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A Novel Crosslinking–Decrosslinking System of Polymers Having Spiro Orthoester Moieties in the Side Chains

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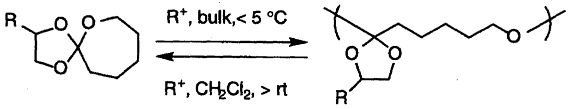
Acid-catalyzed reversible crosslinking–decrosslinking of polymers having spiro orthoester groups in the side chains was carried out. The copolymers obtained by the radical copolymerizations of 2-methylene-1,4,6-trioxaspiro[4.6]undecane with acrylonitrile, methyl, cyclohexyl, and 2-ethylhexyl acrylates were treated with trifluoroacetic acid (5 mol%) at −10 °C for 1 h in CH_2Cl_2 (4.2 M) to afford the crosslinked polymers in 69—99% yields. The crosslinked polymers were then treated with trifluoroacetic acid at a low concentration (0.1 M) in CH_2Cl_2 at room temperature for 1 h to give the original polymers in 55—99% yields. These results strongly support the conclusion that the acid-catalyzed reversible crosslinking–decrosslinking of the polymers possessing the spiro orthoester groups in the side chains could be constructed.

Bio- and photo-degradable polymers have been widely studied for environmental protection.[1] Recyclable polymers are expected to be candidate polymers for overcoming the serious problem. Depolymerization is important in recycling of polymers, and many studies on depolymerization systems have been reported: e.g., poly(methyl methacrylate),[2] polysaccaride,[3] poly(chloroacetaldehyde),[4] poly(2, 2-dialkyl-3-hydroxypropionic acid),[5] and poly(ϵ-caprolactone).[6] However, the degree of the depolymerization in these systems is low. Recently, we have reported that the cationic polymerization of a spiro orthoester proceeds at low temperature via a single ring-opening process to give a poly(cyclic orthoester) (Scheme 1).[7] Since this polymerization is a typical equilibrium polymerization, the obtained polymer can be readily converted to the original monomer by treatment with acid catalyst.

We have also reported a reversible crosslinking–decrosslinking system of a bifunctional monomer and a network polymer by utilizing the equilibrium polymerization of a spiro orthoester (Scheme 2).[8] More recently, we have demonstrated in a preliminary communication that acid-catalyzed complete reversible crosslinking–decrosslinking of a polymer having a spiro orthoester group in the side chain can be constructed.[9] In the present paper, we describe this complete reversible crosslinking–decrosslinking system in detail.



Scheme 1.

Experimental

Measurements. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM EX-90 spectrometer using tetramethylsilane (TMS) as an internal standard in deuteriochloroform. FT-IR spectra were obtained with a JASCO FT/IR-5300. Molecular weight ($\overline{M}_n$) and its distribution ($\overline{M}_w/\overline{M}_n$) were estimated by gel permeation chromatography (GPC) on Tosoh HPLC HLC-8020 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G3000H, G2500H, and G2000H), using tetrahydrofuran (THF) or a lithium bromide solution in *N*,*N*-dimethylformamide (DMF, 5.8 mM) as an eluent, a flow rate 1.0 mL min^{-1}, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Thermal analyses were performed on Seiko Instruments DSC220C and TG/DTA220. Glass transition temperature (T_g) and 10% weight loss temperature (Td_{10}) were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere, respectively.

Materials. Acrylonitrile (AN), methyl, cyclohexyl, and 2-ethylhexyl acrylates, methyl methacrylate (MMA), styrene (St), trifluoroacetic acid (TFA), and tin(IV) chloride ($SnCl_4$) were used after distillation. 2,2′-Azobis(isobutyronitrile) (AIBN) was used as received. Dichloromethane (CH_2Cl_2) was pre-dried with phosphorus pentaoxide and distilled over calcium hydride.

