Photochemical isomerization of *p,p'*-bis(chloromethyl)azobenzene incorporated in poly(tertiary aminostyrene)s by cross linkage

Masato Kijima[*], Kazunori Se[†] and Teruo Fujimoto
Department of Chemistry, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niiagata 940-21, Japan
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A photochromic *p,p'*-bis(chloromethyl)azobenzene (CAB) was prepared as a crosslinking agent. Three poly(tertiary aminostyrene)s prepared via living anionic polymerization were used as reactive polymers: poly(*N,N*-dimethyl-4-vinylphenylamine) (PPA), poly(*N,N*-dimethyl-4-vinylbenzylamine) (PBA) and poly((*N,N*-dimethyl-4-vinylphenethylamine) (PPTA). Films were cast from tetrahydrofuran solution of CAB and the polymers. The crosslinking reaction proceeded during the evaporation of solvent and the annealing of the films at 90°C for >10 h. The result of the swelling test led us to conclude that all the CAB added to the polymer was consumed in the crosslinking reaction. Photochemical isomerization was studied for CAB incorporated in three polymers by cross linkage. The conversions for photochemical isomerization of CAB in three crosslinked films were 35–10% in the stationary state under u.v. irradiation below the glass transition temperature. This indicated that the thermal freedom of CAB was depressed by crosslinking in the glassy state.

(Keywords: photochromism; photochemical isomerization; poly(tertiary aminostyrene)s; *p,p'*-bis(chloromethyl)azobenzene; cross linkage; Menschutkin reaction; glass transition temperature; swelling test)

INTRODUCTION

Photochromism is a reversible change of colours (absorption spectra) in compounds by photoirradiation. The phenomenon is defined in the following way:

$$A \underset{\lambda_2 \text{ or } \Delta}{\overset{\lambda_1}{\rightleftharpoons}} B$$

A photochromic compound A is isomerized to a metastable state B under photoirradiation with u.v. light. B can return to the initial state by photoirradiation with visible light and/or by maintaining the sample in the dark even at room temperature.

A number of photochromic compounds have been studied to obtain colour changeable fibres, new display materials, recording materials, etc.[1]. In such cases, photochromic compounds are incorporated in matrix polymers. Many workers have studied the favourable effect of matrix polymers on isomerization[2–4]. In such studies photochromic compounds were introduced to polymers as additives, pendant groups and components of main chains. The isomerization rate was determined through first-order analysis. The results were quantitatively discussed using the free volume distribution[5–8]. We studied the isomerization of photochromic compounds incorporated in polymers by cross linkage. Azo compounds were used as photoisomerizable low molecular weight chromophores.

Azobenzenes, like spiropyranes, are among the most well-known photochromic compounds. Azobenzene undergoes isomerization from the *trans* to the *cis* form under u.v. irradiation, while the *cis* form reverts to the *trans* form either thermally or photochemically. Azobenzenes have some useful features: their structure is simple and photochemical isomerization can be repeated many times. *p,p'*-Bis(chloromethyl) azobenzene (CAB) was prepared in this study. CAB can react with amino groups by the Menschutkin reaction. Three poly(tertiary aminostyrene)s were used as reactive polymers: poly(*N,N*-dimethyl-4-vinylphenylamine) (PPA), poly(*N,N*-dimethyl-4-vinylbenzylamine) (PBA) and poly(*N,N*-dimethyl-4-vinylphenethylamine) (PPTA)[9]. The poly(tertiary aminostyrene)s react with various halides to form quaternary ammonium salts[10]. Hence, it is expected that CAB is incorporated in the polymers by cross linkage.

In this paper preparation and characterization of the crosslinked films are described, and then the photochemical isomerization of the films is discussed. *Figure 1* schematically shows the structural formula of the crosslinked films.

