

Gelation of telechelic trimethoxysilyl-terminated polyoxazolines

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Summary

Telechelic bifunctional polyoxazoline (poly(*N*-acetyleneimine), PAEI) was prepared by ring-opening polymerization of 2-methyl-2-oxazoline (**1**) in the presence of *p*-(α,α' -dibromo)xylene (**2**) as an initiator. The terminal propagating ends of this polyoxazoline were reacted with 3-aminopropyltrimethoxysilane (**4**) to give telechelic trimethoxysilyl-terminated polyoxazoline (**5**). Gelation of this telechelic polymer was carried out by hydrolysis and condensation of alkoxysilyl groups. By this method, the PAEI gels were obtained in good yields, and their degrees of swelling in the solvent could be controlled successfully by the feed ratios of the initiator to the monomer in the stage of the polymerization of 2-methyl-2-oxazoline. However, the cross-linked products were not stable and gradually dissolved in water. The gels were also swollen in *N,N*-dimethylformamide (DMF). The degrees of swelling of these gels were thus measured in DMF.

Introduction

The synthesis of hydrogels is one of the scientific topics in polymer materials, and they are used in various fields such as household articles, horticulture, coating materials, and civil engineering. Most hydrogels investigated so far have ionic groups such as carboxylic acids and sulfonic acid salts as the hydrophilic group. Recently, the methods for the preparation of non-ionic hydrogels have been explored more and more [4]. We also reported the preparation of cross-linked polyoxazoline by means of partial hydrolysis of this polymer followed by cross-linking reaction [5] or the copolymerization with a bifunctional oxazoline monomer [6]. These gels were immersed in water to form stable hydrogels. This non-ionic hydrogel showed a quite high swelling property in aqueous salt such as 5% aqueous NaCl.

In the polymerization of cyclic imino ethers, several bifunctional initiators such as α,ω -dodecamethylene bis(*p*-toluenesulfonate) [7], bisoxazolinium tosylate from 1,4-tetramethylene(2,2'-bisoxazoline) [8], or bifunctional active halide (1,4-dibromo-2-butene or 3-iodo-2-

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Footnotes 1, 2 and 3, see references

(iodomethyl)-1-propene) [9] have been used to prepare the telechelics or block copolymers. *p*-(α,α' -Dibromo)xylene (**2**) was used as a bifunctional initiator in this study. As **2** has two benzylic halides, these two halides might initiate the polymerization of 2-oxazolines toward two directions rapidly. The living ends of this telechelic polymer were terminated by the amine having trialkoxysilyl group to give the telechelic trialkoxysilyl-terminated PAEI.

Silane coupling agents are widely used in the field of new composite materials [10]. Generally, a silane coupling agent consists of two components, a trialkoxysilyl group and an organic functional group. Previously, we reported the novel silane coupling agent based on PAEI by two methods [11]. These trialkoxysilyl groups are easily hydrolyzed to silanols by acid- or base-catalyzed reaction in the presence of water. The silanol groups are reacted each other to form siloxane linkages. By using these successive reactions i.e., hydrolysis-condensation reactions, the modified glass or porous silica gels can be prepared. This procedure is known as a sol-gel method, and has been studied extensively.

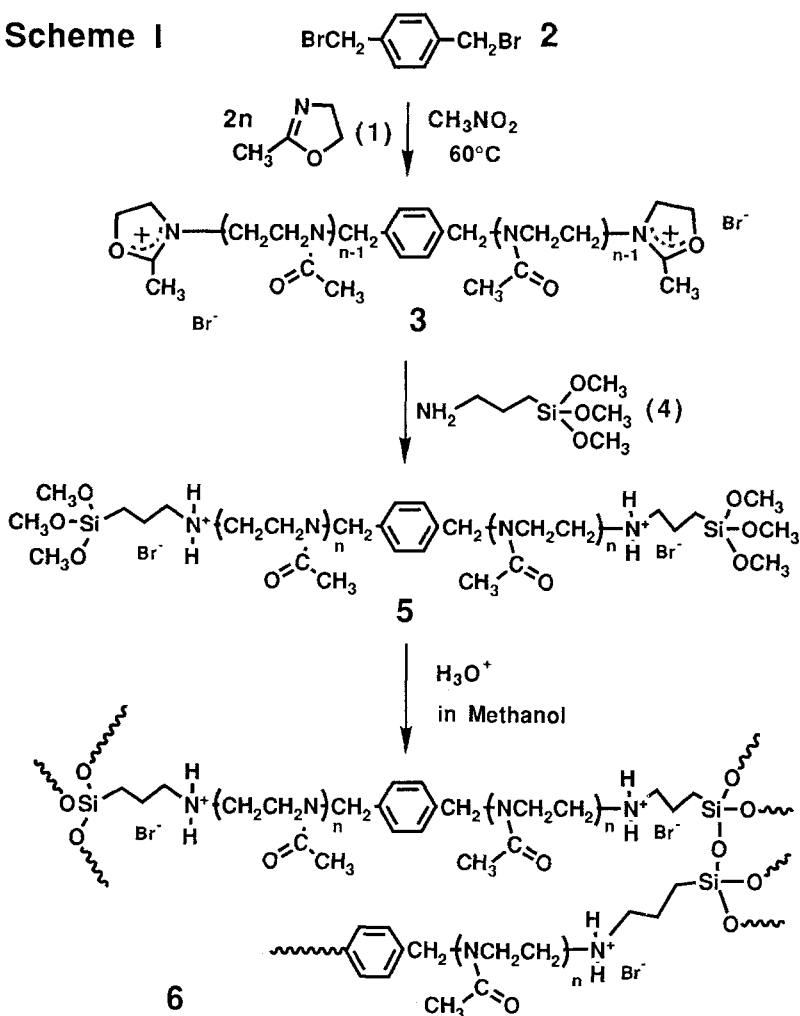
In this paper, the preparation and the gelation of the telechelic trimethoxysilyl-terminated PAEI are described. The stability and the swelling property of the obtained PAEI gel is also discussed.

