



Electron Spin Resonance and Electron Nuclear Double Resonance Studies on the Photoinduced Charge Separation of N-Methylphenothiazine in Phenyltriethoxysilane, Vinyltriethoxysilane and Methyltriethoxysilane Gel Matrices

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Received August 18, 2000

Abstract: The photoproducted cation radical of N-methylphenothiazine (PC₁) doped in the different kind of matrices of phenyltriethoxysilane (PhiTEOS), vinyltriethoxysilane (VTEOS), and methyltriethoxysilane (METOS) was comparatively 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 photoproducted cation radical in the matrices. This was correlatively studied with the polarity and pore size of the gel matrices. The polarity of the matrices was comparatively determined by measuring λ_{\max} values of PC₁ in the different matrices. The relative pore size among the matrices was determined by measuring relative proton matrix ENDOR line widths of the photoproducted cation radical of PC₁. The decay kinetic constants of the cation radical of PC₁ in the different matrices was relatively studied with fitting the biexponential decay curves after exposure into the ambient condition. This is correlatively interpreted with the polarity and pore size of the matrices.

INTRODUCTION

The sol-gel process provides various inorganic oxide glasses without melting and is now well known as synthetic route to trap organic molecules in a solid matrix. Metal alkoxide is used as a starting materials of sol-gel method. Especially, doping organic compounds into inorganic oxide using the sol-gel processes opens a broad range of possibilities for the preparation of optical materials, whose properties can be tuned by selecting organic components (dopants) with appropriate photoactivities, bioactivities, and chemical activities. As examples, organic and organometallic photoactive compounds have been employed to probe the physicochemical structural changes during the sol-gel

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reactions.¹⁻⁵ The sol-gel method has an advantage of thin film preparation over a large area at a comparatively low cost. In this method, metal oxides hydrolyze at relatively low temperature to form porous glass, which are then transformed into dense glasses by sintering. The polymerization process was usually initiated by adding water to a solution of alkoxide in ethanol. Concerning silicon alkoxide precursor such as tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS) and phenyltriethoxysilane (PhiTEOS), the chemical conditions were carefully defined in such a way that nearly complete hydrolysis occurred in a few minutes. This allows us to realize separate condensation with the transformation of siloxane bridges between the hydrolyzed species. Gels turn into the dried materials known as xerogels after conventional drying in air at low temperature. Numerous materials and their applications have been proposed for sensor, optical limiters and information recording materials.⁶⁻¹⁰ For the preparation of optical and electronic materials, functional organic materials have been doped into the gel matrices. Photochromic glasses have been prepared by sol-gel method by doping several kinds of organic materials into the gel matrices.¹¹⁻¹³ The photochromic behavior was related to the microenvironment and structure of the cage within which photochromic molecules were trapped. Among those properties of gel cage, the polarity and pore size of the gel cage critically affected the photochromic kinetics and the normal or reverse photochromism of the gel matrices. For the photochromism of spiropyran in TEOS and polydimethylsiloxane (PDMS), the polarity of the gel cage controlled the photochromic behavior of spiropyran. Also the photochromism of spironaphthooxazine in organic polymer matrices such as polyurethane, polynitrocellulose and vinylcopolymer, the kinetics of photocoloration of spironaphthooxazine can be studied with UV-vis absorption spectrophotometer and decay curve fitting to determine the kinetic constants.¹³ The photoinduced charge transfer between pyrene and N,N'-dimethylaniline on silica gel was studied with fluorescence quenching and transient absorption techniques.¹⁴ The stabilization of $\text{Ru}(\text{bpy})_3^{3+}$ from $\text{Ru}(\text{bpy})_3^{2+}$ at both 77 K and room temperature in silica gel by chemical oxidation with chlorine gas and by the photoinduced electron transfer to suitable electron acceptors is reported.¹⁵ Stabilization at room temperature is of particular interest of potential light energy storage systems. Paramagnetic properties of $\text{Ru}(\text{bpy})_3^{3+}$ is characterized by ESR spectroscopy. The quantity of $\text{Ru}(\text{bpy})_3^{3+}$ yield formed by chlorine gas oxidation can be controlled by the silica gel pore size and decreases with increasing pore size. The $\text{Ru}(\text{bpy})_3^{3+}$ yield is one order of magnitude smaller in 14.0 nm pore size silica gel compared to higher temperature before impregnation with $\text{Ru}(\text{bpy})_3^{3+}$. These results suggested that the oxidation of the $\text{Ru}(\text{bpy})_3^{3+}$ with chlorine gas takes place via a silica gel surface mediated reaction and that the direct reaction of adsorbed $\text{Ru}(\text{bpy})_3^{3+}$ is with a chlorine molecule in the gas phase is less effective. $\text{Ru}(\text{bpy})_3^{3+}$ was also stabilized in silica gel by photolysis in the presence of electron acceptor $\text{S}_2\text{O}_8^{2-}$ (persulfonate ion) with 50% yield or tetrachloro-1,4-benzoquinone (π -chloranil) with a lower yield. Photoionization of N-methylphenothiazine (PC_1) doped into poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) matrices resulted in paramagnetic cation