EXPERIMENTAL

Preparation of CAB

Commercial *p*-nitrobenzyl alcohol (10 g, 0.065 mol) dissolved in dry diethyl ether (350 ml) was added to a

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[*] To whom correspondence should be addressed. Present address: Polymer Research Laboratory, Idemitsu Petrochemical Co. Ltd, Anesaki-kaigan 1-1, Ichihara, Chiba 299-01, Japan

[†] Present address: Faculty of Engineering, Fukui University, Bunkyo, Fukui 910, Japan

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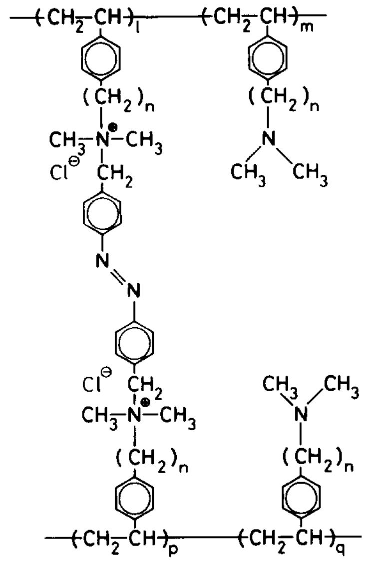

Figure 1 Structural formula of the crosslinked poly(tertiary aminostyrene)s with *p,p'*-bis(chloromethyl)azobenzene

suspension of lithium aluminium hydride (12 g, 0.316 mol) in dry diethyl ether (300 ml) in an ice-water bath[11]. After stirring for 30 min in the bath, the reaction mixture was refluxed with stirring for an additional 2.5 h. A mixture of water (50 ml) and methanol (250 ml) was added to the reaction mixture under ice cooling, and insoluble materials were removed by filtration. After removal of the solvent from the filtrate by evaporation, *p,p'*-bis(hydroxymethyl)azobenzene (3.0 g, 38% yield) was obtained from the residue by recrystallization with methanol: m.p.. 200–204°C; orange, needle-shaped crystals; i.r., 3300 cm^{-1} (ν, O–H), 1020 cm^{-1} (ν, C–O), disappearance of the characteristic band of the nitro group (i.r. spectrophotometer model 260-10, Hitachi Ltd).

To a solution of the product (2.0 g, 8.25 mmol) in tetrahydrofuran (THF) (150 ml) and pyridine (1.4 ml, 17.3 mmol), fresh thionyl chloride (1.4 ml, 19.3 mmol) was added. After stirring for 1 h at room temperature, the reaction mixture was refluxed with stirring for 1 h. Under ice cooling, water (50 ml) was added to the reaction mixture. THF was removed from the reaction mixture by evaporation and the product was extracted from the residue with diethyl ether. Then the product, CAB (1.3 g, 56% yield), was obtained by recrystallization with methanol; m.p. 163–165°C; orange, needle-shaped crystals; i.r., 1260 cm^{-1} (ω, $-CH_2Cl$), disappearance of the i.r. band of the hydroxy group; ^1H n.m.r., 4.66 ppm (s, 4H, $-CH_2Cl$), 7.74 ppm (m, 8H, $-C_6H_8-$) (^1H n.m.r. spectrometer JNM-PMX60, Jeol Ltd, 60 MHz, in $CDCl_3$, TMS standard).

Preparation of polymers

Three monomers were prepared and purified according to previous procedures[9,10]: *N,N*-dimethyl-4-vinylphenylamine, *N,N*-dimethyl-4-vinylbenzylamine and *N,N*-dimethyl-4-vinylphenethylamine. Poly(tertiary aminostyrene)s were prepared via living anionic polymerization. Polymerizations were carried out in a sealed glass apparatus under a pressure of 1.33×10^{-4} Pa at −78°C in THF using essentially the same procedures as those described elsewhere[9]. Cumyl caesium was used as an initiator. Polystyrene (PS; F-10, $M_n = 10.2 \times 10^4$, $M_w/M_n = 1.02$. Tosoh Co.) was used as a reference sample for photochemical isomerization.

Preparation of crosslinked films

Films (10–40 μm thick) were cast from ~2 w/v% THF solution of CAB and the polymers on mercury or on cover glasses floating on mercury. A typical crosslinked film was prepared as follows: 100 mg of PBA and 1 mg of CAB were dissolved in 5 ml of THF. The solution was poured on to six cover glasses (18 mm × 18 mm) floating on mercury in a dish (70 mm in diameter). The solvent was evaporated slowly for 2 days at 25°C. After drying *in vacuo*, the films were annealed at 90°C for >10 h *in vacuo*.

