of a crystallization endotherm at 200 °C in melt-spun material. In contrast, the diol in low-temperature (solution) polymerized polymer appears to be incorporated largely in a head-to-head fashion.

Solid-phase polymerization results in a stable polymer configuration in which the diol is incorporated in a head-to-tail fashion. This configuration is characterized by a 4-fold helical structure. This structure is seen in all samples held at temperatures where ester interchange takes place, regardless of the sequence in the as-polymerized material.

The presence of an extended structure in the nematic phase has important consequences in terms of fiber properties. As-spun fibers have properties which are similar to those obtained from rodlike chains because of this extended structure. The disorder present due to the random incorporation of the diol prevents the formation of large crystallites so that relatively low melting temperatures are found. This has important consequences in that processing temperatures compatible with commercial polyester equipment can be used. High-temperature heat treatment results in fiber tensile properties which are comparable to the best reported for melt-spun fibers. The orientation of these fibers is much higher than generally found for rodlike thermotropic polyesters so that a higher percentage of the ultimate properties is obtained. It is likely that the flexibility of the chain due to the possibility of assuming the cis conformer allows the removal of defects either in spinning or during crystallization.

Registry No. (3,4′-PCOPG diacetate)(T) (copolymer), 75737-94-9; (3,4′-PCOPG diacetate)(T) (SRU), 75796-78-4; (3,4′-PCOPG)(diphenyl terephthalate) (copolymer), 117653-46-0; (3,4′-PCOPG)(terephthaloyl chloride) (copolymer), 117653-47-1.

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A Novel Nonionic Hydrogel from 2-Methyl-2-oxazoline

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ABSTRACT: A novel nonionic hydrogel consisting of poly(*N*-acetylethylenimine) was prepared from 2-methyl-2-oxazoline. Partial alkaline hydrolysis of poly(*N*-acetylethylenimine) was followed by a cross-linking reaction with hexamethylene diisocyanate to produce a gel. The cross-linking reaction proceeded quantitatively in bulk. By use of 1,8-diazabicyclo[5.4.0]undec-7-ene as a catalyst in *N*,*N*-dimethylformamide, the gel was produced under mild conditions. The resulting dried gel was immersed in water to form a stable hydrogel. The water uptake was in up to 72 multiples of the weight of dried gel. This nonionic hydrogel showed also quite a high swelling property in aqueous salt such as 5% aqueous NaCl. The remaining secondary amino groups in the gel after the cross-linking reaction with a diisocyanate influenced the swelling property in water, which could be successfully eliminated by reaction with ethyl isocyanate.

Introduction

Hydrogels have been widely used in a number of applications, e.g., sanitary materials, cosmetics, ingredients for paints or adhesives, food packing, water-holding agents in horti- or agriculture, sealing or packing materials in civil engineering, and some medical applications such as contact lenses[1] or slow-release devices. However, the hydrogels so far depend on carboxylic or sulfonic acids salts as hydrophilic group and, hence, generally do not have satisfactory characteristics toward aqueous salt. Nonionic hydrogels

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Table I
Ring-Opening Polymerization of 2-Methyl-2-oxazoline[a]

run	1, mmol	MeOTs, mmol	$[M]_0/[I]_0$	time, h	$10^{-3}\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
1	58	0.28	209	30	16.4	4.2
2	604	3.17	191	50	14.5	2.2
					8.5[d]	1.3
3	238	0.61	394	72	24.8	2.4
					16.3[d]	1.5
4	248	0.62[c]	403	34	63.5	2.4

[a] Polymerization was carried out in bulk at 120 °C; [M] = [monomer] = [1], [I] = [initiator] = [MeOTs]. [b] Calculated by GPC with polystyrene standard samples. [c] MeOTf was used as an initiator at 100 °C. [d] Polymers after fractionation.

prepared from poly(2-hydroxyethyl methacrylate),[2-4] poly(oxyethylene),[5,6] polyacrylamide,[7,8] poly(2,3-dihydroxypropyl methacrylate),[9] and poly(vinylpyrrolidone)[10] have been reported. The cross-linked poly(*N*-propionylethylenimine) was also prepared in a patent by Dow Chemical Co.[11]

We have studied the ring-opening polymerization of 2-methyl-2-oxazoline for several years.[12] The resulting poly(*N*-acetylethylenimine) (PAEI) can be regarded as a polymer homologue of *N*,*N*-dimethylacetamide (DMAc). It is well-known that DMAc shows unique characteristics of high hydrophilicity and solubilizing organic polymers. Accordingly, PAEI was strongly hydrophilic and well compatible[13] with organic commodity polymers such as poly(vinyl chloride) and polyamides. By using these properties, PAEIs or their copolymers were used as nonionic surfactants[14] or antielectrostatic agents.[15] In addition, PAEI has an amide group, which is easily functionalized. Here we report on a novel nonionic hydrogel consisting of PAEI by using partial hydrolysis followed by a cross-linking reaction.

