ing copolymers, the temperature range of the isotropic state (i.e., range between the clearing and decomposition temperatures) was increased over that for poly(undecyl isocyanate). The results from various analyses showed that all the copolymers undergo decomposition at ~180 °C. The dependence of T_g on alkyl side chain length and copolymer composition was consistent with that for other alkyl side chain polymers.

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Synthesis of Nonionic Hydrogel, Lipogel, and Amphigel by Copolymerization of 2-Oxazolines and a Bisoxazoline[1]

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ABSTRACT: As a novel method for the preparation of a hydrogel based on a polyoxazoline, the copolymerization of 2-methyl-2-oxazoline and 2,2'-tetramethylenebis(2-oxazoline) was carried out with methyl triflate initiator. The obtained gel was isolated almost quantitatively after Soxhlet extraction. The resulting hydrogel showed a high swelling degree both in water and in 5% aqueous sodium chloride. The water uptake was up to 45 multiples of the weight of the dry gel. 2-Oxazoline monomers with various 2-alkyl substituents (methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-octyl) were also copolymerized with the above bisoxazoline to produce gels having a wide variety of swelling characteristics, i.e., from hydrogel to lipogel (organogel) depending on the substituents. The gels from 2-*n*-propyl- or higher alkyl-2-oxazoline showed the characteristic properties of lipogels and were swollen in less polar organic solvents such as toluene or 1,2-dichloroethane. The gel from 2-ethyl-2-oxazoline was a characteristic amphiphilic gel (amphigel), which was swollen both in water and in organic solvents.

Introduction

Hydrogels are known to be one of the most interesting polymeric materials, especially 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, explorations of methods for the preparation of nonionic hydrogels have been reported[2-6] more and more.

Very recently, we reported a novel nonionic hydrogel starting from 2-methyl-2-oxazoline as shown in Scheme I.[7] Generally, poly(2-methyl-2-oxazoline) has unique properties such as high hydrophilicity and good compatibility with several organic polymers.[8] We also demonstrated the partial hydrolysis of poly(2-methyl-2-oxazoline) followed by a cross-linking reaction to give a

Scheme I

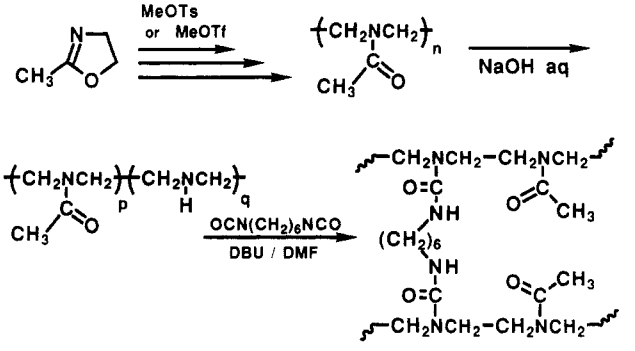


Table I
Preparation of Hydrogel 4 by Copolymerization of 1 and 2[a]

run	1/3	2/3	1/2	yield, %	H_2O content[b] in H_2O	5% NaCl(aq)
1	100	20	5	92	6	6
2	100	10	10	86	15	13
3	100	5	20	68	36	27
4	200	5	40	85	40	31
5	300	5	60	74	45	39
6	500	5	100	92		
7	90	2.5	36	0[c]		

[a] In CH_3CN, 100 °C, 7 h, in sealed tube. [b] g of H_2O/g of dry gel. [c] No gelation was observed after 7 days at 100 °C.

nonionic hydrogel that absorbed water in several multiples of 10.

Here we wish to report a novel method for the preparation of hydrogel based on polyoxazoline by means of copolymerization between 2-methyl-2-oxazoline and a bisoxazoline of 2,2′-tetramethylenebis(2-oxazoline).

In addition, polyoxazoline shows either hydrophilic or hydrophobic (lipophilic) characteristics due to changing the substituents in the acyl group. On this basis, we have prepared a novel nonionic surfactant based on polyoxazoline.[9,10] In the present paper, this quality makes it possible to prepare the so-called lipogel (organogel) and amphigel by copolymerization of 2-alkyl-2-oxazoline and bisoxazoline.

