KINETIC MATRIX EFFECT ON PHOTOCHROMIC REACTIONS OF SPIROBENZOPYRAN DISPERSED IN OR COVALENTLY BOUND TO POLY(ALKYL METHACRYLATE) MATRICES

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Spirobenzopyran (SP) was dispersed (DP) in or covalently bound (CB) to poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(isopropyl methacrylate) (PiPMA) matrices. The extent of coloration due to formation of a merocyanine was smaller in CB than in DP matrices on irradiation of a single pulse of a Nd:YAG laser (355 nm). Photochemical isomerization from a merocyanine to a SP obeyed the first-order kinetics above T_g of the matrix polymer, but not below T_g . The isomerization below T_g was analyzed on the basis of the kinetic matrix effect, by assuming a temperature-independent fast isomerization and a temperature-dependent slow isomerization at lower T than 240 K, but only a temperature-dependent isomerization at higher T than 240 K. The matrix response function time constant, α , for the fast isomerization was larger in CB than in DP matrices. Arrhenius plots of α for the slow isomerization showed discontinuities at characteristic temperatures of matrix polymers.

1. Introduction

Photochromic molecules incorporated in solid materials can be used as a probe for elucidating microenvironments such as microviscosity, polarity, and size and distribution of local free volumes [1-5]. This is due to the high sensitivity of kinetic behaviors of photochromic reactions to microenvironments. Spiropyran (SP) is an appropriate compound for this purpose. A colorless SP isomerizes to a colored merocyanine by UV-light irradiation, while the merocyanine returns back to the SP thermally or by visible-light irradiation. Both isomerizations are accompanied with a large change in molecular

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structure owing to dissociation or recombination of a C-O pyran bond and rotation of a part of the molecule. Both isomerizations also generate a drastic change in polarity because of the zwitter-ion character of the merocyanine.

Thermal and photochemical decolorations of a merocyanine proceed much slower in polymer matrices than in solutions, and deviate from the first-order kinetics below the glass transition temperature, T_g , of the matrix polymer. Kryszewski et al. have proposed that the deviation from the first-order kinetics on thermal decoloration of a merocyanine in poly(alkyl methacrylate) matrices is resulted from a distribution of free volumes around the merocyanine [6]. Richart et al. have analyzed thermal decoloration of a merocyanine in a poly(methyl methacrylate) (PMMA) matrix as a dispersive process both by a stretched exponential equation and by an uncoupled parallel relaxation model in which a Gaussian distribution of activation energies is assumed [7-10]. Horie et al. have measured a photochemical decoloration of a merocyanine in a polycarbonate matrix in a wide range of temperature (80-453 K) and showed influence of molecular motions of the matrix on the decoloration process [11]. Saito et al. have showed that a photochemical coloration process affects the subsequent thermal decoloration process of spiroindolinonaphthoxazine dispersed in a PMMA matrix [12].

Most of kinetic studies have been accomplished using a SP dispersed in polymer matrices. Kinetics of the photochromic reaction reflects microenvironments of a SP dispersed in polymer matrices. When a SP is covalently bound to a matrix polymer, microenvironments of the SP around a polymer backbone or a polymer side chain have been estimated for acrylic and methacrylic polymers [13,14], polyphosphazenes [15], and polysiloxanes [16]. Little attention has been paid to the difference between SPs dispersed in polymer matrices and covalently bound to the matrices except for an early study by Smets et al. [17]. In the present study, we wish to describe the difference in microenvironments between SPs dispersed in polymer matrices and covalently bound to the matrices. A methyl methacrylate (MMA) carrying a SP unit on the ester group is copolymerized with MMA, ethyl methacrylate (EMA), and isopropyl methacrylate (iPMA), while the corresponding isobutyryl derivative of the MMA with a SP unit is dispersed in a poly(methyl methacrylate) (PMMA), a poly(ethyl methacrylate) (PEMA), and a poly(isopropyl methacrylate) (PiPMA) films as a model compound. Using these films, coloration by UV-light irradiation and the subsequent decoloration by visible-light irradiation were carried out in a wide range of temperature.