Results and Discussion

Preparation of Telechelic Trimethoxysilyl-Terminated PAEI (5). Generally, 2-oxazolines are polymerized by using electrophilic initiators such as alkyl halide, alkyl *p*-toluenesulfonate (tosylate), or alkyl trifluoromethanesulfonate (triflate). Here, *p*-(α,α' -dibromo)xylene (**2**) was used as a bifunctional initiator. As shown in Scheme I, the polymerization of 2-methyl-2-oxazoline (**1**) was carried out at 60 °C in nitromethane for several hours, and the oligomer (**3**) having two oxazolinium living ends was terminated by the nucleophilic attack of 3-aminopropyltrimethoxysilane (**4**). Thus, the telechelic trimethoxysilyl-terminated PAEI (**5**) was obtained in a good yield.

Figure 1 illustrates the $^1\text{H-NMR}$ spectrum of the product (**5**). The degree of polymerization (D.P.) of **5** can be calculated from the integral ratio of the ring protons of initiator (δ 7.3) to the acetyl protons (δ 2.0). This value was close to that calculated from the feed ratio of initiator (**2**) to monomer (**1**). The functionality (*f*) of trimethoxysilyl group was also estimated from the integral ratio of the α -protons of silyl group (δ 0.5) to the acetyl protons. Table I summarizes the results of the preparation of telechelic trimethoxysilyl-terminated PAEI (**5**). The functionality (*f*) of trimethoxysilyl group was found to be nearly unity, and the degree of polymerization could be controlled by the feed ratio of the monomer (**1**) to the initiator (**2**). These results were caused by the living nature of the propagating

Scheme I



species in the ring-opening polymerization of 1. In addition, a large excess of 4 makes the quantitative conversion of 3 into 5.

Gelation of Telechelic Trimethoxysilyl-Terminated PAEI (5). As shown in Scheme I, telechelic trimethoxysilyl-terminated PAEI (5) was dissolved in methanol, and the solvent was slowly evaporated at 80°C to yield PAEI gel (6). The results of this gelation are summarized in Table II. In the case of lower molecular weight oligomers (Runs 1 and 2 in Table II), PAEI gels were obtained in relatively good yields. The prepolymer having the relatively high degree of polymerization (D.P.) (Run 3 in Table II) formed PAEI gel in a moderate yield. The hydrolysis-condensation reaction of trialkoxysilyl

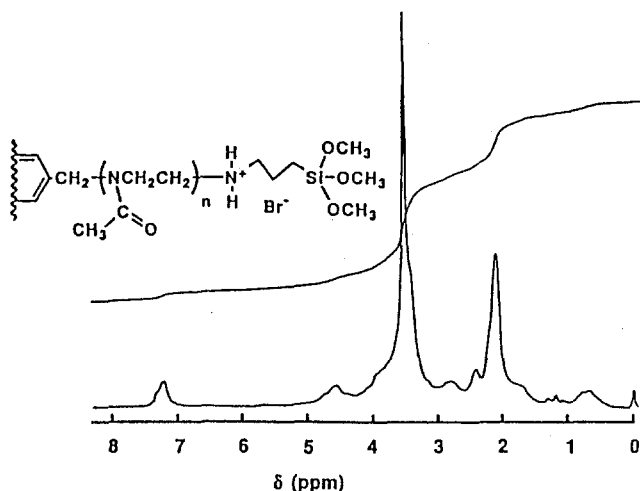


Figure 1. $^1\text{H-NMR}$ spectrum of telechelic trimethoxysilyl-terminated PAEI (5).

