

# Kinetics of Decolorization of Spiroanthoxazine-Doped Photochromic Polymer Films

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Photochromic polymeric films were prepared by doping photochromic dye spiroanthoxazine into polymer resin gels such as polyurethane, vinyl copolymer, and copolymer of vinyl and nitrocellulose at different concentrations. All of the composite films show normal photochromism. The kinetics of the photochromism/decoloration in the films were quantified by fitting biexponential equations to their photochromic decay curves after irradiation. It was observed that the decoration process is faster in vinyl copolymer than that in the copolymer of vinyl and nitrocellulose and is the slowest in the case of polyurethane. The decoloration mechanisms of spiroanthoxazine in those polymeric matrixes have been discussed.

## Introduction

Several materials such as dyes and other chemical systems exhibit a color change when they are exposed to certain types of radiation and regain their original color upon removing the irradiation. This reversible color change process has been called photochromism. Photochromism of organic compounds in heterogeneous systems is a phenomenon of great interest not only for practical applications but also for elucidating primary photochemical reactions.<sup>1–4</sup> The photophysical processes of aromatic carbonyl molecules in solutions and solid matrixes depend on the geometrical and electronic properties of individual molecules, as well as on the physicochemical properties of the surrounding media.<sup>5,6</sup> Photochromism is also accompanied by changes in the refractive index, dielectric constant, enthalpy, and so forth. These modifications other than color change are intrinsic phenomena, which offer vast possibilities of practical applications of these photochromic compounds. As the reversible property variation in photochromic compounds are induced by molecular-level changes, several changes in physical as well as chemical properties may be observed when photoisomerized molecules trigger subsequent rearrangements of microenvironmental states upon light absorption. Therefore, photochromic materials act essentially as transducers and should be called photoresponsive materials, the properties of which change reversibly.

Photochromic systems exhibiting phase transitions with a number of photoresponsive polymers have been studied widely in the areas of micelles, vesicles, and liquid crystals.<sup>7</sup> Such phase transitions are extremely sensitive to changes in the molecular structure of photochromic compounds and have potential significance in practical applications. The decoloration kinetics and color reversibility are the essential properties of photochromic materials for various applications. However, irreversible degradation upon prolonged light irradiation of photochromic materials sometimes restricts their practical uses. The decoloration kinetics of photochromic materials in different matrixes depend on the characteristics of the host, such as the polarity

and rigidity, which critically affect the physical and chemical functions of the photochromic materials. In previous studies, the kinetics and rigidity of the glass gel matrixes and polymeric systems were intensively studied by doping photosensitive organic photochromic and photosensitive compounds.<sup>8–12</sup> The kinetics of the photochromic change of the molecules doped in the polymer matrixes were critically dependent on the kind and structure of the polymer matrixes and glass gel matrixes. The rigidity of the matrix around a photosensitive molecule can control its relaxation kinetics after light excitation. Photoinduced radical yields of photosensitive molecules such as viologens, phenothiazines, and benzidines in inorganic silicate matrixes were studied with electron paramagnetic resonance (EPR) and UV–vis diffuse reflectance spectroscopies.<sup>13–16</sup> Charge recombination of electron–cation pairs formed in polymer solids through two-photon ionization was examined in terms of long-range electron transfer by electron tunneling.<sup>17</sup> In those studies, the yield of the photogenerated radicals was controlled by matrix rigidity and the long-range electron-transfer distance. The photoionization of *N*-methylphenothiazine in poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) matrixes was studied with EPR and electron nuclear double resonance (ENDOR).<sup>18</sup> The decay time of the photogenerated radicals in PEO and PPO at 77 K was studied by determining the amount of the remaining radicals with exposure time. Kinetic constants for biexponential decay of the cation radicals were obtained. The photochromic effect and spatial light modulation in photosensitive-dye-doped polymeric films have also been studied.<sup>19–25</sup>

Spiroanthoxazine, a highly photostable and photosensitive organic dye, was doped into different polymeric gel matrixes such as polyurethane, vinyl copolymer, and a copolymer of vinyl and nitrocellulose in the present study.<sup>26</sup> Those polymer films are commercially available and widely applied for plastic coatings. The photochromic behaviors of the dye doped in polymer matrixes of different polarity and structure are studied.

