28. Synthesis of Organic-Inorganic Polymer Hybrids Containing Transition Metal Salts

By Yoshiki CHUJO,* Shigeo KURE, Hidetake MATSUZI, and Takeo SAEGUSA**

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01

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Abstract: This paper describes the synthesis of polymer hybrids between polyoxazoline and silica gel, in which the transition metal salts are incorporated. Organic-inorganic polymer hybrids were prepared by the acid-catalyzed sol-gel reaction of tetraethoxysilane in the presence of poly (2-methyl-2-oxazoline). To this system were added transition metal salts such as cupric chloride, cupric acetate, nickel chloride or palladium chloride. Cupric or nickel salts gave homogeneous and transparent glasses, while palladium salt caused turbid materials. These homogeneous polymer hybrids containing transition metal salts were subjected to pyrolysis at 600°C to eliminate polyoxazoline segments. The resulting porous silica showed high surface area (around 300 m²/g). In these porous silica gels, the transition metals should be dispersed homogeneously in the matrix, which can be expected as an effective transition metal catalyst-supported inorganic materials (ceramics).

Key words: Organic-inorganic polymer hybrids; sol-gel method; silica gel; polyoxazoline; transition metal salts; hydrogen bonding; pyrolysis; porous silica.

Introduction. Recently, composite materials by the combination of inorganic materials and organic polymers have been attracting attention for the purpose of creating high-performance or high-functional polymeric materials. Previously, the addition of inorganic materials as a filler into organic polymers was very popular to prepare composite materials having high mechanical properties and increased stability. In these cases, organic polymers and inorganic materials form independent phases, in which the interaction at interface plays an important role.

Generally, metal oxide may be regarded as three-dimensional network inorganic polymer consisting of metal-oxygen bonds. The molecular-level dispersion of silica gel is impossible. However, tetraalkoxysilane, a precursor of silica gel in the so-called sol-gel procedure, can be dissolved in organic solvents such as alcohol. Sol-gel process of tetraethoxysilane is composed of three elementary reactions as shown in Scheme 1. Ethoxysilane group is hydrolyzed with either acid or base catalyst to generate silanol group which is the key intermediate of sol-gel process. The linkage of -Si-O-Si- which is the building element of silica gel is formed by the reaction between two silanol groups. It is understood that silica gel is of a three-dimensional network structure consisting of -Si-O-Si- linkage. Some silanol groups remain unreacted, which provide acidic sites. Thus, the sol-gel reaction makes possible to incorporate the organic polymer segments in the network matrix of inorganic polymer.

Very recently, we have explored new composite materials, i.e., molecular hybrids

*) To whom all correspondence should be addressed.

**) Present address: KRI International, 17 Chudoji, Minami-machi, Shimogyo-ku, Kyoto 600, Japan.
between silica gel and organic polymers such as poly (2-methyl-2-oxazoline)(1, polyoxazoline), poly (N-vinylpyrrolidone) (2) or poly (N,N-dimethylacrylamide) (3). In the presence of one of these organic polymers, the sol-gel reaction of tetraalkoxysilane was carried out with acid-catalyst. As a result, colorless, homogeneous and transparent glassy materials were obtained in a wide range of the content of organic polymer. In these hybrids, amide groups of organic polymers were found to play an important role as an acceptor of hydrogen-bonding as illustrated in Fig. 1 in the case of 1. On the other hand, amide groups are also known to have a good interaction with transition metals. Here we describe the synthesis of polymer hybrids between polyoxazoline and silica gel, in which the transition metal salts are incorporated.

![Scheme 1](image1)

![Scheme 2](image2)

**Results and discussion.** Preparation of polymer hybrids containing transition metal salts. As shown in Scheme 2, poly (2-methyl-2-oxazoline) (1, polyoxazoline) was prepared by ring-opening polymerization of 2-methyl-2-oxazoline with an initiator of methyl tosylate. This polymerization is known to proceed in living mechanism. In other words, the molecular weight of the resulting polymer was easily controlled by the feed ratio of monomer (2-methyl-2-oxazoline) to initiator (methyl tosylate).