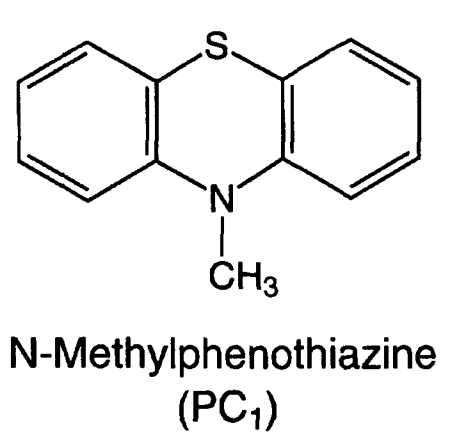


Fig. 1. The structure of N-methylphenothiazine (PC₁).

radical formation.¹⁰ The radicals were identified with ESR and the radical quantity was determined by double integration of the ESR spectra. 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 proton matrix electron nuclear double resonance (ENDOR) linewidths in PEO than in PPO. In solid disordered systems, ENDOR spectrum of a radical often shows a single line called a matrix ENDOR line.¹⁶ This line has 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 the different gel matrices was photoirradiated and the produced phenothiazine cation radical was identified and the relative quantity of radicals was determined with ESR. The stabilization degree of photoproduced radical was determined by estimating the relaxation kinetics of radical by exposing sample at room temperature. The different stability of the radical in the different gel matrices were interpreted in the respect of pore size of gel matrices. The relative pore size of gel matrices was determined by determining proton matrix ENDOR linewidths of their spectra.

EXPERIMENTAL

Materials

N-methylphenothiazine (99%) as Fig. 1 was synthesized as described elsewhere.¹⁷ PhiTEOS (99%), VTEOS (98%) and MTEOS (99%) were obtained from Aldrich Chemical Co. and used without any further purification. House-distilled water was passed through a

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

Preparation of alkoxide sols.

A 2 mM stock solution of PC_1 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 (1mole) and acetone (0.75 mole) was prepared by stirring for 5 min. This solution was added slowly into the mixed solution of water (1 mole) and acetone (0.187 mole) drop by drop and continuously stirred for 30 min. The resulted sol solution keeps molar ratio of alkoxide : water : acetone (1 : 4 : 1.5). Also the completely hydrolyzed sol solution shows a clear solution and stock solution of N-methylphenothiazine was added into the clear solution with volume ratio of alkoxide (2) and N-methylphenothiazine (1) solutions and the solution was stirred for 5 min and kept for 12 hrs more without stirring. The concentration of N-methylphenothiazine in the final sol solution was 0.4 mM. All of this preparation was carried out at room temperature.

Preparation of gel thin films by spin coatings of quartz slide.

Sol solutions for spin coating were filtered with filter paper of 0.2 μm pore size. The filtered sol solution was dropped by three drops on the surface of quartz slide (0.6 x 0.8 cm) in spin coater. The quartz slide was cleaned by successive treatment with saturated KOH solution of isopropanol for 30 min and 1 M sulfuric acid. The treated slide quartz was sonicated in the pure water for 30 min and dried with heat gun. Then it was spin coated at 1000 rpm for 10 sec. The spin coated sol on the substrate was changed to gel by heat treatment at 50 $^\circ\text{C}$ for 48 hrs under the reduced pressure in the vacuum oven. The coated quartz slide was colorless. The thickness of gel films on the quartz slide surface was determined with α -step 500 surface profiler from Tencor Co. and the thickness of MTEOS, VTEOS and PhiTEOS was known approximately as 1.2 μm .