Characterization of the polymers

All the polymer samples were tested on a gel permeation chromatograph (model HLC-803, with high resolution columns G-4000 and GMH6, Tosoh Co.) to estimate the number-average molecular weights, M_n, and the values of M_w/M_n. Narrow distribution PSs (F-1, F-4, F-10 and F-40, Tosoh Co.) were used as the elution standards. The carrier solvent was THF containing *N*-methylpyrrolidine (2 v/v%) to avoid adsorption of the polymers onto the surface of the g.p.c. gels[9].

The glass transition temperatures (T_gs) of the samples were measured by d.s.c. (model DSC-20, Seiko Instruments and Electronics Ltd) with a heating rate of 10°C min^{-1}.

The values of M_n, M_w/M_n and T_g of the polymers are shown in *Table 1*.

Swelling tests

Equilibrium swelling tests were performed at 25°C with THF as a swelling solvent. The films were submerged in the swelling solvent for 6 h. The swelling was achieved in an equilibrium state within 6 h. It was confirmed that the swollen gels did not increase in weight even after 36 h. The volumes of the dry films were determined on the assumption that the polymer density (ρ_p) was 1.01 g cm^{-3} for PBA, independent of the degree of cross linkage. The polymer density was determined by a flotation method.

Measurement of photochemical isomerization

Photoirradiation of the films was carried out with a 150 W xenon lamp (UXL-150D-O, Ushio Ltd) in a lamp house (UI-501, Ushio Ltd). The light was filtered with coloured glass filters (IRA-25S and UV-D33S for $300\,nm < \lambda_1 < 380\,nm$; IRA-25S and Y-44 for

Table 1 Characteristics of the samples used in this study

Polymer	M_n[a] ($\times 10^{-4}$)	M_w/M_n[a]	T_g (°C)[b]
PPA	4.9	1.08	136
PBA	11.0	1.05	
PBA	3.5	1.09	72
PPTA	7.7	1.04	42
PPTA	3.0	1.08	
PS	10.0	1.06	100[c]

[a] Determined from g.p.c. measurements
[b] Determined from d.s.c. measurements
[c] From reference 18

420 nm < λ_2, Toshiba Ltd). The transmission light was followed at 320 nm through a monochromator (CT-10, Japan Spectroscopic Co. Ltd) with a photomultiplier (R374, Hamamatsu Ltd).

U.v. spectra were also measured with a spectrophotometer (model 200-10, Hitachi Ltd).

RESULTS AND DISCUSSION

Preparation of crosslinked films

Quaternary ammonium salts are formed by the Menschutkin reaction of amino groups with alkyl halides. We studied the quaternization reactivity of three poly(tertiary aminostyrene)s, PPA, PBA and PPTA, with n-butyl bromide in *N*,*N*-dimethylformamide[10]. PBA and PPTA were quaternized with ~100% conversion in 4–6 h at 60°C. PPA was also quaternized with >85% conversion in 6 h at 120°C or 12 h at 100°C. We could control the degree of the quaternization of the three poly(tertiary aminostyrene)s from 0 to 100% by using the appropriate reaction time and temperature, even at room temperature[10]. Hence, crosslinked films were prepared by evaporation of the solvent from a mixed solution of the polymer and CAB for 2 days at 25°C. After drying the films *in vacuo*, they were annealed at 90°C for >10 h.

Three crosslinked films, designated P[PA(CAB)$_Y$], P[BA(CAB)$_Y$] and P[PTA(CAB)$_Y$], respectively, where Y is the molar percentage of chloromethyl groups of CAB to *N*,*N*-dimethylamino groups of the polymers. PS film where CAB is dispersed molecularly is designated as P[S(CAB)$_Y$], where Y is the molar percentage of chloromethyl groups of CAB to styrene units of the polymer.

