

# Electron Magnetic Resonance Studies on the Photoinduced Charge Separation of *N*-Methylphenothiazine in the Gel Matrixes of Phenyltriethoxysilane, Vinyltriethoxysilane, and Methyltriethoxysilane

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The photoproduced cation radical of *N*-methylphenothiazine (PC<sub>1</sub>) doped into phenyltriethoxysilane (PhiTEOS), vinyltriethoxysilane (VTEOS), and methyltriethoxysilane (METOS) was studied with electron spin resonance (ESR) and electron nuclear double resonance (ENDOR). The photoinduced charge separation efficiency was determined by integration of ESR spectra which correspond to the amount of photoproduced cation radical in the matrixes. This was correlatively studied with the polarity and pore size of the gel matrixes. The relative polarity of the matrixes was determined by measuring  $\lambda_{\text{max}}$  values of PC<sub>1</sub> in the different matrixes. The relative pore size among the matrixes was determined by measuring relative proton matrix ENDOR line widths of the photoproduced cation radical of PC<sub>1</sub>. The decay kinetic constants of the cation radical of PC<sub>1</sub> in the different matrixes were relatively studied with fitting the biexponential decay curves after exposure at the ambient condition. This is correlatively interpreted with the polarity and pore size of the matrixes.

## Introduction

The sol–gel process provides a low-temperature synthetic route to various inorganic oxide glasses and provides a method to trap organic molecules in a solid matrix.<sup>1–5</sup> Doping organic compounds into an inorganic oxide using sol–gel processes opens a range of possibilities for the preparation of optical materials whose properties can be tuned by selecting appropriate organic components. In this process, metal oxides hydrolyze at relatively low temperature to form porous glass, which are then transformed into dense glasses by sintering. The polymerization process is usually initiated by adding water to a solution of alkoxide in ethanol. With silicon alkoxide precursors, such as tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), and phenyltriethoxysilane (PhiTEOS), the chemical conditions are defined so that nearly complete hydrolysis occurs in a few minutes. The gels turn into dried materials known as xerogels after conventional drying in air at low temperature.<sup>6–10</sup> Photochromic glasses have been prepared by sol–gel methods by doping several kinds of organic materials into the gel matrixes.<sup>11–13</sup> The photochromic behavior was related to the microenvironment and structure of the cage within which photochromic molecules were trapped. The polarity and pore size of the gel cage affects the photochromic kinetic and the normal or reverse photochromism of molecules in the gel matrixes. The polarity of the gel cage controlled the photochromic behavior of spiropyran. The photochromism of spironaphthooxazine in organic polymer matrixes, such as polyurethane, polynitrocellulose, and vinylcopolymer, and the kinetics of photocoloration of spironaphthooxazine, was studied.<sup>13</sup> The photoinduced charge transfer between pyrene and *N,N'*-dimethylaniline on silica gel was studied with fluorescence quenching and transient absorption techniques.<sup>14</sup> The stabilization of Ru(bpy)<sub>3</sub><sup>2+</sup> at both 77 K and room temperature in silica

gel by chemical oxidation with chlorine gas and by photoinduced electron transfer to suitable electron acceptors was reported.<sup>15</sup>

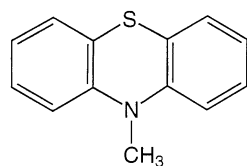
Photoionization of *N*-methylphenothiazine (PC<sub>1</sub>) doped into poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) matrixes resulted in paramagnetic cation radical formation.<sup>10</sup> The amount of radical produced by photoionization is greater in PEO than in PPO and the lifetime of photoproduced radical is relatively longer in PEO than in PPO. These results were interpreted as due to a shorter electron-transfer distance in PEO and to faster radical conversion from phenothiazine cation radical to polymer alkyl chain radicals. This explanation was supported by larger matrix proton electron nuclear double resonance (ENDOR) line widths in PEO than in PPO. In solid disordered systems, the ENDOR spectrum of a radical often shows a single line called a matrix ENDOR line.<sup>16</sup> This line widths have been interpreted as being due to a purely dipolar interaction between an unpaired electron of phenothiazine cation radical and surrounding magnetic protons.

