

Photoinversion Reaction of a Pyrenyl Sulfoxide in Solution and in Polymer Matrices

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ABSTRACT: A pyrenyl-substituted chiral sulfoxide, (*R*)-(+)-1-pyrenyl 4-tolyl sulfoxide (R-TPYS) was synthesized and photoracemized in acetonitrile, benzene, toluene and chloroform. Quantum yields of their photoinversion reactions were 0.02–0.03 from the changes in CD spectra and the rates of decomposition measured by high-performance liquid chromatography (HPLC) during photoirradiation. Quantum yields of photoinversion for R-TPYS in poly(methyl methacrylate) (PMMA) and in polystyrene were almost the same as in solution. It is considered that photoinversion reaction of R-TPYS is not affected by the polymer matrix at room temperature. The reaction at 88 K deviates from the first-order kinetics. The free volume around the sulfoxide in polymer matrix at 88 K does not seem to be enough compared to the sweep volume necessary for the reaction to occur.

KEY WORDS Pyrenyl-Substituted Sulfoxide / Sulfoxide / Photoinversion Reaction / Photoracemization / Chirality / Free Volume / Poly(methyl methacrylate) / Polystyrene /

Characteristic features of reactions in polymer solids are different from those in solutions. In polymer matrices the mobility of reactants is the dominant factor of the reaction. Because the local motion of the main chain and the free rotation of the side chain are not frozen below glass transition temperature, T_g , of matrix polymers, intermolecular or intramolecular reactions can take place sometimes even at temperature below T_g .^{1,2} Reaction rates in polymer solids are controlled by the balance of the molecular motion of a matrix, the free volume required for the reaction and inherent chemical reaction rates. Solid-state reactions in amorphous polymers proceed in three steps as the reaction temperature changes from high to low: (1) reaction rates are determined by chemical reaction paths and are the same as in solution, (2) reaction rates reflect molecular motion of the polymer matrix and proceed heterogeneously, (3) reactions cannot occur because of the absence of molecular motion. The size of the free volume required for reaction to occur determines which changes among the above steps are brought about at transition temperatures (T_g , T_β , T_i) of the matrix polymer. For example, the isomerization of spirobenzopyran which requires large free volume during the reaction shows the change from (1) to (2) at T_g of matrix polymers.^{3,4} In the case of azobenzene which requires smaller free volume for isomerization compared to spirobenzopyran, reaction proceeds in step (1) at room temperature (below T_g) and with decrease in temperature it shows changes from (1) to (2) together with clear deviation from the first-order kinetics.^{5–9} In the case of the photoinversion reaction of a sulfoxide, it might be expected that reaction proceeds similarly as in solution even in a polymer matrix with a small free volume, because photoinversion can be proceeded by the movement of the lone pair and oxygen atom.

Sulfoxide is widely applied to asymmetric synthesis as a chiral auxiliary.¹⁰ It is known that sulfoxides are stable at room temperature but thermal racemization occurs at

about 200°C due to the pyramidal inversion.¹¹ Studies of photochemistry of sulfoxides are mainly concerned with reactions induced by radical pair produced by the cleavage of S–C bonds.^{12–21} Systematic study of the triplet of sulfoxides has been made recently.²² There were some attempts at light induced asymmetric induction of sulfoxides in which a chiral sensitizer was used, but no remarkable results have been reported.^{23–26} Although interest in asymmetric photochemical reactions is growing,²⁷ little noticeable research on photochemistry of sulfoxides as chiral molecules has been made.

It was reported by Mislow *et al.*,^{28–31} that aromatic chiral sulfoxides undergo photoracemization with sensitized or direct light irradiation, which is believed due to the photochemical pyramidal inversion of sulfoxides. But little further research on this reaction has been made in recent years. Consequently the detailed mechanisms of this inversion reaction are not known.