In order to confirm the formation of cross linkage, we carried out d.s.c. measurements and swelling tests on the films. The d.s.c. thermograms of the three poly(tertiary aminostyrene)s showed endothermic steps in the T_gs. *Figure 2* shows the thermograms of P[BA(CAB)$_{9.8}$] films. The value of T_g for PBA was 71.6°C and the value for P[BA(CAB)$_{9.8}$] was ~3°C higher than that of PBA. The value of T_g for P[BA(CAB)$_{9.8}$] also increased with annealing at 90°C. After 10 h, however, T_g became constant. The value was ~1.6°C higher than that of P[BA(CAB)$_{9.8}$] without annealing. The film became insoluble in common solvents such as THF, methanol, etc.[10]. Taking into account the results of quaternization reactivity of poly(tertiary aminostyrene)s with alkyl halide in solution, the cross linkage should be formed during the preparation of the films, and completely finished after annealing for 10 h. Hence, the samples of crosslinked films were annealed at 90°C for 10 h before the photochemical isomerization tests.

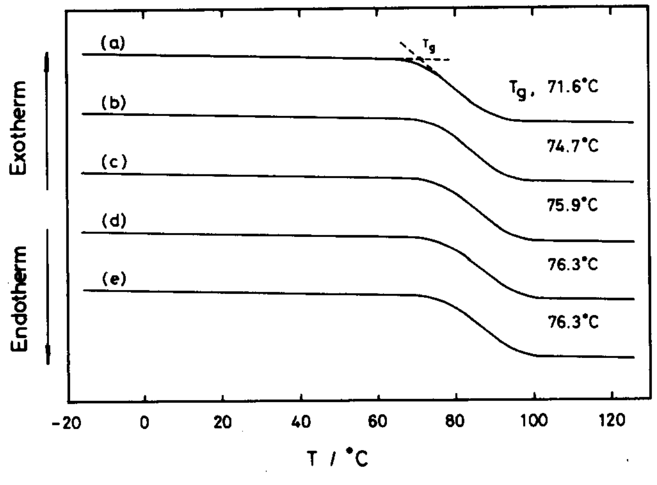

Figure 2 D.s.c. thermograms of (a) PBA and (b) P[BA(CAB)$_{9.8}$]. The specimens were annealed for (c) 4, (d) 10 and (e) 24 h at 90°C. The measurements were carried out with a heating rate of 10°C min^{-1}

Table 2 The degree of swelling in equilibrium with THF at 25°C for P[BA(CAB)$_Y$] films

Polymer	M_n[a] ($\times 10^{-4}$)	(%)[b]	Q_r	ν'_e ($\times 10^5$) (mol cm^{-3})[c]	ν_e ($\times 10^5$) (mol cm^{-3})[d] Small	Hoy
PBA	3.5	0.6	16.0	0.6	1.9	2.1
PBA	3.5	1.0	11.0	3.6	3.7	4.2
PBA	3.5	1.5	7.5	6.6	6.9	7.8
PBA	3.5	1.7	6.0	7.8	10.0	11.0
PBA	11.0	2.2	4.4	13.0	17.0	19.0
PBA	11.0	4.0	3.1	24.0	30.0	33.0

[a] Determined from g.p.c. measurements

[b] The ratio of chloromethyl groups of CAB to tertiary amino groups in the polymer

[c] Apparent effective network concentration calculated from the amount of polymer and CAB in the films

[d] Effective network concentrations calculated from the polymer–solvent interaction parameter (μ) estimated by Small's method ($\mu = 0.34$) and Hoy's method ($\mu = 0.32$), respectively

Swelling tests of crosslinked films

PBA without cross linkage was soluble in alcohols such as methanol, ethanol and n-propanol; in polar solvents such as THF, diethyl ether and chloroform; and in non-polar solvents such as n-hexane and benzene at room temperature. PBA was not soluble in DMF at room temperature but at higher temperature. THF was used as the swelling solvent because the crosslinked PBA was swollen enough with THF at 25°C. The results of the swelling tests are shown in *Table 2*. The degree of swelling (Q_r) decreased with increasing amount of CAB.

The apparent effective network concentration (ν'_e) was calculated from the amounts of CAB and polymer on the assumption that all the CAB reacted with the polymer (*Table 2*).