In the present study, *N*-methylphenothiazine doped into different gel matrixes was photoirradiated and the produced phenothiazine cation radical was identified and the quantity of radicals was determined with ESR. The stabilization degree of the photoproduced radical was determined by determining the decay kinetics of the photoproduced phenothiazine cation radical. The different stabilities of the radical in different gel matrixes is interpreted in terms of the pore size and polarity. The relative polarity of the matrixes was determined with  $\lambda_{\text{max}}$  values of the PC<sub>1</sub>. The relative pore sizes of the gel matrixes was determined from proton matrix ENDOR line widths.

## Experimental Section

**Materials.** *N*-Methylphenothiazine (99%) as Figure 1 was synthesized as described elsewhere.<sup>17</sup> PhiTEOS (99%), VTEOS (98%), and MTEOS (99%) were obtained from Aldrich Chemical Co. and used without further purification. House-distilled

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N-Methylphenothiazine  
(PC<sub>1</sub>)

**Figure 1.** The structure of *N*-methylphenothiazine (PC<sub>1</sub>).

water was passed through a four-cartridge Barnstead Nanopure II purification train consisting of macropure treatment, for removing organics, two ion exchangers, and a 0.2  $\mu\text{m}$  hollow-fiber filter for removing small particles. Its resistivity was 18.3 M $\Omega$ . Organic solvents, such as dichloromethane, chloroform, methanol, and acetone, were either ACS certified spectroanalyzed or HPLC grade. The acids used were reagent grade and used as received from Fisher.

**Preparation of Alkoxide Sols.** A 2 mM stock solution of PC<sub>1</sub> in chloroform was prepared and mixed with each sol solution. Each sol solution was prepared by hydrolysis of alkoxide mixed with water and acetone. The mixed solution of alkoxide (1 mol) and acetone (0.75 mol) was prepared by stirring for 5 min. This solution was added slowly into the mixed solution of water (1 mol) and acetone (0.187 mol) drop-by-drop and continuously stirred for 30 min. The resulted sol solutions have 1:4:1.5 molar ratios of alkoxide:water:acetone. The stock solution of *N*-methylphenothiazine was added into the clear alkoxide solution with a 2:1 volume ratio of alkoxide to *N*-methylphenothiazine, and the solution was stirred for 5 min and kept for 12 h without stirring. The concentration of *N*-methylphenothiazine in the final sol solution was determined as 0.4 mM with UV-vis spectrophotometer (Varian Carry 2000,  $\lambda_{\text{max}} = 310$  nm in chloroform,  $\log \epsilon = 5.02$ ).<sup>17</sup> All of these steps were carried out at room temperature.

**Preparation of Spin Coating Gel Thin Films on Quartz Slides.** A quartz slide was cleaned by successive treatment with a saturated KOH solution of 2-propanol for 30 min and 1 M sulfuric acid. The treated quartz slide was sonicated in the pure water for 30 min and dried with a heat gun. Sol solutions for spin coating were filtered with filter paper of 0.2  $\mu\text{m}$  pore size. The filtered sol solution was dropped on the surface of a quartz slide (0.6  $\times$  0.8 cm) in a spin coater. Then, it was spin coated at 1000 rpm for 10 s. The spin-coated sol on the substrate was changed to a gel by heat treatment at 50  $^{\circ}\text{C}$  for 48 h under reduced pressure in a vacuum oven. The coated quartz slide was colorless. The thickness of the gel films on the quartz slide surface was determined with an  $\alpha$ -step 500 surface profiler from Tencor Co. (Model 230), and the thicknesses of MTEOS, VTEOS, and PhTEOS films were determined as being approximately 1.2–1.3  $\mu\text{m}$ . This procedure was repeated three times to prepare three gel thin films of same type gel matrix by spin coating on quartz slides. The relative polarity of gel matrixes was determined with UV-vis spectrophotometer by measuring  $\lambda_{\text{max}}$  values of PC<sub>1</sub> in the different matrixes.

**Photoirradiation.** Photoirradiation of the quartz slide samples was carried out at 77 K with a 300 W xenon lamp (ILC-LX 300 UV) after freezing with liquid nitrogen. A 10 cm water filter and a Corning No. 7-54 filter (240 nm  $< \lambda < 410$  nm) were placed in the light path to give 70% transmittance at 310 nm. The photoyield of the phenothiazine cation radical reached a plateau after 20 min of photolysis. The samples were photoirradiated for 20 min for ESR experiments and 10 min for ENDOR experiments. The shorter time suppresses radical

conversion for ENDOR experiments so that the local environment of the phenothiazine cation radical is probed.<sup>18–20</sup> The light intensity at the sample position was measured with YSI Kettering model 65 radiometer and was  $1.3 \times 10^3$  W/cm<sup>2</sup>. The Dewar holding the sample tube was rotated at 4 rpm during photolysis to ensure even irradiation of the sample.

