Synthesis of Triethoxysilyl-Terminated Polyoxazolines and Their Cohydrolysis Polymerization with Tetraethoxysilane[1]

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ABSTRACT: Polyoxazoline having a terminal triethoxysilyl group was successfully synthesized by the ring-opening polymerization of 2-methyl-2-oxazoline followed by termination with (3-aminopropyl)triethoxysilane. Triethoxysilyl-terminated telechelic polyoxazoline was prepared by using a bifunctional initiator. Furthermore, polyoxazolines having two or three triethoxysilyl groups were prepared by using diallylamine as a terminator followed by a hydrosilation reaction with triethoxysilane. These triethoxysilyl-terminated polyoxazolines were subjected to acid-catalyzed cohydrolysis polymerization with tetraethoxysilane by the so-called sol–gel method to produce a novel organic–inorganic polymer hybrid, which was a homogeneous transparent glassy composite material. The obtained hybrid showed a higher hydrophilic property in comparison with that of silica gel without polyoxazoline segments.

Introduction

Ring-opening polymerization of 2-methyl-2-oxazoline produces poly(*N*-acetylethylenimine) (polyoxazoline),[4] which can be regarded as a polymer homologue of *N,N*-dimethylacetamide (DMAc). DMAc is known as a unique solvent which has a strong affinity for water and also solubilizing ability for various organic commodity polymers. Similarly, polyoxazoline has been shown to possess a high hydrophilicity and compatibility with organic polymers.[5] On the basis of these characteristics of polyoxazoline, we have explored novel functional polymers of nonionic polymer surfactants[6,7] and nonionic hydrogels.[8–10]

The polymerization of 2-methyl-2-oxazoline is known to be clean; that is, there are no chain transfer and termination reactions under appropriate conditions.[4] The nature of the polymerization makes it possible to synthesize block copolymers with the desired composition and also to introduce reactive functional groups at the end of the polyoxazoline chain.

Recently, we have reported trimethoxysilyl-terminated polyoxazoline as a novel silane coupling agent.[11] This polymer was subjected to reaction with a silanol group at the surface of silica gel to make its surface hydrophilic. However, the polyoxazoline content in the surface-modified silica gel was only 11 wt %, despite the higher feed of silane coupling polyoxazoline.

There has been a considerable research on the so-called "sol–gel" method, by which the metal oxide matrix can be prepared under mild conditions.[12] Generally, metal oxide can be regarded as an inorganic polymer having a three-dimensional network structure. Thus, the sol–gel reaction enables the incorporation of organic polymer segments in the network matrix of an inorganic polymer. By using this system, Wilkes and co-workers have studied novel hybrid materials consisting of silica gel and poly(dimethylsiloxane)[13,14] or silica gel and poly(tetramethylene oxide).[15] The obtained materials showed good optical transparency and very different mechanical behavior relative to pure sol–gel glasses. Mark et al. also reported the reinforcement of poly(dimethylsiloxane) networks by in-situ precipitation of silica.[16–18]

Here we wish to announce a combination of polyoxazoline and sol–gel glass. The combination at the molecular level may be described as "block copolymer consisting of segments of organic and inorganic polymers". The composite material is expected to show novel and promising properties from the viewpoint of the characteristics of polyoxazoline described above.

Results and Discussion

Synthesis of Triethoxysilyl-Terminated Polyoxazoline (6). As described in the Introduction, in the ring-opening polymerization of 2-methyl-2-oxazoline (1), the oxazolinium propagating end remains without being decomposed after the monomer is consumed and is active to receive a nucleophilic attack by amine. Thus, as represented in Scheme I, (3-aminopropyl)triethoxysilane (4) was reacted with the oxazolinium end group of polyoxazoline (3). Subsequent treatment with a basic ion-exchange resin removed *p*-toluenesulfonic acid and produced triethoxysilyl-terminated polyoxazoline (6).

