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Photochemical isomerization of azobenzene incorporated in poly(*N*,*N*-dimethyl-4-vinylphenethylamine-*block*-styrene) diblock copolymer by cross linkage

Kazunori Se*
Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910, Japan

and Masato Kijima† and Teruo Fujimoto
Department of Chemistry, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niigata 940-21, Japan

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Photochemical isomerization of *p,p*′-bis(chloromethyl) azobenzene (CAB) was investigated in poly(*N*,*N*-dimethyl-4-vinylphenethylamine-*block*-styrene) block copolymer [P(PTA-*b*-St)]. The P(PTA-*b*-St) was prepared by anionic living polymerization. Both ends of CAB were attached to amino groups of the PPTA in the P(PTA-*b*-St) by quaternization in order to permit cross-linked films. When the films were irradiated with u.v. light (300 nm $< \lambda_1 <$ 380 nm), CAB underwent photoisomerization from the *trans* to the *cis* form. The photoisomerization did not proceed in a first-order kinetics. Hence, irradiation time-dependence of the results was analysed by the Kohlrausch–Williams–Watts equation. The resultant values of parameter α, *trans* fraction at equilibrium (C_e) and a half-life period ($\tau_{1/2}$), remained constant from 15°C to 30°C, but discontinuously changed at approximately 30°C which is close to the glass transition temperature (T_g) of PPTA. Therefore, the films were first irradiated with u.v. light at 60°C for 2 h, resulting in a 28% content of *cis* form in CAB. Subsequently, when the films were irradiated with visible light (420 nm $< \lambda_2$) at 20°C for 2 h and 90°C for 2 h, the *cis* content of CAB changed to 21% and 0%, respectively. The retention and deletion of the *cis* form was controlled by an alternation of the thermal motion of PPTA above and below the T_g of PPTA in the P(PTA-*b*-St) block copolymer. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Photochromism is a reversible photochemical exchange in molecular structure that results in remarkable changes in absorption spectra[1]. Much attention has been devoted to investigating this phenomenon using reversible recording materials. When a photochromic compound is used as the reversible recording material, problems include sensitivity to photoirradiation, thermal stability, retention of records, and repetition of records[2]. Thermal stability is an important problem to overcome because reverse thermal reactions occur in most organic photochromic compounds.

Two approaches have been attempted in order to overcome this problem. One is the preparation of novel photochromic compounds with thermal stability. Heller *et al.*[3,4] and Irie *et al.*[5,6] synthesized fulgides and diarylethene derivatives, respectively for this purpose. Another approach is to suppress the reverse thermal reactions using polymer matrices[7–15]. Azobenzenes have frequently been investigated in such studies. Azobenzenes undergo photoisomerization from *trans* to *cis* form under u.v. irradiation. The *cis* form can return to the *trans* form thermally or photochemically.

In the present study, we investigated the effects of matrix polymers on the photochemical isomerization of an azobenzene derivative incorporated in poly(tertiary aminostyrenes). *p,p*′-Bis(chloromethyl)azobenzene (CAB) was prepared as a photochromic crosslinking agent for the poly(tertiary aminostyrenes)[16]. CAB was attached to the polymers by quaternization to form cross-linked films[16, 17]. Photochemical isomerization was suppressed by the cross-linked films below the glass transition temperature T_g, of the matrix polymers. However, photochemical isomerization could not be measured at temperatures above the T_g of the matrix polymers due to deformation of the films during the photochemical isomerization[16]. In order to suppress this deformation, CAB was incorporated into the monodispersed diblock copolymer to give the cross-linked film, poly(*N*,*N*-dimethyl-4-vinylphenethylamine-*block*-styrene) [P(PTA-*b*-St)]. The continuous phase of polystyrene (PSt) was

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* To whom correspondence should be addressed

† Present address: Polymer Research Laboratory, Idemitsu Petrochemical Co. Ltd., Ichihara, Chiba 299-01, Japan

intended to suppress the deformation of the films above the T_g of PPTA and below the T_g of PSt.