## Experimental Section

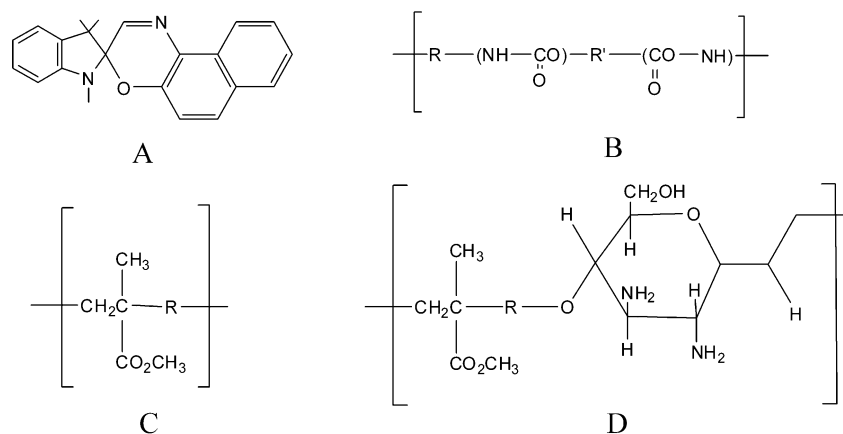
**Materials.** 1,3-Dihydro-1,3,3-trimethyl-spiro[2H]-indole-2,3'-[3H]-naphtho[2,1,b][1,4]-oxazine (Figure 1A) was obtained from Aldrich Chemical Co. and used without any further purification. The polyurethane, vinyl copolymer, and copolymer of vinyl and

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**Figure 1.** The structure of 1,3-dihydro-1,3,3-trimethyl-spiro[2H-indole-2,3-[3H]-naphtho[2,1,b][1,4]-oxazine] (A), polyurethane (B), vinyl copolymer (C), and a copolymer of vinyl and nitrocellulose (D).

nitrocellulose matrixes (Figure 1B, C, and D) were kindly donated by Hyundai Petrochemical Co. (Korea) and used without further purification. Organic solvents, such as dichloromethane, chloroform, methanol, and acetone, were of reagent grade and used as received from Fisher.

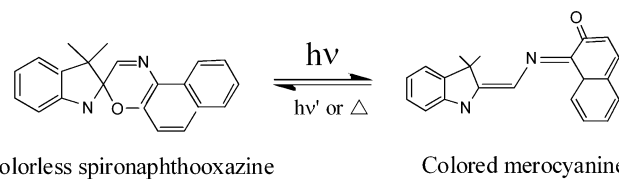
**Preparation of Polymeric Gel Films.** A 0.05 M spironaphthooxazine solution was prepared in the mixed solvent of dichloroform (1 mol) and acetone (1 mol). The spironaphthooxazine solution was mixed into each polymeric resin of polyurethane/cyclohexanone, vinyl copolymer/DMF, and the copolymer of vinyl and nitrocellulose/chloroform, maintaining the spironaphthooxazine at 1, 2, and 3 wt % of the polymeric resins. Each of the prepared polymeric resin was spin-coated onto the glass surface for 10 min at 1000 rpm and dried at 60 °C for 20 min. The thicknesses of the polymeric gel films determined by an  $\alpha$ -step profilometer were between 25 and 30  $\mu\text{m}$ .

**UV–Vis Absorption.** Photoirradiation of the samples was initially carried out at room temperature for 10 min using a 300 W Xe lamp (LX 300 UV) fed by an ILC Technology power supply. This initial irradiation was performed for closing the ring of spironaphthooxazine completely. The light passed through a 10 cm water filter and a glass filter (Corning Glass filter 4-97) to allow the radiations of  $\lambda > 350$  nm. The light intensity at the sample position was 13.85  $\text{mW}/\text{cm}^2$  as measured by the Molecron Detector and Hewlett–Packard 34401 A multimeter. After the initial irradiation, the samples were irradiated again with  $230 < \lambda < 400$  nm for different times using a glass filter (Corning 7-54). The intensity of the light at the sample position was 2.21  $\text{mW}/\text{cm}^2$ . UV–vis absorption spectra of the samples were recorded by a Varian Carry UV–vis spectrophotometer. All of the experiments were carried out at room temperature.