2. Experimental

Materials. A monomer carrying a spiropyran chromophore, 1,3,3-trimethyl-6'-nitro-8'-methacryloxymethylspirobenzopyran (SMA), was synthesized according to the literature [17]. MMA, EMA, and iPMA (Tokyo Kasei) were distilled under nitrogen at reduced pressures. Copolymers of SMA and MMA (CP(SMA-MMA)), SMA and EMA (CP(SMA-EMA)), and SMA and iPMA (CP(SMA-iPMA)) were synthesized by free-radical polymerization of monomer mixtures using AIBN initiator (1.0×10^{-3} mol %) at 70 °C for 10 hours and following 120 °C for 12 hours in a DMF solution (50 wt%) for CP(SMA-MMA) or in toluene solutions (50 wt%) for CP(SMA-EMA) and CP(SMA-iPMA). The copolymers were reprecipitated several times by pouring chloroform solutions into methanol for CP(SMA-MMA) and CP(SMA-EMA) or into diethylene glycol for CP(SMA-iPMA). The number average molecular weights (M_n) of the copolymers were 6.2×10^4 for CP(SMA-MMA),

1.0×10^5 for CP(SMA-EMA), and 3.7×10^4 for CP(SMA-iPMA) as determined by HPLC with GPC column, KF-802 and KF-80M (SHODEX). The compositions of the copolymers were determined by absorption spectra of chloroform solutions, and the mole fraction of SMA was 2×10^{-3} for all copolymers.

PMMA (Aldrich, $M_n = 1.0 \times 10^6$) was reprecipitated three times by pouring a DMF solution into methanol. PEMA was synthesized in the same manner as CP(SMA-EMA), and $M_n = 1.0 \times 10^5$. PiPMA was synthesized in the same manner as CP(SMA-iPMA), and $M_n = 7.6 \times 10^4$. A model compound of SMA was the corresponding isobutyryl derivative, 1,3,3-trimethyl-6'-nitro-8'-isobutyroxymethylspirobenzopyran (BSP), which was synthesized according to the literature [17]. A spiroopyran having no ester group, 1,3,3-trimethyl-6'-nitrospirobenzopyran (HSP) (Tokyo Kasei), was purified by recrystallization from hexane.

SP	R
SMA	$\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$
BSP	$\text{CH}_2\text{OCOCH}(\text{CH}_3)_2$
HSP	H

Film Preparation. Copolymer films and polymer films containing BSP or HSP were prepared on quartz plates by means of the cast method from chloroform solutions. The concentrations of BSP or HSP in PMMA, PEMA, and PiPMA films were 2×10^{-3} in the mole fractions. The films were $8 \mu\text{m}$ thick, and their absorbances at 355 nm were 0.1 ± 0.01 .

Measurements. Figure 1 shows set up of an experimental apparatus for measurements of photoisomerizations between a SP and a merocyanine. A film on a quartz plate was set in a cryostat and kept at a constant temperature ranging from 153 to 400 K. Coloration of the film was carried out by

Fig.1 Schematic diagram of apparatus for measurements of the transient absorption in photochromic reactions with laser pulse excitation.

irradiation of a single pulse at 355 nm from a pulsed Nd:YAG laser (SL-803, SPECTRON) at a fluence of 16 mJ cm^{-2} . Monitor light from a Xe lamp (150 W) was collimated with a lens, passed through a cut-off filter (UV-42, SIGMA KOKI), and passed perpendicularly through a film in the cryostat. The intensity of the monitor light at 576 nm was detected with a photomultiplier tube. Signals from the photomultiplier tube were converted to absorbances at 576 nm, A , with a log-amplifier using reference signals from a photodiode, and stored on a personal computer (PC-9801, NEC) through a storage scope (DSO 4074, GOULD) or a digital multimeter (TR6846, ADVANTEST). The temporal resolution of the absorption measurement was $100 \mu\text{s}$.

3. Results and Discussion

Coloration by UV Pulse Irradiation. Copolymer films and polymer films containing BSP or HSP turned to blue-violet by irradiation of a single pulse of the third harmonics of a Nd:YAG laser (355 nm). The extent of coloration due to formation of a merocyanine was estimated from the absorbance at 576 nm immediately after the laser pulse, A_0 . Plots of A_0 vs. temperature (T) were shown for BSP in PMMA, CP(SMA-MMA), and HSP in PMMA films (Fig.2). Values of A_0 were independent of T below T_g of PMMA (376 K) and increased rapidly with T above T_g . According to the free volume concept proposed by Kryszewski et al. [14], it is assumed that only SPs located at a site with the free volume, v_f , larger than an activation volume, v_a , can isomerize to the merocyanine. The temperature-independence of A_0 below T_g indicates that the accumulation of the site with $v_f \geq v_a$ does not change when the microbrownian motion of the polymer backbone is frozen in a longer time scale than $100 \mu\text{s}$.

Fig.2 Plots of A_0 vs. temperature for BSP in PMMA (O), CP(SMA-MMA) (●), and HSP in PMMA (▽) films.