Figure 1 illustrates the ^{1}H NMR spectra of 3, 5, and 6 in the case of $n = 3$. The top spectrum is the spectrum of oxazolinium-terminated polyoxazoline (3), in which the propagating oxazolinium end group is recognized from the following peaks; δ 2.4 (CH_3 of the oxazolinium ring), 4.2–4.9 (CH_2CH_2 of oxazolinium), 2.3 (CH_3 of tosylate), 7.2–7.9 (aromatic). In the middle spectrum, which is the spectrum of the intermediate polymer (5) after the end-capping reaction with 4, the peaks due to the oxazolinium group described above disappeared, while the methyl (δ 1.3) and methylene (3.8) protons of the ethoxy group of the terminal triethoxysilyl moiety and the methylene (0.6) protons adjacent to the silicon atom were observed. In the spectrum of triethoxysilyl-terminated polyoxazoline (6) (bottom spectrum), the peaks due to the tosylate group completely disappeared. In all cases, the integral ratios are in good agreement with the expected structures for 3, 5, and 6, respectively. These results strongly support the complete transformation reactions in Scheme I.

Triethoxysilyl-Terminated Telechelic Polyoxazoline (10). Telechelic polyoxazoline having two triethoxysilyl groups at the α- and ω-termini was prepared using a bifunctional initiator (8) (Scheme II). 8 was obtained from the reaction of 2,2′-tetramethylenebis(2-oxazoline) (7) with

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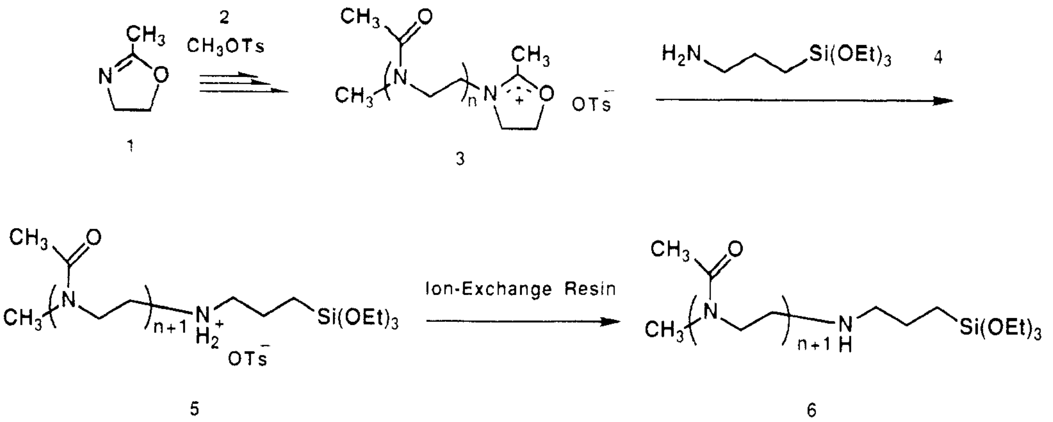
Scheme I