Next, the effective network concentration ν_e was estimated from the swelling of crosslinked polymer. A crosslinked polymer is insoluble in any solvent but swells with some solvents by suppression of elasticity due to network structures. In the swelling equilibrium state, the modified Flory–Rehner's equation is valid[12]

$$\nu_e = \frac{-2[v + \mu v^2 + \ln(1 - v)]}{V_s(2v^{1/3} - v)} \qquad (1)$$

where V_s is the molar volume of solvent, μ is the polymer–solvent interaction parameter, and v is a volume fraction of polymer in a gel, which is the reciprocal of Q_r:

$$v = \frac{V_p}{V_G} = 1 + \left[\frac{\rho_p}{\rho_s}\left(\frac{W_G}{W_p} - 1\right)\right]^{-1} \qquad (2)$$

$$Q_r = 1/v \qquad (3)$$

where V_G and V_p are the volumes of gel and dry polymer, respectively, W is weight and ρ is density. Subscripts s, p and G refer to the solvent, polymer and gel, respectively. This treatment could be applied not only to crosslinked rubber but also to other polymers in the amorphous state[13].

When $v^{1/3} \gg v/2$ (Q_r is large), equation (1) can be rewritten as[12]

$$\nu_e = \frac{1}{Q_r^{5/3} V_s}(1/2 - \mu) \quad (4)$$

When the value of μ is known, ν_e can be calculated from equation (4).

The polymer–solvent interaction parameter μ is expressed as[14]

$$\mu = \mu_z + \frac{V_s}{RT}(\delta_s - \delta_p) \quad (5)$$

where δ_s and δ_p are the solubility parameters of the solvent and polymer, respectively, and μ_z is a small constant (empirically 0.2–0.3), depending upon the coordination number of the lattice assumed in the entropy calculation[14].

According to Small[15], δ_p can be estimated from the summation of molar-attraction constants (F) for the constitutional repeating unit of polymer with both the molecular weight of the repeating unit (M) and the density of the polymer (ρ_p):

$$\delta_p = \rho_p \frac{\sum F}{M} \quad (6)$$

By using the F values estimated by Small, the solubility parameter of PBA δ_p was estimated to be 9.7. With the F values recently estimated by Hoy[16], δ_p becomes 9.8. The solubility parameter of THF δ_s is 9.1. When μ_z in equation (5) is 0.3, μ was estimated to be 0.34 (from F values by Small) or 0.32 (from F values by Hoy). Then, ν_e values were estimated by using equation (4) (see *Table 2*).

As shown in *Figure 3*, the plot of ν_e' *versus* $Q_r^{-5/3}$ gives a straight line. This result suggests that equation (4) can be applied for ν_e'. Both values of ν_e, determined from Small's number and Hoy's number for the same film are somewhat larger than that of ν_e', as shown in *Figure 3*. This discrepancy probably comes from a difference in μ estimated by Small's method or Hoy's method. If a more exact value of μ was used, ν_e would approximately agree with ν_e'. It is concluded that all of the CAB added to the polymer forms the cross linkage between the amino groups of the polymer.

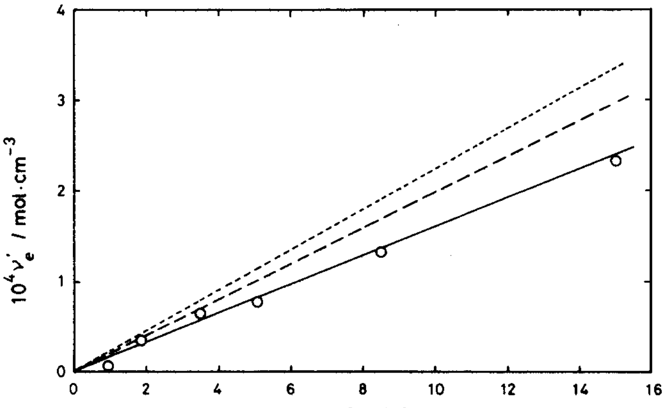

Figure 3 Plots of apparent effective network concentration (ν_e') *versus* $Q_r^{-5/3}$ for P[BA(CAB)$_Y$] films in THF at 25°C: (---) effective network concentration (ν_e) calculated by Small's method ($\mu = 0.34$); (------) ν_e calculated by Hoy's method ($\mu = 0.32$)