Experimental Section

Materials and Instruments. 2-Methyl-2-oxazoline (1), 2-ethyl-2-oxazoline (**6a**), methyl trifluoromethanesulfonate (**3**), and all solvents were dried and distilled under nitrogen. 2,2′-Tetramethylenebis(2-oxazoline) (bisoxazoline; **2**), 2-*n*-propyl-2-oxazoline (**6b**), 2-*n*-butyl-2-oxazoline (**6c**), and 2-*n*-octyl-2-oxazoline (**6d**) were prepared according to the method reported previously.[11]

IR spectra were obtained with a Hitachi 260-50 grating spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 (60 MHz). GPC was carried out on a Toso CCPD (TSK gel G4000) using *N,N*-dimethylformamide (DMF) with 0.4% triethylamine as an eluent after calibration with standard polystyrene samples. Gas chromatographic analysis (GC) was made on a Shimadzu GC-6A instrument.

Copolymerization of 2-Methyl-2-oxazoline (1) and Bisoxazoline (2). In a typical procedure, a mixture of **1** (0.65 g, 7.6 mmol), **2** (0.075 g, 0.38 mmol), **3** (0.0125 g, 0.076 mmol), and acetonitrile (5 mL) was placed in a 30-mL glass ampule and heated at 100 °C for 7 h. The obtained gel was purified by Soxhlet extraction with dichloromethane, followed by drying in vacuo and finally freeze-drying with benzene: yield 0.49 g (68%).

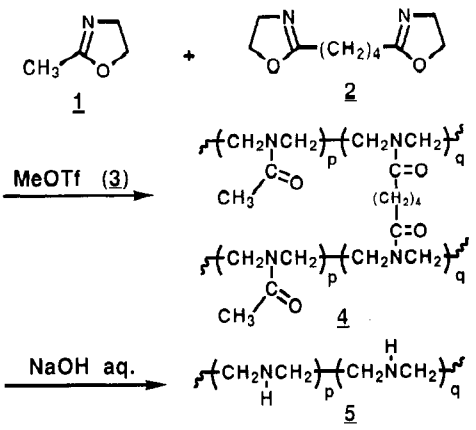
Hydrolysis of the Obtained Gel. The gel (0.88 g) prepared from **1** and **2** (run 2 in Table I) was immersed in 5% aqueous sodium hydroxide. The resulting mixture was heated at 100 °C for 74 h. A white solid was precipitated after cooling and purified by recrystallization from water: yield of **5** 0.42 g (95%).

Copolymerization of 2-Alkyl-2-oxazoline (6) and Bisoxazoline (2). In a typical example, a mixture of 2-*n*-propyl-2-oxazoline (**6b**) (2.59 g, 23 mmol), **2** (0.23 g, 1.2 mmol), **3** (0.039 g, 0.24 mmol), and acetonitrile (15 mL) was placed in a 50-mL sealed glass ampule and heated at 100 °C for 40 h. The resulting gel was isolated by Soxhlet extraction with dichloromethane followed by freeze-drying with benzene: yield 2.14 g (76%).

Swelling Properties. The swelling equilibrium of the obtained gel was determined as follows. The gel (0.1 g) was immersed in deionized water (50 mL) at room temperature for 24 h. The swollen hydrogel was weighed after filtration by using a 1G4 glass filter (17 mmHg, 5 min). The water uptake was calculated from the equation $(W' - W)/W$, where W is the weight of the dried gel and W' the weight of the swollen hydrogel.

The swelling degrees in some organic solvents such as *N,N*-dimethylformamide (DMF), 1-propanol, 1,2-dichloroethane, diethylene glycol dimethyl ether (diglyme), and toluene were measured by a method similar to that described above for swelling in water.

Scheme II



Results and Discussion

Synthesis of Hydrogel. Generally, 2-oxazolines are polymerized by using electrophilic initiators such as alkyl halide, alkyl *p*-toluenesulfonate (tosylate), or alkyl trifluoromethanesulfonate (triflate).[8] Here, methyl triflate was used for a rapid initiation. As shown in Scheme II, the copolymerization between **1** and **2** produced a gel. This one-step method is very simple and easy for the preparation of polyoxazoline gel.

The results of the gelation are summarized in Table I. The gel was obtained in a good yield when the feed ratio of **2** to **3** was higher than 5. In run 7, no gelation was observed. GPC analysis of the polymer obtained in this case (soluble in acetonitrile) showed that the degree of polymerization was 155. This value was relatively larger than the calculated one from the feed ratio of (1 + 2) to 3 (92.5) by assuming that only one oxazoline group in **2** was polymerized to give a linear polyoxazoline. Accordingly, some cross-linking reaction should take place under this condition. However, the concentration of the cross-linking points was not enough to form a gel. The obtained gels in runs 1–5 were white solid and absorbed water to form a colorless hydrogel. The hydrogel was stable and had strength enough to bear handling.

