ESR Study of a Nitroxide Radical in Sol-Gel Glasses

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Abstract. A spin probe TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy) was dissolved in a tetraethyl orthosilicate sol-gel reaction system and measured by electron spin resonance spectroscopy at 295 K. The nitrogen hyperfine coupling constant was from 1.64–1.66 mT in the sol-gel solutions. The values were sensitive to the ethanol-to-water ratio of the solutions. The hyperfine coupling constant in the xerogels was 1.70 mT, which was almost the same as that in water, indicating that the probe molecules were trapped in silica pores with water adsorbed on the silica surfaces. The motion of TEMPOL in the xerogels was considerably slower than in the sol-gel solutions. The local viscosity estimated was from 70–90 cP. The ESR spectra of TEMPOL were altered during the sol-gel process, indicating that adsorbed water on the silica surfaces has an important role for trapping organic molecules in sol-gel glasses.

Keywords: silica, TEMPO, ESR, doped sol-gel, TEOS

1. Introduction

The sol-gel technique enables the preparing of inorganic glasses containing organic molecules [1–5]. Such an organic-doped glass system allows for the possibility of new innovative applications. In addition, the doping of organic molecules in inorganic glasses by the sol-gel process has received considerable interest from another direction of study: viz., use of dopant molecules as probes in the sol-gel process. For example, fluorescence photoprobes are frequently used for the study of the environmental polarity of sol-gel glasses and molecular motion in the sol-gel process [1–5].

There have been many studies regarding ESR for spin probes in colloidal and biological systems. One of the stable spin probes often used is 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPOL), which has two important advantages: (1) nitrogen hyperfine coupling constant $A_N$ is sensitive to solvent polarity because of the pseudoionic resonance structure of the nitroxide; and (2) the rotational correlation times are functions of the solvent viscosity [6]. Therefore, the ESR spectrum of TEMPO provides information on the local polarity and the local viscosity of the microenvironment surrounding the TEMPO probe.

In this study, we have reported on the ESR spectra of TEMPOL in the sol-gel systems derived from tetraethyl orthosilicate. The hyperfine coupling constant and correlation times were measured during the sol-gel process. We could obtain changes in the micro-polarity and microviscosity of the sol-gel systems from these measurements, which gave us detailed information on the sol-gel systems regarding a molecular scale.

2. Experimental Section

Chemicals. The spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPOL) was purchased from Aldrich and used without further purification. Tetraethyl orthosilicate (TEOS) obtained from Tokyo Kasei and ethanol of a spectroscopic grade were used without further purification. The water used was de-ionized and distilled.
Table 1. Hyperfine coupling constants of TEMPOL and corresponding H2O vol% in EtOH-H2O mixtures which gives the same AN for three preparation conditions of the sol-gel solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TEOS</th>
<th>EtOH</th>
<th>H2O</th>
<th>AN/mT</th>
<th>H2O vol% in EtOH-H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>4</td>
<td>11</td>
<td>1.640</td>
<td>25</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>4</td>
<td>16</td>
<td>1.655</td>
<td>40</td>
</tr>
<tr>
<td>A3</td>
<td>1</td>
<td>4</td>
<td>21</td>
<td>1.660</td>
<td>45</td>
</tr>
</tbody>
</table>

Sample Preparation. Sol-gel solutions were prepared from TEOS, water, and ethanol. When the probe molecules were introduced into sol-gel solutions, TEMPOL was dissolved into ethanol at 10^-4 M. Compositions of the sol-gel solutions can be seen in Table 1. The solutions were adjusted to pH3 by an addition of HCl and stirred for a few hours at room temperature. The solutions were placed in plastic beakers sealed with pinholed film at room temperature. For ESR spectral changes with aging time, a sol-gel solution was kept in a flat cell for aqueous solution measurements.

Measurement. ESR spectra were measured with a JEOL JES-RE1X spectrometer at 295 K. The microwave power was 4 mW and the modulation amplitude was 0.02 mT. Nitrogen hyperfine coupling constant AN was measured between the maxima and between the minima in the first derivative spectra of the triplet. Experimental errors were ±0.005 mT for nitrogen hyperfine coupling constant AN and ±15% for the correlation times. Viscosity was measured by a Cannon-Fenske viscometer. Surface measurements and analysis of xerogels by the nitrogen gas adsorption method were carried out with an ASAP 2000 and ASAP-PC1 (Micromeritics-Shimadzu). Xerogels were vacuum-treated at 200°C for 15 h to degas. The specific surface area was estimated by the BET method and the pore size distribution was calculated by assuming the pores to be cylindrical in shape (BJH method).

3. Results and Discussion

Figure 1 shows how the nitrogen hyperfine coupling constant, AN, of TEMPOL varies with the percentage of water in ethanol-water mixtures. As was found previously, AN increased with an increase in polarity of the solvents [6]. Figures 2 indicates the ESR spectra of TEMPOL (sample A2) as measured in the starting sol-gel solution (after a few h) and sol-gel glasses (xerogels) at 1100 and 1700 h after preparation. The ESR spectra for the solution exhibited the usual three-line pattern, but the spectra for the xerogels showed a broader width and different peak heights, thus indicating that the motion of the probe was more restricted in the xerogels than in the sol-gel solution as will be discussed later. The signal intensity became weaker with an increase in the aging time: 1 : 0.53 : 0.16 for t = 0, 1100 and 1700 h. This is possibly due to the decomposition of TEMPOL. The values of AN in the sol-gel solutions were sensitive to the preparation conditions as shown in Table 1: AN increased from 1.64 to 1.66 mT with an increase in the water content in the solutions. The apparent water vol% for the sol-gel solutions corresponding to the same AN in the ethanol-water mixtures was 25–45%, estimated from the calibration curve in Fig. 1. Therefore, it is considered that the TEMPOL probes in the sol-gel solution are mainly dissolved in the solvent phase of ethanol and water. Naturally, the solvent compositions in the sol-gel solutions changed from the initial mixing because water was consumed and ethanol was produced by hydrolysis of TEOS.

The ESR spectra become asymmetric due to a decrease in the rotational motion of the probes as the viscosity of the solution is increased. The characteristic parameter for the probe motion is rotational correlation time, which is approximated by the following formula:

$$\tau_c = 6.6 \times 10^{-9} \Delta H [ ( h_{-1} / h_{+1} )^{1/2} - 1 ]$$

in which $\Delta H$ is the width of the low-field line (in mT); and $h_{-1}$ and $h_{+1}$ are the heights of the low, and high field peaks [7, 8].

Figure 3 shows the relationship between the correlation times and the viscosity in glycerol-water mixtures.