When films are used as the reversible recording material, the photochemical isomerization changes remarkably according to the external conditions. Photochemical isomerization rate from *trans* to *cis* form in CAB under photoirradiation with u.v. light is fast above the T_g of PPTA, and some of the *trans* form changes to the *cis* form (corresponding to the process of optical recording). The reaction rate of reverse thermal isomerization from *cis* to *trans* form in CAB is slow below this temperature, and some of the *cis* form remains despite photoirradiation with visible light (corresponding to the process of record retention). Finally, the photochemical isomerization rate from *cis* to *trans* in CAB is fast above this temperature, and all of the *cis* form returns to *trans* form (corresponding to deletion of the records). We attempted to control the photochemical isomerization of the CAB incorporated into the block copolymer by using the changes that are observed in the thermal motion of PPTA above and below the T_g of PPTA.

EXPERIMENTAL

Materials

p,p'-Bis(chloromethyl)azobenzene (CAB) was prepared according to the method described in a previous paper[16] using commercial *p*-nitrobenzyl alcohol as the starting material. *N,N*-Dimethyl-4-vinylphenethylamine (PTA) and cumyl potassium were also prepared as the monomer and initiator, respectively according to a previously described method[18]. Poly(*N,N*-dimethyl-4-vinylphenethylamine) (PPTA), which was prepared in a previous experiment[16], was used as a reference polymer [$M_n = 7.7 \times 10^4$, $M_w/M_n = 1.04$, determined by g.p.c. measurement with standard poly(styrene)s]. Poly(styrene) (PSt) was also used as a reference polymer for the matrix [standard poly(styrene): F-10, $M_n = 1.02 \times 10^5$, $M_w/M_n = 1.02$, Tosoh Co.].

Preparation of a diblock copolymer

Styrene (St) and *N,N*-dimethyl-4-vinylphenethylamine (PTA) for use as monomers and THF for use as a solvent were purified according to the conventional method for anionic living polymerization[18–20]. Preparation of the diblock copolymer was performed by sequential addition of the PTA and St to the polymerization solution. Polymerization was performed in a sealed glass apparatus at −78°C in THF under a pressure of 10^{-5} torr, following essentially the same procedures as described in previous studies[18–20].

Molecular characterization

All polymer samples were tested using gel permeation chromatography (Tosho Co., Model HLC-803, high resolution columns of GMH6 × 2) to estimate number-average molecular weights, M_n, and molecular weight distribution. Narrow distribution polystyrenes were used as the elution standard (standard polystyrenes, F-1, F-4, F-10, and F-40, Tosoh Co.). THF containing 2 v/v% of *N*-methylpyrrolidine was used as the carrier solvent in order to suppress adsorption of the polymers on the surface of the g.p.c. gels[18].

Preparation of cross-linked films

Films measuring 10–40 μm in thickness were cast from 2 w/v% THF solution of CAB and the polymer on cover glasses (18 mm × 18 mm) floating on mercury. The solvent was evaporated at 25°C for 2 days. After drying *in vacuo*, the films were annealed at 90°C for at least 10 h *in vacuo*[16].

Measurement of photochemical isomerization

Photochemical isomerization was investigated in the CAB incorporated in the polymers using a previously described method[16]. Photoirradiation of the films was performed using a 150 W xenon lamp (UXL-150D-O, Ushio Co.) in a lamp house (UI-501, Ushio Co.). The light passed through glass filters to produce u.v. light (IRA-25S and UV-D33S for $300\,\mathrm{nm} < \lambda_1 < 380\,\mathrm{nm}$, Toshiba Co.) and the visible light (IRA-25S and Y-44 for $420\,\mathrm{nm} < \lambda_2$, Toshiba Co.). In order to estimate the degree of photochemical isomerization, intensity of the transmitted light was measured at 320 nm using a monochromator (CT-10, Japan Spectroscopic Co.) and a photomultiplier (R374, Hamamatsu Co.). The film was set between a hand-made aluminous cell with a heater and a thermocouple. Temperature was monitored and controlled using a digital thermocontroller.