The pyramidal structure of sulfoxides with the sulfur atom in its center is shown in Figure 1. In the present study, a pyrenyl-substituted sulfoxide was synthesized for the first time. The C–S bond of this sulfoxide cannot be cleaved easily because of direct bonding between aromatic carbon and sulfur atom. There are few sulfoxides which emit fluorescence at room temperature.²² Pyrenyl-substituted sulfoxide emits strong fluorescence. Longer wavelength absorption and strong fluorescence emission would make this molecule suitable for dynamics and excited singlet state measurements. In the present paper the pyrenyl sulfoxide was photoracemized in solution and in polymer matrices and the quantum yields of its photoinversion reaction were estimated and discussed in relation to the required free volume for the photoinversion reaction (sweep volume).

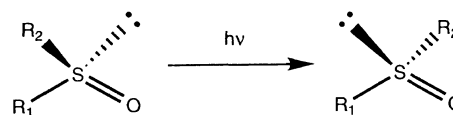


Figure 1. Photoinversion reaction of a sulfoxide.

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EXPERIMENTAL

Instrumentation

All UV-visible absorption measurements were performed with a JASCO UVIDEK 660 UV/VIS spectrophotometer. IR spectra were obtained with a JASCO IR-700 infrared spectrophotometer. NMR spectra were measured with JEOL JNM-GX400 FT-NMR spectrometer. Luminescence spectra were recorded with a Hitachi 850 fluorescence spectrophotometer. Optical rotatory power was obtained with a JASCO DIP-360 digital polarimeter. CD spectra were recorded with a JASCO J-500A spectropolarimeter. Melting points were measured with a Meihohsha sharp melting pointer. High-performance liquid chromatography (HPLC) was carried out with a JASCO UVIDEK 100-IV UV detector equipped with Wakosil 5SIL (4.6 mm \times 200 mm) column (Wako) and JASCO 807-IT integrator. Optical purity was measured with a Shimadzu SPD-6A UV detector and Hitachi D-2500 integrator with Daicel Chiralcel OD (4.6 mm \times 250 mm). All solvents and reagents were obtained from Tokyo Kasei and used without further purification, unless otherwise noted. In UV absorption and fluorescence measurements and photoracemization, all solvents were of spectrograde or luminasol grade (Wako) and used as received.

Synthesis of (R)-(+)-1-Pyrenyl 4-Tolyl Sulfoxide (R-TPYS)

R-TPYS was synthesized from the sulfinate with pyrenylmagnesium bromide by a method analogous to that of Andersen.^{32,33} A solution of 2.78 g (10 mmol) of bromopyrene in 20 ml anhydrous tetrahydrofuran (THF) was dropped into 0.315 g (13.8 mmol) of magnesium in 10 ml THF under nitrogen atmosphere. After reflux for 1 h, the mixture was cooled to -78°C and a solution of 2.95 g (10 mmol) of (1*S*,2*R*,5*S*)-(+)-menthyl-(*R*)-*p*-toluenesulfinate ($[\alpha]_{\text{D}}^{20} + 201.0^{\circ}$, c 2.0 g dl^{-1} , acetone) in 20 ml THF was added dropwise for 2 h with stirring and cooling in an ice bath. 30 ml of aqueous ammonium chloride (1.25 M) were added. After stirring for 15 min, the THF solution was removed by decanting. The water layer was extracted with dichloromethane. A mixture of THF and dichloromethane solution was evaporated, dissolved again in dichloromethane and dried over anhydrous sodium sulfate. The product was isolated by column chromatography on silica gel (Wako Gel C-200, eluent benzene:THF = 20:1) and purified by recrystallization in benzene and hexane. 0.527 g of a yellow crystal were obtained with a 15.5% yield. Melting point was 153–155 $^{\circ}\text{C}$. The specific rotation: $[\alpha]_{\text{D}}^{25} + 1.05 \times 10^3^{\circ}$ (c = 1.00 g dl^{-1} , dichloromethane). Enantiomer excess: 98.8% (determined by chiral HPLC column, eluent hexane:isopropyl alcohol = 9:1, flow rate 0.5 ml min^{-1} , monitored at 254 nm).