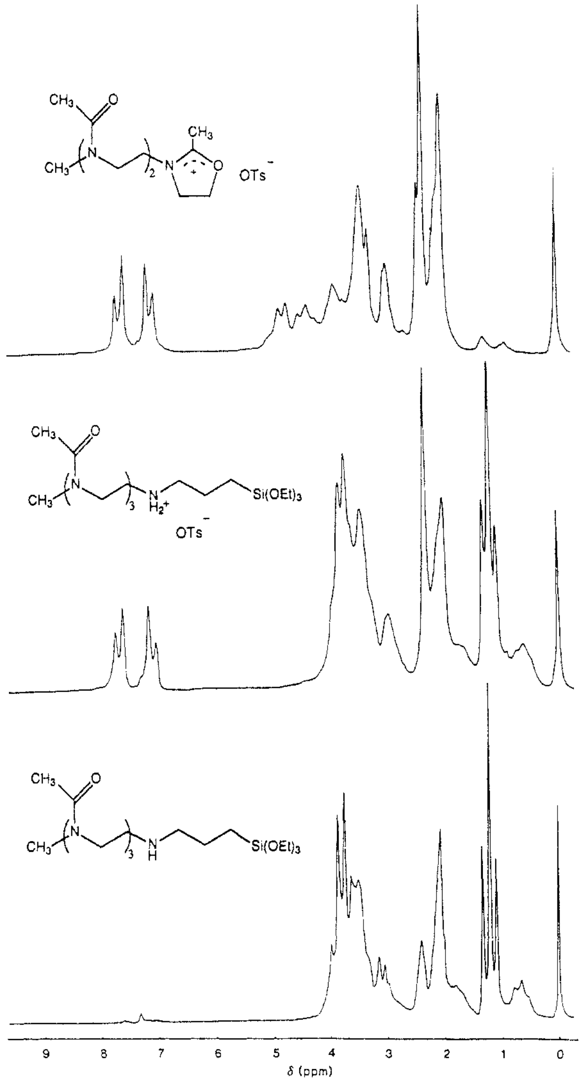


Figure 1. ^1H NMR spectra of **3**, **5**, and **6**.

an excess of **2** and isolated by reprecipitation. **8** was pure enough for the subsequent polymerization of **1**. After polymerization, the oxazolinium-terminated telechelic polyoxazoline (**9**) was subjected to reaction with **4** followed by treatment with an ion-exchange resin to give **10**.

Table I summarizes the results of the preparation of monofunctional (**6**) and bifunctional (**10**) triethoxysilyl-terminated polyoxazolines. The molecular weight of the obtained polymer (**6** or **10**), which was calculated from the ^1H NMR spectrum, could be easily controlled by the feed ratio of initiator and monomer.

Table I. Synthesis of Triethoxysilyl-Terminated Polyoxazolines (6 or 10)[a]

run	initiator	time (h)	yield (%)	$\bar{M}_n$[b]
1	MeOTs	5	66	510
2	MeOTs	11	100	1040
3	MeOTs	10	100	1610
4	8	8.5	84	1960

[a] In CH_3CN, 80 °C. [b] Calculated from ^1H NMR.

Table II. Synthesis of Triethoxysilyl-Terminated Polyoxazolines (14 or 16)

run	polyoxazoline silane coupling agent	condition[a] Si–H/$CH_2{=}CHCH_2$	time (days)	yield (%)	$\bar{M}_n$[b]
1	14	4.0	6	73	1120
2	16	1.7	4	45	1400

[a] In 1,2-dichloroethane, at 83 °C, catalyst = H_2PtCl_6. [b] Calculated from ^1H NMR.

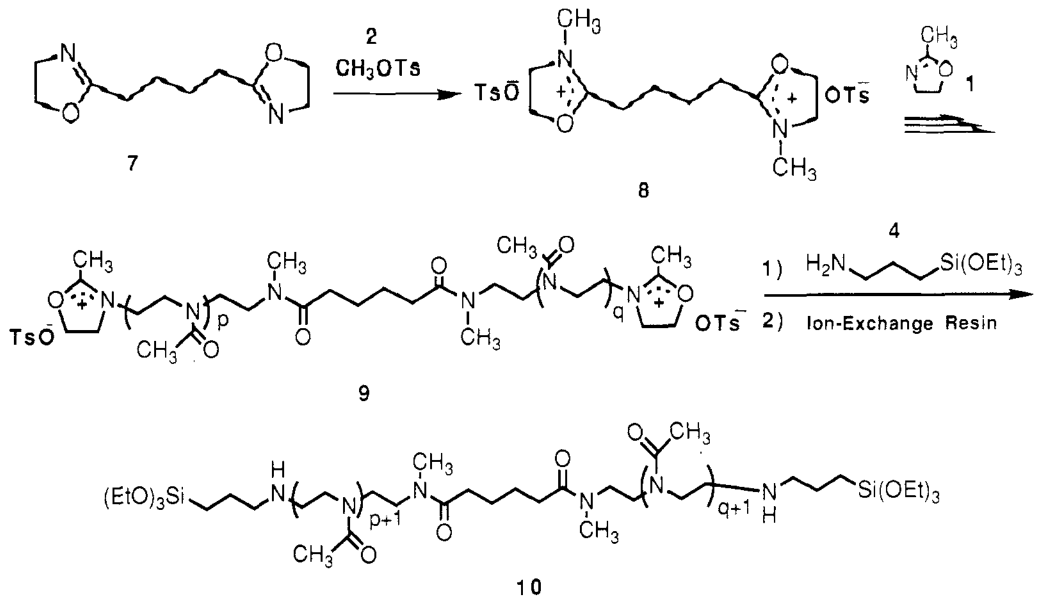
Polyoxazolines Having Two or Three Triethoxysilyl Groups (14 or 16). As an alternative method for the preparation of triethoxysilyl-terminated polyoxazolines, a hydrosilation reaction was used. In the polymer prepared by ring-opening polymerization of 2-methyl-2-oxazoline (**1**) with methyl tosylate (**2**) initiator, the propagating oxazolinium end group remains reactive after the monomer is consumed. As shown in Scheme III, the nucleophilic attack of diallylamine (**11**) on this oxazolinium salt (**3**) was followed by treatment with the ion-exchange resin to produce polyoxazoline having two allyl groups at one end (**12**). The hydrosilation reaction of the C=C of this allyl group with triethoxysilane (**13**) was carried out in the presence of chloroplatinic acid catalyst. From the results of the ^1H NMR spectrum of the obtained polymer, two triethoxysilyl groups were effectively introduced into one end of polyoxazoline.