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 < λ < 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.¹⁸⁻²⁰ The light intensity at the sample position was measured with YSI Kettering model 65 radiometer and was $1.3 \times 10^3 \text{ Wcm}^{-2}$. 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 the 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 (Wilmad Glass Co.) filled with liquid nitrogen and secured in a TE102 cavity. The loaded Q factor of this cavity was measured as about 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 amplitude, 20 mT sweep width, 7 scan accumulations, 56 s scan time constant, 9.501 GHz microwave frequency and 1.25×10^5 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 JES-PX software. After 20 min photoirradiation at 77 K, the radical yield was measured at 77 K after subsequent 5 min exposures to room temperature and then plunged into liquid nitrogen. The radical yield data were normalized by dividing the radical yield of PC₁ in MTEOS after 20 min photoirradiation at 77 K.

ENDOR spectra were recorded with a Bruker 350 ENDOR unit. Radiofrequency modulation was performed at constant magnetic field which resulted in a first derivative ENDOR spectrum. Each spectrum was accumulated for 64 scans. Typical experimental conditions were 1.97 mW microwave power and 100 W radiofrequency power. A Bruker ER 4111 ENDOR variable temperature nitrogen flow unit was used in the measuring the peak-to-peak separation distance of the first derivative signal.

Kinetic Data Manipulation.

The radical yield decay curves of N-alkylphenothiazine were fitted to the following biexponential using Sigmaplot software.

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

A(t) is the ESR intensity after photolysis, A₁ and A₂ are contributions of the k₁ and k₂ rate processes and A_{th} is the contribution from thermal decay.

RESULTS AND DISCUSSION

Photoinduced electron transfer from phenothiazines to interface water of molecular assemblies like micelles, reverse micelles and vesicles is well known from previous

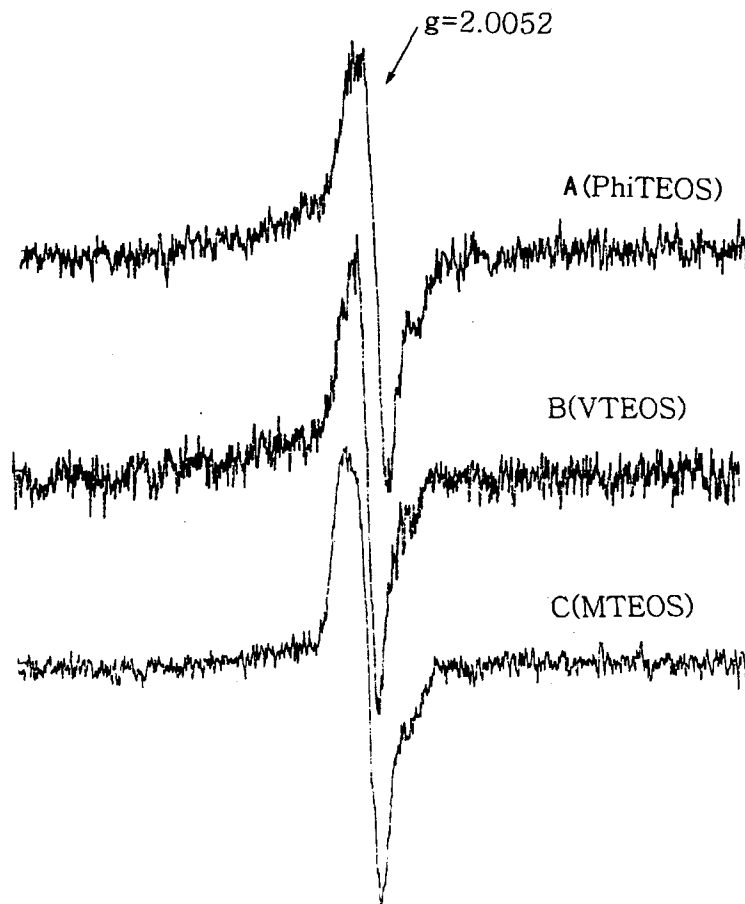


Fig. 2. X-band ESR spectra of PC_1 in methyltriethoxysilane (MTEOS), vinyl triethoxysilane (VTEOS), and phenyltriethoxysilane (PhiTEOS) matrices after 20 min photoirradiation at 77 K.

studies.¹⁷⁻²⁰ 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 photoproduct radical yields by integration of the spectra and to identify the photoproduct radicals by hyperfine structure and g -factor of the produced radicals.

