C is a parameter characterizing the rigidity of the matrix and $f_c = V_c/V_0$ is the critical free-volume fraction. The value of f_c is assumed to depend on temperature, according to equation (5), owing to the local fluctuation of free volume caused by the local molecular relaxation within the excited-state lifetime. The quantity f_{c0} is a hypothetical f_c at 0 K where the local fluctuation of free volume can be ignored

$$f_c = f_{c0} - \beta T \quad (5)$$

The distribution $G(f)$ of the fractional local free volume takes the form of a gamma distribution according to Robertson²³

$$G(f) = \frac{\lambda}{\Gamma(\alpha)} (\lambda f)^{\alpha-1} \exp(-\lambda f) \quad (6)$$

The parameters α and λ are defined by

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

where \bar{f} is the mean fractional free volume, $\Delta \kappa$ is the difference in compressibility between liquid and glass k_B is the Boltzmann constant and T is the temperature. The values $\bar{f} = 0.025$, $\Delta \kappa = 4.2 \times 10^{-10} \text{ Pa}^{-1}$ for PC and PhR and $2.55 \times 10^{-10} \text{ Pa}^{-1}$ for PMMA and PVA²⁴, and $V_0 = 4.96 \text{ nm}^3$ were used for the calculation. The variance of the distribution given by equations (6) and (7) is given by

$$\overline{\delta f^2} = \frac{\Delta \kappa k_B T}{V_0} = \frac{\alpha}{\lambda^2} \quad (8)$$

The value of the variance for vinyl polymers (PMMA and PVA) is about 0.6 times smaller than that for aromatic polymers (PC and PhR). This supports our experimental results for photoisomerization, showing the difference in the final *cis* fraction between vinyl-type polymers and main-chain aromatic polymers. The distribution functions $G(f)$ and their integrated curves are shown in *Figure 6*.

The schematic illustrations of $G(f)$ and relative reactivity $k(f)/k_0$ are shown in *Figure 7*. At low temperatures, such as that of liquid helium, the fluctuation width of the local free volume around the photo-probe is very narrow (*Figure 7a*). It broadens with increasing temperature, and the lower limit f_c for a freely mobile photoisomerization site becomes smaller in accordance with equation (5), as shown in *Figure 7b*.

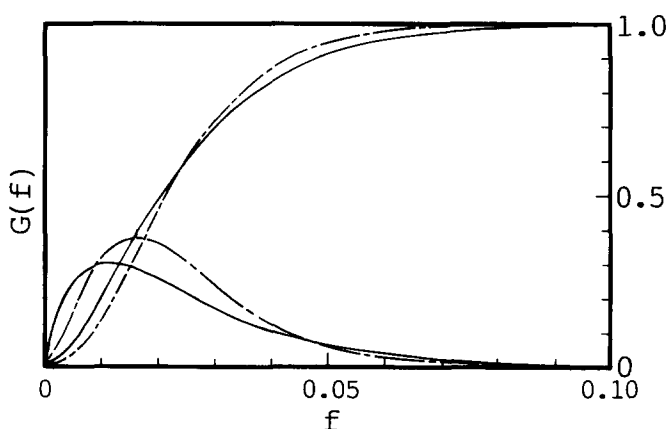


Figure 6 The shapes of the free-volume distributions and their integral curves for polycarbonate (—) and PMMA (---) according to equations (6) and (7)

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 reaction

$$[\text{tr}]_t/[\text{tr}]_0 = \int_0^{\infty} G(f) \left\{ \frac{A}{A+B} \exp[-k(f)t] + \frac{B}{A+B} \right\} df \quad (9)$$

where *A* and *B* are the apparent rate coefficients for *trans* to *cis* and *cis* to *trans* photoisomerizations. Since local fluctuation of the matrix polymer chain becomes larger at higher temperatures, a small difference in local free volume below f_c might cause a large difference in reactivity in the polymer solid. So, the parameter *C* in equation (4) was assumed to be larger at higher temperatures. Thus we tried to fit the calculation separately at each temperature to the experimental result. The results of the calculation according to the free-volume fluctuation model are shown as solid lines in Figure 1. The model fits well with the experimental results. The values of critical free volume, f_c and *C* used for the simulation at each temperature are shown in Figure 8. The values of β (the slope of f_c versus temperature) and the ranges of *C* are shown in Table 1. Constant values of β for all polymers correspond to the straight and almost parallel lines for the temperature dependences of f_c in these polymers. The values of the matrix rigidity index *C* are influenced by the existence of hydrogen bonding.