Similarly, allyl tosylate (**15**) and diallylamine (**11**) were used as an initiator and as a terminator, respectively, in the ring-opening polymerization of 2-methyl-2-oxazoline (**1**). After the hydrosilation reaction with triethoxysilane (**13**), polyoxazoline having three triethoxysilyl groups at the α-, ω-, and ω-ends (**16**) was produced (Scheme IV). All conversions were monitored by ^1H NMR spectroscopy and proved to proceed almost quantitatively.

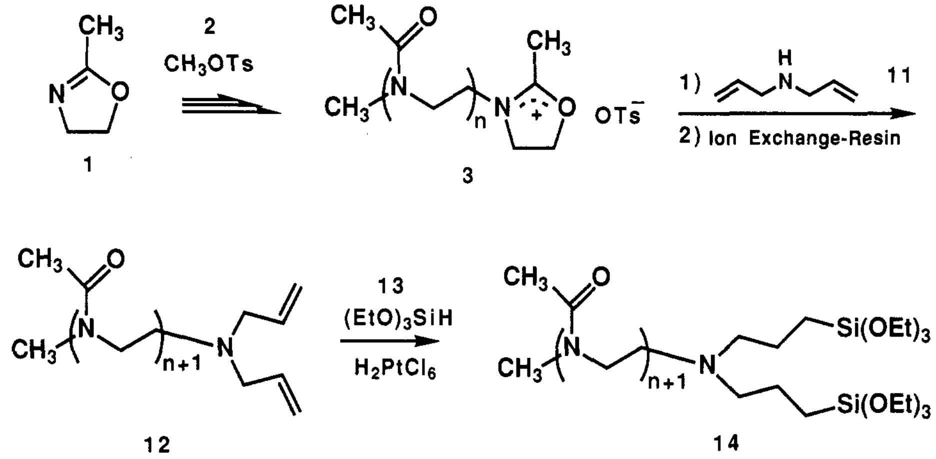
Table II summarizes the results of the synthesis of polyoxazolines having two or three triethoxysilyl groups by means of a hydrosilation reaction.

Cohydrolysis Polymerization of Triethoxysilyl-Terminated Polyoxazoline (6 or 10) with Tetraethoxysilane. An Organic–Inorganic Polymer Hybrid. As illustrated in Scheme V, acid-catalyzed hydrolysis of a mixture of triethoxysilyl-terminated polyoxazoline (**6**) and tetraethoxysilane produced successfully a polyoxazoline-modified silica gel (**17**), which was purified by Soxhlet

