Photochromism of 2-Chloro-*N*-salicylideneaniline in Amorphous Polymer Solids

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ABSTRACT: Photochromism of 2-chloro-*N*-salicylideneaniline, Sa(H,2-Cl), molecularly dispersed in amorphous polymer matrices was investigated under conventional steady-state irradiation. The final conversion of photochromic reaction in amorphous polymers was found to decrease with temperature due to notable influence on a thermal back reaction. The effect of polymer matrix on the thermal decay reaction was explained by the half-life ($1/t_{1/2}$) of the colored species and concept of free volume of polymer matrices: the values at 20°C for Sa(H,2-Cl) in poly(methyl methacrylate) (PMMA), polystyrene (PS), and polycarbonate (PC) were 11.1, 3.0, and 2.5 min, respectively. This indicates that the size of free volume of PMMA is the smallest in the three polymers at room temperature. Arrhenius plots of $1/t_{1/2}$ for PC and PS broke obviously at 20 and 14°C in contrast to a linear relationship for PMMA, and apparent activation energies for the thermal decay reactions in both polymers were approximately half above the break points.

KEY WORDS 2-Chloro-*N*-salicylideneaniline / Photochromism / Thermal
Decay Reaction / Half-Life of the Colored Species / Photochromic Probe /
Free Volume /

Photochromism in polymer matrices has aroused much interest in connection with applications to EDRAW (erasable and directly reading and writing) memories,¹ and it has also been regarded as a molecular probe method for obtaining information of molecular motion of polymers in glassy state.² Reactions in amorphous polymer solids are generally governed by mobility and heterogeneity of reaction sites, so that photochromic processes may be retarded by polymer matrices compared with the liquid phase, and processes in amorphous polymers often deviate from first-order kinetics even if apparently elementary first-order reactions.³

Salicylideneaniline and its derivatives (anils) are well-known organic photochromic compounds and their photochromism has been investigated in pure crystalline states and various matrices.^{4–6} In general, the photochrom-

ism of anils in liquid solutions does not appear under conventional steady-state irradiation, because the photo-reaction yield of anils is relatively low and thermal reversion is extremely fast compared with other photochromic compounds. Therefore, the viscosity effect of solutions as well as other matrix effects on photochromism have been measured by laser-flash photolysis.^{5,7}

In this paper, the photochromism of 2-chloro-*N*-salicylideneaniline which is molecularly dispersed in amorphous polymer matrices was investigated under conventional steady-state irradiation at room temperature, and the matrix effects of polymer on the photochromism are discussed by comparing the thermal decay reactions in poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC), and others. The effect of polymer matrices on the thermal decay reactions was elu-

culated by values of half-life of colored species. The molecular motion of polymers below T_g was estimated by kinetics of thermal decay reactions.

EXPERIMENTAL

Materials

2-Chloro-*N*-salicylideneaniline [Sa(H,2-Cl)] was prepared by the direct condensation of salicylaldehyde and o-chloroaniline in ethanol at 20°C. Recrystallization from ethanol afforded a pale yellow crystal, mp 83–84°C. Polymers and their parameters used are shown in Table I. PMMA was used as received from Tokyo Kasei Co. and the others were from Aldrich Chem. Co. Solvents were dehydrated with molecular sieve 3A before use.

Sample Preparation

The sample films were prepared by two methods.

Solvent-Casting Method. A 0.5 g portion of polymer was dissolved in 2 ml of appropriate solution (Table I) containing 0.02 mmol Sa(H,2-Cl). The mixture was poured onto $9 \times 38 \text{ mm}^2$ glass plate and allowed to stand in a dark place at room temperature for one day. The glass plate was placed in a dark-brown desiccator and dried under reduced pressure at room temperature for a week.

Melting Method. A polymer and Sa(H,2-Cl) (same composition as above) was melted as

fast as possible on a glass plate at a relevant temperature (Table I) and then covered tightly with another glass plate by pressing to afford a sandwiched film approximately $10 \mu\text{m}$ in thickness.