Average values of A_0 below T_g , $(A_0)_{AV}$, were summarized for copolymer films and polymer films containing BSP or HSP in Table.1. The copolymer films showed smaller $(A_0)_{AV}$ than BSPs in the corresponding polymer films. This indicates that the concentration of the site with $v_f \geq v_a$ is larger for SPs covalently bound to the matrices than for SPs dispersed in the same matrices. The isomerization to a merocyanine occurs through rotational motions of both the indoline ring and the pyran ring for the dispersed SP, while it occurs only through a rotational motion of the indoline ring for the covalently

bound SP because the pyran ring is bound to the polymer backbone. The value of $(A_0)_{AV}$ increased consistently with size of the alkyl group bound to the polymer backbone for copolymer films, whereas the order of PMMA<PiPMA<PEMA was observed for $(A_0)_{AV}$ in BSP in the polymer films. HSP in PMMA film showed larger $(A_0)_{AV}$ than BSP in PMMA film. This is because HSP requires smaller v_s than BSP owing to smaller molecular size of HSP than BSP.

Table 1. The average values of A_0 , $(A_0)_{AV}$, below T_g

SP in polymer film	$(A_0)_{AV}$	Copolymer film	$(A_0)_{AV}$
BSP in PMMA	0.06	CP(SMA-MMA)	0.02
BSP in PEMA	0.19	CP(SMA-EMA)	0.03
BSP in PiPMA	0.10	CP(SMA-iPMA)	0.05
HSP in PMMA	0.17		

Kinetic Analysis of Photochemical Decoloration Process. Blue-violet colors due to a merocyanine generated in copolymer films and polymer films faded by irradiation of monitor light from a Xe lamp. This decoloration corresponds to photochemical isomerization from the merocyanine to the SP. Concentration of the merocyanine relative to the initial concentration, $[MC]_t/[MC]_0$, was calculated from A/A_0 . Photochemical decoloration of the film was analyzed by the first-order kinetics above T_g (337 K), but not below T_g (Fig.3). The similar results were observed in all copolymer films and polymer films containing BSP or HSP, while decoloration in copolymer films occurred faster than in the corresponding polymer films. The non-exponential relation below T_g clearly shows the existence of the kinetic matrix effect of polymer films, and that a part of the merocyanine is located at a site with $v_f < v_s$. The isomerization of the merocyanine is controlled by fluctuation in size of the local free volume. The phenomenological expression based on the concept of the dispersive reaction kinetics is applied for the isomerization kinetics,

Fig.3 First-order kinetic plots of photochemical decoloration for BSP in PEMA film at various temperatures.

$$\ln ([MC]_t/[MC]_0) = -\alpha t^\beta \quad (1)$$

or

$$\ln (\ln ([MC]_0/[MC]_t)) = \ln (\alpha) + \beta \ln (t), \quad (2)$$

where α is the matrix response function time constant and β is the dispersive parameter indicating the extent of deviation from the first-order kinetics. Figure 4 showed linear relations of the decoloration of a merocyanine to time according to eqn.(2) except for 253 and 183 K. Values of β were obtained from slopes of the linear lines, and plotted against T for copolymer films and polymer films containing BSP and HSP (Fig.5). The initial slope was taken as β at lower T . Values of β were scattered between 0.4 and 0.6 below T_g (376 K for PMMA, 337 K for PEMA, and 353 K for PiPMA), and increased rapidly to unity above T_g .

Fig.4 Plots of $\ln(\ln([MC]_0/[MC]_t))$ vs. $\ln(t)$ in photochemical decoloration of merocyanine for BSP in PEMA film according to eqn.(2) at various temperatures.

Fig.5 Plots of β vs. temperature for BSP in PMMA (○), BSP in PEMA (△), BSP in PiPMA (□), HSP in PMMA (▽), CP(SMA-MMA) (●), CP(SMA-EMA) (▲), and CP(SMA-iPMA) (■) films.

Since β was 0.5 in average, decoloration of the merocyanine was analyzed according to eqn.(1) with $\beta = 0.5$ for polymer films containing BSP (Fig.6) and copolymer films (Fig.7). Plots of $\ln ([MC]_t/[MC]_0)$ vs. $t^{0.5}$ showed linear lines at higher T , but not at lower T . The initial slopes of these lines were almost equivalent at lower T . Since the initial slopes were larger for copolymer films than for BSP in the corresponding polymer films, the merocyanine isomerizes faster in copolymer films than in the corresponding polymer films. The isomerization from the merocyanine to the SP below T_g was analyzed by assuming a temperature-independent fast isomerization and a temperature-dependent slow isomerization at lower T than 240 K, but only a temperature-dependent isomerization at higher T than

Fig.6 Plots of $\ln ([MC]_t/[MC]_0)$ vs. $t^{0.5}$ for BSP in PMMA, BSP in PEMA, and BSP in PPMA films.