RESULTS AND DISCUSSION

*Preparation of poly(*N,N*-dimethyl-4-vinylphenethylamine-*block*-styrene)*

Table 1 shows the experimental conditions and results of the preparation of the poly(*N,N*-dimethyl-4-vinylphenethylamine-*block*-styrene) block copolymers [P(PTA-*b*-St)] from *N,N*-dimethyl-4-vinylphenethylamine (PTA) and styrene (St) by anionic copolymerization. Preparation of the diblock copolymers was performed by sequential addition of the two monomers. After the PTA was polymerized for 10 h, St was added to the polymerization solution. When the first monomer was added to the initiator solution, it instantly showed a characteristic red of the styryl anion. The red colour did not alter after the addition of the second monomer to the polymerization solution. The colour remained unchanged until polymerization was terminated by the

Table 1 Experimental conditions[a] and result for the preparation of poly(*N,N*-dimethyl-4-vinylphenethylamine-*block*-styrene) diblock copolymer

First monomer		Second monomer		Solvent						
PTA	Time	St	Time	THF	Initiator[b]	Yield	PSt cont.	$10^{-4}M_n$		
g	h	g	h	ml	10^{-4} mol	%	%	Calc[c]	Obs[d]	M_w/M_n
3.4	10	3.9	3.5	160	1.5_8	100	53	4.6	3.9	1.0_7

[a] Polymerization was carried out at −78°C under a pressure of 10^{-6} torr

[b] Cumyl potassium

[c] Calculated from the amounts of monomer and initiator

[d] Determined from g.p.c. measurements using standard polystyrenes

addition of methanol. The block copolymer was prepared in the 100% conversion.

The g.p.c. elution curve of the P(PTA-*b*-St) block copolymer showed a sharp peak. The number-average molecular weight, M_n, was 3.9×10^4 and the M_w/M_n value was 1.07 as determined from g.p.c. measurements with standard polystyrenes. The kinetic molecular weight, M_k, was 4.6×10^4, as calculated from the amounts of monomer and initiator. The value of M_n was somewhat smaller than that of M_k. The values of M_n of PPTA were also uniformly smaller than those of M_k[18].

A well-defined polymer must be used to prepare a film with a fine micro-phase separated structure. Therefore, a P(PTA-*b*-St) block copolymer was used for the photochemical isomerization. As shown in *Table 1*, the PSt content of the block copolymer was 53 w/w%. From the common morphological results of the block copolymers[21], the phases of PSt and PPTA were expected to form the continuous phases, such as with the lamella structure.

Preparation of the cross-linked films

Cross-linked films were prepared from a mixture of THF solutions of CAB and the diblock copolymer P(PTA-*b*-St) by evaporation of the solvent, as described in a previous study. Cross-linked films of PPTA were also prepared according to the same procedure. Polystyrene film containing CAB was also prepared by the solvent-cast method for use as a reference sample. CAB can be attached to the poly(tertiary aminostyrenes) by quaternization due to the chloromethyl groups at the two *para*-positions[16,17]. Most of the added CAB was found to cross-link with the polymers in the films based on the following findings[16].

(a) When *n*-butylbromide reacted with PPTA in methanol at 45°C for 6 h, the degree of quaternization of the PPTA was 95%. Hence, the experimental conditions of the solvent-cast method (2 days at 25°C for the solvent-cast and 10 h at 90°C for the annealing) permits the preparation of cross-linked films in a 100% conversion. (b) The cross-linked films were not soluble in any common solvents, but the films without cross-linkage were soluble in common solvents. (c) The glass transition temperature (T_g) of poly(*N*,*N*-dimethyl-4-vinylbenzylamine) (PBA) was 72°C, as determined by d.s.c. After evaporation for 2 days, T_g for the P[PBA(CAB)$_{9.8}$] shifted to the higher temperature side by 3°. After annealing at 90°C for 10 h, T_g shifted to the higher temperature side by an additional 1.5°. The T_g shifts correspond to the formation of the network structure. (d) Based on the swelling test of PBA with methanol in the range of 3–16, the effective network-concentration of P[BA(CAB)$_{1.5}$] was determined to be 3.6×10^{-5} mol cm^{-3}. The apparent effective network-concentration was 3.7×10^{-5} mol cm^{-3}, as determined from the quantities of CAB and PBA. These values are not significantly different.

