Photoisomerization and Thermal Isomerization Behavior of Azobenzene Derivatives in Liquid Crystalline Polymer Matrices

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ABSTRACT: The trans to cis photoisomerization and cis to trans thermal isomerization of azobenzene derivatives molecularly dispersed in two types of polymer liquid crystals (PLCs), nematic and smectic PLCs, were investigated with reference to the inner free volume of the PLC matrices. The size distribution and the fluctuating nature of the inner free volume were examined, and it was found that the nematic phase posesses more inner free volume than the smectic phase.

Introduction

Polymer liquid crystals (PLCs) have attracted great interest for several applications,[1-9] particularly for optical image storage systems. The photochemical phase transition has also been extensively studied as the working principle for optical image storage.[6] This is an isothermal transition triggered by a photochemical reaction of the guest photoresponsive molecule. Photoisomerization of azobenzene and spiropyran derivatives, for example, was found to induce the isothermal phase transition in low-molecular-weight LCs as well as PLCs. The photochemical phase transition in PLCs is promising for optical image storage in view of high resolution, high stability of the stored image, and relatively quick response (<50 ms).[6a,e]

Such a phase transition is composed of two processes: the photochemical reaction (photoisomerization) of a guest molecule and the subsequent phase transition of the host. Although the second process has been investigated in detail by time-resolved measurements of birefringence,[6e,f] few studies have been performed on the photoisomerization behavior of photoresponsive molecules in PLC matrices.

The liquid crystalline (LC) phase is an ordered assembly of rod-shaped rigid molecular units called mesogens, providing an anisotropic environment on the molecular scale. In a series of studies on liquid crystalline solvents as mechanistic probes, Weiss et al. have employed various low-molecular-weight LCs as *anisotropic* matrices and explored thermal reactions and photoreactions in such environments.[10] They have found that in the LC phase, reactions proceed anisotropically. A number of amorphous polymers have also been employed as matrices for photochemical reactions, since polymer binders are essential for the practical use of photochemical systems.[11-13] Photoisomerization reactions of azobenzene derivatives in amorphous polymer films were used to evaluate the free volume. If various azo compounds, each requiring some free volume to isomerize, are incorporated into polymers, the photoisomerization behavior yields information on the size distribution of the free volumes.[11-13]

In this study, the photoisomerization reactions of azobenzene derivatives in two types of PLCs were explored. Several types of PLCs are known which exhibit nematic, smectic, and cholesteric phases. Particularly, nematic and smectic-A phases contrast strongly in the packing of the mesogens so that the distribution of free volumes is expected to be different between these phases. In the present study, PLCs with the same structure in the mesogens and the main chain but with a different spacer length between them were employed and the photoisomerization behavior of two azobenzene derivatives requiring a different size of the free volume for isomerization was explored in these PLCs. Although the PLCs used in this study possess a very similar structure (Figure 1), one is nematic whereas the other exhibits both nematic and smectic-A phases. Thus, the effect of the LC phases on the isomerization behavior of the probe molecules can be studied in detail without any ambiguity due to different structures of the mesogens.

Experimental Section

Preparation of Samples. The structures of host PLCs and azobenzene derivatives used in this study are shown in Figure 1. Poly(4′-methoxyphenyl 4-(((acryloxy)alkyl)oxy)benzoate)s, in which the number of carbon atoms in the alkyl spacer is 3 (PAPB3) and 6 (PAPB6), were used as the matrix PLCs, and azobenzene derivatives, 4,4′-dimethoxyazobenzene (DMAB) and 3,4,5,3′,4′,5′-hexamethoxyazobenzene (HMAB), were used as the photoresponsive probe molecules. The synthesis of these PLCs was described elsewhere.[6a] PAPB3 is nematic and PAPB6 has both nematic and smectic phases. The azobenzene derivatives were synthesized by coupling of the corresponding methoxy-substituted anilines via the Bogoslovski reaction and were purified by recrystallization from ethanol.[6b,14,15]

The number-average molecular weights (M_n) of the PLCs were determined by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8 + G2500H8; eluent, chloroform), and the phase transition temperatures of the PLCs were determined with a differential scanning calorimeter (DSC; Seiko I&E SSC-5000). The thermodynamic properties of the PLCs are given in Table I.