Results and Discussion

Preparation of the Hydrogel. The preparation of the hydrogel is represented in Scheme I. Ring-opening polymerization of 2-methyl-2-oxazoline (**1**) was carried out in the presence of methyl *p*-toluenesulfonate (methyl tosylate) (at 120 °C) or methyl trifluoromethanesulfonate (methyl triflate) (at 100 °C) as an initiator. This polymerization proceeded via a cationic oxazolinium ring, which was opened by the nucleophilic attack of monomer through an S_N2 mechanism. Table I summarizes the results of the ring-opening polymerization of **1**. The molecular weights of the resulting poly(*N*-acetylethylenimine) (**2**) were controlled by the feed ratio of the initiator to the monomer (**1**). However, the molecular weight distribution of **2** was relatively broad in the case of high molecular weight **2**. Thus, the obtained polymers (runs 2 and 3) were subjected to fractionation for the following hydrolysis reactions as shown in Table I.

The partial hydrolysis of **2** was carried out in aqueous sodium hydroxide solution to form poly(*N*-acetylethylenimine)/poly(ethylenimine) copolymer (**3**). This might be random copolymer because of no specific selectivity in hydrolysis. The degree of hydrolysis was controlled by the concentration of sodium hydroxide and also by the reaction time, which was successfully determined by titration and ^{1}H NMR. Figure 1 illustrates the ^{1}H NMR spectra of poly(*N*-acetylethylenimine) before and after the alkaline hydrolysis. From the integral ratio between the methylene protons adjacent to secondary amino group and those adjacent to acetamide group, the degree of hydrolysis could be calculated. This value was very close to that by titration with perchloric acid as summarized in Table II. In the hydrolysis for a long time, i.e., 67 h, an equimolar amount of amide group to the amount of NaOH was completely hydrolyzed. This means that the degree of hydrolysis can be controlled by the ratio of the amount of NaOH to that of amide groups. Thus, 2.4–24.0 mol % of the amide groups in **2** were hydrolyzed to form secondary amino groups.

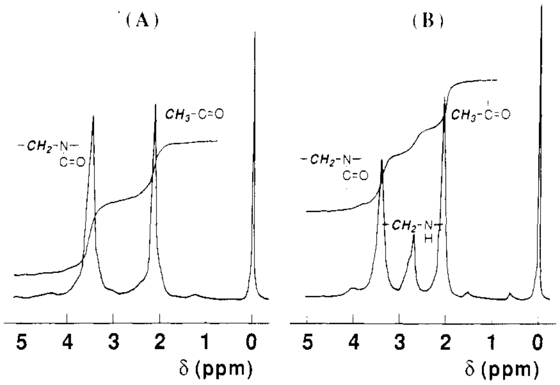


Figure 1. ^{1}H NMR spectra of poly(*N*-acetylethylenimine) (A) before and (B) after partial hydrolysis.

Table II
Partial Hydrolysis of Poly(*N*-acetylethylenimine)

run	2: $10^{-3}\bar{M}_n$[a]	NaOH/NCOMe	temp, °C	time, h	hydrolysis, % NMR[b]	hydrolysis, % titr[c]
1	16.4	2.54	100	0.5	12.5	
2	8.5	0.47	100	0.5	7.2	7.0
3	11.4	0.47	100	0.5	5.0	4.9
4	10.8	0.27	100	67	24.0	
5	10.8	0.15	100	67	17.0	
6	10.6	0.10	100	67		10.2
7	63.5	0.02	100	65		2.4

[a] Calculated by GPC. [b] Calculated from ^{1}H NMR spectra. [c] Determined by titration.

Table III
Cross-Linking Reaction in Bulk

run	2: $10^{-3}\bar{M}_n$[a]	hydrolysis,[b] %	NCO/NH	gel,[c] %
1	16.4	12.5	1.11	100
2	16.4	18.2	1.21	95
3	14.5	3.4	1.19	93
4	14.5	3.4	0.65	55
5	14.5	3.4	0	0
6	8.5	7.2	0.98	76
7	8.5	7.2	0.53	62

[a] Calculated by GPC. [b] Calculated from ^{1}H NMR spectra. [c] Isolated yield after Soxhlet extraction with dichloromethane.