When the films were prepared from the mixed solution of PPTA and PSt, they showed heterogeneous white turbidity, corresponding to a macro-phase separated structure. However, the films prepared from P(PTA-*b*-St) were transparent and homogeneous. Therefore, micro-phase separated structure were suspected to have been formed in these films[22].

Cross-linked films are designated as P[St(CAB)$_Y$], P[PTA(CAB)$_Y$], and P[(PTA-*b*-St)(CAB)$_Y$], which are prepared from PSt, PPTA, and P(PTA-*b*-St), respectively. The subscript Y refers to the mol% of the chloromethyl groups for added CAB to the tertiary amino groups of the polymer.

Photochemical isomerization from trans *to* cis *form*

Figure 1 shows the photochemical isomerization from *trans* to *cis* form for each film. The degree of photoisomerization is described as the ratio of A_t/A_0, where A_0 and A_t are the initial absorbance and the absorbance after irradiation with u.v. light ($300\,\mathrm{nm} < \lambda_I < 380\,\mathrm{nm}$) for time *t*, respectively. This ratio represents the fraction of *trans* which was not converted to *cis* form in CAB. CAB was isomerized in approximately 65% at 20°C for 15 min in the case of CAB dispersed in PSt, forming non-cross-linked film. When CAB was incorporated in the film of P[PTA(CAB)$_{1.3}$], it was isomerized in approximately 15% at 20°C for 30 min. The gap between these values indicates that the thermal freedom of CAB was suppressed by the cross-linked polymers.

At temperatures above T_g, the cross-linked film of P[PTA(CAB)$_{1.3}$] is in a rubbery state. CAB in a rubbery state is thought to be capable of smooth isomerization by irradiation, in contrast with that in a glassy state. However, as shown in *Figure 1*, the *trans* fraction did not decrease with increasing time of the irradiation at 60°C. Furthermore, unexpected behaviour was observed: the *trans* fractions of CAB appeared to increase with increasing time of irradiation with u.v. light. This behaviour may be attributable to deformation of the film due to conformational changes in the cross-linked chains. The process should be utilized to induce photostimulated mechanical motions such as bending, twisting, and expansion.

In order to suppress the deformation of the films above the T_g of PPTA, P(PTA-*b*-PSt) block copolymer was prepared. The continuous phase of PSt in the block

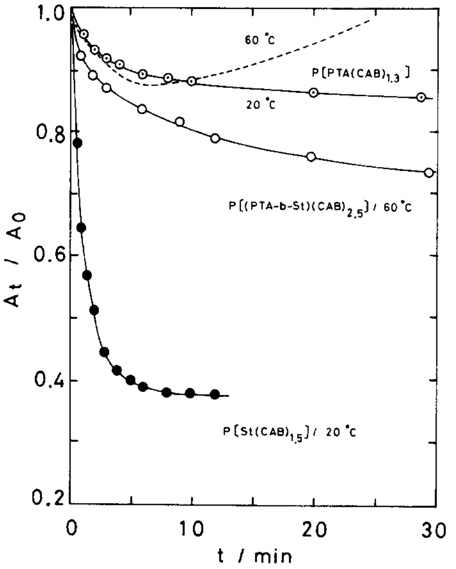

Figure 1 Photochemical isomerization of CAB from *trans* to *cis* form at a fixed temperature in the following films: P[(PTA-*b*-St)(CAB)$_{2.5}$] at 60°C (○), P[PTA(CAB)$_{1.3}$] at 20°C (⊙), P[PTA(CAB)$_{1.3}$] at 60°C (- - - - -) and P[St(CAB)$_{1.5}$] at 20°C (●). Absorbance (A_t) was detected at 320 nm after irradiation with ultraviolet light ($300\,\mathrm{nm} < \lambda_I < 380\,\mathrm{nm}$) for time, *t*, which is plotted as an axis of the abscissa on the figure. The value of A_t/A_0 represents the fraction of *trans* form which was not converted to *cis* form in CAB