The structure of *N*-methylphenothiazine (PC_1) is shown in Fig. 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 nm < λ < 410 nm region. The photoirradiation of PC_1 doped into the MTEOS, VTEOS and PhiTEOS matrices showed a pale pink color which is characteristic of the phenothiazine

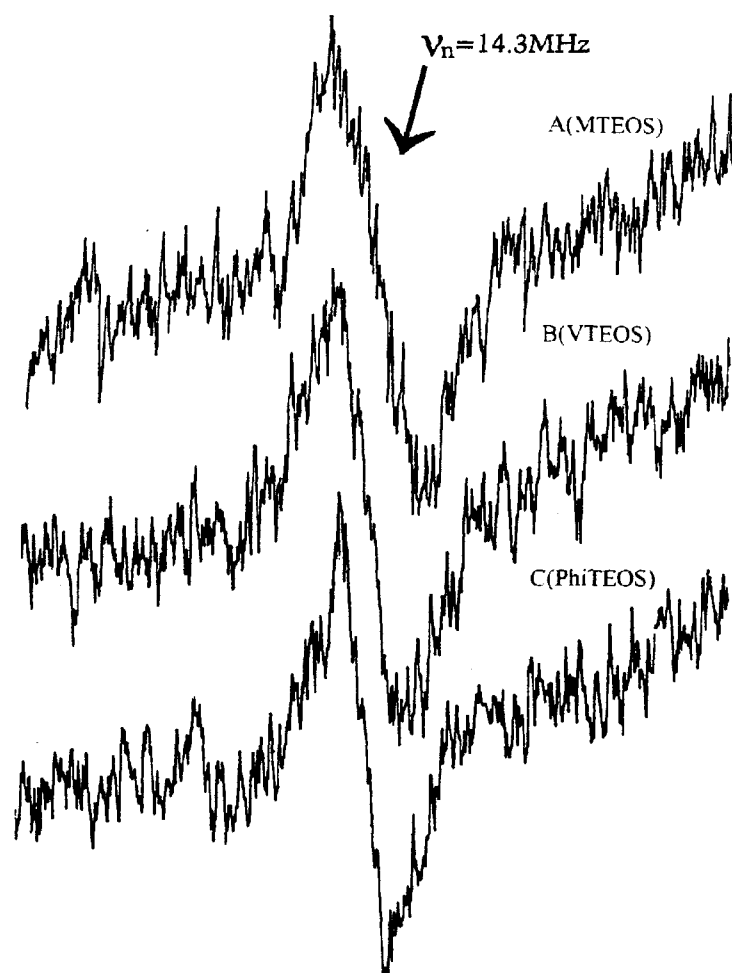


Fig. 3. Proton matrix ENDOR spectra of PC_1 in methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS) and phenyltriethoxysilane (PhiTEOS) matrices at 141 K after 10 min photoirradiation at 77 K.

cation radical. 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_1 doped into MTEOS, VTEOS and PhiTEOS matrices after 20 min photoirradiation are shown in Fig. 2. A characteristic broad singlet appears at $g = 2.0052$. This assignment is consistent with reported g -values.^{13,17-20} Also, each sample is pink color which is characteristic of phenothiazine cation radicals.^{13,17-20} The weak multiplet signals are due to radical conversion of phenothiazine cation radical into organic groups of gel matrices.