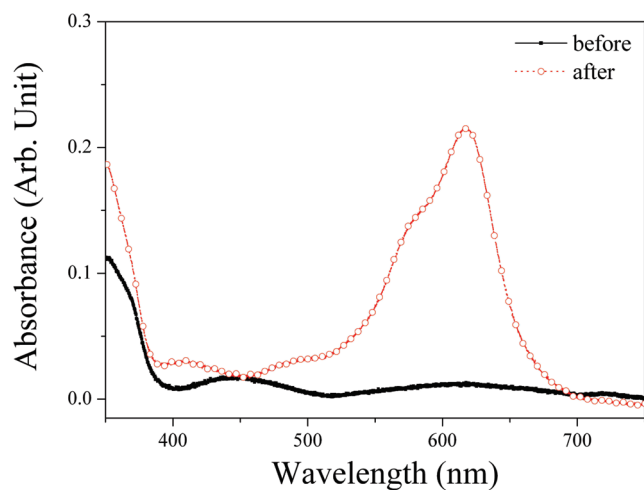
**Data Manipulation Using Origin 6.0 Software.** The absorption intensity decay at  $\lambda_{\text{max}}$  was studied for all of the samples until 20 min after photoirradiation. The intensity decay curves were fitted with exponential functions of Origin 6.0 software to obtain the pre-exponential constants ( $A_{\text{th}}$ ,  $A_1$ , and  $A_2$ ) and kinetic constants ( $k_1$  and  $k_2$ ) of the biexponential kinetic equation to study the photochromic kinetics of the spironaphthooxazine-doped polymeric gel films.

## Results and Discussion

The structures of 1,3-dihydro-1,3,3-trimethyl-spiro[2H-indole-2,3-[3H]-naphtho[2,1,b][1,4]-oxazine] (A), polyurethane (B), vinyl copolymer (C), and the copolymer of vinyl and nitrocellulose (D) are shown in Figure 1. The structures of the closed and



**Figure 2.** The structure of the closed and opened forms of spironaphthooxazine during coloration by irradiation of light and decoloration without light.

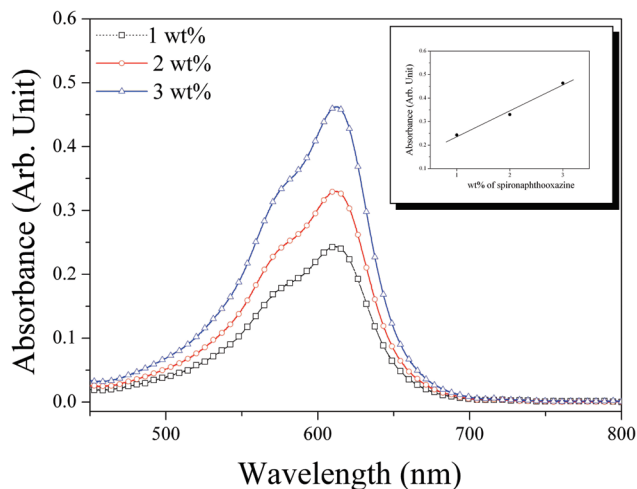


**Figure 3.** Optical absorption spectra of spironaphthooxazine in the copolymer of vinyl and nitrocellulose before (—●—) and after (—○—) irradiation of light in the range of  $230 < \lambda < 420$  nm for 20 min.