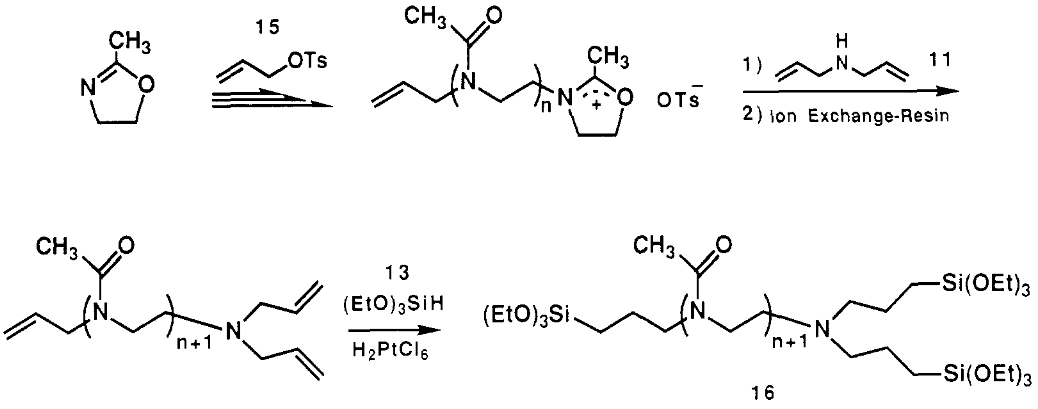
Scheme II



Scheme III



Scheme IV



extraction with chloroform to remove the unreacted polyoxazoline. The telechelic triethoxysilyl-terminated polyoxazoline (**10**) also produced composite material (**18**), in which polyoxazoline segments were connected through their α- and ω-positions to the silica matrix.

The obtained gels before Soxhlet extraction were homogeneous and transparent even in the case of high (50%) content of polyoxazoline. In comparison with a pure sol–gel glass prepared from tetraethoxysilane alone, the produced composite material showed improved flexibility. Usually, the incorporation of organic commodity polymers into a silica glass causes phase separation, and, consequently, the obtained composite glass is opaque or turbid. The homogeneity of the so-called "block copolymer of polyoxazoline and silica gel" in the present study may be due to the chemical bonding at the end of polyoxazoline and also due to the interaction between the amide group in polyoxazoline and silica through hydrogen bonding. This explanation can be illustrated as shown in Figure 2. The hydrogen bonding in **17** was supported by the shift of the carbonyl stretching band of polyoxazoline from 1637 cm^{-1} (polyoxazoline itself) to 1621 cm^{-1} (in **17**) in its IR spectrum. Thus, the molecular-level combination between an organic polymer (polyoxazoline) and an inorganic polymer (silica

Table III. Synthesis and Water Adsorption Property of POZO–Silica Gel Polymer Hybrids

run	POZO	DP^a	POZO/Si(OEt)$_4$	wt loss (TGA) (%)	POZO (wt %)^b	H_2O content^c
1	$(EtO)_3Si$—	9.0	1/2	49.0	50.0	2.98
2	$(EtO)_3Si$—	9.0	1/10	29.4	15.6	1.87
3	$(EtO)_3Si$—	14.4	1/2	47.5	47.2	2.26
4	$(EtO)_3Si$—	14.4	1/10	27.3	14.2	1.63
5	$(EtO)_3Si$—$Si(OEt)_3$	16.1	1/2	50.3	53.1	3.46
6	$(EtO)_3Si$—$Si(OEt)_3$	16.1	1/10	28.5	17.9	1.92
7			0	18.2	0	1.53

^{a} Calculated from feed ratio. ^{b} Calculated from elemental analysis. ^{c} Grams of wet gel/gram of dried gel.

