

Aging Effect on the Thermal Bleaching Reaction of Photomerocyanine Form of Spiroanthoxazine Doped in Polystyrene Film

In-Ja Lee

Department of Chemistry, College of Natural Science, Dongguk University, Kyongju-si, Kyongpook 780-714, Korea

Received November 13, 2000

Keywords : Thermal bleaching, Spiroanthoxazine, Dispersive kinetic, Local free volume, Aging.

It is well known that the reactions of photochromic compounds doped in amorphous solids deviate from the single exponential kinetics even if their elementary steps are unimolecular reactions which lead to the first-order reaction in solutions.¹⁻⁷ Examples are thermal back reactions of photochromic compounds of azobenzenes,^{1,2} stilbenes² and indolinospiro compounds.³⁻⁷ These results imply that the photochromic and thermochromic reactions of the compounds dispersed in or linked to the polymer chain may be widely used to obtain the information regarding on the disorder and the local free volume of the polymer.

Various models have been proposed to account for the deviation from the first-order reaction of the thermal back reaction of the photochromic compounds dispersed in the amorphous solids. Among them the bi-exponential decay,⁴ stretched exponential decay,⁵ local free volume model^{1,2} and dispersive kinetic model^{3,6,7} are the most frequently used. Although each model utilized different methods and assumptions to derive the governing equations, there is a point of sameness, that is, that all require a distribution of relaxation times or free volume to explain the anomalous behavior in the polymer matrices.

The distribution of the relaxation times has its origin in the inherent structural disorder of the amorphous solids below glass transition temperature T_g . Below T_g , the amorphous solids are not in the equilibrium state. Because the guest molecules dispersed in the polymer matrices are coupled to the local environment, which vary point by point, the different guest molecule sees different energy and different local free volume. The amorphous solid in the non-equilibrium state slowly approach toward an equilibrium. This slow approach is termed physical aging and is known to affect various characteristics of the amorphous solids and the reactions in the solids. Examples are local free volume,^{1,2} dielectric constant relaxation,⁸ and x-ray scattering.⁹

In this work, the aging effect on the thermal bleaching reaction of spiroanthoxazine doped in the polystyrene film has been measured using laser photolysis method and analyzed using the dispersive kinetics. The results are interpreted by combining the concept of the local free volume.

Experimental Section

Spiroindolinanthoxazine (SNO) was purchased from Tokyo Kasei Kogyo Co. and used without further purifica-

tion. Polystyrene (PS) and spectrograde toluene were purchased from Aldrich. Thin films of PS containing 3% SNO were prepared by using solvent-cast method from toluene.

The photocoloration of the samples was achieved by a single pulse from a pulsed N₂ laser (337 nm, Laser Photonics LN-1000). A yellow He-Ne laser (594 nm, Edmund G3941) was used as a probe beam and a PMT (R928) was used to detect the change in probe beam intensity. The time traces of the transmission after cessation of photoirradiation were collected using an oscilloscope (HP54600B) and were transferred to a personal computer for data analysis. The temperature of the sample was maintained within ± 0.1 °C of the desired temperatures using a cryostat (Janis VPF-475) and a temperature controller (Lakeshore Model 330).

Analysis of Kinetics of Thermal Bleaching Reaction

The thermal bleaching reaction of photomerocyanine (PMC) follows the first-order reaction in solutions and the concentration of PMC varied with time as $[PMC] = [PMC]_0 e^{-kt}$, where $[PMC]_0$ is initial concentration, t is elapsed time and k is rate constant, which is expressed as Arrhenius equation $k = A e^{-E_a/RT}$. Here, A is frequency factor and E_a is activation energy.

Because the energy of PMC doped in polymer depends on the large number of internal coordinates, it is appropriate to assume that the activation energy for the reaction of PMC below T_g is subject to a distribution. Similar assumption is employed in the hole-burning spectroscopy to interpret the hole growth kinetics.¹⁰⁻¹² In the case of reactions consisting of many decoupled contribution, the concentration of PMC as a function of time is expressed as the convolution of a distribution function of the activation energy, $g(E_a)$, and the individual decay function.^{3,6,7,10-12}

$$[PMC] = [PMC]_0 \int g(E_a) e^{-k(E_a)t} dE_a \quad (1)$$

where $[PMC]_0$ is concentration of PMC at the end of the laser pulse. The gaussian distribution is utilized for $g(E_a)$ in this paper. For the numerical integration, Bode's approximation has been utilized.