**TABLE 1:  $\lambda_{\text{max}}$  Values of Spiroapththooxazine in the Different Matrixes**

matrixes	copolymer of vinyl and nitrocellulose	polyurethane	vinyl copolymer
$\lambda_{\text{max}}$ (nm)	614	617	612

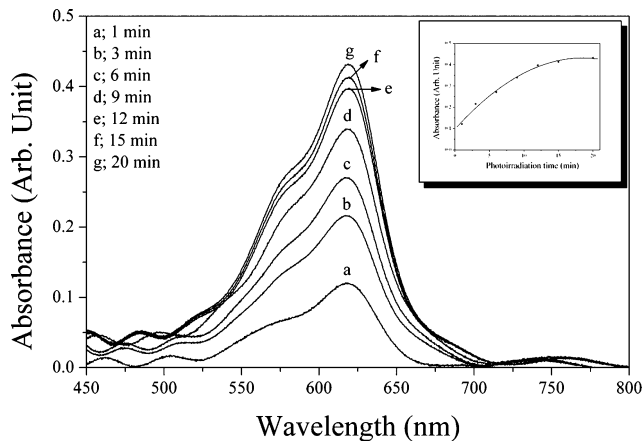
and open forms of spironaphthooxazine during coloration by irradiation and during decoloration in darkness are shown in Figure 2. The optical absorption spectra of spironaphthooxazine incorporated into the copolymer of vinyl and nitrocellulose, before and after irradiation of light in the  $230 < \lambda < 420$  nm range, are shown in Figure 3. The absorption spectra obtained after UV irradiation present two peaks, a weak shoulder at about 580 nm and an intense band at about 620 nm. Appearance of the weak absorption band in the visible region indicates that a thermal equilibrium was established between the blue open ring



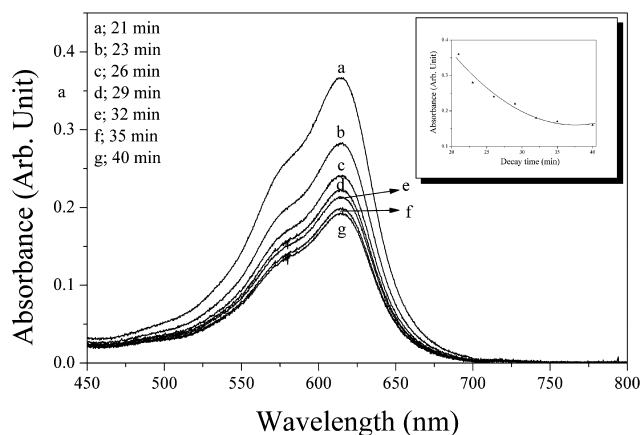
**Figure 4.** Optical absorption spectra of spiroanthoxazine in a copolymer of vinyl and nitrocellulose at different concentrations, after 20 min of irradiation in the range of  $230 < \lambda < 420$  nm. The inset shows the variation of maximum absorbance with spiroanthoxazine concentration.

and colorless closed ring forms, as shown in Figure 2. The  $\lambda_{\max}$  values of the opened form of spiroanthoxazine doped into the different polymeric matrixes are presented in Table 1. A gradual blue shift of  $\lambda_{\max}$  of the open form of spiroanthoxazine while being incorporated into polyurethane versus that incorporated into the copolymer of vinyl and nitrocellulose and further versus that into vinyl copolymer matrixes was observed. Positive solvatochromism is the characteristic of compounds having a weakly polar ground state, implying a small charge delocalization. As the polarity and hydrogen bonding ability of polyurethane  $>$  that of the copolymer of vinyl and nitrocellulose  $<$  that of the vinyl copolymer, the observed change in  $\lambda_{\max}$  values for the opened form spiroanthoxazine incorporated into the polymers is expected. Effects of the polarity and hydrogen bonding ability on the photochromic kinetics have been reported earlier.<sup>8–11</sup>