Measurements of Photoisomerization

The films were irradiated at a distance of 10 cm from a 75 w high pressure mercury lamp with a combination of filters (Toshiba UV-D35 and UV-31), 310–400 nm-pass wave-length. The resulting spectral changes were recorded by means of a Shimadzu UV-160 spectrophotometer. The sample film was put into a glass cell and the temperature of the cell was kept constant during irradiation and absorption measurements at a given temperature.

RESULTS AND DISCUSSION

Temperature Effects on Photochromism of Sa(H,2-Cl) in PMMA Film and Its Thermal Decay Reaction

Photochromism of Sa(H,2-Cl) in PMMA film prepared by the melting method was investigated at 0–40°C. Figure 1 shows the absorption spectra of the film before and after irradiation (D_∞ and D_0 , respectively) and the thermal decay in the dark at 0°C. The photo-induced product observed as the *trans*-keto species of Sa(H,2-Cl) in liquid solutions⁷ appeared with relatively long life when dispersed in PMMA.

The optical density at 475 nm increased with

Table I. Polymers used and parameters

Polymer ^a	MW ^{b1}	Density ^b	T_g ^c /K	Solvent ^d	T^e /°C
PMMA	7000–7500 ^{b2}	1.170	383	CH ₃ Cl	310
PC	medium	1.200	423	CH ₂ Cl ₂	280
PS	280000	1.047	373	C ₆ H ₆	250
PBMA	high	1.070	300	CH ₃ Cl	120
LDPE	—	0.915	205	—	150

^a PMMA, poly(methyl methacrylate); PC, polycarbonate; PS, polystyrene; PBMA, poly(butyl methacrylate); LDPE, polyethylene, low density. ^b From manufacturer's handbook. ^{b1} Average molecular weight. ^{b2} Degree of polymerization. ^c From Polymer Handbook. ^d Solvent for casting method. ^e Temperature for melting method.

Figure 1. Changes in visible absorption spectra of PMMA film containing 2-chloro-*N*-salicylideneaniline at 0°C. D_0 , after irradiation; D_∞ , before irradiation and completely recovered; thermal decay were recorded at 1-min intervals after irradiation.

irradiation time and leveled off after 30 min irradiation. The final absorbance changes (D_0) at 475 nm decreased markedly with increasing temperature (Figure 2). This means that the temperature dependence of the back reaction is large compared with that of photoinduced forward reaction.

To elucidate the thermal decay reaction of the colored product, absorption changes at 475 nm were measured with time at various temperatures. Figure 3 illustrates the decay curves at various temperatures, where the ordinate is the extent of thermal decay reaction. Although the thermal decay reaction of Sa(H,2-Cl) in solution followed first-order kinetics,⁷ the reaction in amorphous polymer obviously deviated from first order, presumably due to the heterogeneity of polymer matrices. The effects of the heterogeneity of matrix on the reactions have been discussed well for azobenzene in terms of the model of the free volume distribution. A part of photochromic compounds functions as a reactive site in polymer matrices, where the local free volume around photochromic species is larger than the critical free volume, so that the final conversion of photoisomerization for azobenzene decreases with decreasing temperature due to decrease in free volume of polymer matrices.^{8,9} However, the relationship between

Figure 2. Final absorbance changes at 475 nm for PMMA film containing 2-chloro-*N*-salicylideneaniline.

Figure 3. Thermal decay curves of the colored product of 2-chloro-*N*-salicylideneaniline in PMMA film at various temperatures.

the final conversion of photoisomerization of anils and temperature was different with azobenzene. The volume required for isomerization of anils is thus small compared with azobenzene.

The half-life of the colored species in different polymer matrices was measured at various temperatures, and the reciprocal number of the half-life was used as the apparent rate constant. The apparent rate of the thermal decay reaction increased with temperature as shown in Figure 4. The value of half-life in PMMA, was 11.1 min at 20°C. By using the flash photolysis technique, the decay time of

Figure 4. Apparent rate constant for the thermal decay reaction of the colored product of 2-chloro-*N*-salicylideneaniline in PMMA film.