copolymer was expected to suppress the deformation of the film under irradiation above the T_g of PPTA. When CAB was incorporated in the film of P[(PTA-*b*-St)(CAB)$_{2.5}$], CAB was isomerized in approximately 15% at 20°C for 30 min. The conversion was probably the same as that of P[PTA(CAB)$_{1.3}$], suggesting that CAB is incorporated in the PPTA phase in P[(PTA-*b*-St)(CAB)$_{2.5}$] by cross-linkage in a similar manner as in P[PTA(CAB)$_{1.3}$]. As shown in *Figure 1*, we succeeded in measuring the photoisomerization of CAB in the block copolymer at 60°C, which is a higher temperature than the T_g of PPTA.

Analysis of kinetics of photochemical isomerization from trans *to* cis *form*

As shown in *Figure 2*, a plot of $-\ln[(C_t - C_e)/(C_0 - C_e)]$ vs. t for each film was not linear within most of the range of t[23], where C_0, C_t, and C_e are *trans* fractions at initial state ($t = 0$), time t, and equilibrium state ($t = ?$), respectively. The *cis* fraction of CAB in equilibrium state, $(C_0 - C_e)$, was determined from the intercept of a plot of C_t vs. $1/t$. The kinetics of photochemical isomerization from *trans* to *cis* form of CAB was found not to proceed in a first-order kinetics in the films. Such deviation from the first-order plots has been discussed on the basis of the distribution of free volume[11–13]. That is to say, there is a distribution of isomerization rates in the glassy state. The different isomerization rates of CAB are thought to correspond to the molecular motions of CAB in sufficient and/or insufficient free volume[15,24,25].

The departures from the first-order kinetics in polymer matrices have been analysed quantitatively by Saito *et al.*[26] and Tomioka *et al.*[27] using a phenomenological procedure based on the Kohlrausch–Williams–Watts (KWW) equation[28,29]. A time-dependent reaction rate constant, k_t can be defined as

$$-\mathrm{d}\ \ln\left[(C_t - C_e)/(C_0 - C_e)\right]/\mathrm{d}t = k_t \qquad (1)$$

By using KWW equation[28,29], k_t can be expressed as

$$k_t = \kappa t^{\alpha - 1} \qquad (2)$$

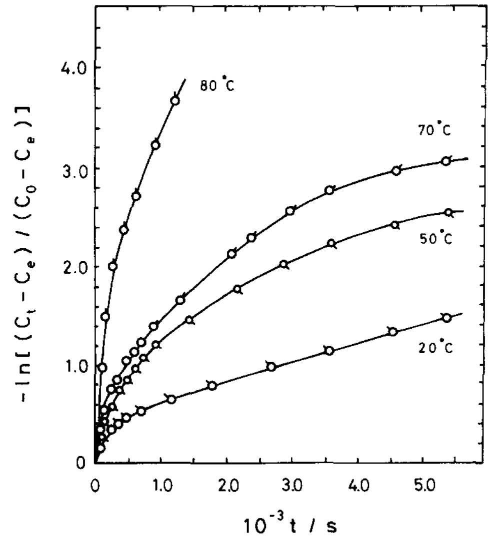

Figure 2 Typical plots of $-\ln[(C_t - C_e)/(C_0 - C_e)]$ vs. t for the photochemical isomerization of CAB from *trans* to *cis* form in the following films: P[St(CAB)$_{0.59}$] at 20°C (ɒ), P[(PTA-*b*-St)(CAB)$_{2.85}$] at 50°C (Q) and 70°C (σ), and P[(PTA-*b*-St)(CAB)$_{2.74}$] at 80°C (ó)

Substituting the above expression for k_t in equation (1) and the subsequent integration of equation (1) yields,

$$-\ln\left[(C_t - C_e)/(C_0 - C_e)\right] = (\kappa/\alpha)t^{\alpha} \qquad (3)$$