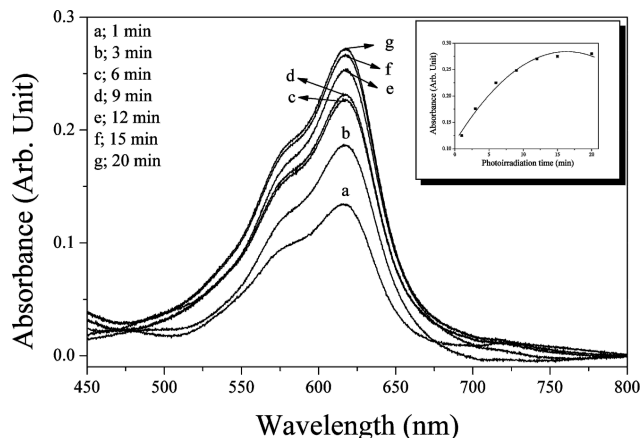
Absorption spectra of spiroanthoxazine incorporated into the copolymer of vinyl and nitrocellulose matrix with different concentrations after 20 min of light irradiation are shown in the Figure 4. The intensity of the absorption peaks increased linearly with the increase of spiroanthoxazine concentration in the polymeric matrix (inset of Figure 4). Variation of the absorption intensity and consequently the absorption peak height of the absorption maxima for the spiroanthoxazine-incorporated copolymer of vinyl and nitrocellulose matrix with irradiation time ( $230 < \lambda < 420$  nm) is shown in Figure 5. The intensity of the 614 nm absorption band reaches the plateau upon light irradiation approximately after 18 min. Longer irradiation time causes a saturation of the absorption intensity, resulting in the decoloration. The decoloration of spiroanthoxazine incorporated into the copolymer of vinyl and nitrocellulose after 20 min of light irradiation was studied by recording its absorption spectra at different time delays in the dark (Figure 6). The absorption intensity decay (inset of the Figure 6) curve follows the first-order kinetics. The increase of absorption intensity with irradiation time and its decay upon decoloration for the spiroanthoxazine incorporated into the vinyl copolymer are shown in Figures 7 and 8, respectively. The increase and decrease of absorption intensity in this case and also that for the spiroanthoxazine incorporated into the polyurethane matrix revealed the same trends as those for incorporation into the copolymer of vinyl and nitrocellulose



**Figure 5.** The optical absorbance change during coloration at 614 nm of spiroanthoxazine in the copolymer of vinyl and nitrocellulose by irradiation of light in the range of  $230 < \lambda < 420$  nm versus irradiation time.

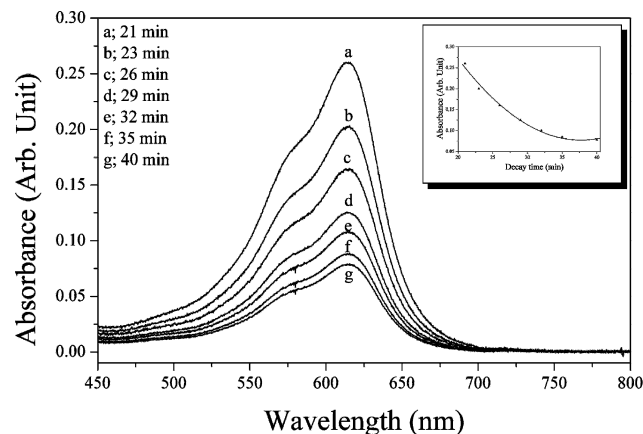


**Figure 6.** The optical absorbance change during decoloration at 614 nm of spiroanthoxazine in the vinyl copolymer after 20 min of irradiation of light in the range of  $230 < \lambda < 420$  nm. The absorbance intensity decay is shown in the inset.

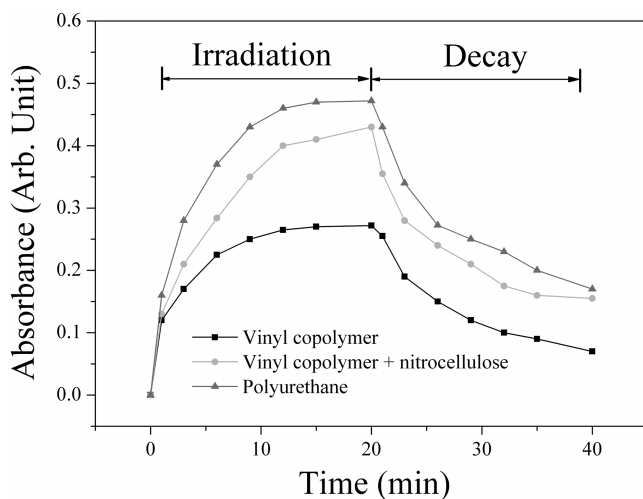


**Figure 7.** The optical absorbance change during coloration at 612 nm of spiroanthoxazine in the vinyl copolymer by irradiation of light in the range of  $230 < \lambda < 420$  nm versus irradiation time.

matrixes. The behaviors of spiroanthoxazine incorporated into all of the polymeric matrixes studied here manifested normal photochromism, which indicates that the used polymer matrixes are not polar enough to induce drastic change in the microenvironment of spiroanthoxazine required for observing reverse photochromism. The reverse photochromism can occur only in the highly polar microenvironment of the matrixes.