The PLCs were dissolved in chloroform solutions of the azobenzene derivatives and cast onto glass plates (film thickness ~ 20 μm). The concentration of the azobenzene derivatives was 0.3 mol % on the basis of the mesogenic units. After drying at room temperture, the samples were washed with ethanol to remove the probe molecules from the surface of the films, heated under vacuum at 60 °C for several hours, and annealed at a temperature of $T/T_{NI} = 0.99$ so as to exhibit the liquid crystalline phase.

Dimethyl sulfoxide (DMSO; Spectrosol grade) was used as a solvent for reference experiments. DMSO was chosen as a reference medium because both DMAB and HMAB were very soluble in it, allowing the isomerization behavior to be explored at high temperatures.

Measurements of Photoisomerization and Thermal Isomerization. Sample films set in a thermostated block were irradiated at 370 nm with a Jasco CRM-FA irradiator. The change in the light intensity transmitted through the sample was monitored with a photodiode, and the data were collected with a microcomputer. The absorption spectra of the sample before and after irradiation were measured on a Hitachi UV320

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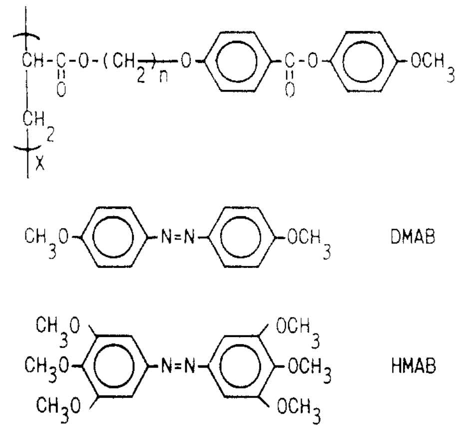

Figure 1. Structures of PLCs and azobenzene derivatives used in this study.

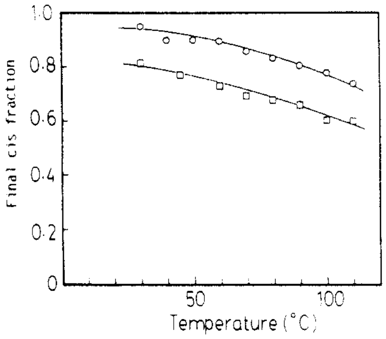

Figure 2. Temperature dependence of the final cis fraction of DMAB (○) and HMAB (□) in DMSO.

Table I
Thermodynamic Properties of PLCs Used in This Study

	M_n	M_w/M_n	phase transitn temp, °C	ΔH_{NI}, kJ/mol	ΔS_{NI}, J/(mol K)
PAPB3	4000	1.24	g 27 n 63 i	0.35	1.01
PAPB6	4300	1.26	g 18 s 83 n 104 i	0.76	2.02

spectrometer. The sample film was irradiated with monochromatic light until the trans–cis photoisomerization reached the photostationary state at a given temperature. The light was then cut off, and the film was moved to a thermostated block in the spectrometer and the absorbance of the azobenzene dopant at the absorption maximum (λ_{max} = 370 nm) was measured as a function of time after irradiation.

Reference experiments for the photoisomerization and the thermal back-reaction of azobenzene derivatives in a dilute solution were carried out in DMSO using a 1-mm quartz cell. The concentration of the azobenzene derivative in DMSO was adjusted so as to give nearly the same absorbance at λ_{max} as the sample films (ABS = 0.60).

Results and Discussion

Extent of Photoisomerization in the Photostationary State. The cis fraction, Y, was determined by