When a parameter α takes unity, k_t become κ corresponding to an inherent reaction rate constant and the resultant equations (1) and (3) become an equation of the first-order kinetics. Thus the parameter α concerns with the deviation of reaction kinetics from the first order reactions. The values of k_t could be determined from equation (1), and the following equation concerning k_t was derived from equation (2):

$$\log k_t = (\alpha - 1)\log t + \log\kappa \qquad (4)$$

As shown in *Figure 3*, a plot of log k_t vs. log t for each film gave a straight line. The parameter α was determined from the slopes of the lines. *Figure 4* showed the relationship between the thus-obtained parameter α and temperature, at which the photochemical isomerization from *trans* to *cis* form of CAB proceeded in the polymer matrices. The α values were

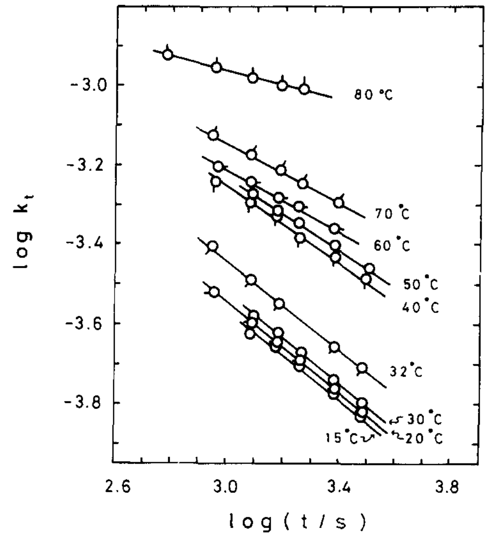

Figure 3 Plots of log k_t vs. log t for each P[(PTA-*b*-St)(CAB)$_Y$] film which was measured at a fixed temperature: Y = 0.82 at 15°C (○); Y = 0.59 at 20°C (ɒ); Y = 2.74 at 30°C (-o), 32°C (ρ), and 80°C (ó); Y = 2.85 at 40°C (ϙ), 50°C (Q), 60°C (o-), and 70°C (σ). Analysis was carried out using equation (3)

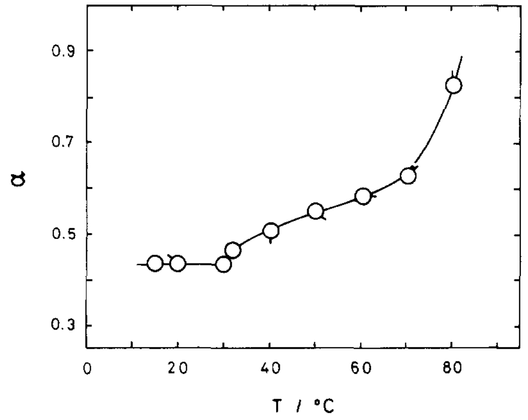

Figure 4 A relationship between the parameter α and temperature, at which the photochemical isomerization from *trans* to *cis* form of CAB proceeded in the P[(PTA-*b*-St)(CAB)$_Y$] polymer matrices. The characteristics of samples for each symbol in the figure are the same as those described in the figure caption of *Figure 3*

small below 30°C and increased with increasing temperature above 30°C and finally took a value close to 0.9 above approximately 80°C. The resultant temperature dependence of the α values is the same as those of spirooxazine in poly(*n*-butyl methacrylate) reported by Saito *et al.*[26] and of spyropyrans in poly(methyl methacrylate) reported by Tominaga *et al.*[27]. Namely, segmental motions of matrix polymers affect the molecular environment around CAB. Thus, the parameter α increased and progressively reached to unity with increasing temperature.

As shown in *Figure 3*, the k_t values, although depend on t, increased with increasing temperature. Because the treatment of absolute reaction rate constants in non-first order reaction system is difficult, further details of discussion of k_t and κ were not conducted in the present paper.