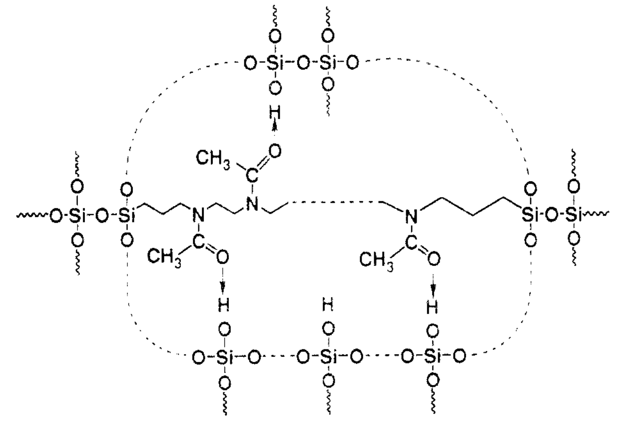
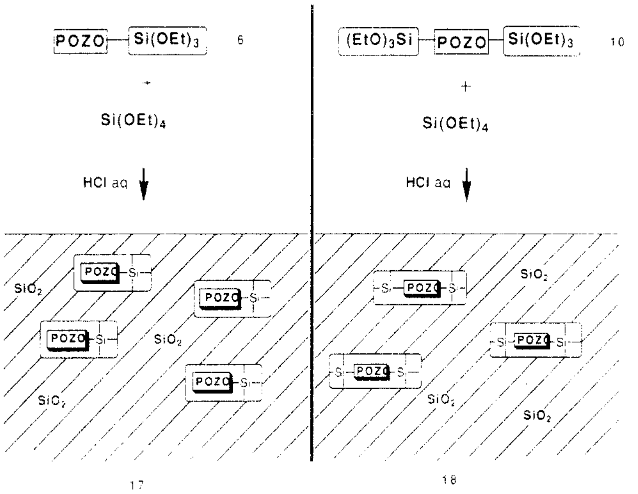


Figure 2. Illustrative interaction between a polyoxazoline segment and the silica matrix in a polymer hybrid.

Scheme V



gel) has been accomplished, for which the terminology "organic–inorganic polymer hybrid" is proposed.

The results of the preparation of polyoxazoline–silica polymer hybrids are summarized in Table III together with their water adsorptions (vide infra). Three kinds of polyoxazolines, two monofunctional polyoxazolines (**6**) with different degrees of polymerization and one bifunctional polyoxazoline (**10**), were used for this cohydrolysis polymerization. The feed ratio of polyoxazoline to tetraethoxysilane was varied from 1/2 to 1/10. The polyoxazoline content in the obtained hybrid was estimated by means of thermogravimetric analysis (TGA), in which the weight loss of this hybrid was measured by raising the temperature to 900 °C. For example, a sample (run 3 in Table III) lost 48% of its weight above 600 °C under nitrogen as shown in Figure 3. This weight loss can be ascribed mainly to the loss of organic components, the polyoxazoline segment in the gel, and water or ethanol molecules produced by the reaction between two silanol groups or from the unhydrolyzed ethoxysilyl groups and adsorbed in the gel. As shown in Table III, the weight loss by TGA increased with an increase of the feed ratio of polyoxazoline.

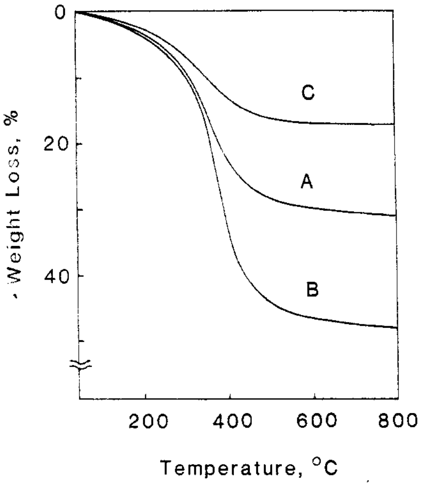


Figure 3. Thermogravimetric analyses of polyoxazoline–silica gel polymer hybrids (A, run 2; B, run 3 in Table III) and of silica gel without polyoxazoline segments (C, run 7 in Table III).

The polyoxazoline content was also estimated from the % N from the elemental analysis as shown in Table III. This value also increased with increasing feed ratio of polyoxazoline. Thus, it should be noted here that the polyoxazoline content in the polymer hybrid can be controlled by the feed ratio of polyoxazoline to tetraethoxysilane.