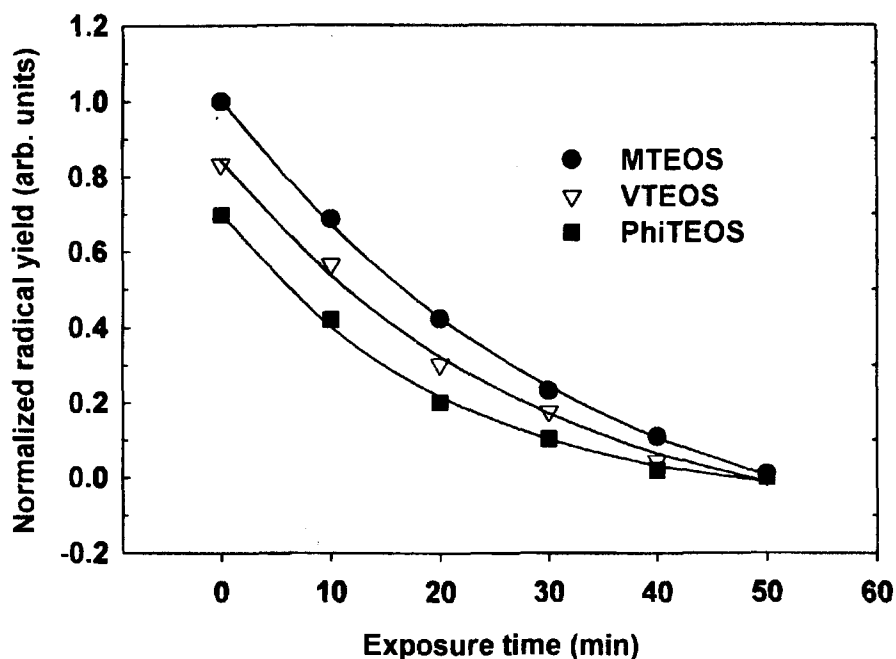


Fig. 4. Normalized radical yield of PC_1 in methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), and phenyltriethoxysilane (PhiTEOS) matrices versus the exposure time of the samples at room temperature. The decay curves fitting biexponential equation show the relaxation process of produced radical.

This is already reported in the previous studies.^{13,17-20} As the photoirradiation time is increased, the signal intensity of the phenothiazine radical decreases in parallel with increasing signal of the organic group radical. This together with a loss of pink color indicates radical conversion from a primary phenothiazine cation radical to organic radical during photoirradiation.

Proton matrix ENDOR spectra of PC_1 in MTEOS, VTEOS and PhiTEOS after 10 min photoirradiation are shown in Fig. 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 linewidths of the ENDOR spectrum of PC_1 in PhiTEOS, VTEOS and MTEOS matrices are 0.82, 0.95 and 1.02 MHz, respectively. The increasing order of ENDOR linewidth as MTEOS > VTEOS > PhiTEOS obtained from gel matrices samples. The broader linewidth of proton ENDOR linewidths indicates that higher proton density around phenothiazine cation radical results in the greater dipolar interaction between organic group of gel matrices and phenothiazine cation radical. The broader ENDOR linewidth indicates the shorter

interaction distance of phenothiazine cation radical with organic functional group of gel matrices.

Fig. 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_1 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_1 in gel matrices was increased as $MTEOS < VTEOS < PhiTEOS$. The exact decay rate constants of PC_1 in gel matrices are shown in Table 1. No ESR signal is obtained after 60 min exposure to room temperature for four gel samples. In this study, N-methylphenothiazine was doped into gel matrices and photoinduced electron transfer from phenothiazine resulted in charge separation. The acceptor is probably water which is hydrogen bonded to the oxygen of gels. Water interacting with the oxygen of alkoxide gels and polymers such as polyethylene oxide (PEO) and polypropylene oxide (PPO) are well known.^{1,2,21} 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 in gel matrices as $MTEOS < VTEOS < PhiTEOS$ as shown in Fig. 4 can be explained by a shorter electron transfer distance and by a faster radical conversion rate as $MTEOS > VTEOS > PhiTEOS$. The relative interaction distance between a phenothiazine cation radical and organic group of gel matrices is related to the proton matrix ENDOR linewidth which measures the local proton density around the phenothiazine cation radical. A higher proton density indicates a more compact structure which indicates a shorter interaction distance. A shorter interaction distance results in a higher radical yield of PC_1^+ in gel matrices as decreasing order of $MTEOS < VTEOS < PhiTEOS$. Thus, the higher radical yield in gel matrices as decreasing order of $MTEOS < VTEOS < PhiTEOS$ as shown in Fig. 4 is supported by the decreasing order of proton matrix ENDOR linewidth of PC_1^+ in gel matrices as shown in Fig. 3.

Photoproduct radical yield of PC_1 doped into gel matrices is also partially controlled by radical conversion during photoirradiation. The radical from a phenothiazine cation radical to a organic group of gel matrices suppresses back electron transfer to the phenothiazine cation radical. This results in a decreasing order of radical yield of PC_1^+ in gel matrices as decreasing same order of proton matrix ENDOR line width as shown in Fig. 3. The similar results were already reported in the previous studies in the organic molecular assemblies and polymer matrices.^{13,17-20} The similar effect of gel matrix structure on the normal and reverse photochromism of spironaphthooxazine was studied with UV-vis absorption spectroscopy.¹⁰