Results and Discussions

Figure 1 shows the change of normalized absorbance of

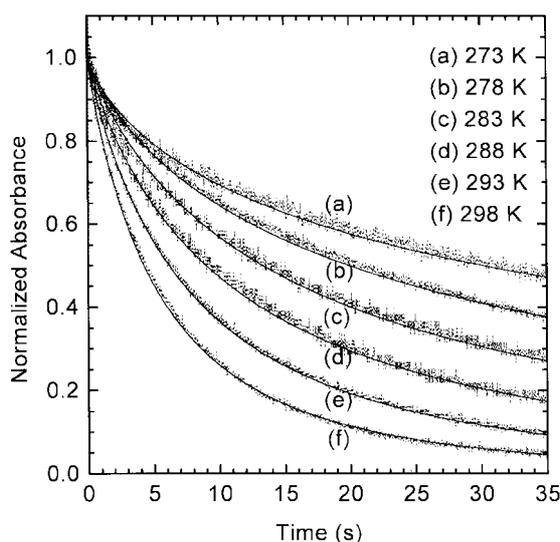
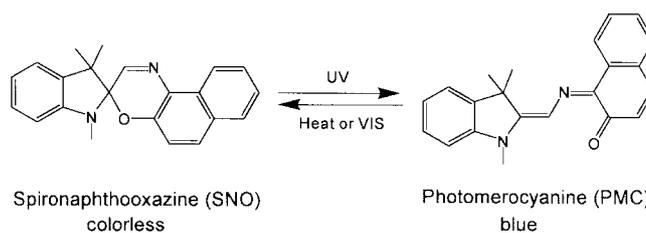


Figure 1. Theoretical fit to the thermal bleaching reaction of PMC form of SNO doped in PS. For all different temperatures, same fitting parameters were used. The dotted lines are experimental data and the solid lines represent fits obtained using Eq. (1). The fitting parameters are listed in Table 1.

PMC in PS as a function of time at various temperatures. The sample used was made 10 days prior to the measurement. The noisy curves are experimental data and the solid curves are theoretical best fits obtained with Eq. (1) using the same mean activation energy, 55.0 kJ/mol, and the same pre-exponential factor $1.05 \times 10^9 \text{ s}^{-1}$ for all temperatures studied. In fact, the frequency factor depends on the temperature because the rate constant k for the unimolecular reaction is expressed as $k = \{ek_B T/h\} e^{\Delta S^\ddagger/R} e^{-E_a/RT}$. Here k_B is Boltzmann constant and h is Planck constant. However, k is not affected by the frequency factor as much as by the activation energy. Therefore, only the temperature dependent parameter used in the fitting procedure is the standard deviation of the activation energy, σ and the fitting parameters are listed in Table 1. It is previously reported that the activation energy of the thermal bleaching reaction of PMC is greatly influenced by the solvent polarity although the reaction mechanism is same for all solvents studied.¹³ For example, the activation energy varies from 61.46 kJ/mol in toluene to 92.10 kJ/mol in methanol. The fact that the activation energy

Table 1. Thermal aging effects on the thermal bleaching reaction of PMC doped in PS

parameters	days	10	38
		E_a (kJ/mol)	55
A (s^{-1})/ 10^{10}		0.105	0.00029
σ (J/mol)	298 K	3150	3700
	293 K	3200	4000
	288 K	3400	4300
	283 K	3600	4600
	278 K	3800	4900
	273 K	4000	5200



Scheme 1

measured in PS is 55 kJ/mol, which is close to those in the various nonpolar solvents (61.46–63.83 kJ/mol) indicates that the molecular environments in PS are similar to those in nonpolar solvents.