Synthesis of 2-Methylene-1,4,6-trioxaspiro[4.6]undecane (1). **1** was prepared by the reaction of epichlorohydrin and ϵ-caprolactone catalyzed by $Et_2O{\cdot}BF_3$, followed by dehydrochlorination with sodium methoxide according to the previously reported method.[10]

Copolymerization of 1 and AN. Typical procedure: To a mixture of **1** (343 mg, 2.02 mmol) and AN (110 mg, 2.07 mmol) in a polymerization tube was introduced AIBN (13.4 mg, 0.0816 mmol). The tube was cooled, degassed, sealed off, and heated at 60 °C for 24 h. The resulting mixture was diluted with CH_2Cl_2 (5 mL) and poured into hexane (100 mL) to precipitate a solvent-insoluble polymer (**2**). $\overline{M}_n$ 45800, $\overline{M}_w/\overline{M}_n$ 2.27, T_g 100 °C, Td_{10} 335 °C. Anal. Found : C, 63.14; H, 7.55; N, 7.29%. The copolymerization ratio was calculated to be **1** : AN = 45 : 55 (molar ratio) from the elemental analysis. ^1H NMR ($CDCl_3$) δ = 0.5—2.5 (m), 2.6—3.5

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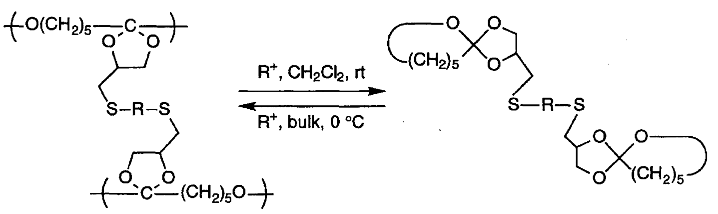


Scheme 2.

(m), 3.5—4.3 (m); IR (KBr) 2932, 2861, 2242, 1447, 1370, 1240, 1040, 961 cm^{-1}.

Copolymerization of 1 and Methyl Acrylate. The copolymerization was carried out similarly to that of **1** and AN. Spectral data of the copolymer obtained in Run 1 in Table 2; ^{1}H NMR ($CDCl_3$) $\delta = 1.2$—2.9 (m), 3.7 (broad s); IR (KBr) 2949, 2859, 1738, 1445, 1370 cm^{-1}.

Copolymerization of 1 and Cyclohexyl Acrylate. The copolymerization was carried out similarly to that of **1** and AN. Spectral data of the copolymer obtained in Run 3 in Table 2; ^{1}H NMR ($CDCl_3$) $\delta = 1.0$—2.9 (m), 3.3—4.0 (m), 4.7 (broad s); IR (KBr) 2936, 2859, 1732, 1453, 1368 cm^{-1}.

Copolymerization of 1 and 2-Ethylhexyl Acrylate. The copolymerization was carried out similarly to that of **1** and AN. Spectral data of the copolymer obtained in Run 4 in Table 2; ^{1}H NMR ($CDCl_3$) $\delta = 0.8$—1.1 (m), 1.2—2.9 (m), 3.4—4.2 (m); IR (KBr) 2959, 2932, 2861, 1734, 1464, 1368, 1173 cm^{-1}.

Ternary Copolymerization of 1, AN, and St. The copolymerization was carried out similarly to the copolymerization of **1** and AN. Spectral data of the copolymer obtained in Run 2 in Table 3; ^{1}H NMR ($CDCl_3$) $\delta = 1.2$—4.0 (m), 6.7—7.3 (m); IR (KBr) 3029, 2930, 2238, 1956, 1495, 1453, 1368, 1071, 961, 762, 702 cm^{-1}.

Ternaly Copolymerization of 1, AN, and MMA. The copolymerization was carried out similarly to the copolymerization of **1** and AN. Spectral data of the copolymer obtained in Run 3 in Table 3; ^{1}H NMR ($CDCl_3$) $\delta = 0.8$—4.3 (m); IR (KBr) 2949, 2240, 1732, 1449, 1370 cm^{-1}.