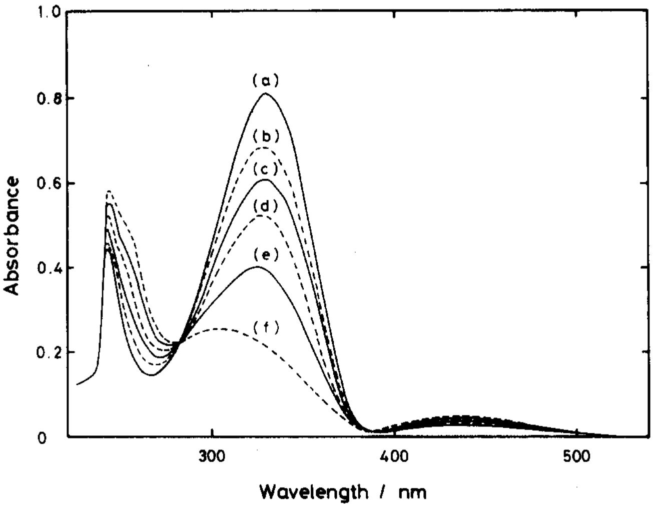

Figure 4 Change of absorption spectra of CAB with u.v. (300–380 nm) irradiation time in methanol: (a) $t = 0$; (b) $t = 45$; (c) $t = 60$; (d) $t = 90$; (e) $t = 150$; (f) $t = 600$ s

Photochemical isomerization of CAB

Figure 4 shows u.v. spectra of CAB in methanol. As shown in *Figure 4*, the maximum in the u.v. absorption spectrum, λ_{max}, in the solution was 330 nm. When the solution was irradiated with u.v. light (300 nm $< \lambda_1 <$ 380 nm), the u.v. absorption spectra showed a blue shift. The absorbance at λ_{max} decreased with increase in the absorbance of 240 nm. This is attributed to the photochemical isomerization of the *trans* to the *cis* form for CAB. When visible light (420 nm $< \lambda_2$) was used or the solution was allowed to stand in darkness, the u.v. spectrum was restored to the original spectrum, the extent of which depends on the irradiation time. This behaviour arises from the photochemical isomerization of the *cis* to the *trans* form for CAB. Isosbestic points were observed at 385 and 280 nm. Observation of isosbestic points indicates that there is no side reaction.

Similar behaviour was observed in the crosslinked films of P[BA(CAB)$_{1.5}$], as shown in *Figure 5*. The λ_{max} of CAB for P[PA(CAB)$_{1.5}$] was 320 nm, while that for polymer PBA was ~280 nm. Absorbance of the polymer at 320 nm was <3% of P[BA(CAB)$_{1.5}$] and this was sufficiently small to ignore the absorbance due to the polymer. Hence, a change of absorbance of P[BA(CAB)$_{1.5}$] at 320 nm was measured to determine the fraction of *trans* to *cis* form of CAB.

Figure 6 shows a change of photochemical isomerization of *trans* to *cis* form with time at 25°C. The degree of isomerization was described as the ratio of A_t/A_0, where A_0 and A_t are the initial absorbance and the absorbance at time t, respectively. In the case of CAB dispersed in PS, P[S(CAB)$_{0.94}$], which was non-crosslinked film, CAB was isomerized in ~65% after the irradiation of λ_1 for 30 min. When CAB was incorporated in both films of P[PA(CAB)$_{1.2}$] and P[PTA(CAB)$_{1.3}$], CAB was, however, isomerized in ~10%. These facts indicate that the thermal freedom of CAB was depressed by crosslinked polymers in the glassy state. On the other hand, the photochemical isomerization of P[BA(CAB)$_{1.4}$] continued to proceed slowly after 30 min and reached ~35% after 2 h. Photochemical isomerization of crosslinked CAB might be based on local motion of the polymer side chains in the glassy state. The molecular motion of CAB was in any event depressed by crosslinked polymers in the glassy state.