IR (KBr): ν 1046 cm^{-1} (S=O), 1593, 1493 cm^{-1} (aromatic C=C), 3042 cm^{-1} (aromatic C-H). ^1H NMR (CDCl_3): δ 7.2, 7.6 (d, 4H, tolyl-H), 8.1–8.6 (m, 9H, pyrenyl-H), 2.3 (s, 3H, Ar-C-H₃). *Elemental Analysis* Calcd for C₂₃H₁₆OS: C, 81.14%; H, 4.74%; S, 9.42%. Found: C, 81.20%; H, 5.01%; S, 9.50%. CD: λ_{max} ($\Delta\epsilon$) (acetonitrile solution): 221 (6.9), 232 (–6.0), 246 (24.6), 277 (–19.4), 303 (6.4), 333 (14.1), 349 (15.9), 375 (1.3).

Photoracemization in Solution

Solutions of 2.5 ml of 1×10^{-5} – 2×10^{-5} M R-TPYS in acetonitrile, benzene, toluene and chloroform were irradiated with 365 nm light from a 250-W high pressure mercury lamp (Ushio USH-250D) with a combination of interference filter (Toshiba, KL-36) and color filter (Toshiba, UV-25). Ellipticity (optical activity) changes were traced with CD spectra. Irradiation was continued until peaks of CD spectra disappeared. Light intensity before and after irradiation was measured at 436 nm using an interference filter (Toshiba KL-44) and color filter (Toshiba L-39) with an Advantest TQ8210 optical powermeter calibrated by chemical actinometry (potassium ferrioxalate actinometry). UV spectra before and after photoracemization were obtained to check for by-products. Aliquots of solution during irradiation (0.5 ml) were sampled. Solutions during and after irradiation were quantified by HPLC to determine the rates of decomposition of TPYS during photoracemization.

Photoracemization in Polymer Matrices

1 mm thick polymer films containing R-TPYS (0.80×10^{-4} – 1.0×10^{-4} M) on quartz plates were prepared using the solvent-cast method and irradiated with 365 nm light from the high pressure mercury lamp in the same way as for the solution.

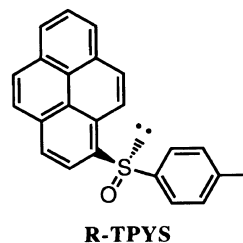
Photoracemization in Polymer Matrices at a Low Temperature

Poly(methyl methacrylate) (PMMA) films containing R-TPYS (9.79×10^{-5} M) prepared by the solvent-cast method were set in the cryostat (Oxford DN1754), cooled to 88 K and irradiated at 365 nm with the high pressure mercury lamp.

RESULTS AND DISCUSSION

Characterization of R-TPYS

Chiral sulfoxides are synthesized by allowing optically-active sulfinate esters to react with Grignard reagents *via* an inversion mechanism.^{32,33} Therefore the synthesized chiral sulfoxide has *R* configuration. Optical rotation power, $[\alpha]_{\text{D}}^{25}$, of the synthesized R-TPYS was $+1.05 \times 10^3^{\circ}$ at the sodium D line. Sulfoxides of *R* configuration have positive rotation except for only a few cases.³³



The absorption spectra of R-TPYS in acetonitrile are shown in Figure 2 (solid line). Absorption of the pyrenyl group is observed at 280 nm, 340 nm and 352 nm. New weak absorption is observed in the longest wavelength region at 380 nm. 0–0 transition between ground and excited singlet states for pyrene (26900 cm^{-1} ; 371 nm) is not permitted by selection rules because of the same