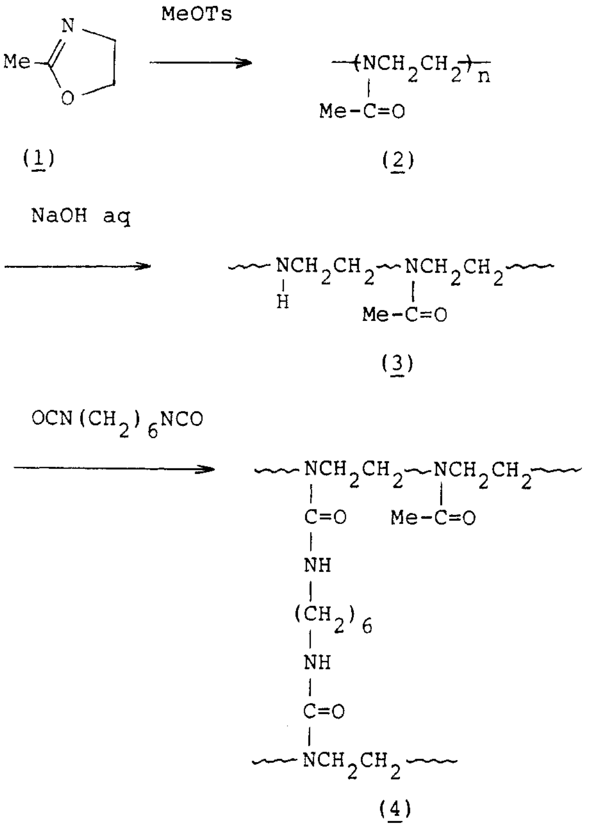
Table IV
Cross-Linking Reaction Catalyzed by DBU in DMF

run	2: $10^{-3}\bar{M}_n$[a]	hydrolysis,[b] %	NCO/NH	DBU/NCO	temp, °C	time, h	gel,[c] %
1	11.4	5.0	0.41	0.54	20	0.5	43
2	63.5	2.4	0.85	0.89	25	0.5	50
3	24.8	3.9	0.59	0.11	60	3.0	99

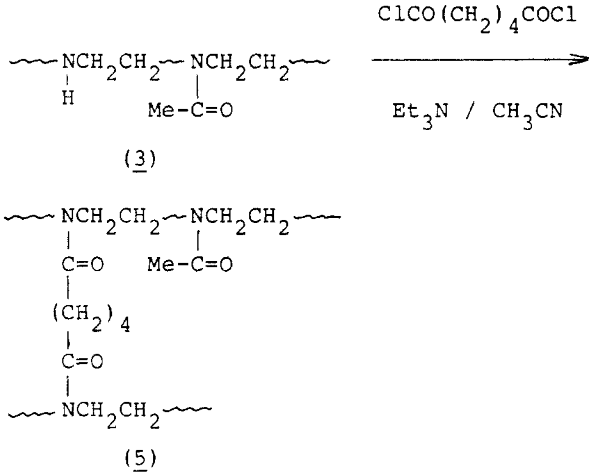
[a] Calculated by GPC. [b] Calculated from ^{1}H NMR spectra. [c] Isolated yield after Soxhlet extraction with dichloromethane.

The cross-linking reaction was carried out at 100 °C by using hexamethylene diisocyanate as a cross-linker. Table III shows the results of the cross-linking reaction in bulk. When a slight excess of cross-linker was used (runs 1–3 in Table III), the resulting gel (**4**) was obtained almost quantitatively after Soxhlet extraction of the soluble part with methylene chloride. Without cross-linker, no gel was formed (run 5). Furthermore, the prepolymer (**2**), which contained no secondary amino groups, produced no gel by the reaction with cross-linker. Table IV summarizes the

Scheme I



Scheme II



results of the cross-linking reaction in *N,N*-dimethylformamide (DMF) by using 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) as a catalyst. The gel was formed under milder conditions in comparison with those in bulk without catalyst. Even at room temperature, gel **4** was obtained in a moderate yield.

As a cross-linker, a diacid chloride such as adipoyl chloride was also used to prepare gel **5** as shown in Scheme II. The cross-linking points of **5** consisted of an amide group, which might cause a different swelling behavior in comparison with the urea group cross-linked gel (**4**).