As illustrated in Scheme 3, organic-inorganic polymer hybrids were prepared by the acid-catalyzed sol-gel reaction of tetraethoxysilane in the presence of 1. After drying, a homogeneous and transparent glassy material was produced. These homogeneous
hybrids were obtained in a wide range of compositions, which demonstrated the characteristic properties of 1. To this system were added transition metal salts such as cupric chloride, cupric acetate, nickel chloride or palladium chloride. The results are summarized in Table I. Without 1, the transition metal salts were found to be separated from silica gel (Run 6, Table I). This result supports the role of polyoxazoline, which enables the transition metal salts to disperse in the silica matrix. In other words, amide carbonyl groups have good interaction with the residual silanol group of silica gel through hydrogen bonding. This hydrogen bonding was supported by IR spectra, in which the stretching bands (1634 cm⁻¹) due to amide carbonyl groups of 1 were shifted to the lower wavenumbers region (1622 cm⁻¹) after the formation of hybrids. In addition, the transition metal salts should be highly dispersed in the hybrid matrix due to the strong interaction with amide groups of polyoxazoline. Thus, cupric or nickel salts gave homogeneous and transparent glasses (Runs 1–5, Table I), while palladium salt caused turbid materials.

Table I. Polyoxazoline-silica polymer hybrids containing transition metal salts

<table>
<thead>
<tr>
<th>Run</th>
<th>D.P.¹ of 1</th>
<th>Salt</th>
<th>1/Si(OEt)₄/Salt</th>
<th>Appearance</th>
<th>Weight loss</th>
<th>1 Content² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.8</td>
<td>NiCl₂-6H₂O</td>
<td>1/10/8.0×10⁻²</td>
<td>homogeneous</td>
<td>29.9</td>
<td>19.7</td>
</tr>
<tr>
<td>2</td>
<td>5.7</td>
<td>NiCl₂-6H₂O</td>
<td>1/27.0×10⁻²</td>
<td>homogeneous</td>
<td>30.8</td>
<td>15.2</td>
</tr>
<tr>
<td>3</td>
<td>5.8</td>
<td>Cu(OAc)₂</td>
<td>1/10/6.1×10⁻²</td>
<td>homogeneous</td>
<td>29.7</td>
<td>18.6</td>
</tr>
<tr>
<td>4</td>
<td>5.7</td>
<td>CuCl₂</td>
<td>1/10/4.0×10⁻²</td>
<td>homogeneous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.7</td>
<td>CuCl₂</td>
<td>1/10/4.0×10⁻²</td>
<td>homogeneous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>—</td>
<td>CuCl₂</td>
<td>0/10/4.0×10⁻²</td>
<td>separated</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹) Determined by ¹H NMR.
²) Calculated from elemental analysis (N%).

The polymer hybrids obtained above were relatively rigid and brittle due to four crosslinking points in silica gel matrix. Instead of tetraethoxysilane, methyltrimethoxysilane was used as a starting silicate for the purpose of the preparation of flexible polymer hybrids. Acid-catalyzed sol-gel reaction of methyltrimethoxysilane was carried out in the presence of 1 and cupric chloride to give a homogeneous colored glassy material. Casting of the sol-gel reaction mixture upon the surface of teflon gave a transparent film. In a similar way, a thin coating film of polymer hybrid containing cupric salt was formed on the surface of tubular alumina without cracking. Furthermore, from the viscous reaction solution, a homogeneous and tough fiber was successfully drawn. These results indicate that the flexible polymer hybrids containing transition metal salts were obtained by this method. These materials can be expected as a hybrid membrane for various applications such as gas-permeable membrane and catalytic matrix, which should be our next target.