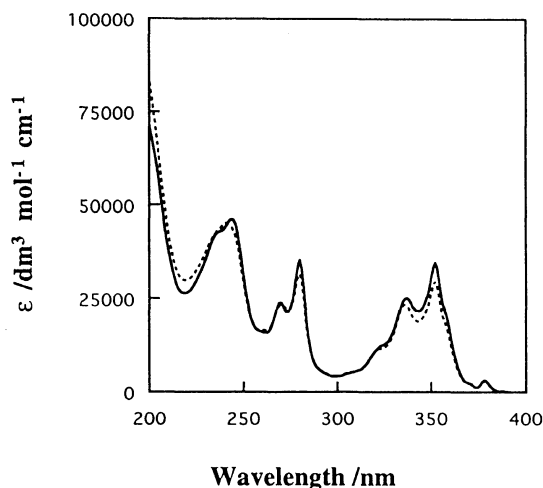


Figure 2. UV spectra of R-TPYS in acetonitrile (solid line: before irradiation; dotted line: after irradiation for 5520 s).

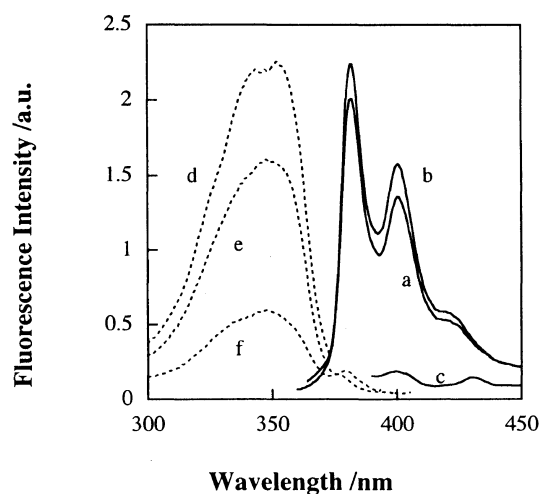


Figure 3. Fluorescence spectra of R-TPYS in benzene (1.12×10^{-5} M). (solid lines: emission spectra excited at 340 nm (a), 354 nm (b), and 380 nm (c); dotted lines: excitation spectra monitored at 382 nm (d), 402 nm (e), and 425 nm (f)).

symmetry of electronic states.^{34,35} Distortion of symmetric electronic states of the sulfoxide is supposed to loosen the symmetry-forbiddenness, so it produce new absorption at 380 nm. The absorption spectra were measured for R-TPYS in various solvents such as acetonitrile, hexane, benzene, dichloromethane, methanol, and *iso*-butyl alcohol, and absorption peaks were observed to red-shift (0–4 nm) at 340 nm, 350 nm, and 380 nm absorption in polar solvents. Therefore these are π - π^* absorptions of the pyrenyl group.

Fluorescence spectra of R-TPYS in benzene excited at 340 nm, 354 nm, and 380 nm are shown in Figure 3. Almost the same emission spectra were observed for 340 nm, 354 nm, and 380 nm excitation. The solvent effects are also observed. The peaks of fluorescence red-shifted somewhat (2–3 nm) in polar solvents. This solvent effect on fluorescence spectra does not contradict the case for absorption spectra.

Photoracemization in Solution

The change in CD spectra of R-TPYS in acetonitrile during photoirradiation at 365 nm is shown in Figure 4. The decrease in optical activity in solution caused by

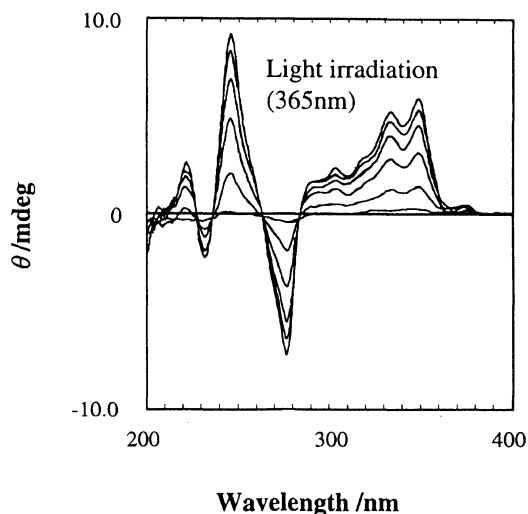


Figure 4. Change in CD spectra of R-TPYS in acetonitrile (1.13×10^{-5} M) during photoirradiation at 365 nm (irradiation time: 0 s, 180 s, 480 s, 1200 s, 2640 s, 5520 s from the top).