Swelling Property in Water. The dried gel was immersed in distilled water for 24 h to form a stable hydrogel with an equilibrium water content. The swelling property of the resulting hydrogel was estimated by the water content. The water uptake was calculated from eq 1, where

$$\frac{W'-W}{W} \tag{1}$$

W is the weight of the dried gel, *W′* the weight of the swollen hydrogel. In aqueous salt, the water content including the weight of sodium chloride was similarly calculated according to eq 1. The results of the swelling properties are summarized in Table V. In this table, the molecular weights between cross-linking points were also shown after the hypothetical calculation by assuming that (i) the hydrolysis of amide group in **2** proceeded at random and (ii) the reaction of isocyanate group with secondary amino group was quantitative, regardless of the molecular weights of **2** or **3**. When a nearly equimolar amount of diisocyanate to amino group in **3** was used, the equilibrium swelling degree (water content) increased with increasing molecular weight of the backbone segments between nearest bridges. The water contents of these gels (runs 1–4 in Table V) in 5% aqueous NaCl solution did not decrease much compared with those in water. This result is taken as one of the characteristic properties of a nonionic hydrogel. In runs 5 and 6, where the amount of diisocyanate was less than the equimolar amount of secondary amino group, some amino groups should remain unreacted. These gels absorbed water to a much higher extent. For example, the absorbed water by the gel in run 7 was up to 72 multiples of the weight of dried gel. However, a big decrease of the equilibrium swelling degree was observed in aqueous salt. The decrease may be due to the effect of the remaining secondary amino groups in **4** (vide infra).

The swelling equilibrium in water was reproducible. Table VI shows the swelling degree of regenerated gel after one cycle of swelling and drying. Within experimental error, the first swelling and the second one showed almost the same values of water content. All these hydrogels were stable and had sufficient strength to be handled.

To examine the effect of remaining secondary amino groups on the swelling equilibrium, the gel possessing amino groups was subjected to reaction with ethyl isocyanate as shown in Scheme III. The starting gel (**6**) contained secondary amino groups in 1.9 mol %, determined by titration. After the reaction with ethyl isocyanate, the amino group was converted to an ethylurea

Table V
Swelling Equilibrium in Water

run	**2**: $10^{-3}\bar{M}_n$[a]	hydrolysis,[b] %	NCO/NH	MW[c] btwn cl pts	H_2O content[d] in H_2O	5% $NaCl_{aq}$
1	16.4	18.2	1.21	500	2	2
2	8.5	7.2	0.98	1200	10	8
3	14.5	3.4	1.19	2500	14	11
4	63.5	2.4[e]	1.16	3500	38	37
5	14.5	3.4	0.65	3900	45	19
6	14.5	3.4	0.79	3200	63	29
7	24.8	3.9	0.59	3700	72	25

[a] Calculated by GPC. [b] Calculated from ^{1}H NMR spectra. [c] The number-average molecular weight between cross-linking points. [d] Grams of H_2O/grams of dried gel. [e] Determined by titration.

Table VI
Regeneration of Hydrogel

run	gel[a]	H_2O content[b] 1st[c]	2nd[d]
1	1	2	2
2	3	14	15
3	5	45	55

[a] The number of the gel corresponds to the run number in Table V. [b] Grams of H_2O/grams of dried gel. [c] H_2O content for the original gel. [d] H_2O content for the regenerated gel after one cycle of swelling and drying.

Scheme III

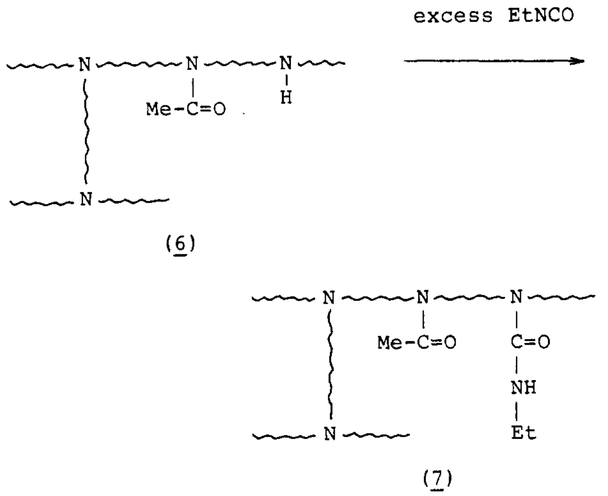


Table VII
Swelling Equilibrium of the Gel[a] before and after Treatment with EtNCO

run	EtNCO/NH	unreacted[b] NH, %	H_2O content[c] in	
			H_2O	5% $NaCl_{aq}$
1		1.9	72	25
2	excess	0.9	59	31
3	excess	<0.5	26	27