Table I. Synthesis of Telechelic Trimethoxysilyl-Terminated PAEIs (5)^{a)}

Run	Feed Ratio (1/2)	Reaction Time (h)	Yield (%)	D.P. ^{b)}	f ^{c)}
1	5.1	2	90	4.5	1.03
2	9.9	4	100	8.4	1.06
3	10.2	4	98	9.3	1.03
4	21.4	6	90	21.8	1.05
5	38.0	8	99	48	1.03

a) Polymerization was carried out at 60°C under nitrogen.

b) Degree of polymerization (D.P.) was determined by $^1\text{H-NMR}$ (acetyl protons vs ring protons).

c) Functionality (f) was determined by $^1\text{H-NMR}$ (α -protons of Si vs ring protons).

groups at both termini caused to form the cross-linkages of the PAEI oligomer (5) by the treatment with the protic media at high temperature. First of all, the trimethoxysilyl-termini were hydrolyzed by the protic media to form silanol-terminated PAEI and then the condensation of these silanol-termini in an intermolecular manner took place immediately to give PAEI gels (6).

Swelling Properties. In water, these gels (6) were dissolved within 30 minutes, and had not enough stability to be handled as a hydrogel. In DMF, however, they were relatively stable, and their

swelling property could be estimated. The degrees of swelling of the obtained gel (6) in DMF are summarized in Table II. The degrees of swelling in DMF increased with increasing the degree of polymerization (D.P.) of the prepolymer (5). Taking account of the living mechanism in the polymerization of 2-oxazolines, it can be concluded that the degree of swelling could be controlled by the feed ratio of the initiator (2) to the monomer (1).

Table II. Gelation Reaction of 5^{a)}

Run	Prepolymer ^{b)}		Gel Yield (%)	Degree of Swelling ^{c)} in DMF
	D.P.	f		
1	8.4	1.06	77	0.23
2	21.8	1.05	92	4.24
3	48	1.03	43	9.02

a) 5; 200 mg, methanol; 0.40 mL, at 80°C.

b) Degree of polymerization (D.P.) and functionality (f) were determined by ¹H-NMR.

c) g-Solvent / g-dried gel after swelling for 1 hour in DMF.

Experimental Section

Materials and Instruments. All solvents and reagents were used as supplied except the following cases. Nitromethane was distilled from phosphorus pentoxide under nitrogen. Acetonitrile was distilled from calcium hydride, and redistilled from phosphorus pentoxide. 2-Methyl-2-oxazoline (1) was distilled from potassium hydroxide. 3-Aminopropyltrimethoxysilane (4) was distilled under reduced pressure. *p*-(α,α' -Dibromo)xylene (2) was dried *in vacuo* before use.

IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. ¹H-NMR spectra were obtained on a Hitachi R-600 (60MHz), or on a JEOL JNM-JX-400 (400 MHz) spectrometer. All NMR spectra were recorded in the deuterated solvent relative to the internal standard tetramethylsilane.

Preparation of Telechelic Trimethoxysilyl-Terminated PAEI (5). A typical procedure for the preparation of trimethoxysilyl-terminated PAEI (5) is as follows. To a solution of *p*-(α,α' -dibromo)xylene (2) (0.535 g, 2.03 mmol) in 10 mL of nitromethane, 1.76 g (20.7 mmol) of 2-methyl-2-oxazoline (1) was added and the resulting mixture was refluxed at 60°C. After heating for several hours, the resulting polymer solution was treated with 0.916 g (5.11 mmol) of 3-aminopropyltrimethoxysilane (4) and kept heating for another 12 hours. The pale-yellow polymer (5) was obtained by precipitation with diethyl ether (3.01 g, 98 %). The

molecular weight and the functionality of the resulting polymer (5) was determined by $^1\text{H-NMR}$.

Gelation of Telechelic Trimethoxysilyl-Terminated PAEI (5). A typical gelation reaction is described as follows. The trimethoxysilyl-terminated PAEI (5) (0.353 g) was dissolved in small amount of methanol (0.7 mL), and the solvent was rapidly evaporated at 80°C under air. Heating for 3.5 hours gave an insoluble product. After the purification by washing with methanol and drying *in vacuo*, PAEI gel (6) was obtained in a yield of 0.246g (77 %). The swelling equilibrium of the obtained gel in DMF was examined by the method previously reported [5, 6].

References and Notes

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