Photochromism of 4-Hexadecyl-4'-methoxysalicylideneaniline in Polycarbonate: Kinetic Study on the Thermal Decoloration in Heterogeneous Matrix

Ming Yin, Tetsuo Kuwabara, and Masato Nanasawa*
Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Yamanashi University, 4 Takeda, Kofu 400

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A multi-process model consisting of a distribution of rate constant of each process was proposed to explain the thermal decoloration of the colored species of 4-hexadecyl-4'-methoxysalicylideneaniline in polycarbonate matrix. The kinetic equation deduced from this model indicates that the lifetime of the colored species linearly increases with time for the decoloration in heterogeneous matrix.

Photochromism in amorphous polymers has received considerable attention due to its specific features different from those in solutions. The most important fact is that the reactions following first-order kinetics in solutions show strong deviations from the exponential kinetics in amorphous polymers.[1] For some reactions such as the decoloration of merocyanines, the deviation is interpreted by assuming the existence of photochrome aggregation or different isomers.[2,3] However, the specific kinetic behavior for a number of photochromic compounds in amorphous polymer is mainly caused by the microheterogeneity of system such as the distribution of free volume of polymer.[1,4,5] To express the kinetics of the reaction in heterogeneous matrix, the first attempt has been made on the basis of a biphasic process,[6] and others have been made by use of the stretched exponential.[7] Recently, a model concerning with the distribution of free volume has been proposed.[8,9]

In this paper, a model based on multi-process was proposed to explain the decoloration of 4-hexadecyl-4'-methoxysalicylideneaniline (***SB***, Figure 1) in polycarbonate (PC). The kinetic equation in terms of the extent of reaction was deduced from this model for the decoloration in heterogeneous matrix.

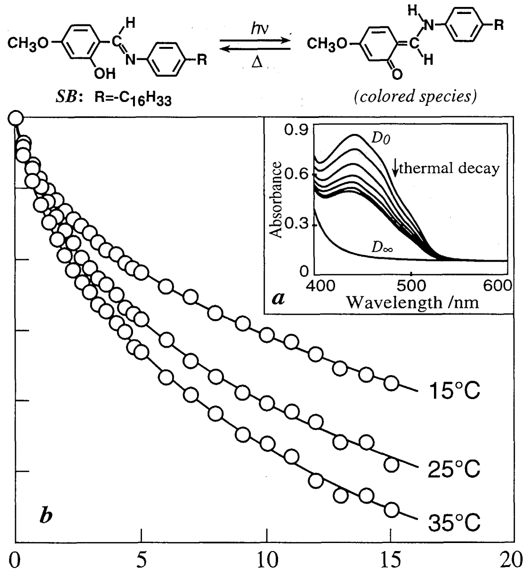

Figure 1. ***a***: Absorption spectra of PC film containing 4-hexadecyl-4'-methoxysalicylideneaniline at 15 °C. D_∞, before irradiation; D_0, immediately after irradiation. ***b***: Kinetic plots of ln*R* *vs.* time, where *R* is the extent of thermal decoloration.

Anil of ***SB*** was prepared by the condensation of 4-methoxysalicylaldehyde with 4-hexadecylaniline in ethanol at 40 °C, and recrystallized from ethanol. The film of PC containing 0.3 $\mathrm{mmol \cdot g^{-1}}$ of ***SB*** was prepared by using a solvent-cast method from chloroform. Irradiation was carried out by using 310-400 nm light.

Figure 1a shows the spectra of ***SB*** in PC before and immediately after irradiation, and its thermal decoloration at 15 °C. The extent of decoloration is given as[10]

$$R = \frac{A_t - A_\infty}{A_0 - A_\infty} \tag{1}$$

where A is the absorbance of the colored species of ***SB*** at λmax=440 nm, A_∞, A_0 and A_t express the absorbance before, immediately after irradiation, and at time *t* after irradiation, respectively. Figure 1b shows the kinetic plots of thermal decoloration of the colored species of ***SB*** in PC at various temperatures. The thermal decolorations obviously deviate from the first-order kinetics.

Considering a decoloration in heterogeneous matrix, it is assumed that the colored species fade in many process due to the heterogeneity of matrix, and that each process independently follows the first-order kinetics. For this multi-process, the total extent of decoloration which is defined as the ratio of concentration of the colored species to the initial concentration (c/c_0), can be described in terms of the sum of extents of each process.[3,4] It is given as

$$R = \sum_i a_i R_i = \sum_i a_i e^{-k_i t} \tag{2}$$

where a_i is the mole fraction of the colored species in the i-th process and k_i is its rate constant. In this model, the rate constants of each process depend on the microheterogeneity of matrix. If the number of process tends to infinite, the rate constants can be considered to taking a continuous distribution. Then eq. 1 can be formulated as a definite integral as

$$R = \int_0^\infty \xi(k) e^{-kt} dk \tag{3}$$

where k is the rate constant and ξ is a density function of the rate constant. Generally, the distribution of rate constant reflects that of the free volume of polymer. If the rate constant is distributed according to a gamma distribution which is usually used as a relatively general continuous distribution to describe the random processes, ξ is given by[11]

$$\xi(k) = \frac{\lambda}{\Gamma(\alpha)}(\lambda k)^{\alpha-1} e^{-\lambda k} \qquad (\alpha>0,\ \lambda>0) \tag{4}$$

where $\Gamma(\alpha)$ is the Gamma function, α and λ are adjustable parameters. From eqs. 3 and 4, the final solution of the integral for the total extent of decoloration is derived as[12]