[a] $\bar{M}_n$ of prepolymer, 24800; hydrolysis, 3.9%; NCO (cross-linker)/NH, 0.59. [b] Determined by titration. [c] Grams of H_2O/grams of dried gel.

group. As summarized in Table VII, the gel with 0.9 mol % of free amino group showed that the water content decreased compared with that of **6**. After almost quantitative conversion of **6** to **7**, water was absorbed in 26 multiples of the weight of dried gel. In both gels **6** and **7**, the water contents in 5% aqueous NaCl solution were held constant. This result shows that the remaining secondary amino groups act as a kind of ionic group to increase the swelling equilibrium in water. Gel **7** showed again the characteristic property of a nonionic hydrogel, that is, the same values of water content were obtained both in water and in aqueous salt.

The obtained gels in this study can be used as a novel nonionic hydrogel. Taking account of the compatibility of the poly(*N*-acetylethylenimine) segment with other organic commodity polymers, the resulting hydrogel might be a promising polymeric material. The application of these hydrogels is an ongoing study in our group.

Experimental Section

Materials and Instruments. 2-Methyl-2-oxazoline (**1**), methyl *p*-toluenesulfonate (methyl tosylate), methyl trifluoromethanesulfonate (methyl triflate), hexamethylene diisocyante, ethyl isocyanate, adipoyl chloride, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and all solvents were dried and distilled under nitrogen. IR spectra were determined on a Hitachi 260-50 grating spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ on a Hitachi R-20B (60 MHz) or on a JEOL JNM-JX-400 (400 MHz) instrument. GPC was carried out on a Toso CCPD (TSK gel G4000) after calibration with standard polystyrene samples.

Polymerization of 1. As a typical procedure, a mixture of **1** (20.3 g, 238 mmol) and methyl tosylate (0.113 g, 0.606 mmol) was placed in a 40-mL glass ampule and sealed under nitrogen, which was then heated at 120 °C for 72 h. The resulting poly(*N*-acetylethylenimine) (**2**) was isolated by dissolving in MeOH and precipitation into diethyl ether. Yield was 18.9 g (93%). **2** was purified by fractionation with MeOH and diethyl ether and drying in vacuo.

Partial Hydrolysis of 2. A typical procedure was as follows. **2** (7.27 g, run 6 in Table I) was dissolved in 40 mL of 1 N aqueous NaOH (40 mmol) solution and refluxed for 40 min. Water was removed under reduced pressure. **3** was extracted with methylene chloride and dried in vacuo. The degree of hydrolysis was determined by the ^1H NMR spectrum and also by titration with perchloric acid in the presence of methyl violet B as an indicator.

Cross-Linking Reaction in Bulk. Under nitrogen, **3** (0.623 g, run 1 in Table II), hexamethylene diisocyanate (0.086 g, 0.511 mmol), and methylene chloride (5 mL) were placed in a 30-mL flask. After evaporation of methylene chloride, the mixture was heated at 100 °C for 3.5 h. The resulting gel (**4**) was subjected to Soxhlet extraction with methylene chloride and drying in vacuo. Yield was 0.709 g (100%).

Cross-Linking Reaction in DMF. Under nitrogen, **3** (0.992 g, run 1 in Table II), hexamethylene diisocyanate (0.020 g, 0.119 mmol), DBU (32.5 mg, 0.212 mmol), and DMF (3 mL) were placed in a 50 mL flask and stirred at room temperature (25 °C) for 30 min. The isolation of the gel (**4**) was carried out by the same method described above. Yield was 0.509 g (50%).

Swelling Property of 4. The swelling equilibrium of the resulting gel in water was estimated as follows. As a typical example, **4** (0.157 g, run 4 in Table III) was immersed in ion-exchanged water (100 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 absorbed water was 45 multiples of the weight of dried gel.

Reaction with Ethyl Isocyanate. The gel (0.990 g, run 3 in Table IV), ethyl isocyanate (1.80 g, 25.3 mmol), DBU (0.042 g, 0.276 mmol) and DMF (20 mL) were placed in a 50-mL flask equipped with a reflux condenser and heated at 80 °C for 1 h under nitrogen atmosphere. The resulting gel (**7**) was isolated by Soxhlet extraction and drying as for **4**. Yield was 0.698 g (71%).

Registry No. DBU, 6674-22-2; NaOH, 1310-73-2; NaCl, 7647-14-5; MeOTf, 333-27-7; H_2O, 7732-18-5; 2-methyl-2-oxazoline (homopolymer), 26375-28-0; 2-methyl-2-oxazoline (SRU), 38796-76-8.

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