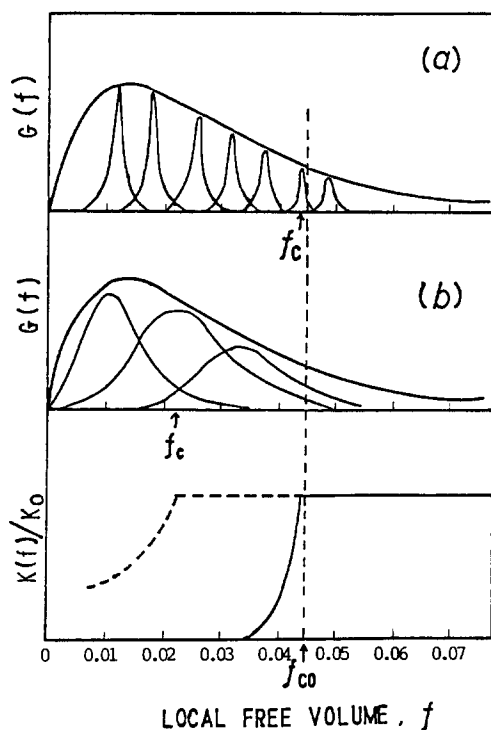


Figure 7 Schematic illustration of the fractional free-volume distribution $G(f)$ (a) at 4 K and (b) at higher temperatures and reactivity $k(f)/k_0$ according to the free-volume fluctuation model. The solid line in the reactivity diagram corresponds to 4 K and the dashed line corresponds to a higher temperature

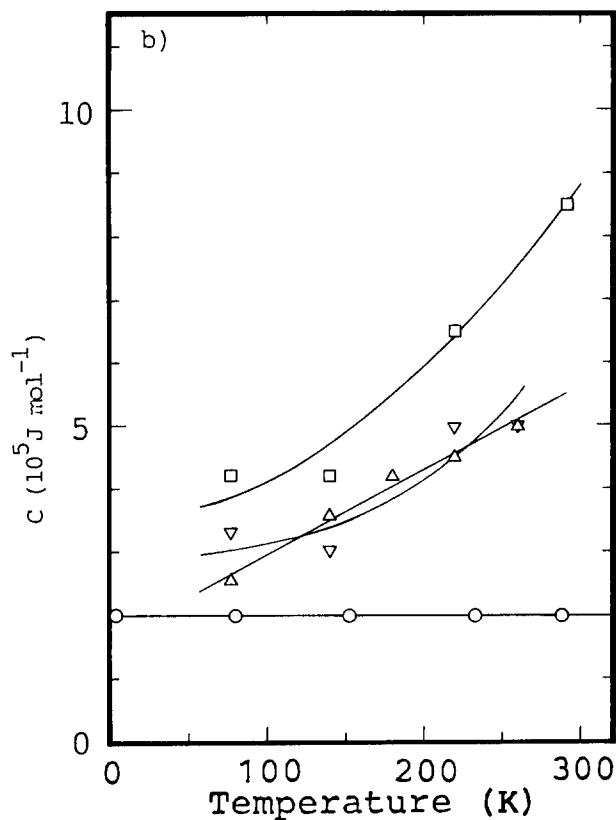
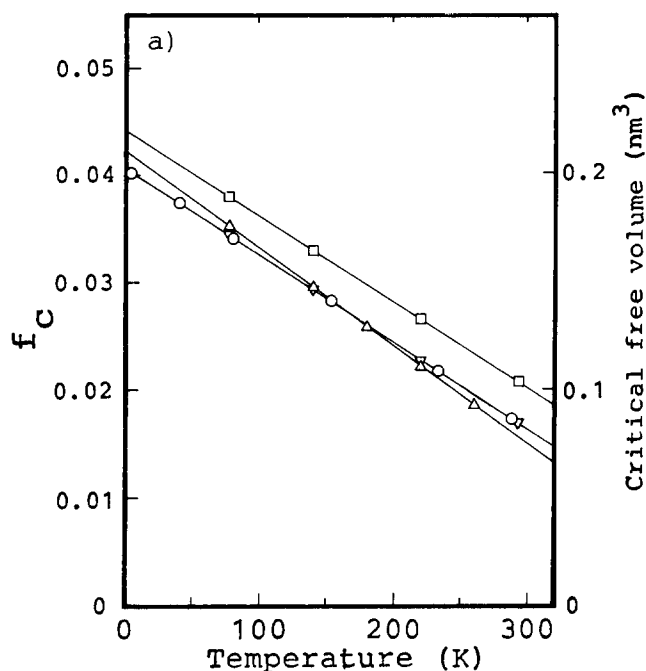