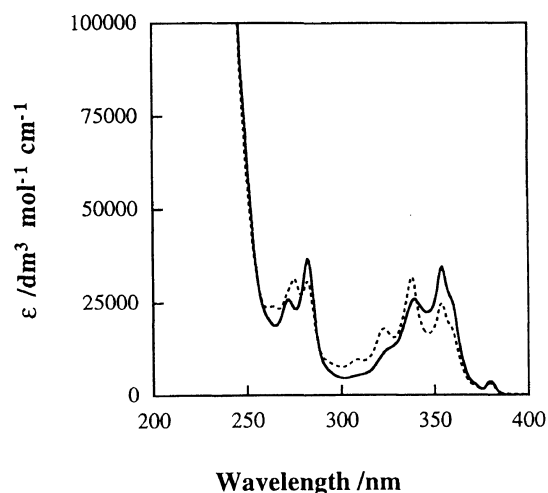


Figure 5. UV spectra of R-TPYS in chloroform (solid line: before irradiation; dotted line after irradiation for 5580 s).

photoracemization was recognized. Almost the same changes in CD spectra were recognized for four solvents (acetonitrile, benzene, toluene, and chloroform). As is shown in Figure 2, there was some change in UV spectra of acetonitrile and benzene solutions after irradiation. Changes were recognized in UV spectra of toluene and chloroform solutions after irradiation as are shown in Figure 5, suggesting that some by-products exist in toluene and chloroform solution.

The rates of photoinversion are expressed in eq 1–5,

$$-\frac{dC_R(t)}{dt} \cdot S \cdot l \times 10^{-3} = (A_R(t) \cdot \Phi - A_S(t) \cdot \Phi) S \quad (1)$$

$$-\frac{dC_S(t)}{dt} \cdot S \cdot l \times 10^{-3} = (A_S(t) \cdot \Phi - A_R(t) \cdot \Phi) S \quad (2)$$

$$A_R(t) = I_0 \cdot (1 - 10^{-OD}) \cdot \frac{C_R(t)}{C_0} \quad (3)$$

$$A_S(t) = I_0 \cdot (1 - 10^{-OD}) \cdot \frac{C_S(t)}{C_0} \quad (4)$$

$$C_R(t) - C_S(t) = C_0 \cdot \exp\left(-\frac{2 \cdot I_0(1 - 10^{-OD})\Phi \times 10^3}{C_0 \cdot l} \cdot t\right) \quad (5)$$

where I_0 is the number of irradiated photons per unit time and unit cross section, S is the area of the irradiated cross section, $C_R(t)$ and $C_S(t)$ are concentration of R-TPYS and S-TPYS ((S)-(-)-1-pyrenyl 4-tolyl sulfide), respectively, and functions of time, ε is the molar extinction coefficient of R- and S-TPYS, l is the thickness of system, $A_R(t)$ and $A_S(t)$ are the numbers of photons per unit time and unit cross section which R-TPYS and S-TPYS absorb, respectively, Φ is the quantum yield of photoinversion reaction and t is time. It is obvious that the quantum yields of photoinversion reaction for R-TPYS and S-TPYS are equal because of symmetry.