Water Adsorption of Polymer Hybrid. As described in the Introduction, polyoxazoline has a high hydrophilicity, which may improve the hydrophilic property of silica gel by incorporating the polyoxazoline segments. Table III shows the water adsorption of hybrid materials. In comparison with the silica gel without polyoxazoline segments (run 7), the hybrid was found to show a higher water adsorption property. Especially, the gels with 50% polyoxazoline segments (runs 1, 3, and 5) showed a much higher hydrophilicity. As can be expected, the water adsorption property increased with increasing polyoxazoline content.

The hydrophilicity of the polymer hybrid was also influenced by the molecular weight of the polyoxazoline segments used. The number of polyoxazoline segments of the sample of run 1 having almost the same polyoxazoline content as that of run 3 should be much higher because the degree of polymerization of a polyoxazoline segment is lower. This sample showed a higher hydrophilic property than that of run 3. This means that the number of polyoxazoline segments must be more effective than the length of the polyoxazoline for the water adsorption property of the resulting polymer hybrid. This tendency is also observed in the sample of run 2 in comparison with that of run 4.

In addition, the gels from telechelic polyoxazoline (runs 5 and 6) adsorbed more water than those from monofunctional polyoxazoline. However, detailed examinations are required for the elucidation of these phenomena.

Conclusions. A polyoxazoline–silica gel polymer hybrid was successfully obtained by the cohydrolysis polymerization between triethoxysilyl-terminated polyoxazoline and tetraethoxysilane. The study of the mechanical behavior of the present hybrid is now under investigation. Taking account of the good compatibility of the polyoxazoline segment with other organic commodity polymers, the present polymer hybrid makes it possible to produce an interesting functional composite material.

The present study has demonstrated the hydrophilicity of hybrid gels based on the hydrophilic property of poly(2-methyl-2-oxazoline). Generally, polyoxazolines have a wide spectrum from hydrophilic to lipophilic nature depending on the *N*-acyl groups. For example, the polymers from higher alkyl derivatives (butyl or higher) show hydrophobicity (lipophilicity). From this point of view, triethoxysilyl-terminated polymer from 2-alkyl-2-oxazoline can be used to prepare a lipophilic or amphiphilic polymer hybrid. This will be the next target of our research.

The TGA results indicate that the polyoxazoline segments can be eliminated by the pyrolysis of the present polymer hybrid. This means that the pyrolysis of the polyoxazoline–silica hybrid at a temperature below the fusion point of silica gel produces a silica having micropores. A preliminary experimental example showed the production of a porous silica with 800 m^2/g surface area and with 0.5 cm^3/g pore volume from a polyoxazoline–silica hybrid by this procedure. Further studies on the pyrolysis of our hybrids are now underway and will be reported in a forthcoming paper.

Experimental Section

Materials and Instruments. 2-Methyl-2-oxazoline (1), methyl *p*-toluenesulfonate (methyl tosylate) (2), (3-aminopropyl)triethoxysilane (4), diallylamine (11), triethoxysilane (13), tetraethoxysilane, and all solvents were dried and distilled under nitrogen. 2,2′-Tetramethylenebis(2-oxazoline) (7)[19] and allyl *p*-toluenesulfonate (allyl tosylate) (15)[11,20] were prepared according to the methods reported previously.

IR spectra were obtained on a Hitachi 260-50 grating spectrophotometer. ^{1}H NMR spectra were recorded in CDCl$_3$ on a Hitachi R-600 (60 MHz) instrument. Gas chromatographic analysis (GC) was performed on a Shimadzu GC-6A instrument. Gel permeation chromatographic analysis (GPC) was carried out on a Tosoh CCPD (TSK Gel G2500) after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was performed on a Shimadzu DT-30 instrument under nitrogen.