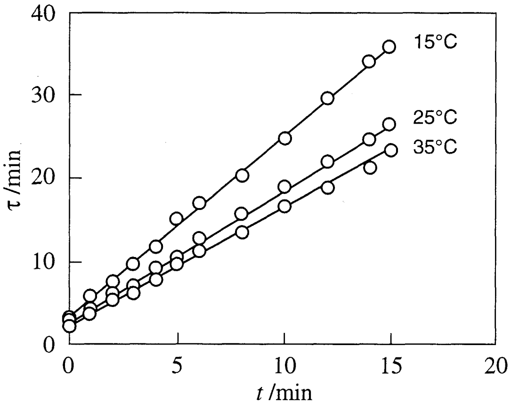

Figure 2. Relation between the lifetime of the colored species and time for the thermal decoloration of 4-hexadecyl-4'-methoxysalicylideneaniline in PC at various temperatures.

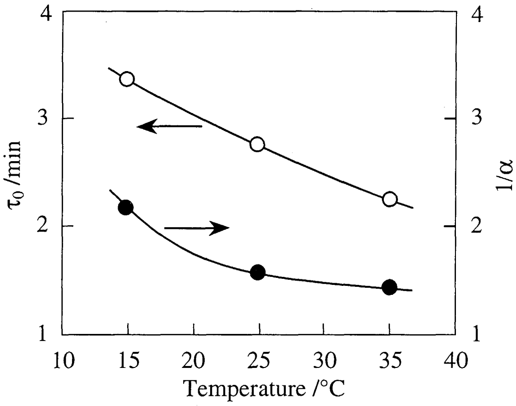

Figure 3. Temperature dependence of the kinetic parameters in equation 7 for the thermal decoloration of 4-hexadecyl-4'-methoxysalicylideneaniline in PC.

$$R = \left(\frac{\lambda}{t+\lambda}\right)^{\alpha} \tag{5a}$$

or

$$\ln R = \alpha \ln \lambda - \alpha \ln(t+\lambda) \tag{5b}$$

For the decoloration of ***SB*** in PC, the experimental data were in good agreement with this equation (the solid lines in Figure 1b). The parameters α and λ were evaluated by fitting the equation to the experimental plots of ln*R* *vs.* time performed on computers with the nonlinear least-squares method.

If τ and k' are defined as,

$$\tau \equiv \frac{1}{k'} \equiv \left(-\frac{d\ln R}{dt}\right)^{-1} \tag{6}$$

k' can be regarded as the apparent rate of decoloration, representing the variation in ln*R* with time, and τ can be regarded as the lifetime of the colored species. Then the kinetic equation (eq. 5b) can be written as

$$\tau = \tau_0 + t/\alpha \tag{7}$$

where $\tau_0=\lambda/\alpha$ is the initial value (t=0) of the lifetime. For a decoloration obeying the first-order kinetics in homogeneous matrix, it is well known that the lifetime defined by eq. 6 is a constant independent of time. However, eq. 7 indicates that the lifetime of the colored species linearly increases with time for the decoloration in heterogeneous matrix. Thus, the slope (1/α) of the line represents the deviation of reaction from the first-order kinetics, *i.e.*, the larger the slope of line is, the greater the deviation of reaction is. The decoloration will obey the first-order kinetics if 1/α is equal to zero as an extreme case.

From the kinetic plots showed in Fig. 1b, the lifetimes for the decoloration of ***SB*** in PC were obtained according to eq. 6. Figure 2 shows the plots of the lifetime *vs.* time at various temperatures. It is obvious that the lifetime linearly increases with time in the decoloration process of ***SB*** in PC. The values of the kinetic parameters τ_0 and 1/α were obtained from the intercept and slope of the straight lines, respectively, and their temperature dependence are shown in Figure 3. Both the initial lifetime τ_0 and 1/α decrease with increasing temperature.

The decrease in the value of 1/α indicates that the decoloration in polymer matrix tends towards a homogeneous process with increasing temperature. Generally, the distribution of free volume of polymer becomes narrower as temperature increases, and disappears above Tg.[13] It suggests that the value of 1/α tends to zero and the decoloration will proceed as a homogeneous process following the first-order kinetics above Tg of the polymer matrix. The details are now under investigation.

References and Notes

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12 Combination of eqs. 3 and 4 leads to

$$R = \int_0^{\infty} \frac{\lambda}{\Gamma(\alpha)} (\lambda k)^{\alpha-1} e^{-(\lambda+t)k} dk \tag{8}$$

where Γ(α) is the Gamma function defined by

$$\Gamma(\alpha) = \int_0^{\infty} x^{\alpha-1} e^{-x} dx \qquad (\alpha > 0) \tag{9}$$

If *k* is substituted by $y = (\lambda + t)k$, eq. 8 can be rewritten as

$$R = \left(\frac{\lambda}{\lambda+t}\right)^{\alpha} \cdot \frac{1}{\Gamma(\alpha)} \int_0^{\infty} y^{\alpha-1} e^{-y} dy \tag{10}$$

According to the definition of Gamma function (eq. 9), it is obvious that

$$\int_0^{\infty} y^{\alpha-1} e^{-y} dy = \Gamma(\alpha)$$

Therefore, eqs. 5a and 5b are obtained.
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