**Electron Magnetic Resonance Experiments.** ESR spectra were recorded at X-band using a JEOL JES-PX1050 FT-ESR Spectrometer with 100 kHz field modulation. The irradiated sample tube was placed in a quartz ESR Dewar (Wilma Glass Co.) filled with liquid nitrogen and secured in a TE<sub>102</sub> cavity. The loaded  $Q$  factor of this cavity is approximately 1700. The microwave power was maintained at 1.97 mW, which is well below the saturation level for irradiated phenothiazine gel samples. The standard spectrometer settings used in these ESR experiments were 0.281 mT modulation field, 20 mT sweep width, 7 scan accumulations, 56 s scan time constant, 9.501 GHz microwave frequency, and  $1.25 \times 10^5$  receiver gain. The average value of the photoinduced radical yield was determined from triplicate experiments for each system by double integration of the first derivative ESR spectra using the JES-PX software. After 20 min photoirradiation at 77 K, the radical yield was measured at 77 K and after subsequent 5 min exposures to room temperature and then plunging into liquid nitrogen. The radical yield data were normalized by dividing with the radical yield of PC<sub>1</sub> in MTEOS after 20 min photoirradiation at 77 K.

Proton matrix ENDOR spectra were recorded at 141 K using a Bruker 350 ENDOR unit. A Bruker ER 4111 VT nitrogen flow variable temperature unit was used to control and monitor the temperature in the ENDOR cavity. The radio frequency (rf) power was constant at 100 W and was frequency modulated at 12.5 kHz. The resulting microwave response at the center of the desaturated ESR line was synchronously detected at the rf modulation frequency, resulting in a first derivative presentation of the ENDOR spectrum. Each spectrum was accumulated for 64 scans. The ENDOR line width was obtained by measuring the peak-to-peak separation distance of the first derivative signal. The ENDOR line widths are an average of three experiments.

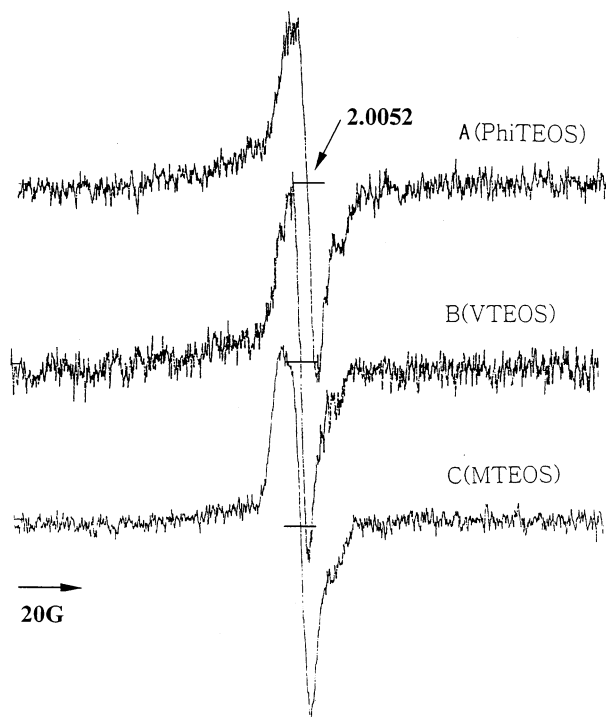
**Kinetic Data Manipulation.** The total radical yield decay curves of *N*-alkylphenothiazine were fitted to the following biexponential using Sigmaplot software.

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{\text{th}}$$

$A(t)$  is the ESR intensity after photolysis;  $A_1$  and  $A_2$  are contributions of the  $k_1$  and  $k_2$  kinetic constants of the rate processes for the back-electron transfer between phenothiazine cation radical and electrons separated from phenothiazine during photoinduced charge separation.  $A_{\text{th}}$  is the contribution from thermal decay. Here, the thermal decay means that the recombination reaction of phenothiazine cation radical with electron in the surroundings of the matrixes. So total decay consists of decay by back-electron transfer and thermal decay.

