Polymer Bulletin 21, 353–356 (1989)

Polymer Bulletin

Synthesis of an amphigel by the terpolymerization of 2-methyl-2-oxazoline, 2-alkyl-2-oxazoline, and bis-oxazoline

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SUMMARY

The terpolymerization of 2-methyl-2-oxazoline, 2-alkyl-2-oxazoline (alkyl = n-butyl, n-octyl, n-dodecyl), and 2,2'-tetramethylenebis(2-oxazoline) was carried out with methyl trifluoromethanesulfonate initiator. The obtained gel was isolated in a moderate yield after Soxhlet extraction. The resulting gel showed a characteristic property as an amphiphilic gel (amphigel), i.e., it was swollen both in water and in organic solvents such as N,N-dimethylformamide (DMF), n-propanol, 1,2-dichloroethane, diethyleneglycol dimethyl ether (diglyme) and toluene.

INTRODUCTION

A considerable effort of research has been made in the area of preparation of non-ionic hydrogels in connection with the exploration of functional polymeric materials.(1-5) Previously, we reported the synthesis of a novel non-ionic hydrogel based on poly(2-methyl-2-oxazoline) by the partial hydrolysis and the subsequent cross-linking reaction.(6) This gel absorbed water in several multiples. We have also explored recently an alternative method for the preparation of non-ionic polyoxazoline hydrogel, which was carried out by the copolymerization between 2-methyl-2-oxazoline and bis-oxazoline. (7) These gels showed high swelling degree both in water and in 5% aqueous sodium chloride solution.

On the other hand, we have been studying on the chemistry of the polymerization of various 2-oxazolines, in which polyoxazoline was found to have a wide spectrum from hydrophilic to lipophilic nature depending on the N-acyl groups.(8) Actually, a lipogel (lipophilic gel) was prepared by the copolymerization between 2-oxazoline with a medium to long alkyl group and a bis-oxazoline. This lipogel was swollen in less polar organic solvents such as toluene and 1,2-dichloroethane.(7)

We wish to describe here a combination between hydrophilic polyoxazoline segment and lipophilic one. Thus, the terpolymerization of 2-methyl-2-oxazoline, 2-alkyl-2-oxazoline, and a bis-oxazoline was carried out to produce amphigel (amphiphilic gel), which is swellable both in water and in organic solvents.

RESULTS AND DISCUSSION

Preparation of Polyoxazoline Gel (5)

A hydrophilic monomer, a lipophilic monomer and a bifunctional one were employed in the terpolymerization. Thus, a mixture of 2-methyl-2-oxazoline (**1**), 2-(n-butyl)-2-oxazoline (**2a**), and 2,2'-tetramethylenebis(2-oxazoline) (bis-oxazoline) (**3**) was polymerized at 60°C in the presence of methyl trifluoromethanesulfonate (methyl triflate) (**4**) as an initiator. GC analysis indicated that no monomers (**1**,**2a** and **3**) remained unreacted after the gelation, i.e., the conversions of all three monomers were almost quantitative. The soluble parts during Soxhlet extraction should include a linear polymer and a cross-linked one, which has not enough cross-linking points to form a gel. By replacing of **2a**, 2-(n-octyl)-2-oxazoline (**2b**) and 2-(n-dodecyl)-2-oxazoline (**2c**) were also used for this terpolymerization to

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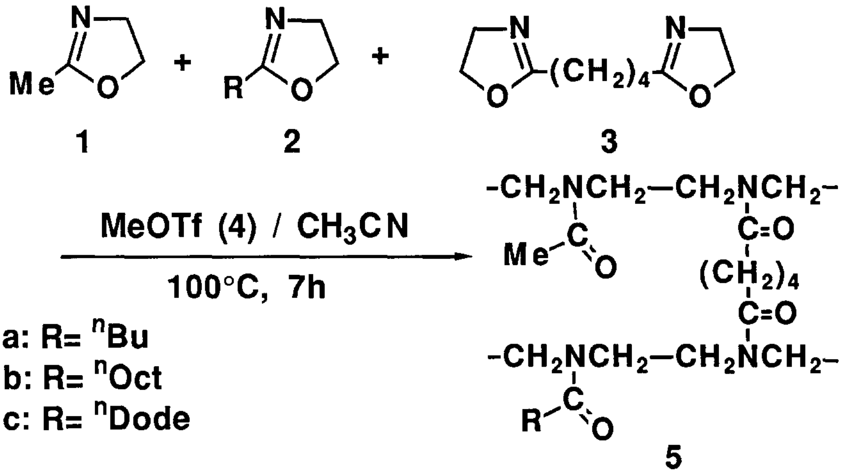
Scheme 1



produce the corresponding gels (**5b** and **5c**) as represented in Scheme 1. In all three cases, the isolated yields of gels after purification were moderate as summarized in Table I. For a comparison of their swelling degrees, the feed ratios among **1**, **2**, **3** and **4** in all three cases were kept constant, i.e., 50:50:5:1.