Synthesis of Triethoxysilyl-Terminated Polyoxazoline (6). A typical procedure is as follows. Under nitrogen, a mixture of 2-methyl-2-oxazoline (1) (2.81 g, 0.33 mmol), methyl tosylate (2) (0.68 g, 3.66 mmol), and acetonitrile (15 mL) was placed in a 50-mL flask equipped with a reflux condenser and stirred at 80 °C for 11 h. To the reaction mixture was added (3-aminopropyl)triethoxysilane (4) (0.92 g, 4.17 mmol) at 0 °C. The resulting solution was stirred at room temperature for 11 h followed by treatment with an ion-exchange resin of Amberlyst A-21. Triethoxysilyl-terminated polyoxazoline (6) was isolated by reprecipitation from chloroform by *n*-hexane and drying in vacuo. The yield of 5 was 3.75 g (100% based on 1).

Triethoxysilyl-Terminated Telechelic Polyoxazoline (10). Bifunctional initiator (8) was prepared as follows. In a 50-mL flask equipped with a reflux condenser, 2,2′-tetramethylenebis(2-oxazoline) (7) (0.494 g, 2.52 mmol), methyl tosylate (2) (1.12 g, 6.05 mmol), and acetonitrile (10 mL) were placed and heated at 80 °C for 6.5 h. The obtained 8 was purified by reprecipitation from acetonitrile by diethyl ether. The yield of 8 was 0.99 g (69%).

A mixture of 8 (1.22 g, 14.4 mmol), 1 (0.507 g, 89.2 mmol), and acetonitrile (10 mL) was heated at 80 °C for 7.5 h. Addition of 4 (0.478 g, 2.16 mmol) was followed by treatment with an ion-exchange resin to give telechelic triethoxysilyl-terminated polyoxazoline (10), which was purified by reprecipitation from chloroform by *n*-hexane. The yield of 10 was 1.53 g (84% based on 1).

Synthesis of Polyoxazolines Having Two or Three Triethoxysilyl Groups (14 or 16) by Hydrosilation Reactions. In a typical example, a mixture of 1 (2.96 g, 34.8 mmol), 2 (0.774 g, 4.16 mmol), and acetonitrile (15 mL) was placed in a 50-mL flask with a reflux condenser and heated at 80 °C for 12 h under nitrogen. After addition of diallylamine (11) (0.803 g, 8.26 mmol), the reaction mixture was stirred at room temperature for 2 days and then at 45 °C for 2 days followed by treatment with an ion-exchange resin. The obtained polyoxazoline having two allyl groups at one end (12) was isolated by reprecipitation from chloroform by *n*-hexane. The yield of 12 was 3.07 g (90%).

In a 100-mL flask equipped with a reflux condenser, 12 (3.07 g), chloroplatinic acid catalyst (4.63 × 10^{-3} mmol), and 1,2-dichloroethane (20 mL) were placed under nitrogen. Triethoxysilane (13) (3.42 g, 20.8 mmol) was added dropwise, and the reaction mixture was stirred at 83 °C for 4 days. Then another amount of 13 (1.73 g, 0.106 mmol) and chloroplatinic acid (2.62 × 10^{-3} mmol) were added and the stirring was continued at 83 °C for 3 days. The obtained polymer (14) was purified by reprecipitation from chloroform by *n*-hexane. The yield of 14 was 3.48 g (73%).

A similar procedure was used to prepare polyoxazoline having three triethoxysilyl groups (16).

Reactions of 6 or 10 with Tetraethoxysilane by the Sol–Gel Method. In a typical procedure, 6 (0.394 g) and tetraethoxysilane (1.97 g, 9.44 mmol) were dissolved in ethanol (3 mL). Aqueous 1 N 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 yield of polymer hybrid (17) was 0.831 g.

The reaction of telechelic polyoxazoline (10) with tetraethoxysilane was carried out by a procedure similar to that described above for 6.

Water Adsorption of Polyoxazoline–Silica Gel Polymer Hybrids (17 and 18). The water adsorption of the obtained polyoxazoline–silica gel polymer hybrid was estimated as follows. The gel (0.186 g) was immersed in deionized water (100 mL) at room temperature for 6 h. The wet silica gel was weighed after filtration with a 1G4 glass filter (17 mmHg, 5 min). The water uptake was calculated from the following equation; W'/W, where W is the weight of the dried silica gel and W' is the weight of the wet silica gel.

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