## Results and Discussion

Photoinduced electron transfer from phenothiazines to interface water of molecular assemblies such as micelles, reverse micelles, and vesicles is well-known from previous studies.<sup>17–20</sup> This photoinduced electron transfer is controlled by the electron-transfer distance between electron donor and acceptors, the type and density of interface charge of the molecular assemblies, and the orientation of the photoionizable molecules with respect to the interface. ESR has been used to determine the amount of photoproduced radical yields by integration of the spectra and



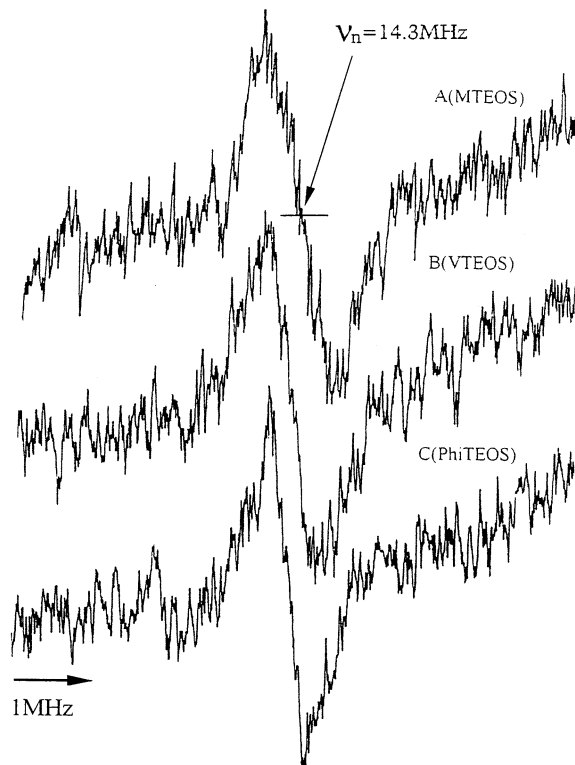
**Figure 2.** X-band ESR spectra of PC<sub>1</sub> in methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), and phenyltriethoxysilane (PhiTEOS) matrixes after 20 min photoirradiation at 77 K.

to identify the photoproduct radicals by hyperfine and *g*-factor parameter of the produced radicals.

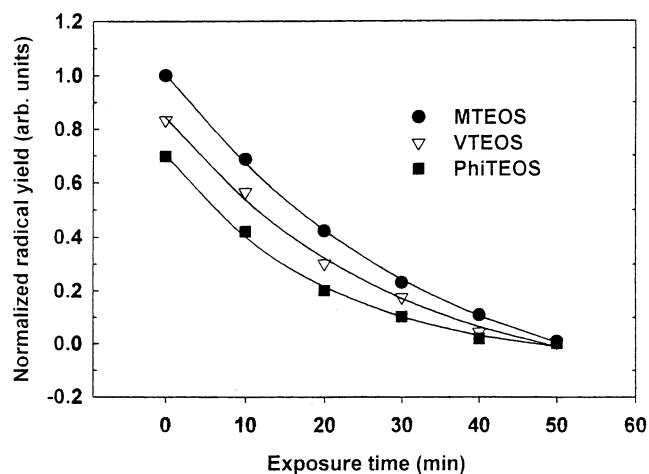
The structure of *N*-methylphenothiazine (PC<sub>1</sub>) is shown in Figure 1. No ESR spectra is observed from the samples which do not contain phenothiazine. This indicates that phenothiazine is the only photosensitive molecule absorbing ultraviolet light in the  $240 < \lambda < 410$  nm region. The photoirradiation of PC<sub>1</sub> doped into the MTEOS, VTEOS, and PhiTEOS matrixes showed a pale pink color which is characteristic of the phenothiazine cation radical.<sup>13,17–20</sup> The intensity of this pink color increased, reached a maximum, and decreased with increasing irradiation time. The doubly integrated ESR intensity reached a plateau after 20 min photoirradiation.