Particular attention should be paid to C_e and a half-life period, $\tau_{1/2}$[27] of the photochemical isomerization from *trans* to *cis* form of CAB. *Figure 5* shows the temperature dependence of C_e of P[St(CAB)$_Y$], P[PTA(CAB)$_Y$], and P[(PTA-*b*-St)(CAB)$_Y$]. The value of C_e of P[St(CAB)$_Y$] probably remained constant in the temperature range from 15°C to 60°C, but increased rapidly at temperatures above 60°C. A similar temperature dependence of C_e was reported in a study on azobenzene dispersed in polycarbonates[24,25]. In contrast, the C_e value of P[PTA(CAB)$_Y$] was constant in the temperature range from 15°C to 30°C. Above approximately 30°C, which is probably the glass transition temperature of PPTA, measurement of photoisomerization could not be performed due to deformation of the film. The value of C_e of P[(PTA-*b*-St)(CAB)$_Y$] was also constant in the range from 15°C to 30°C, and decreased rapidly at 30°C. Above 30°C, C_e showed the same temperature dependence of that of P[St(CAB)$_Y$]. This phenomenon reflects the thermal freedom of CAB, which increases rapidly at the glass transition temperature of PPTA[16].

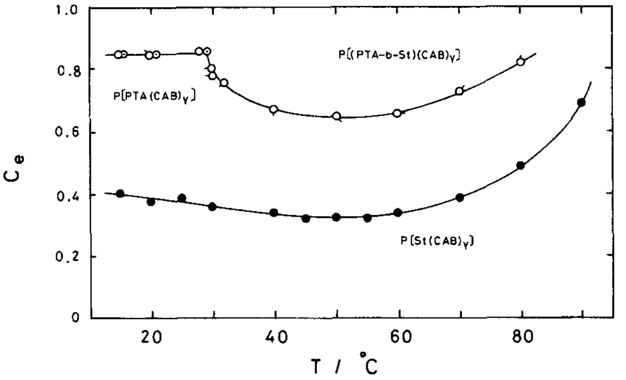

Figure 5 Temperature dependence of the *trans* fraction at equilibrium state (C_e) of P[St(CAB)$_Y$] film (●), P[PTA(CAB)$_Y$] film (⊙), and P[(PTA-*b*-St)(CAB)$_Y$] film (○). The C_e values was determined from the intercept of a plot of C_t vs. $1/t$ at a fixed temperature which is plotted as an axis of the abscissa on the figure

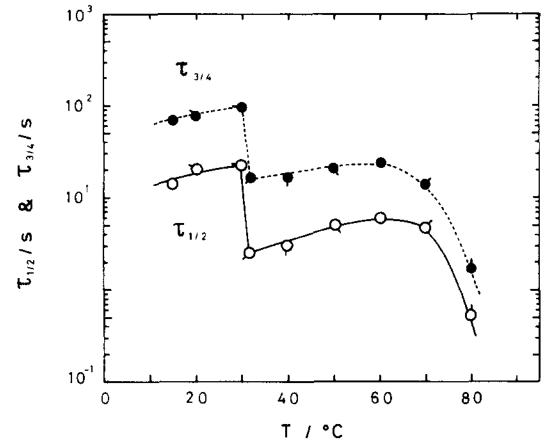

Figure 6 Temperature dependence of a half-life period, $\tau_{1/2}$ (○) and a three fourths-life period, $\tau_{3/4}$ (●) of photochemical isomerization of CAB from *trans* to *cis* form. The characteristics of samples for each symbol in the figure are the same as those described in the figure caption of *Figure 3*

A half-life period, $\tau_{1/2}$[27] and a three fourths-life period, $\tau_{3/4}$ were determined from the times at which the $(C_t - C_e)/(C_0 - C_e)$ values attained to 50% and 75%, respectively. *Figure 6* shows the resultant temperature dependence of $\tau_{1/2}$ and $\tau_{3/4}$ of P[(PTA-*b*-St)(CAB)$_Y$]. Both values of $\tau_{1/2}$ and $\tau_{3/4}$ increased slightly with increasing temperature in the range from 15°C to 30°C. However, both values decreased discontinuously at approximately 30°C. The thermal freedom of CAB should increase rapidly at the glass transition temperature of PPTA, as with the temperature dependence of C_e. Above approximately 30°C, both values of $\tau_{1/2}$ and $\tau_{3/4}$ increased slightly with temperature, and finally decreased markedly above approximately 70°C.