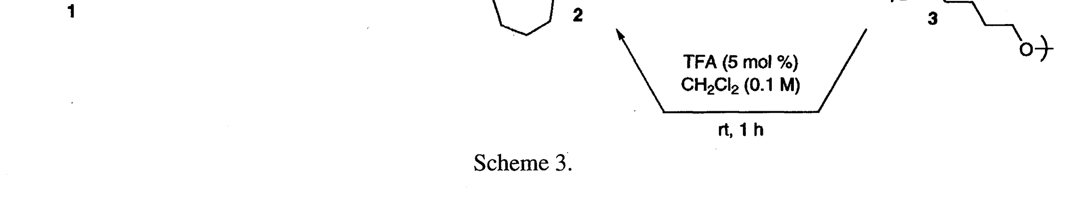
Crosslinking of the Copolymer (2) Typical procedure: To a solution of **2** (131 mg, 1.26 mmol) in CH_2Cl_2 (0.3 mL), TFA (5.7 µL, 0.063 mmol) was introduced at −10 °C under an argon atmosphere. After stirring for 1 h, the reaction was quenched by the addition of triethylamine (3 drops), followed by the addition of CH_2Cl_2 (5 mL) and stirred for 5 min. The swelled gel was washed with hexane (20 mL) five times. After repeating this procedure five times, the obtained gel (**3**) was dried at 50 °C in vacuo. Yield 99%. IR (KBr) 2241 (CN), 1071 and 950 cm^{-1} (C–O–CH_2).

Crosslinking of the copolymers 4 and 6. The crosslinking of **4** and **6** was carried out similarly to that of **2**. IR (KBr) of the crosslinked polymer obtained in Run 1 in Table 2: 2951, 1742, 1441, 1383 cm^{-1}. IR (KBr) of the crosslinked polymer obtained in Run 3 in Table 2: 2938, 2859, 1732, 1453, 1368 cm^{-1}. IR (KBr) of the crosslinked polymer obtained in Run 4 in Table 2: 2932, 2861, 1734, 1464 cm^{-1}. IR (KBr) of the crosslinked polymer obtained in Run 2 in Table 3: 3061, 3029, 2930, 2238, 1495, 1453, 1368, 1071, 762, 702 cm^{-1}. IR (KBr) of the crosslinked polymer obtained in Run 3 in Table 3: 2930, 2241, 1736, 1640, 1441, 1071 cm^{-1}.

Decrosslinking of the Crosslinked Polymer. Typical procedure: To a mixture of **3** (88 mg, 0.846 mmol) and CH_2Cl_2 (10 mL), TFA (3.3 µL, 0.042 mmol) was added at room temperature under an argon atmosphere. The solvent-insoluble gel disappeared after 1 h. The reaction was quenched by the addition of triethylamine (3 drops). After the reaction mixture was filtered, the filtrate was evaporated to give **2**. Yield 0.085 g (97%). $\overline{M}_n$ 54000, $\overline{M}_w/\overline{M}_n$ 2.21.

Results and Discussion

1. Radical Copolymerization of 1 with AN. First, radical homopolymerization of **1** was carried out at 60 °C for 24 h in the presence of AIBN as an initiator to afford no polymer due to vinyl ether structure of **1**. Therefore, the copolymerization of **1** with a vinyl monomer having an electron-withdrawing group, AN, was carried out under similar conditions to afford the corresponding copolymer (**2**) in satisfactory yield (Scheme 3, Table 1). Unimodal GPC curves of the obtained copolymers might strongly support the proceeding of copolymerizations. The structure of **2** was confirmed by the ^{1}H NMR spectrum (Fig. 1). The composition of **2** was determined by the integration ratio of the four α-methylene protons of the ether oxygen (3.5—4.5 ppm) of **1** unit to the methine proton (2.6—3.4 ppm) of AN unit in the ^{1}H NMR spectrum. No carbonyl absorption in the IR spectrum indicates that no side reaction such as isomerization of **1** proceeds. The unit molar ratio of **1** in the copolymer was slightly smaller than the monomer feed ratio except for Run 1 in Table 1. The polymers obtained in Runs 3—5 were soluble in CH_2Cl_2, $CHCl_3$, THF, and DMF, but the polymers obtained in Runs 1 and 2 were not completely soluble in CH_2Cl_2, $CHCl_3$, and THF. This might be due to the lower solubility of polyacrylonitrile in organic solvents. The T_g and Td_{10} under nitrogen of **2** were 86—117 and 318—338 °C, respectively.