Figure 8 Temperature dependence for (a) f_c and the values of fractional critical free volume and (b) the matrix rigidity index *C* for the photoisomerization of azobenzene in: (O) polycarbonate; (Δ) PMMA; (∇) phenoxy resin; (\square) poly(vinyl alcohol)

Table 1 Parameters for the photoisomerization of azobenzene in various polymers fitted to the free-volume fluctuation model

	PC	PMMA	PhR	PVA
β (K^{-1})	8.0×10^{-5}	7.9×10^{-5}	8.0×10^{-5}	7.4×10^{-5}
<i>C</i> (J mol^{-1})	2.0×10^5	$(2.6-5.0) \times 10^5$	$(2.0-4.9) \times 10^5$	$(4.2-8.5) \times 10^5$

Table 1 shows that the values of C for phenoxy resin are larger than that for polycarbonate, and those for poly(vinyl alcohol) are also larger than those for PMMA at the same temperature. These larger values of C for the hydrogen-bonding polymers (PhR and PVA) suggest that the local mobility in the polymer chains is restricted by the hydrogen bonding. The difference in the temperature dependence of parameter C among the polymers may be related to the existence or absence of side chains that are included in the hydrogen bonding.

In conclusion, the good fitting of the experimental results to the free-volume fluctuation model suggests that this kinetic model, which considers the free-volume distribution and its local fluctuation, can usefully describe the characteristics of photoisomerization reactions in amorphous polymer solids.

ACKNOWLEDGEMENT

This work was supported in part by Grants-in-Aid for Scientific Research on the Priority Area of 'Macromolecular Complexes' from the Ministry of Education, Science and Culture, Japan.

REFERENCES

- 1 Smets, G. *Adv. Polym. Sci.* 1983, **50**, 17

- 2 Horie, K. and Mita, I. *Adv. Polym. Sci.* 1989, **88**, 77
- 3 Paik, C. S. and Morawetz, H. *Macromolecules* 1972, **5**, 171
- 4 Eisenbach, C. D. *Makromol. Chem.* 1978, **179**, 2489
- 5 Paik Sung, C. S., Lamarre, L. and Tse, M. K. *Macromolecules* 1979, **12**, 666
- 6 Eisenbach, C. D. *Ber. Bunsenges. Phys. Chem.* 1980, **84**, 680
- 7 Sung, C. S. P., Lamarre, L. and Chung, K. H. *Macromolecules* 1981, **14**, 1839
- 8 Lamarre, L. and Sung, C. S. P. *Macromolecules* 1983, **16**, 1729
- 9 Sung, C. S. P., Gould, I. R. and Turro, N. J. *Macromolecules* 1984, **17**, 1447
- 10 Victor, J. G. and Torkelson, J. M. *Macromolecules* 1987, **20**, 2241
- 11 Yu, W. C., Sung, C. S. P. and Robertson, R. E. *Macromolecules* 1988, **21**, 355
- 12 Mita, I., Horie, K. and Hirao, K. *Macromolecules* 1989, **22**, 558
- 13 Mita, I., Naito, T. and Horie, K. *J. Photopolym. Sci. Technol.* 1988, **1**, 303
- 14 Naito, T., Horie, K. and Mita, I. *Eur. Polym. J.* 1990, **26**, 1295
- 15 Naito, T., Horie, K. and Mita, I. *Macromolecules* 1991, **24**, 2907
- 16 Naito, T., Horie, K. and Mita, I. *Polym. J.* 1991, **23**, 809
- 17 Naito, T., Kunishige, M., Yamashita, T., Horie, K. and Mita, I. *React. Polym.* 1991, **15**, 185
- 18 'Kobunshi Shinsozai Binran' (Ed. Japanese Society of Polymer Science), Maruzen, 1990, p. 87
- 19 Murov, S. L. 'Handbook of Photochemistry', Marcel Dekker, New York, 1973, p. 119
- 20 Deanin, R. D. 'Polymer Structure, Properties and Applications', Cahners Books, Boston, 1972, p. 201
- 21 Elias, H.-G. 'Macromolecules', Vol. 1, Plenum Press, New York, 1977, p. 164
- 22 Edward, J. T. *J. Chem. Educ.* 1970, **47**, 261
- 23 Robertson, R. E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 173
- 24 Wendorff, J. H. and Fischer, E. W. *Koll. Z. Z. Polym.* 1973, **251**, 876