Photochemical isomerization of *trans* to *cis* form for azobenzene in methanol is a function of irradiation time. The apparent reaction rate is expressed as a first-order equilibrium reaction:

$$\frac{C_0 - C_e}{C_t - C_e} = \exp[(k_1 + k_{-1})t] \qquad (7)$$

where k_1 and k_{-1} are the apparent isomerization rate constants of *trans* to *cis* and *cis* to *trans*, respectively. C_0, C_t and C_e are *trans* fractions in the initial state ($t = 0$), at time t and in the stationary state ($t = \infty$), respectively. The *trans* fraction of CAB in the stationary state C_e was determined from the intercept of a plot of C_t *versus* $1/t$. The value C_e is 0.36 for CAB in 5.7×10^{-5} M methanol solution. The values of C_e for P[PA(CAB)$_{1.2}$], P[BA(CAB)$_{3.4}$], P[PTA(CAB)$_{1.3}$] and P[S(CAB)$_{0.94}$] in the films are 0.90, 0.66, 0.86 and 0.40, respectively.

Figure 7 shows the plots of $\ln[(C_0 - C_e)/(C_t - C_e)]$ *versus* t for the photochemical isomerization of CAB in methanol solution and in the films. The apparent reaction rate ($k_1 + k_{-1}$) of the *trans* to the *cis* form of CAB in methanol was determined from the slope of the straight line in the plot. The value ($k_1 + k_{-1}$) is 1.6×10^{-2} s^{-1}. However, the plots for CAB in the films were not linear. Such deviation from first-order plots was quantitatively discussed on the basis of the distribution of free volume[5–8]. There is a distribution of isomerization rates in the glassy state. There is a distribution of isomerization rates in the glassy state. The faster and slower processes may correspond to molecular motions of CAB in sufficient and insufficient free volumes, respectively[8]. The latter process may proceed in the local motion of side chains of the crosslinked polymers.

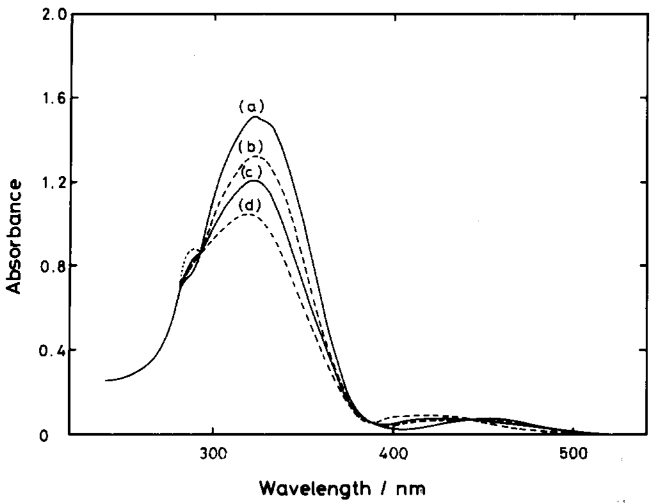

Figure 5 Change of absorption spectra of CAB with u.v. (300–380 nm) irradiation time for P[BA(CAB)$_{15}$] film: (a) $t = 0$; (b) $t = 2$; (c) $t = 6$; (d) $t = 30$ min

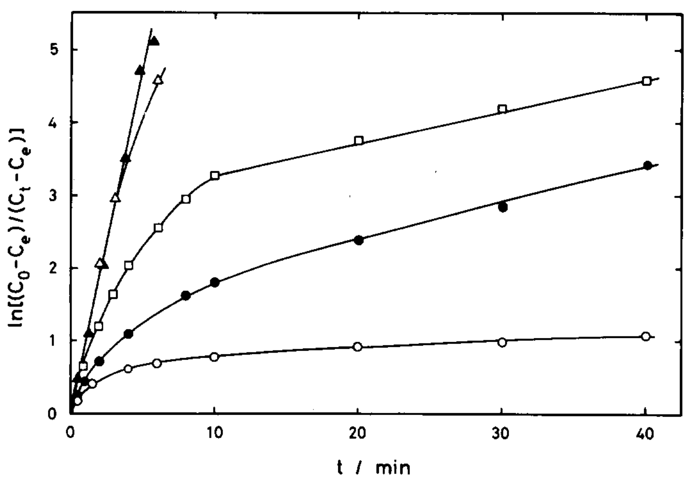

Figure 7 Plots of $\ln[(C_0 - C_e)/(C_t - C_e)]$ *versus* t for the photochemical isomerization of CAB in methanol (▲) and in the films at 30°C (below T_g of the four polymers): (△) P[PA(CAB)$_{1.2}$]; (□) P[S(CAB)$_{0.94}$]; (●) P[PTA(CAB)$_{1.3}$]; (○) P[BA(CAB)$_{3.4}$]