Scheme 3.

Table 1. Radical Copolymerization of **1** and AN[a)]

Run	Feed ratio **1** : AN mol%	Yield[b)] — %	$\overline{M}_n^{c)}$	$\overline{M}_w/\overline{M}_n^{c)}$	Unit ratio **1** : AN mol% ^{1}H NMR	EA	$T_g^{d)}$ °C	$Td_{10}^{e)}$ °C
1	20 : 80	94	202000[f)]	2.98	25 : 75[g)]	21 : 79	116	318
2	40 : 60	94	120000[f)]	2.50	37 : 63[g)]	38 : 62	117	336
3	50 : 50	90	40900	2.36	39 : 61	40 : 60	104	334
4	60 : 40	82	37600	1.71	49 : 51	55 : 45	86	338
5	80 : 20	31	28300	1.59	50 : 50	53 : 47	101	332

a) Conditions; initiator AIBN, bulk, 60 °C, 24 h. b) Methanol-insoluble part. c) Estimated by GPC based on polystyrene standards; eluent THF. d) Determined by DSC. e) Determined by TGA under nitrogen. f) Eluent, eluent, LiBr solution in DMF (5.8 mM). g) Chloroform-soluble part.

Table 2. Radical Copolymerization of **1** and Acrylates and Crosslinking-Depolymerization of **4**

			4						**5**			Depolymerization to **4**		
Run	R	Feed ratio **1** : acrylate mol%	Yield — %	Unit ratio **1** : acrylate mol%	$\overline{M}_n^{e)}$	$\overline{M}_w/\overline{M}_n^{e)}$	$T_g^{f)}$ — °C	$Td_{10}^{g)}$ — °C	Yield — %	$T_g^{f)}$ — °C	$Td_{10}^{g)}$ — °C	Yield — %	$\overline{M}_n^{e)}$	$\overline{M}_w/\overline{M}_n^{e)}$
1	Me	50 : 50	99[a)]	45 : 55[c)]	62000	2.62	67	342	99	38	259	85	63000	2.77
2	Me	33 : 66	99[a)]	34 : 66[c)]	36000	2.59	48	347	75[h)]	39	325	99	57000	2.18
3	Cyclohexyl	50 : 50	69[b)]	32 : 68[d)]	61000	2.51	67	347	71	71	312	99	70000	2.09
4	2-Ethylhexyl	50 : 50	77[b)]	34 : 66[d)]	101000	2.06	−9	348	55[i)]	−10	333	82	162000	3.18

a) Hexane-insoluble part. b) Methanol-insoluble part. c) Determined by elemental analysis. d) Determined by ^{1}H NMR. e) Estimated by GPC based on polystyrene standards; eluent THF. f) Determined by DSC. g) Determined by TGA under nitrogen. h) 6 M. i) −10 °C.

Table 3. Radical Ternary Copolymerization of **1** and Crosslinking-Depolymerization of **6**

		6						**7**			Depolymerization to **6**		
Run	Feed ratio **1** : AN : St or MMA mol%	Yield — %	Unit ratio[c)] $x:y:z$ mol%	$\overline{M}_n^{d)}$	$\overline{M}_w/\overline{M}_n^{d)}$	$T_g^{e)}$ — °C	$Td_{10}^{f)}$ — °C	Yield — %	$T_g^{e)}$ — °C	$Td_{10}^{f)}$ — °C	Yield — %	$\overline{M}_n^{d)}$	$\overline{M}_w/\overline{M}_n^{d)}$
1	20 : 40 : 40 (St)	90[a)]	11 : 44 : 45	95000	1.99	111	342	57[g)]	114	340	99	92000	1.70
2	33 : 33 : 33 (St)	64[a)]	17 : 44 : 39	59000	2.03	115	342	54	115	343	99	62000	1.89
3	33 : 33 : 33 (MMA)	99[b)]	39 : 39 : 22	63000	2.19	85	320	46	99	306	99	71000	1.89

a) Methanol-insoluble part. b) Hexane-insoluble part. c) Determined by elemental analysis. d) Estimated by GPC based on polystyrene standards; eluent THF. e) Determined by DSC. f) Determined by TGA under nitrogen. g) 5.5 M.