Sa(H,2-Cl) in liquid solution had been measured as $55 \mu\text{s}$ at 20°C .⁷ This means that the thermal decay reaction is highly restricted in polymer matrices, so that the photoinduced color species can be held at room temperature.

Effect of Free Volume of Polymer on the Photochromism of Sa(H,2-Cl)

The photoconversion of anils proceeds by migration of hydrogen of *o*-hydroxy group to imine-nitrogen and an additional *cis-trans* isomerization. Rearrangement of the molecular framework of anils was affected by rigid crystal states,¹⁰ viscosity of solution¹¹ and T_g of polymers.⁶ Figure 5 shows Arrhenius plots of the apparent rate constant for thermal back reactions of Sa(H,2-Cl) in PMMA, PC, and PS films, and Table II gives the values of the apparent activation energy for the thermal decay reaction in different ranges of temperature. It is obvious that the rate of thermal decay reaction varies with the matrix, and the rate in PMMA is the slowest of the three matrices at room temperature. The rate of the thermal decay reaction in PC is slower than that in PS

Figure 5. Arrhenius plots of the apparent rate constant for 2-chloro-*N*-salicylideneaniline in PMMA (O), PC (□), and PS (Δ).

Table II. Half-lives at 20°C and apparent activation energies for thermal decay reactions

Polymer matrices	PMMA	PC	PS
$t_{1/2}/\text{min}$	11.1	3.0	2.5
$E_a/\text{kJ mol}^{-1}$	58.2	69.0	50.7
	(0–40°C)	(0–20°C)	(0–14°C)
		33.3	26.6
		(20–40°C)	(14–20°C)

at low temperatures, but becomes faster at relatively high temperatures. In contrast to the linear relationship for the Arrhenius plot of PMMA, plots for PC and PS broke obviously at 20 and 14°C , respectively. The apparent activation energies of the thermal decay reaction in PC and in PS decreased by half above the break points.

The glassy state of an amorphous polymer is generally a thermodynamic nonequilibrium state, in which polymer molecules aggregate with an extra energy and excess free volume, so that the rate of thermal decay reaction in polymer matrices should depend on the size of free volume of polymer. From experimental results, the size of free volume of PMMA is smaller than that of PC or PS at 20°C , and there is no obvious relationship between T_g

and size of free volume. The breaks on the Arrhenius plots reflect changes of free volume, and subglass transition of PC and PS appears at 20 and 14°C, respectively. This is similar to phosphorescence decay of benzophenone in polymers.¹²

Since the size of free volume differs not only with the kind of polymer but specific structure as well as thermal history involving the physical processing and annealing, we also investigated the photochromism of Sa(H,2-Cl) in low density polyethylene, and poly(butyl methacrylate) films prepared by the melting or solvent-casting method. However, color development was observed only at low temperature (approximately -50°C). We assumed that the size of free volume of these polymer films was too large to restrict the thermal back reaction of anils, thus the photochromism of anils was not observed at room temperature.

CONCLUSIONS

1. Spectra of colored product of Sa(H,2-Cl) molecularly dispersed in polymer matrices were obtained with relatively long life under the conventional steady-state irradiation at room temperature.

2. The final conversion of photochromic reaction decreased with increasing temperature. Thermal decay reaction of Sa(H,2-Cl) in polymer matrices deviated from first-order kinetics, and the rate of the thermal decay

reaction is estimated to be 1×10^{-7} times that in liquid solution in the literature.

3. The half-lives of the thermal decay reactions for Sa(H,2-Cl) varied with polymer matrices due to differences in free volume. A linear relationship was obtained for the Arrhenius plot of PMMA, but plots for PC and PS broke at 20 and 14°C, respectively.

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