Ellipticity at 349 nm, $\theta(t)$, is expressed by eq 6. The quantum yield of photoinversion reaction Φ is obtained from changes in $\theta(t)$ by eq 12.

$$\theta = 33 \times \Delta OD \quad (6)$$

$$\Delta \varepsilon = \varepsilon_{lR} - \varepsilon_{rR} = \varepsilon_{rS} - \varepsilon_{lS} \quad (7)$$

$$OD_l(t) = \{\varepsilon_{lR} \cdot C_R(t) + \varepsilon_{lS} \cdot C_S(t)\}l \quad (8)$$

$$OD_r(t) = \{\varepsilon_{rR} \cdot C_R(t) + \varepsilon_{rS} \cdot C_S(t)\}l \quad (9)$$

$$\Delta OD(t) = OD_l(t) - OD_r(t) = \Delta \varepsilon(C_R(t) - C_S(t))l \quad (10)$$

$$C_R(t) - C_S(t) = 2C_R(t) - C_0 = \frac{\Delta OD(t)}{\Delta \varepsilon \cdot l} = \frac{\theta(t)}{33 \cdot \Delta \varepsilon \cdot l} \quad (11)$$

$$\ln\left(\frac{\theta(t)}{\theta_0}\right) = -\frac{2 \cdot I_0(1 - 10^{-OD}) \times 10^3}{C_0 \cdot l} \Phi \cdot t = -A \cdot \Phi \cdot t \quad (12)$$

where ε_{lR} and ε_{rR} are the molar absorptivities of R-TPYS for left-circularly-polarized light (l-CPL) and right-circularly-polarized light (r-CPL) and ε_{lS} and ε_{rS} are also molar absorptivities of S-TPYS for l-CPL and r-CPL, respectively.

The wavelength distribution of irradiated light intensity was calculated from the wavelength distribution of mercury lamp intensity, wavelength dependence of the sensitivity of the optical powermeter and transmittance of the filters. Absolute light intensity for each wavelength was calculated from the wavelength distribution of the incident light and light intensity measured with optical powermeter, and converted to the number of irradiated photon, I_0 , per unit time and unit cross section. Optical density, OD , was measured from UV spectra before irradiation. Parameter, A , was obtained from OD , I_0 , C_0 and l .

First-order plots of the ellipticity, $\theta(t)$, against time in acetonitrile are shown in Figure 6. The quantum yields of photoinversion reaction, Φ , were calculated from the slopes of the first-order plots. The values of Φ in four solvents are given in Table I. Experimental error of Φ was within 10%.

Although side reactions are ignored in the calculations, it is possible that optical activity in solution decreased also owing to side reactions. The loss of TPYS in solution

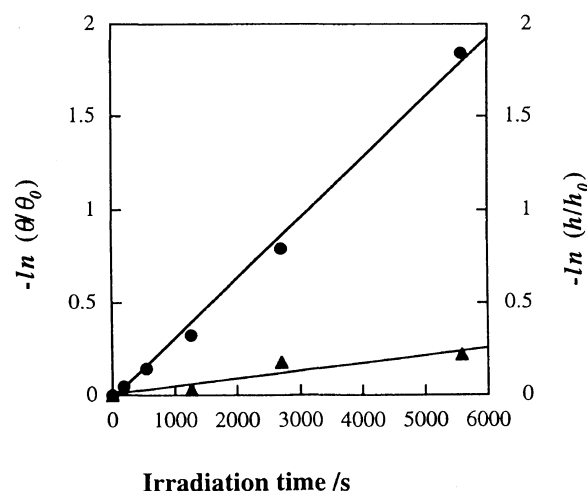


Figure 6. First-order plots for photoracemization of R-TPYS in acetonitrile at room temperature (●, $-\ln(\theta(t)/\theta_0)$; ▲, $-\ln(h(t)/h_0)$).

Table I. Quantum yields of photoinversion reactions, Φ , photolysis, Φ_{dec} , and net inversion, Φ_{inv} , for R-TPYS in acetonitrile, benzene, toluene, and chloroform at room temperature. Concentrations are $1-2 \times 10^{-5}$ M