_Porous silica by pyrolysis of polymer hybrids._ Pyrolysis of the homogeneous
polymer hybrids in air brings about the weight loss due to the decomposition of the component of 1. When the range of pyrolysis temperature is high enough for the complete decomposition of 1 and lower enough than the fusion point of silica gel, porous silica is assumed to be produced.8,9,10 Thus, the homogeneous polymer hybrids containing transition metal salts were subjected to pyrolysis at 600°C to eliminate polyoxazoline segments as illustrated in Scheme 4. The complete elimination of 1 was supported by the result of elemental analysis, from which no nitrogen content was observed after pyrolysis. The results of analyses of the resulting porous silica are summarized in Table II. The porous silica obtained by this procedure showed high surface area (around 300 m²/g). Fig. 2 illustrates the pore-size distribution of the porous silica (Run 2, Table II) thus obtained. The average radius of the pores are found to be around or even less than 10 angstrom. This result strongly supports the molecular dispersion of 1 at the stage of hybrid. In these porous silica gels, the transition metals should be dispersed homogeneously in the matrix, which can be expected as an effective transition metal catalyst-supported inorganic materials (ceramics).

<table>
<thead>
<tr>
<th>Run</th>
<th>Salt</th>
<th>D.P. 3)</th>
<th>POZO/TEOS /Salt</th>
<th>Pore volume 1) (cc/g)</th>
<th>Surface area 2) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiCl₂·6H₂O</td>
<td>5.6</td>
<td>1/10/8.0×10⁻²</td>
<td>0.073</td>
<td>302</td>
</tr>
<tr>
<td>2</td>
<td>Cu(OAc)₂</td>
<td>5.6</td>
<td>1/10/6.1×10⁻²</td>
<td>0.344</td>
<td>371</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.026</td>
<td>15</td>
</tr>
</tbody>
</table>

1) Calculated by BJH method.
2) Calculated by BET method.
3) D.P. = Degree of polymerization.

Fig. 2. Pore-size distribution of porous silica after pyrolysis of polymer hybrid containing cupric acetate.

Experimental section. Instruments and materials. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. ¹H-NMR spectra were obtained on a Hitachi R-600 (60 MHz), or on a JEOL JNM-JX-400 (400 MHz) spectrometer. All ¹H-NMR spectra were recorded in CDCl₃ solutions with tetramethylsilane internal standard. GPC analysis was carried out on a Shodex PAK K-802 or AC-803 by using chloroform as an eluent after
calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was performed on a Shimadzu DT-30 instrument under nitrogen.

2-Methyl-2-oxazoline, methyl p-toluenesulfonate (methyl tosylate), tetraethoxysilane, methyltrimethoxysilane, and all solvents were dried and distilled under nitrogen. Cupric acetate, cupric chloride, nickel chloride, and palladium chloride were commercially available and used without further purification.

Ring-opening polymerization of 2-methyl-2-oxazoline. A typical procedure is as follows. Under nitrogen, a mixture of 2-methyl-2-oxazoline (10.2 g, 120 mmol), methyl tosylate (3.72 g, 20.0 mmol), and acetonitrile (50 mL) was placed in a 100-mL flask equipped with a reflux condenser and stirred at 80°C for 11 hours. The obtained polyoxazoline (1) was isolated by reprecipitation from chloroform into diethyl ether and drying in vacuo. Yield of 1 was 13.9 g (100%). The degree of polymerization of 1 (D.P. = 5.7) was determined by 1H-NMR spectrum using the peaks due to methyl protons of acetyl group (1.99 ppm) and those for phenyl protons of tosyl group (7.40 ppm).

Preparation of organic-inorganic polymer hybrids containing transition metal salts. In a typical procedure, 1 (2.50 g), tetraethoxysilane (25.0 g), and cupric chloride (0.10 g) were dissolved in ethanol (10 mL). Aqueous 1N HCl (0.171 g) was added, and the reaction mixture was allowed to stand at room temperature for several days. After the solvent had evaporated, the remaining glassy silica gel was purified by Soxhlet extraction with chloroform.

The reaction of methyltrimethoxysilane was carried out by a procedure similar to that described above for tetraethoxysilane.

Pyrolysis of polymer hybrids. As a typical procedure, the polymer hybrid containing cupric acetate (0.85 g) was heated at 600°C for 24 hours. The porous silica obtained was subjected to elemental analysis and the measurement of surface area.

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References