The molecular structure of obtained gel (**5**) has not been elucidated because of its insoluble nature. However, from the results of GC analysis in the binary copolymerization between **1** and **3**, the reactivity of **3** should be much higher than that of **1**. (7) In addition, **2** has a similar polymerization reactivity to that of **1**. From these results, it is assumed that the distributions of the units of (**1**+**2**) and **3** in the terpolymer (**5**) are not statistically random, while those of **1** and **2** are random. Accordingly, the length of the random copolymer chain consisted of **1** and **2** segments between cross-linking points was shorter at earlier stage and longer at later stage of terpolymerization.

Swelling Properties in Water and in Organic Solvents

The swelling degrees of the obtained gels (**5**) both in water and in some organic solvents are summarized in Table I. For example, the water uptake by the gel (**5a**) from **1**, **2a** and **3** was 29 multiples of the weight of dried gel. This gel showed a characteristic property as a

Table I Swelling degrees of polyoxazoline gels

R	Yield (%)	Swelling Degrees[a]					
		H_2O	DMF	n-PrOH	CH_2ClCH_2Cl	Diglyme	$C_6H_5CH_3$
ⁿBu	69	29	30	23	31	4	2
ⁿOct	63	8	23	20	30	8	8
ⁿDode	63	5	6	11	39	4	9

a) g-solvent / g-dry gel

b) ROZO / MeOZO / BisOZO / MeOTf 50/50/5/1, 100°C, in CH_3CN

hydrogel, which was stable and had strength enough to bear at handling. Furthermore, this gel (**5a**) was swollen also in DMF, n-propanol or 1,2-dichloroethane. It should be noted that this gel can be characterized as an amphiphilic gel (amphigel).

The gel (**5b**) from **2b** was swollen much less in water compared with the gel (**5a**) from **2a**. However, this gel adsorbed a wide variety of solvents, from water to toluene at moderate swelling degrees. In the case of the gel (**5c**) from **2c**, the swelling degrees in water, DMF or n-propanol decreased in comparison with the gel from **2a** or **2b**. On the other hand, the gel (**5c**) was much swollen in 1,2-dichloroethane or in toluene. The order of the polarity of the solvents used is as follows: water > DMF > n-propanol > 1,2-dichloroethane > diglyme > toluene. Accordingly, it can be concluded that the gel from polyoxazoline with higher N-acyl group is inclined to adsorb less polar solvents. Compared with the copolymer gel from **2** and **3** (7), the gel prepared by terpolymerization of **1**, **2** and **3** showed a wide swelling property in water and in organic solvents.

EXPERIMENTAL

Materials and Instruments

2-Methyl-2-oxazoline (**1**), methyl trifluoromethanesulfonate (methyl triflate) (**4**) and all solvents were dried and distilled under nitrogen. 2,2'-Tetramethylenebis(2-oxazoline) (bisoxazoline) (**3**), 2-(n-butyl)-2-oxazoline (**2a**), 2-(n-octyl)-2-oxazoline (**2b**) and 2-(n-dodecyl)-2-oxazoline (**2c**) were prepared according to the method reported previously.(9) These all oxazoline monomers gave satisfactory data in their ^{1}H-NMR and IR spectra.

IR spectrum was obtained with a Hitachi 260-50 grating spectrophotometer. ^{1}H-NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-20B (60MHz). Gas chromatographic analysis (GC) was made on a Shimadzu GC-6A instrument.

Terpolymerization of 2-Methyl-2-oxazoline (1), 2-(n-Butyl)-2-oxazoline (2a) and Bisoxazoline (3)

A mixture of **1** (0.65g, 7.6mmol), **2a** (0.97g, 7.6mmol), **3** (0.15g, 0.76mmol), **4** (0.025g, 0.15mmol), and acetonitrile (10ml) was placed in a 30ml glass ampoule and heated at 100°C for 7 hours. The obtained gel was purified by Soxhlet extraction with dichloromethane, followed by drying in vacuo and finally by freeze-drying with benzene. Yield was 1.2g (69%).

Terpolymerization of 1, 2-(n-Octyl)-2-oxazoline (2b) and 3

In a 30ml glass ampoule, **1** (0.33g, 3.8mmol), **2b** (0.70g, 3.8mmol), **3** (0.075g, 0.38mmol), **4** (0.013g, 0.075mmol), and acetonitrile (4.5ml) were heated at 100°C for 7 hours. The obtained gel was purified by similar procedure as that of **2a**. Yield was 0.69g (63%).

Terpolymerization of 1, 2-(n-Dodecyl)-2-oxazoline (2c) and 3

1 (0.33g, 3.8mmol), **2c** (0.92g, 3.8mmol), **3** (0.075g, 0.38mmol), **4** (0.013g, 0.075mmol), and benzene (2ml) were sealed in a 30ml glass ampoule and heated at 100°C for 7 hours. Yield was 0.83g (63%) after purification.

Swelling Properties

The swelling equilibrium of the obtained gel was determined as follows. The gel (0.10g) was immersed in ion-exchanged water (50ml) at room temperature for 24 hours. The swollen hydrogel was weighed after filtration by using 1G4 glass filter (17mmHg, 5minutes). The water uptake was calculated from the following equation; (W'-W)/W, where W; weight of the dried gel and W'; weight of the swollen hydrogel.

The swelling degrees in some organic solvents such as DMF, n-propanol, 1,2-dichloroethane, diglyme and toluene were measured by a similar method described above for swelling in water.

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Accepted March 7, 1989 S