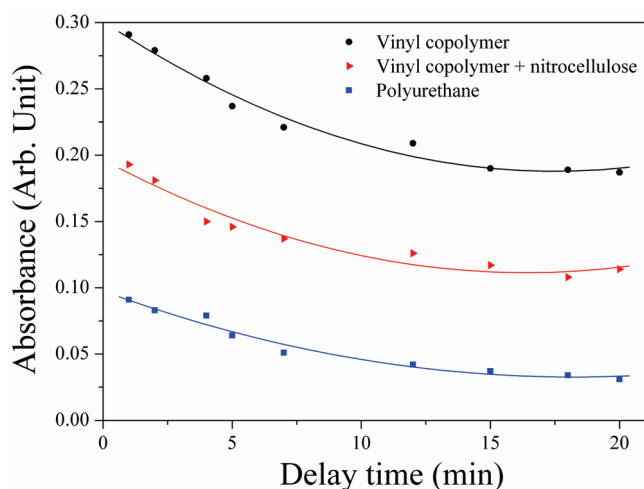
**Figure 8.** The optical absorbance change during decoloration at 612 nm of spironaphthooxazine in the vinyl copolymer after 20 min of irradiation of light in the range of  $230 < \lambda < 420$  nm. The inset shows the absorbance decay with delay time.



**Figure 9.** Optical absorbance at  $\lambda_{\max}$  of spironaphthooxazine doped in the vinyl copolymer (—■—), the copolymer of vinyl and nitrocellulose (—●—), and polyurethane (—▲—) with irradiation of light in the range of  $230 < \lambda < 420$  nm for 20 min and without light for 20 min more.

Previous studies have demonstrated that the open merocyanine form of the spironaphthooxazine can be formed instantly in highly polar tetraorthosilicate (TEOS) gel, as the zwitterionic structural form of merocyanine can be easily stabilized in the highly polar TEOS gel matrix,<sup>8,9</sup> leading to a reverse photochromism of spironaphthooxazine in the TEOS gel matrix. In the present study, the used polymer matrixes were not highly polar to induce reverse photochromism in spironaphthooxazine. The coloration and decoloration processes of spironaphthooxazine in each of the used polymer matrixes are shown in Figure 9, where the  $\lambda_{\max}$  of absorption was monitored during 20 min of UV irradiation ( $230 < \lambda < 420$  nm) and after 20 min of delay in darkness. All of the samples show normal photochromism.

The kinetics of the thermal bleaching or ring closure (decoloration) was studied following the fading of color at  $\lambda_{\max}$  of the open form of spironaphthooxazine. The kinetics of the photochromism in these polymer gels was quantified using simple biexponential models in order to take into account the inhomogeneous distribution of free volume in the polymer gel matrixes and to compare the photodynamics among them. The absorbance decay curves due to the decoloration process of spironaphthooxazine in different polymer matrixes are shown in Figure 10. All of the decay curves follow biexponential



**Figure 10.** Optical absorbance decay at 616.6 nm of spironaphthooxazine doped in the vinyl copolymer (●), a copolymer of vinyl and nitrocellulose (left-pointed triangle), and polyurethane (■) during the decoloration process after initial irradiation in the range of  $230 < \lambda < 420$  nm for 20 min.

**TABLE 2: Kinetic Constants of the Biexponential Equation for the Decoloration of the Opened Form of Spironaphthooxazine Doped at Different Matrixes**

constants	copolymer of vinyl and nitrocellulose	polyurethane	vinyl copolymer
$A_{th}$	0.1800	0.0257	0.0719
$A_1$	0.0695	0.0394	0.0742
$k_1$	0.1710	0.1293	0.3771
$A_2$	0.0620	0.0364	0.0745
$k_2$	0.1293	0.0330	0.1330

relations. The kinetic constants extracted from the biexponential fittings of the absorption decay curves for all of the samples are presented in Table 2.