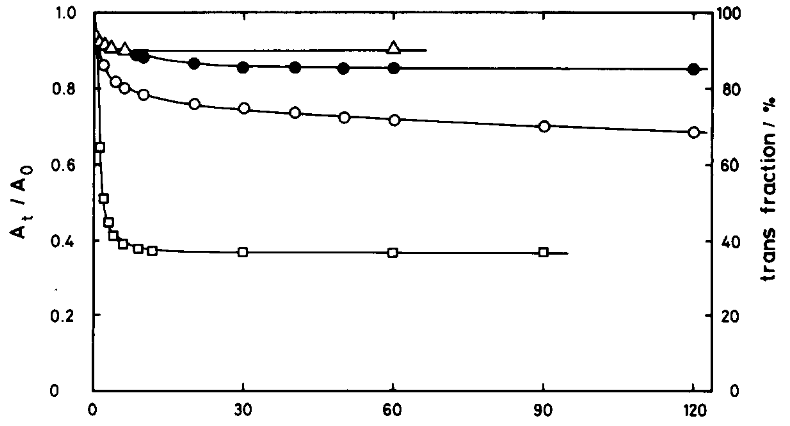

Figure 6 Change of absorbance (320 nm) *versus* u.v. (300–380 nm) irradiation time at 30°C (below T_g of each polymer): (△) P[PA(CAB)$_{1.2}$]; (●) P[PTA(CAB)$_{1.3}$]; (○) P[BA(CAB)$_{3.4}$]; (□) P[S(CAB)$_{0.94}$]

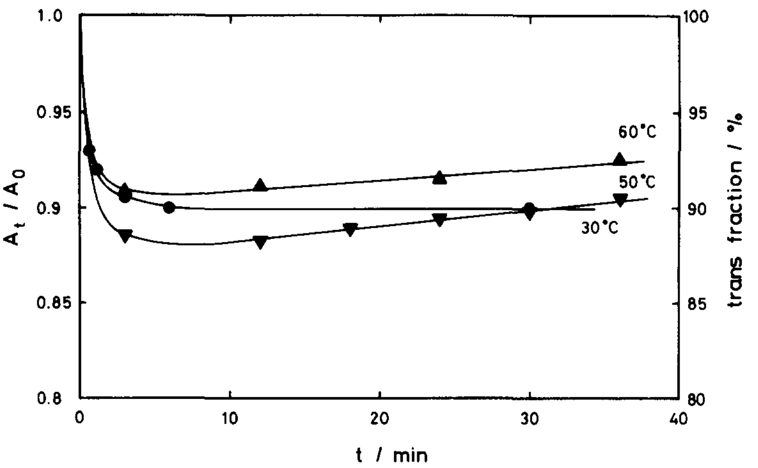

Figure 8 Change of absorbance (320 nm) *versus* u.v. (300–380 nm) irradiation time for $P[PTA(CAB)_{2.0}]$ film below and above T_g (42°C) of PPTA

At temperatures above T_g, the crosslinked films are in the rubbery state. Hence, it is expected that CAB in the rubbery state can be photoisomerized more than in the glassy state[6,7,17]. But, as shown in *Figure 8*, the *trans* fractions of $P[PTA(CAB)_{2.0}]$ did not decrease with increasing irradiation time after 5 min irradiation. Furthermore, peculiar behaviour was observed: the *trans* fractions of CAB apparently increased with u.v. irradiation after ~5 min. This behaviour may be attributed to the deformation of the films due to conformational changes of the crosslinked polymer chains[17].

In conclusion, crosslinked polymers were prepared and characterized by using the swelling test, and photochemical isomerization of CAB was depressed by cross linkage in the glassy state.

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