$$Y = \frac{1 - A/A_0}{1 - \epsilon_{cis}/\epsilon_{trans}} \qquad (1)$$

where A_0 is the initial absorbance at λ_{max}, A is the absorbance at λ_{max} after irradiation, and ϵ_{cis} and ϵ_{trans} are the molar absorption coefficients of the cis and trans isomers at λ_{max}, respectively. In this equation, we used $\epsilon_{cis}/\epsilon_{trans}$ = 0.056 for DMAB (λ_{max} = 369.5 nm) and 0.062 for HMAB (λ_{max} = 370.4 nm). The final cis fractions of DMAB and HMAB at the photostationary state in DMSO solutions are plotted against the irradiation temperature in Figure 2. DMAB and HMAB are characterized by the number of OCH_3 substituents on the phenyl rings of the azobenzene molecules; thus, with an increasing number of OCH_3 substituents, the diameter of the azobenzene increases. As seen in Figure 1, this change in shape should result in an increasing free volume required for the photoisomerization. The final cis fraction was somewhat different for DMAB and HMAB but showed a similar dependence on the irradiation temperature. The reduced cis fraction observed for HMAB may be explicable in terms of the sterically hindered structure of the cis isomer owing to the triple substitution on both phenyl rings. The thermal cis to trans isomerization is faster in HMAB than in DMAB. This is because the cis isomer of HMAB is sterically crowded and thermodynamically unstable compared to *cis*-DMAB, leading to the reduced cis fraction of HMAB in the photostationary state.

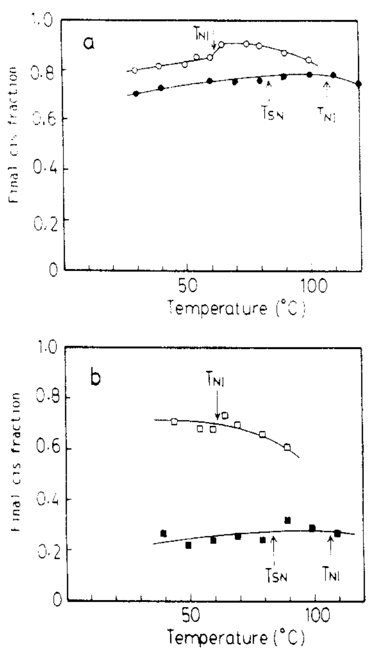

Figure 3. Temperature dependence of the final cis fraction of DMAB and HMAB in PLCs. (a) DMAB: (○) PAPB3; (●) PAPB6. (b) HMAB: (□) PAPB3; (■) PAPB6. Arrows in the figure indicate the phase transition temperature of the PLCs.

The final cis fractions of DMAB in the PLCs are shown in Figure 3a. The final cis fraction in PAPB3 was larger by about 10% than that in PAPB6 in the temperature range examined. On the other hand, when HMAB was isomerized in the PLCs, the final cis fraction was greatly suppressed in PAPB6 compared to that in PAPB3 (Figure 3 b). These results seem to indicate that the size of the free volume in PAPB3 and PAPB6 is different since DMAB and HMAB should require a different free volume for the isomerization. The number of sites where the free volume was large enough for DMAB to photoisomerize differed between PAPB3 and PAPB6 by only ~10%, while the number of sites in which HMAB can photoisomerize was found to be very different in PAPB3 and PAPB6. These results may be interpreted in terms of packing states of mesogens in each PLC. In PAPB6, which is smectic, the mesogens are closely packed, so that the size of the free volume is much reduced compared to that in the nematic liquid crystal, PAPB3.

We also wish to note the different temperature dependence of the final cis fraction in the PLCs from that in DMSO. With rising temperature, the final cis fraction decreased in DMSO because of the enhanced cis–trans thermal isomerization at high temperatures. Although a similar tendency was observed in the PLCs above T_{NI}, the final cis fraction increased with rising temperature below T_{NI} in both PLCs. This temperature dependence seems

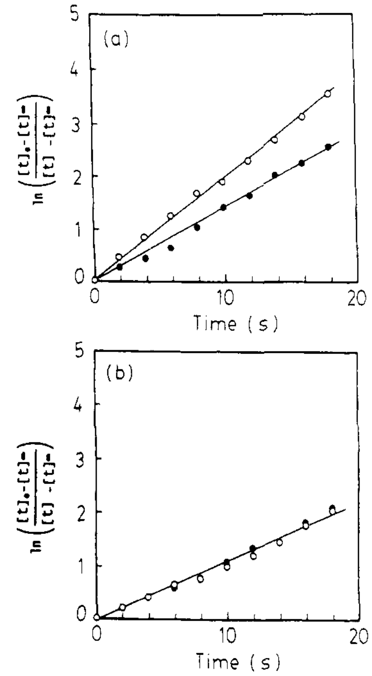

Figure 4. First-order plots for the trans → cis photoisomerization of DMAB and HMAB in PLCs. (a) DMAB in PAPB3 (○) and in PAPB6 (●); (b) HMAB in PAPB3 (○) and in PAPB6 (●). Irradiation temperature, 50 °C.

to suggest that the isotropic states of the PLCs are as *fluid* as DMSO but the LC states are *rigid* enough to suppress the trans–cis photoisomerization of both DMAB and HMAB. In fact, above T_{NI}, the final cis fraction of DMAB in PAPB3 and PAPB6 was nearly the same as in DMSO. In the LC state, fluidity becomes large with rising temperature, resulting in a higher cis fraction in the photostationary state.