ESR spectra of PC<sub>1</sub> doped into MTEOS, VTEOS, and PhiTEOS matrixes after 20 min photoirradiation are shown in Figure 2. A characteristic broad singlet appears at  $g = 2.0052$ . This assignment is consistent with reported *g*-values.<sup>13,17–20</sup> The weak multiplet signals are possibly due to radical conversion of phenothiazine cation radical into an organic gel radicals. This is already reported in previous studies.<sup>13,17–20</sup> As the photoirradiation time is increased, the signal intensity of the phenothiazine radical decreases in parallel with an increasing signal of the organic group radicals. This together with a loss of pink color indicates radical conversion from a primary phenothiazine cation radical to an organic gel radical during photoirradiation.

Proton matrix ENDOR spectra of PC<sub>1</sub><sup>+</sup> in MTEOS, VTEOS and PhiTEOS after 10 min photoirradiation are shown in Figure 3. The ENDOR transition is centered at 14.3 MHz, which is characteristic of a proton in the 0.3377 T magnetic field. The organic group proton line widths of the ENDOR spectrum of PC<sub>1</sub> in PhiTEOS, VTEOS, and MTEOS matrixes are 0.82, 0.95, and 1.02 MHz, respectively. A broader proton ENDOR line width indicates a higher proton density around the phenothiazine cation radical which indicates a shorter interaction distance of phenothiazine cation radical to the organic groups of the gel matrixes.



**Figure 3.** Proton matrix ENDOR spectra of PC<sub>1</sub> in methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), and phenyltriethoxysilane (PhiTEOS) matrixes at 141 K after 10 min photoirradiation at 77 K.



**Figure 4.** Normalized radical yield of PC<sub>1</sub> in methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), and phenyltriethoxysilane (PhiTEOS) matrixes versus the exposure time of the samples at room temperature. The decay curves fitting biexponential equation show the relaxation process of produced radical by recombining with electron.

Figure 4 shows data on the total radical yield after 20 min photoirradiation at 77 K followed by several 5 min exposures to room temperature. The total radical yield of PC<sub>1</sub> in MTEOS was the highest and is normalized to unity. The amount of photoproduct radical biexponentially decreased with increasing total exposure time to room temperature. The slope of the biexponential decay curve of PC<sub>1</sub><sup>+</sup> in the gel matrixes increased as MTEOS < VTEOS < PhiTEOS. The decay rate constants of PC<sub>1</sub><sup>+</sup> in the gel matrixes are shown in Table 1. No ESR signal is obtained after 60 min exposure to room temperature for the four gel samples. In this study, *N*-methylphenothiazine was doped into the gel matrixes and photoinduced electron



**TABLE 1: Constants for Biexponential Decay of Photoproducted *N*-Methylphenothiazine Doped Into MTEOS, VTEOS, and PhiTEOS Matrixes<sup>a</sup>**

constants	MTEOS	VTEOS	PhiTEOS
$A_{th}$	0.29	0.19	0.08
$A_1$	0.67	0.54	0.39
$k_1$	0.03	0.05	0.05
$A_2$	0.62	0.49	0.40
$k_2$	0.03	0.04	0.05

<sup>a</sup> The estimate parameter error is  $\pm 0.005$ .

transfer from phenothiazine resulted in charge separation. The acceptor is probably water which is hydrogen bonded to the oxygens of the gels. Water interacting with the oxygen of alkoxide gels and polymers such as poly(ethylene) oxide and poly(propylene) oxide are well-known.<sup>1,2,21</sup> This is supported by a decreased radical yield with increasing sample gelation time which removes some of this water. The decreasing radical yield of  $PC_1^+$  MTEOS > VTEOS > PhiTEOS as shown in Figure 4 can be explained by a shorter electron-transfer distance and by a faster radical conversion rate. The relative interaction distance between a phenothiazine cation radical and the organic group of the gel matrixes is related to the proton matrix ENDOR line width which measures the local proton density around the phenothiazine cation radical. A higher proton density indicates a more compact structure because of the shorter interaction distance. A shorter interaction distance results in a higher radical yield of  $PC_1^+$ . Thus, the higher radical yield as shown in Figure 4 correlates with the decreasing order of proton matrix ENDOR line widths of  $PC_1^+$  as shown in Figure 3.