The rigidity and pore size of gel matrices around a photosensitive phenothiazine molecule possibly affect the photoproduct radical yield of phenothiazine by the interaction distance of it with surrounding organic group of gel matrices and relaxation kinetics of photoproduct radicals. Photoproduct radical yields of viologens, phenothiazines and benzidines in inorganic silicates matrices were studied with ESR and UV-vis diffuse

reflectance spectroscopies.²²⁻²⁶ 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.²⁷ In those studies, the photoproduced radical yield was controlled by the matrix rigidity and the long range electron transfer distance. The photochromism of spironaphthooxazine molecule in gel matrices was studied with UV-vis and IR spectroscopies.¹¹⁻¹³ The effect of polarity and pore size of alkoxide gels such as TEOS, MTEOS, VTEOS and PhiTEOS matrices on the kinetics of photochromism between opened and closed form of spironaphthooxazine was comparatively studied by measuring optical absorbance. The normal and reverse photochromism of spironaphthooxazine of it were critically affected by the microenvironment such as polarity and rigidity of the gel matrices. PhiTEOS, VTEOS and MTEOS showed the normal photochromism and TEOS showed a reverse photochromism. The polarity of the gel matrices was investigated with the red shift of λ_{max} of the opened form of the spironaphthooxazine molecule as a decreasing order of PhiTEOS < VTEOS < MTEOS < TEOS. The higher polarity of TEOS gel matrix stabilize the zwitterionic structure of the opened form of the spironaphthooxazine. This lead to the reverse photochromism of the spironaphthooxazine in TEOS gel matrix. The kinetics of the normal photochromism of decoloration process was comparatively studied with biexponential equation. This was carried out by fitting the constants of the biexponential equation. The determined kinetic constant among PhiTEOS, VTEOS and MTEOS showed a decreasing order of PhiTEOS > VTEOS > MTEOS. This was interpreted as the polar microenvironment of the gel matrices suppresses the decoloration reaction of the opened form of the spironaphthooxazine because zwitterionic structure of the opened form of the spironaphthooxazine can be stabilized more in the polar gel matrix. This results in a greater activation energy for the decoloration reaction. This was also along with the pore size of gel matrix. The relative pore size among PhiTEOS, VTEOS and MTEOS matrix was tentatively interpreted as the important parameters contribute for the kinetic constants of the normal photochromism of spironaphthooxazine. The kinetic parameters of the thermal fading for spironaphthooxazine doped gels is also dependent on the pore size of matrix because the dynamics are clearly slowed down in the less restricted matrix.

Table 1. Constants for biexponential decay of photoproduced N-methylphenothiazine doped into MTEOS, VTEOS and PhiTEOS matrices.

Constants	MTEOS	VTEOS	PhiTEOS
A_{th}	0.2866	0.1893	0.0791
A_1	0.6680	0.5398	0.3877
k_1	0.0298	0.0532	0.0489
A_2	0.6241	0.4934	0.3955
k_2	0.0297	0.0351	0.0489

The same trend of the thermal decay of photoinduced charge separation of N-methylphenothiazine doped in MTEOS, VTEOS and PhiTEOS gel matrices are shown in Table 1 and Fig. 4. The photoproduced radical yield was appeared as a decreasing order of TEOS < VTEOS < PhiTEOS. This can be interpreted by the charge separated state of phenothiazine can be stabilized in the most polar gel matrix of MTEOS. This interpretation can be supported by the previous report on the relative polarity of gel matrix among MTEOS, VTEOS and PhiTEOS. This results in the highest radical yield of phenothiazine in MTEOS matrix. The least polar PhiTEOS gel matrix surely results in the lowest radical yield of phenothiazine. The kinetics of the thermal back reaction was analyzed in terms of a biexponential decay. The kinetic constants of thermal decay of photoproduced radical are shown as decreasing order of MTEOS < VTEOS < PhiTEOS. This can be interpreted as the recombination dynamics of photoproduced radical can be slowed down in the less pore size of gel matrix than larger pore size of gel matrix. This results in the increasing order of kinetic constants of thermal recombination of photoproduced phenothiazine cation radical as MTEOS < VTEOS < PhiTEOS gel matrices. The relative pore size of gel matrix is already discussed in the proton matrix ENDOR linewidths of photoproduced phenothiazine cation radical.

Acknowledgments

This work was financially supported by the Chaired Research Equipment Assistance Programm 2000 of Korea Basic Science Institute.

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