Rate of Photoisomerization. When a *trans*-azobenzene with an initial concentration of $[t]_0$ is irradiated at λ_{max}, the rate of the change in the *trans*-azobenzene concentration, [t], as it approaches its equilibrium value, $[t]_\infty$, is given by[13b]

$$-d[t]/dt = A[t] - B[c] - K[c] \qquad (2)$$

where A and B are the rate constants, for the trans to cis and the cis to trans photoisomerizations, respectively, and K is the rate constant for thermal cis to trans isomerization. Here, [c] ($=[t]_0 - [t]$) is the concentration of the *cis*-azobenzene. When the photostationary state is attained, we obtain

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

and hence the change in [t] can be given by

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

Examples of first-order plots according to eq 4 for the trans–cis photoisomerization of DMAB in PLC matrices are shown in Figure 4a. The reaction was first order both in PAPB3 and in PAPB6 in the time region indicated but deviated from first order in the later stage of the reaction. It was observed that DMAB photoisomerized faster in PAPB3 than in PAPB6. However, when HMAB isomerized in PLC matrices, no significant difference was observed in the first-order plots in PAPB3 and PAPB6 (Figure 4b).

We define a time $T_{0.5}$ by $[t]_0 - [t]_{T_{0.5}} = ([t]_0 - [t]_\infty)/2$. The values of $T_{0.5}$ obtained for the photoisomerization of DMAB and HMAB in DMSO solutions are plotted against the irradiation temperature in Figure 5. As seen in this figure, $T_{0.5}$ was insensitive to the irradiation temperature. However, when DMAB was incorporated into the PLC matrices, $T_{0.5}$ was strongly affected by the irradiation temperture (Figure 6a). Values of $T_{0.5}$ were smaller in PAPB3 than in PAPB6 in the temperature range examined.

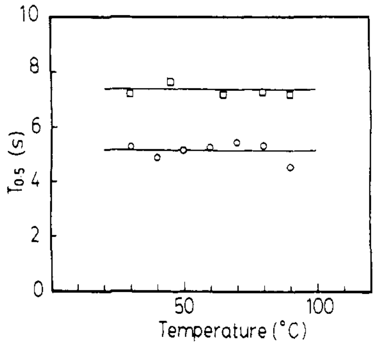

Figure 5. Temperature dependence of $T_{0.5}$ in the photoisomerization of DMAB (○) and HMAB (□) in DMSO.

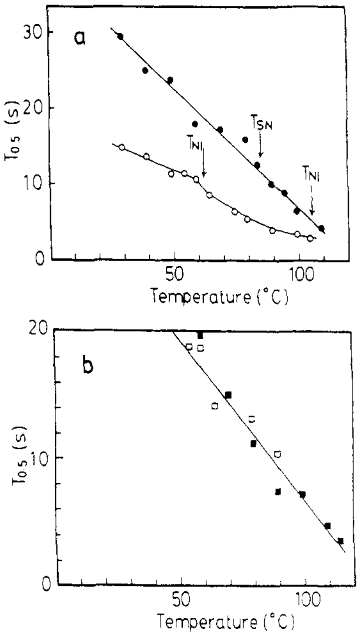

Figure 6. Temperature dependence of $T_{0.5}$ in the photoisomerization of DMAB and HMAB in PLCs. (a) DMAB: (○) PAPB3; (●) PAPB6. (b) HMAB: (□) PAPB3; (■) PAPB6.