The photoproducted radical yield of  $PC_1^+$  doped into gel matrixes is also partially controlled by radical conversion during photoirradiation. Similar results were already reported in previous studies in organic molecular assemblies and polymer matrixes.<sup>13,17–20</sup>

The polarity and pore size of gels around a photosensitive phenothiazine molecule possibly affect the photoproducted radical yield of phenothiazine by the interaction distance of it with an organic group of the gel matrixes and the decay kinetics of photoproducted radicals. Photoproducted radical yields of viologens, phenothiazines and benzidines in inorganic silicate matrixes were studied with ESR and UV–vis diffuse reflectance spectroscopies.<sup>22–26</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>27</sup> In those studies, the photoproducted radical yields were controlled by the matrix rigidity and the long-range electron-transfer distance. The photochromism of spironaphthooxazine molecule in gel matrixes was studied with UV–vis and IR spectroscopies.<sup>11–13</sup> The effect of polarity and pore size of alkoxide gels such as TEOS, MTEOS, VTEOS, and PhiTEOS matrixes on the kinetics of photochromism between the opened and closed form of spironaphthooxazine was comparatively studied by measuring optical absorbance. The normal and reverse photochromism of spironaphthooxazine were affected by polarity and rigidity of the gel matrixes. PhiTEOS, VTEOS, and MTEOS showed normal photochromism and TEOS showed a reverse photochromism. The polarity of the gel matrixes was correlated with the blue shift of  $\lambda_{max}$  of the opened form of the spironaphthooxazine molecule and increase as PhiTEOS < VTEOS < MTEOS < TEOS. The higher polarity of the TEOS gel matrix stabilizes the zwitterionic structure of the opened form of spironaphthooxazine. This leads to reverse photochromism of the spironaphthooxazine in a TEOS gel matrix. The kinetics of the normal photochromism of the decoloration

process was comparatively studied with the biexponential equation. The determined kinetic constants among PhiTEOS, VTEOS and MTEOS showed a decreasing order of PhiTEOS > VTEOS > MTEOS. This was interpreted as the polar microenvironment of the gel matrixes suppressing the decoloration reaction of the opened form of the spironaphthooxazine because the zwitterionic structure of the opened form of the spironaphthooxazine can be stabilized more in a more polar gel matrix. This results in a greater activation energy for the decoloration reaction. This was also related with the pore size of the gel matrix. The relative pore sizes among PhiTEOS, VTEOS, and MTEOS matrix were tentatively interpreted as important parameters for the kinetic constants of the normal photochromism of spironaphthooxazine. The kinetic parameters of the thermal fading for spironaphthooxazine-doped gels are also dependent on the pore size of matrix because the dynamics are clearly slowed in a more restricted matrix.

The same trends of the total decay of photoinduced charge separation of *N*-methylphenothiazine doped in MTEOS, VTEOS, and PhiTEOS gel matrixes are shown in Table 1 and Figure 4. The photoproducted radical yield decreases as MTEOS > VTEOS > PhiTEOS. This can be interpreted as the charge separated state of phenothiazine being stabilized in the most polar gel matrix of MTEOS. This interpretation is supported by measuring  $\lambda_{max}$  values of  $PC_1$  in the different matrixes as 313.3 nm in PhiTEOS, 312.0 nm in VTEOS, and 311.1 nm in MTEOS. These values indicate the decreasing relative polarity of the gel matrixes as MTEOS > VTEOS > PhiTEOS. This results in the highest radical yield of phenothiazine in MTEOS matrix due to the more stabilization of charge separated polar state of phenothiazine cation radical. This suppresses the recombination of phenothiazine cation radical and electron through back-electron transfer between phenothiazine cation radical and electron separated from phenothiazine. The least polar PhiTEOS gel matrix surely results in the lowest radical yield of phenothiazine. The kinetics of total decay consists of two contributions. The first is the recombination reaction between phenothiazine cation radical and electrons which are electron separated from phenothiazine by photoinduced electron transfer. The second is the recombination reaction between phenothiazine cation radical and the electrons which exist in the surroundings in matrixes. The second is thermal decay. Both were analyzed in terms of a biexponential decay. The kinetic constants by back-electron electron-transfer reaction decay of the photoproducted radical increases as MTEOS < VTEOS < PhiTEOS. This can be interpreted as a recombination of photoproducted radicals can be slowed more in the smaller pore size gel than in the larger pore size gel because of more stabilized charge separated state in a more polar and smaller pore size. The contribution constants of thermal decay and back-electron transfer show a decreasing order as MTEOS > VTEOS > PhiTEOS. This indicates that the total decay was also more suppressed in a more polar and smaller pore of the matrixes even with faster kinetic constants.

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