Solvent	Quantum yields		
	Φ	Φ_{dec}	Φ_{inv}
Acetonitrile	2.6×10^{-2}	4.4×10^{-3}	2.4×10^{-2}
Benzene	2.8×10^{-2}	5.4×10^{-3}	2.5×10^{-2}
Toluene	3.0×10^{-2}	4.9×10^{-3}	2.8×10^{-2}
Chloroform	3.0×10^{-2}	4.4×10^{-3}	2.8×10^{-2}

during light irradiation was measured by HPLC. The ratio of decomposition is less than 20% after 92 min of irradiation in acetonitrile solution. The quantum yields of photolysis of TPYS, Φ_{dec} , were obtained from the first-order plots (Figure 6) of the peak area (expressed as $h(t)$) of TPYS and light intensity. Experimental error of Φ_{dec} was within 20%. Since decrease in optical activity during light irradiation was induced also by the loss of TPYS, the net quantum yields of photoinversion, Φ_{inv} , were recalculated from Φ and Φ_{dec} by using eq 13 and are listed in Table I,

$$2\Phi = 2\Phi_{inv} + \Phi_{dec} \quad (13)$$

where 2Φ is equal to quantum efficiency of loss of optical activity, $2\Phi_{inv}$ is equal to that of photoracemization induced by net photoinversion. It seems that neither Φ_{inv} nor Φ_{dec} are affected by solvent (Table I). Φ_{inv} and Φ_{dec} are estimated to be 0.02–0.03 and 0.004–0.005, respectively, irrespective of the solvent.

The photolysis of sulfoxides has been investigated in detail.^{12–21} According to these reports, it is supposed that side reactions are initiated by C–S bond cleavage and radical formation. The UV spectra of acetonitrile and benzene solution after irradiation changed very little but changes were recognized for toluene and chloroform solution. It seems that differences in UV spectra of TPYS after light irradiation are due to those in by-products produced by the photolysis.

Photoracemization in Polymer Matrices

The peak of CD spectra, $\theta(t)$, decreased during

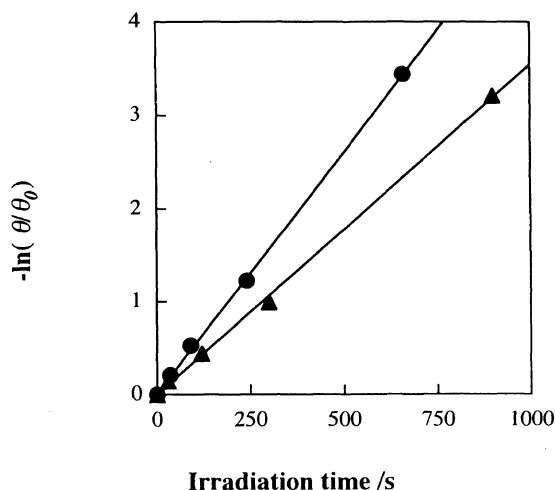


Figure 7. First-order plots for photoracemization of R-TPYS in polystyrene (●) and PMMA (▲) at room temperature.

Table II. Quantum yields of photoinversion reactions, Φ , for R-TPYS in PMMA and polystyrene

Polymer	Temperature	Concentration/ M	Quantum yields
PMMA	r.t.	9.79×10^{-5}	2.7×10^{-2}
PMMA	88 K	9.79×10^{-5}	1.6×10^{-2}
			(Initial stage)
Polystyrene	r.t.	8.64×10^{-5}	3.0×10^{-2}

photoirradiation at 365 nm to polymer films (polystyrene and PMMA) doped with R-TPYS at room temperature. UV spectra did not change after photoracemization. Although the rates of photolysis of TPYS in polymer films could not be measured, the rates of photolysis should not be larger than in solution. Similarly to the photoinversion in solution, straight lines were obtained for the first-order plots of $\theta(t)$ against time as shown in Figure 7, and quantum yields of photoinversion were determined from the slopes of the first-order plots. The quantum yields, Φ , are 2.7×10^{-2} and 3.0×10^{-2} for R-TPYS in PMMA and polystyrene, respectively, at room temperature (Table II). These values were almost the same as in solution (0.02–0.03). It is supposed that photoinversion reaction occurs in polymer films at room temperature with the same efficiency as in solution. The effect of polymer matrix was not observed. Photochemical reactions in polymer solids at a temperature below T_g are usually observed to deviate drastically from first-order kinetics.² Present results may be due to the small sweep volume required for the photoinversion, compared to the free volume expanded by thermal fluctuation in these polymer matrices at room temperature.