Polymerization Mechanism. GC analysis indicated that no monomers (**1** and **2**) remained unreacted after the gelation; i.e., the conversions of two monomers were almost quantitative.

The structure of the obtained gel (**4**) was supported by its IR spectrum and alkaline hydrolysis. The IR spectrum of **4** shows the stretching band at 1630 cm^{-1}, which is assignable to C=O of the acyl group. The alkaline hydrolysis of **4** (run 2 in Table I), performed by using aqueous sodium hydroxide, produced a linear poly(ethylenimine) (**5**) as shown in Scheme II. The structure of **5** was characterized by IR and ^1H NMR spectra. GPC analysis of **5** showed the following results: $\bar{M}_n$ = 5090, $\bar{M}_w$ = 5200, $\bar{M}_w/\bar{M}_n$ = 1.02. The degree of polymerization (118) of **5** was very close to that calculated by the feed ratio of (1 + 2) to 3 (110). In addition, the narrow molecular weight distribution of **5** is taken to support the living mechanism in this copolymerization.

Table II
Swelling Degrees[a] of Polyoxazoline Gels[b]

R in 7	yield, %	swelling degree in solvent					
		H_2O	DMF	*n*-PrOH	CH_2ClCH_2Cl	diglyme	$C_6H_5CH_3$
Me	68	36	14	15	4	2	0
Et	73	28	25	17	27	3	1
n-Pr	76	5	21	20	29	8	1
n-Bu	86	5	20	20	27	3	5
n-Oct	87	5	3	7	19	3	10

[a] g of solvent/g of dry gel. [b] ROZO/BisOZO (2)/MeOTf (100/5/1), 100 °C, CH_3CN, sealed tube.

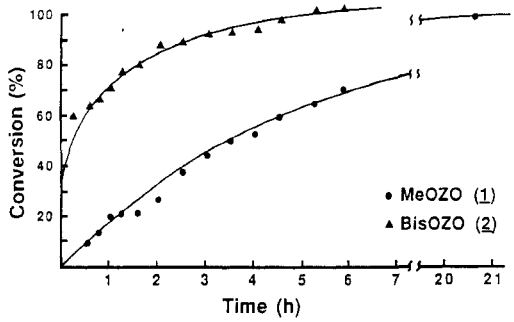


Figure 1. Time–conversion curves for 2-methyl-2-oxazoline (1) and bisoxazoline (2) in the copolymerization in acetonitrile at 80 °C.

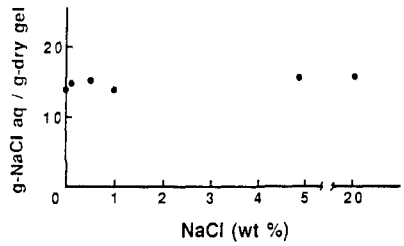
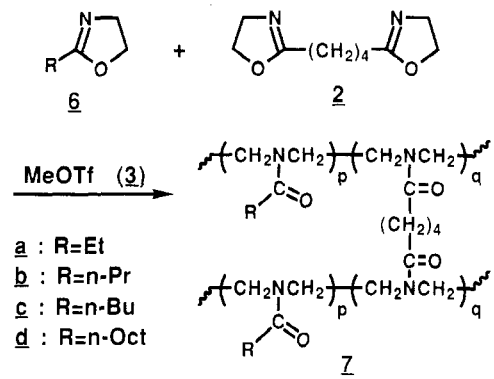


Figure 2. Swelling degrees of polyoxazoline gel (4) in various concentrations of aqueous sodium chloride.

Scheme III



The present gelation was influenced by the concentration of monomers. For example, the experiment under the same condition as that of run 3 in Table I except for the amount of solvent (20 mL, 4 times as large as that of run 3) showed no gelation even after 7 days of heating.

Figure 1 illustrates the time–conversion curve of the present copolymerization (1:2:3 = 100:10:1, at 80 °C) by GC analysis. Under this condition, the gelation was observed after 21 h of heating. The following two results should be pointed out from Figure 1. (i) The reactivity of 2 is much higher than that of 1. 1 has still remained unreacted at about 30% at the time of 100% conversion of 2. (ii) The gelation took place after 100% conversion of 1. That is, no gelation was observed before 1 had been consumed. From these results, it is assumed that the distributions of the monomeric units of 1 and 2 in the copolymer are not statistically random. Consequently, the length of the polymer chain between cross-linking points was shorter at an earlier stage and longer at a later stage of copolymerization. Thus, the calculated value of the chain length (molecular weight) between two cross-linking points on the basis of the feed ratio of 1 to 2 is to be taken as an overall average value during the whole course of copolymerization.