Fig.7 Plots of $\ln ([MC]_t/[MC]_0)$ vs. $t^{0.5}$ for CP(SMA-MMA), CP(SMA-EMA), and CP(SMA-PPMA) films.

240 K. The experimental data were fitted to the following equation,

$$[MC]_t/[MC]_0 = F \exp(-\alpha_1 t^\beta) + (1-F) \exp(-\alpha_2 t^\beta) \quad (3)$$

where α_1 and α_2 are matrix response function time constants for the fast and the slow isomerization, respectively, and F is the fraction of the fast isomerization. The existence of two isomerizations may be explained by two kinds of merocyanine isomers, such as *cis*- and *trans*-isomers. However, no evidence was obtained for two isomers. The existence of two isomerizations is attributed to heterogeneous

Fig.8 Arrhenius plots of α_1 (○) and α_2 (□) for BSP in PMMA, BSP in PEMA, and BSP in PiPMA films.

Fig.9 Arrhenius plots of α_1 (○) and α_2 (□) for CP(SMA-MMA), CP(SMA-EMA), and CP(SMA-iPMA) films.

distribution of v_f [11]. At lower T than 240 K, F was approximately 0.7.

Arrhenius plots Arrhenius plots of α_1 and α_2 were shown for polymer films containing BSP (Fig.8) and for copolymer films (Fig.9). The plots of α_2 showed a manifest discontinuity at the β -transition temperature, T_β , above which molecular motions of the side chain ester groups occur. On the other hand, α_1 was temperature-independent. Values of α_1 for the copolymer films were larger than those for BSP in the corresponding polymer films. This was shown in Figs.6 and 7 in which the fast isomerization of the merocyanine for the copolymer films at lower T occurs faster than for BSP in the corresponding polymer films.

The plot for BSP in PMMA film showed an additional discontinuity at T_β' above T_β . Since the discontinuity at T_β' was observed only for BSP in PMMA film, T_β' is assumed to be related to an interaction between ester groups of BSP and PMMA side chains. When the ester group of the pyran ring interacts with the ester groups of PMMA side chains below T_β , a rotational motion of the pyran ring is restricted and the ring closure occurs only through a rotational motion of the indoline ring. When T increases above T_β' , the ring closure can occur through rotational motions of both the indoline ring and the pyran ring. This leads to decrease in the activation energy and results in discontinuity in the Arrhenius plot at T_β' . In copolymer films, on the other hand, the pyran ring is fixed to the polymer side chain and the ring closure occurs only through a rotational motion of the indoline ring. Therefore, T_β' was not observed in the copolymer films. The reason why T_β' was not observed for BSP in PEMA and PiPMA films is explained by steric hindrance of side chain alkyl groups against the interaction between the ester groups. This assumption is supported by the linear Arrhenius plot of α_2 above T_β for HSP with no ester group in PMMA film (Fig.10).

Fig.10 Arrhenius plots of α_1 (○) and α_2 (□) for HSP in PMMA film.

Values of T_β and T_β' in the Arrhenius plots of α_2 were summarized for polymer films containing BSP or HSP and copolymer films in Table.2. Values of T_β for the copolymer films were almost equal to those for the corresponding polymer films containing BSP. This indicates that effect of polymer matrix on the slow isomerization was similar in SPs dispersed in poly(alkyl methacrylate) matrices and

covalently bound to the matrices.

Table 2. T_g and T_g' in the Arrhenius plots of α_2 .

SP in polymer film	T_g/K	T_g'/K	Copolymer film	T_g/K
BSP in PMMA	183	315	CP(SMA-MMA)	208
BSP in PEMA	220	—	CP(SMA-EMA)	221
BSP in PiPMA	205	—	CP(SMA-iPMA)	205
HSP in PMMA	230	—		

4. Conclusion

Photochromic reactions of SP incorporated in poly(alkyl methacrylate) matrices were affected by molecular motions of the matrix polymer both for SPs dispersed in the matrices and covalently bound to the matrices. Fraction of SP located at the site at which SP can isomerize to a merocyanine by UV-light irradiation was larger in dispersed SP than in covalently bound SP. The kinetic matrix effect on photochemical isomerization from a merocyanine to SP was similar in dispersed SP and covalently bound SP. The interaction between ester groups of SP and PMMA side chains influenced on the isomerization in SP dispersed PMMA film but not in the corresponding copolymer film.

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