The kinetics of the thermal unimolecular reactions of spironaphthooxazine from metastable species to stable ones did not proceed as first-order kinetics. In fact, it was generally accepted that the common observation of nonexponential isomerization kinetics in polymer gel matrixes indicates the site-specific matrix effects by imposing a distribution of localized barriers on the steric requirements of the reaction.<sup>27–29</sup> Attribution of the deviation from first-order kinetics to the conformational statistics of the matrixes was confirmed by the approach to a single-exponential decay pattern. The results can be analyzed by using the Gaussian model developed by Albery et al., which has been applied to porous silica by Samuel and co-workers.<sup>30</sup> The basic assumption of the model is that the distribution of rate constants,  $k$ , is governed by the normal distribution of free energy. Kinetic data concerning the thermal bleaching reaction of spironaphthooxazine in polymer gel matrixes has been previously analyzed as a biexponential process.<sup>31</sup> In this case; the thermal ring closure of the spironaphthooxazine can be described by the equation

$$A(t) = A_{1e}^{-k_1 t} + A_{2e}^{-k_2 t} + A_{th} \quad (1)$$

where  $A(t)$  was the optical density of spironaphthooxazine at 623 nm and  $A_1$  and  $A_2$  were contributed to the initial optical density  $A_0$ .  $A_{th}$  reflects the thermal equilibrium between the closed and the opened forms of spironaphthooxazine.

In this simple model, the spiroanthoxazine molecule in the copolymer of vinyl and nitrocellulose, polyurethane, and vinyl copolymer matrixes was thermally decolorized with different rate constants. From the viewpoint of a uniform distribution of free volume, the separated constants  $k_1$  and  $k_2$  should be understood as empirical mean values between the fast and the slow kinetic constants. The constants extracted from the fitting of the experimental data for different samples by using the biexponential relation were analyzed to deduce the mean activation energy for the equilibrium. The density constants ( $A_1$ ,  $A_2$ , and  $A_{th}$ ) indicate the contribution of each thermal decoloration reaction of spiroanthoxazine in the polymer gel matrixes. The decreasing values of the kinetic constants ( $k_1$  and  $k_2$ ), vinyl copolymer > copolymer of vinyl and nitrocellulose > polyurethane matrix, indicate the increasing stability of the open form of the spiroanthoxazine in the polymer gel matrix, vinyl copolymer < copolymer of vinyl and nitrocellulose < polyurethane. The lowest values of the kinetic constants obtained for the polyurethane matrix indicate that the opened form of spiroanthoxazine is more stable in polyurethane, which has higher polarity and hydrogen bonding ability than the other matrixes used in the present study. The high polarity and hydrogen bonding ability of polyurethane suppress the decoloration process of spiroanthoxazine, offering stability to the zwitterionic structure of the open form of spiroanthoxazine. On the other hand, the vinyl copolymer matrix has the lowest polarity and no hydrogen bonding ability. This results in the highest kinetic constant values of thermal back reaction of spiroanthoxazine in the polymer.

The kinetic parameters of the thermal fading for spiroanthoxazine doped in the polymer gels should also be dependent on the rigidity of the matrixes in parallel with the polarity of the matrixes. In the previous studies,<sup>8,9</sup> this is clearly shown by determining proton matrix electron nuclear double resonance (ENDOR) line widths. The results on the proton matrix ENDOR line widths of photogenerated *N*-methylphenothiazine cation radicals in the these polymer gel matrixes were reported earlier.<sup>32</sup>

## Conclusions

The decreasing kinetic constant of the decoloration of spiroanthoxazine in the polymer matrix as vinyl copolymer > nitrocellulose + vinyl copolymer > polyurethane matrix indicate the increasing stability of the opened form of the spiroanthoxazine in the polymer gel matrix as vinyl copolymer < nitrocellulose + vinyl copolymer < polyurethane. The greater polarity of the gel matrixes suppresses the kinetics of the decoloration by the greater stability of the zwitterionic structure of the opened spiroanthoxazine in the gel matrixes.

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