Upon ultraviolet irradiation, SNO experiences heterolytic cleavage of C–O spirobond of oxazine ring and then immediate rotation of a part of the molecule to achieve coplanarity to give PMC (Scheme 1). Then the open PMC thermally fades to the closed SNO. As long as the local free volume around PMC molecule in the amorphous solids is greater than the critical free volume, the rate of the thermal back reaction of PMC may be independent on the local free volume and follow the first-order reaction. However, when the local free volume is smaller than the critical free volume, the rotation around the bridge between the two rings is restricted and some of PMC in a strained conformation may be trapped during the UV irradiation below T_g . Similar considerations were given for the thermal back reaction of azobenzenes.¹⁴ Because partially relaxed PMCs are in higher energy state than the fully relaxed PMCs, they could have smaller activation energy for the thermal back reaction and, therefore, revert back to SNO at a faster rates than the fully relaxed PMCs. Table 1 lists the standard deviation of the activation energy, σ , obtained by the dispersive kinetic analysis. The large σ value implies that the microscopic environment around PMC is quite heterogeneous. The increase of σ with decreasing temperature are attributed to the restriction of mobility in the polymer solids at lower temperatures, which give rise to the decrease in the local free volume.

Figure 2 shows the change of normalized absorbance of PMC in PS as a function of time measured on tenth day (PMC_{10th}) and thirty-eighth day (PMC_{38th}) after the sample has been made. In general, at 298 K the rate of the thermal back reaction of PMC_{10th} is similar to that of PMC_{38th} except in the initial part, where the rate of PMC_{38th} was faster than that of PMC_{10th}. The separation of adjacent curves for PMC_{38th} is smaller than that for PMC_{10th}. Because the smaller temperature effect on the reaction rate corresponds to the smaller activation energy, Figure 2 implies that the activation energy decreases with aging. The fitting parameters on PMC_{38th} obtained from the dispersive kinetic analysis are also listed in the Table 1. It shows that with aging the activation energy and the frequency factor decreases while the standard deviation of the activation energy increases. These results are interpreted as follows: because quite large fraction of sites has local free volume similar to or larger than the critical free volume when the polymer is initially

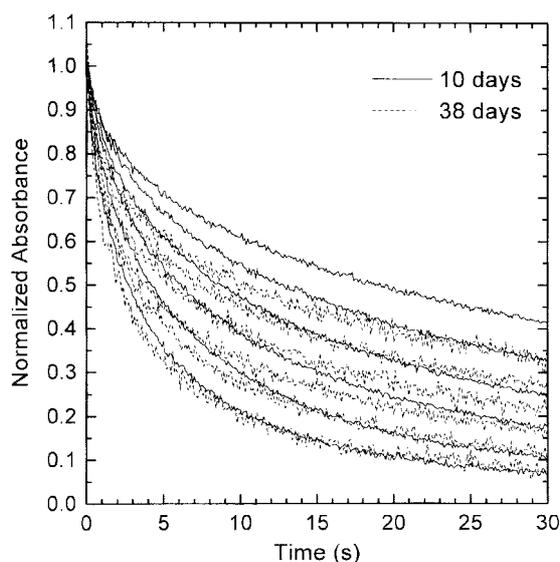


Figure 2. Aging effects on the thermal bleaching reaction of PMC in PS at various temperatures. Probe wavelength was 594 nm. Temperatures of the sample are 298 K, 293 K, 288 K, 283 K, 278 K, and 273 K from the bottom for each set of data.

made below T_g , the mean of the activation energy is close to those in the nonpolar solvents¹³ and its standard deviation is relatively small. Because with aging the local free volume of these sites slowly decreased and their fraction decreases, the average activation energy becomes smaller and the standard deviation becomes larger. The fact that the frequency factor A , which is expressed as $A = \{ek_B T/h\} e^{\Delta S^\ddagger/R}$, decreases with aging implies the decrease in the activation entropy. As mentioned in the previous paper,¹³ ΔS^\ddagger is negative in the nonpolar environments due to the formation of an ordered transition state having orthogonal SNO geometry with C-O bond cleavage. Therefore, the decrease in ΔS^\ddagger with aging indicates the production of PMC having larger entropy and it may be explained by fact that the decrease in the local free

volume around SNO causes PMC in a strained conformation.

In summary, the thermal bleaching reaction of PMC form of SNO doped in PS has been studied by the flash photolysis method and the results are analyzed using the dispersive kinetics. The activation energy of the reaction is similar to those obtained for nonpolar solvents and its standard deviation is large due to significant heterogeneity of the microscopic environment around PMC. With aging, the activation energy decreases while its standard deviation increases. These results are interpreted in terms of the local free volume around PMC.

Acknowledgment. This work was supported by Dongguk University Research Fund, 2000.

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