This behavior can be interpreted in terms of mobility of polymer segments. At temperatures above τ_g, polymer segments are mobile and the size of the free volume fluctuates, leading to the progress of reaction at the site where initially the free volume was too small.[12] The photoisomerization reaction of DMAB in PLC matrices above T_g is considered to involve first sties where the free volume is sufficient and follow the fluctuation of free volumes activated by the rise in temperature. Therefore, the photoisomerization reaction in the PLC matrices above T_g was affected strongly by the irradiation temperature. The difference in the temperature dependence of the reaction rates in PAPB3 and PAPB6 indicates that the extent of thermal fluctuation of free volumes of the size in which DMAB can photoisomerize is different. However, for HMAB in PLC matrices, no difference was observed in $T_{0.5}$ between PAPB3 and PAPB6 (Figure 6b). Thus, the thermal fluctuation of free volumes of different size occurs differently in PAPB3 and PAPB6.

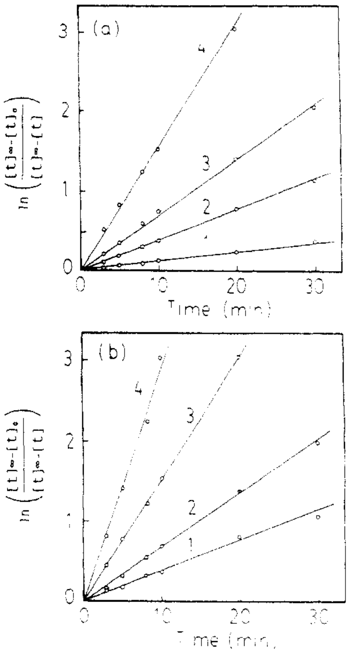

Figure 7. First-order plots for the thermal cis → trans isomerization of DMAB in PLCs. (a) DMAB in PAPB3: (1) 40; (2) 50; (3) 60; (4) 70 °C. (b) DMAB in PAPB6: (1) 50; (2) 60; (3) 70; (4) 80 °C.

Thermal Cis to Trans Isomerization. Thermal cis to trans isomerization was also examined. For the thermal cis to trans isomerization

$$\ln \frac{[t]^{H}_{\infty} - [t]^{H}_{0}}{[t]^{H}_{\infty} - [t]} = Kt \tag{5}$$

where $[t]^{H}_{0}$ is the concentration of the trans azobenzene after the photoirradiation and $[t]^{H}_{\infty}$ is the concentration of the trans form when the thermal isomerization ceased. First-order plots according to eq 5 for DMAB in the PLC matrices are shown in Figure 7. In the temperature range 40–80 °C, the profile was almost the same in PAPB3 and PAPB6, and an activation energy of 16.1 kcal/mol was obtained from the Arrhenius plots. Figure 8 shows the first-order plots for the thermal cis to trans isomerization of HMAB in the PLC matrices. The profile was again almost the same in PAPB3 and in PAPB6. Thus, although the trans to cis photoisomerization of DMAB proceeded at a different rate in PAPB3 and in PAPB6 (Figure 4), reflecting the difference in the nature of the phase structures of these PLCs, in the case of the cis to trans thermal isomerization, the reaction rate was the same in PAPB3 and PAPB6. The *trans*-azobenzene is a molecule with a rodlike shape, so it can be dispersed in LC phases without disturbing the mesogenic orientation of the LC phases. On the other hand, the *cis*-azobenzene is bent, and hence it disturbs the phase structure around the molecule. The fact that the thermal cis to trans isomerization of DMAB and HMAB had the same rate in PAPB3 and PAPB6 seems to indicate that the trans–cis photoisomerization of the azobenzene derivatives, preceding the thermal reaction, disorganized the LC phase structure around the probe molecules and produced sufficiently large free volumes for the thermal reaction of both azobenzene derivatives.

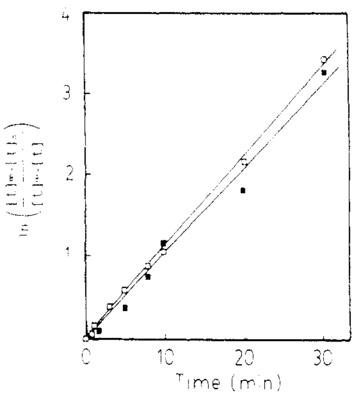

Figure 8. First-order plots for the thermal cis → trans isomerization of HMAB in PAPB3 (□) and PAPB6 (■) at 60 °C.

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