Swelling Properties in Water. The swelling degrees of the obtained gel (4) both in water and in 5% aqueous sodium chloride are summarized in Table I. The equilibrium swelling degree increased with increasing the feed ratio of 1 to 2. The water uptake was up to 45 multiples of the weight of dried gel. The swelling degrees in 5% aqueous sodium chloride did not decrease much compared with the values in water. This result is taken as one of the characteristic properties of a nonionic hydrogel (vide infra).

In run 6 in Table I, the gel was obtained after Soxhlet extraction with dichloromethane. However, this gel was immersed in water to become soluble. It may be said that the cross-linking points were enough to form a gel in dichloromethane under reflux (Soxhlet extraction) but not enough in water to maintain its hydrogel state.

As mentioned above, the swelling degree in aqueous salt solution did not decrease an order of magnitude compared with that in water. However, careful analysis of these results has revealed that a 0–20% decrease of the equilibrium swelling degree was observed in aqueous salt. The decrease may be explained by the effect of the remaining unreacted oxazoline rings of 2 in the polymer pendant groups, which act as a kind of ionic group to cause the decrease of swelling degree in an ionic water. This assumption is supported by the following experiments. After the gel obtained in run 4 of Table I is dried in vacuo at 120 °C for 2 h, the resulting gel was found to be swollen in aqueous sodium chloride by changing the concentration of the salt. During the drying procedure, further reaction (cross-linking reaction) of the remaining oxazoline ring with the propagating oxazolinium ring occurred, and the swelling degree decreased to a lower level (15 multiples of the weight of dried gel), which remained unchanged in aqueous salt solutions of varying salt concentrations, as shown in Figure 2. This property again shows strongly the characteristics of nonionic hydrogel.

Synthesis of Lipogel and Amphigel. As mentioned in the Introduction, polyoxazoline shows either hydrophilicity or lipophilicity by changing the substituents. Scheme III illustrates the copolymerization of 2-alkyl-2-oxazoline (6) and bisoxazoline (2) using methyl triflate initiator. After Soxhlet extraction, a gel was obtained in a good yield. The results are summarized in Table II together with the swelling degrees both in water and in some organic solvents.

The gel from 2-methyl-2-oxazoline (**1**), which showed a high swelling degree in water as a hydrogel, was also swollen in DMF or in 1-propanol. However, this gel was not much swollen in less polar solvents such as diglyme or toluene. On the other hand, the gel from 2-*n*-octyl-2-oxazoline (**6d**) was swollen in toluene or in 1,2-dichloroethane and swollen much less in polar solvents such as water or DMF. Thus, this gel is taken as a lipogel. The gels from 2-*n*-propyl-2-oxazoline (**6b**) and from 2-*n*-butyl-2-oxazoline (**6c**) showed the intermediate properties between the gel from **1** and that from **6d**. These gels absorbed DMF, 1-propanol, and 1,2-dichloroethane in 20–30 multiples of the weight of dried gel.

It is noteworthy that the gel from 2-ethyl-2-oxazoline (**6a**) was swollen both in water and in organic solvents such as DMF or 1,2-dichloroethane. This gel can be characterized as an amphiphilic gel.

Conclusions

The present copolymerization method is convenient for the preparation of nonionic hydrogel based on polyoxazoline. 2-Oxazolines with various 2-alkyl substituents produced a wide variety of gels, i.e., hydrogel, lipogel, and amphigel.

Recently, nonionic gels such as poly(*N*-isopropylacrylamide)[12] or polypeptide[13] have been reported to show volume-phase transitions with temperature. These systems are said to have a lower critical solution temperature (LCST).[14] These LCST phenomena can be regarded as a muscle-type action. The polyoxazoline gels in the present study also have potential to offer a model of muscle, which will be the next target of our research.

The good compatibility of polyoxazoline segment with other organic polymers allows production of a composite gel by the combination of the gel obtained in this work and other materials. In addition, it should be interesting that the functional groups are introduced to the present polyoxazoline gel to give a novel type of polymeric functional material, which is now under investigation in our group.

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Registry No. **1**, 1120-64-5; **2**, 36931-59-6; **5**, 26913-06-4; (**1**)(**2**) (copolymer), 124919-84-2; (**2**)(**6a**) (copolymer), 124919-86-4; (**2**)(**6b**) (copolymer), 124919-85-3; (**2**)(**6c**) (copolymer), 124919-87-5; (**2**)(**6d**) (copolymer), 124919-88-6.