Photoinversion in Polymer Matrix at a Low Temperature

A PMMA film doped with R-TPYS was refrigerated to 88 K, and irradiated at 365 nm. $\theta(t)$ of the sample decreased during light irradiation for 5 h, and peaks of CD spectra disappeared. UV spectra of the sample did not change after 50 min irradiation and slightly changed after 5 h irradiation. For 50 min irradiation,

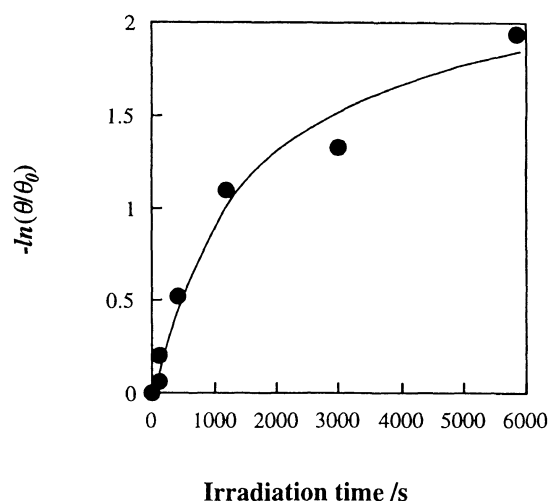


Figure 8. First-order plots for photoracemization of R-TPYS in PMMA at 88 K.

optical activity of the sample dramatically decreased. The decrease in $\theta(t)$ and no change of UV spectra mean that photoracemization proceeds even at 88 K in PMMA matrix.

The reaction deviates from the first-order kinetics as shown in Figure 8. This agrees with our previous results^{5–9} for the photoisomerization of azobenzene, azonaphthalene, etc. in various polymer matrices. The quantum yield for the initial stage of the photoinversion reaction at 88 K is estimated to be 0.016 from the initial slope of the first-order plots and plots for conversion above 20% ($\ln \theta/\theta_0 = 0.223$) begin to deviate from a straight line. The obtained initial quantum yield is much larger than that of photolysis at room temperature. Consequently, photoinversion reaction proceeds in PMMA at 88 K. Since there is distribution of free volume in polymer matrices, molecules in amorphous polymer solids react when (1) there is enough free volume around reaction sites and reactions proceed freely as in solution, (2) free volume is not so enough and reactions are controlled by molecular motions of polymer chains, (3) free volume is smaller than sweep volume and reactions cannot occur. Since the thermal fluctuation of polymer chains is restricted and the number of sites where TPYS cannot freely undergo inversion increases at low temperatures, first-order plots deviate from a straight line.

CONCLUSION

R-TPYS was photoracemized in acetonitrile, benzene, toluene, and chloroform solutions. Quantum yields of the photoinversion reaction were 0.02–0.03 from changes of the CD spectra, $\theta(t)$, and the rates of photolysis obtained by HPLC during photoirradiation. Quantum yields of photolysis were estimated to be 0.004–0.005 and one order of magnitude smaller than that of photoinversion. Although the rate of photolysis in polymer matrices was not measured, quantum yields of photoinversion for the samples in PMMA and in polystyrene seem to be almost the same as in solution. The photoinversion reaction of R-TPYS proceeds linearly based on the first-order kinetics and is not affected by

the polymer matrices at room temperature. The reaction at 88 K deviates from the first-order kinetics above 20% conversion. The restriction of chain mobility at 88 K decreases the number of sites which have sufficiently large free volume around sulfoxides in the polymer matrix, compared to the size of sweep volume for the reaction to occur, and hence photoinversion is controlled by the local chain motion in the intermediate stage of photoracemization at 88 K.

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