In conclusion, the temperature dependence of $\tau_{1/2}$ and $\tau_{3/4}$ was found to be the same behaviour as those of parameter α and C_e. Photochemical isomerization from *trans* to *cis* form of CAB was suppressed by the crosslinked films below T_g of PPTA matrix polymer and the suppression was discontinuously removed from CAB at T_g of PPTA with increasing temperature. The photochemical isomerization of CAB proceeded in a homogeneous molecular environment above T_g and specially in a completely homogeneous state like a liquid above approximately 70°C.

Photochemical isomerization from cis *to* trans *form*

When the films are used as reversible optical recording materials, the process of optical recording, the process of retention of the records, and the process of deletion of the records must be considered carefully. The process of optical recording corresponds to photochemical isomerization from *trans* to *cis* form of CAB, that was described in the previous paragraph. The other processes are related to the photochemical isomerization from *cis* to *trans* form of CAB.

The process of the photoisomerization from *cis* to *trans* form was investigated by irradiation with visible light (420 nm $< \lambda_2$) and by storing the sample in darkness below the T_g of PPTA. As shown in *Figure 5*, two films of P[(PTA-*b*-St)(CAB)$_{1.5}$] were first irradiated with u.v. light at 60°C and 20°C for 2 h. After 2 h under the irradiation with visible light, the *trans* fractions of P[(PTA-*b*-St)(CAB)$_{1.5}$] became 72% at 60°C and 86% at 20°. Next, these two films were irradiated with visible light at 20°C (below the T_g of PPTA). After 3 h under the irradiation with visible light, the *trans* fractions of the former film irradiated with u.v. light at 60°C for 2 h varied from 72% to 82%, and the *trans* fractions of the latter film irradiated with u.v. light at 20°C for 2 h varied from 86% to 92%. In the former case, 18% of the *cis* fraction remained in P[(PTA-*b*-St)(CAB)$_{1.5}$] under visible light, whereas 8% remained in the latter case. *Trans*

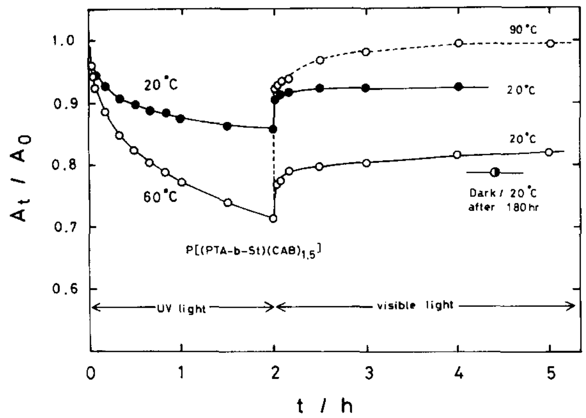

Figure 7 Photochemical isomerization of CAB from *trans* to *cis* form and from *cis* to *trans* form of P[(PTA-b-St)(CAB)$_{1.5}$] film. The film was first irradiated with ultraviolet light at 60°C (○) and 20°C (●) for 2 h. Next, these films were irradiated with visible light at 20°C. The result of a reverse thermal reaction is also described by storing the film in darkness at 20°C for 180 h (◑). The film after irradiation with ultraviolet light at 60°C for 2 h was finally irradiated with visible light at 90°C (- -○- -)

fraction of the former film also varied from 72% to 79% after storing the film in darkness at room temperature for 180 h. Hence, approximately 20% of the CAB remained in the *cis* form. Retention of the *cis* form was achieved using polymer chains of PPTA below the T_g.

The deletion of the *cis* form was also studied by the measurement of the photoisomerization of *cis* to *trans* form of P[(PTA-b-St)(CAB)$_{1.5}$] after irradiation with visible light at 90°C. As shown in *Figure 5*, when the film was irradiated with visible light at 90°C (above the T_g of PPTA) for 3 h after irradiation with u.v. light at 60°C for 2 h, the *trans* fraction returned from approximately 72% to 100%. The *cis* form can be deleted completely by irradiation with visible light at 90°C, although 18% of the *cis* form remained at 20°C. Therefore, the retention and/or deletion of the *cis* form was controlled by alternation of the thermal motion of PPTA below and above the T_g of PPTA of the P(PTA-b-St) block copolymer.

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