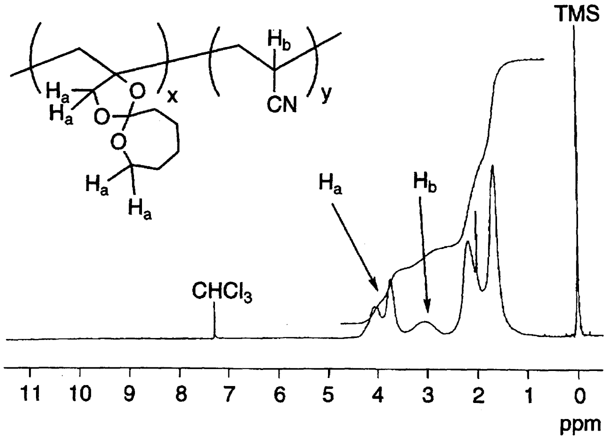


Fig. 1. ^{1}H NMR spectrum (solvent $CDCl_3$, 90 MHz) of the copolymer obtained in the radical polymerization of **1** and AN (Run 3 in Table 1).

2. Reversible Crosslinking-Decrosslinking of the Copolymer. Treating of **2** ($x:y=44:56$) with TFA (5 mol%) at −10 °C for 1 h in CH_2Cl_2 (4.2 M, 1 M = 1 mol dm^{-3}) afforded the crosslinked polymer (**3**), which was insoluble in all solvents. The T_g (76 °C) of **3** was lower than that (100 °C) of **2**. Treating of **3** with TFA (5 mol%) at room temperature for 1 h in CH_2Cl_2 (0.1 M) regenerated **2** in 97% yield (Scheme 3). The GPC profiles (Fig. 2) before crosslinking and after decrosslinking confirmed the acid-catalyzed reversible crosslinking-decrosslinking of the polymer possessing the spiro orthoester group in the side chain. The $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the recovered **2** was 54000 and 2.21, respectively, which were nearly the same values as those of **2** before crosslinking. No side reaction such as fission of the polymer main chain should proceed during the crosslinking and decrosslinking reactions.

3. Concentration Effect on Crosslinking. The crosslinking reaction of **2** ($\overline{M}_n$ 38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : AN = 44 : 56) at 0 °C in the presence of TFA (5 mol%) was carried out in several concentrations (2—8 M) in CH_2Cl_2. The relationship between the concentration of **2** and the yield of **3** in the reaction is illustrated in Fig. 3. Compound **3** was not obtained in lower concentration such as 2 and 3 M, but was obtained in higher concentration, and the yield of **3** increased as the concentration increased. Formation of solvent-soluble crosslinked polymers was suggested, since some increases of the molecular weights were observed in the GPC profiles (Fig. 4) in the crosslinking reactions in 2 and 3 M solutions. Although the molecular weights of the solvent-soluble parts obtained in the reactions in 4—6 M looked to be lower that of **2**, large amounts of solvent-insoluble crosslinked polymers were formed in these cases, as shown in Fig. 3.

4. Temperature Effect on Crosslinking. Figure 5 illustrates the relationship between the crosslinking temperature and yield of **3** in the crosslinking reaction of **2** ($\overline{M}_n$

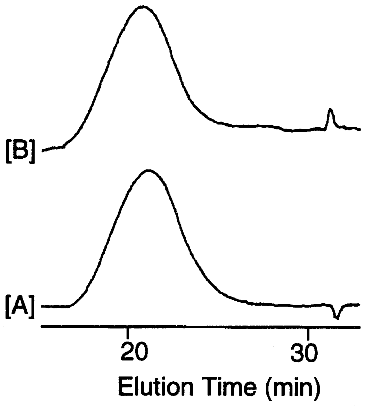


Fig. 2. GPC profiles of **3** before crosslinking and after decrosslinking. [A]: Before crosslinking, $\overline{M}_n$ 46000, $\overline{M}_w/\overline{M}_n$ 2.27. [B]: After decrosslinking $\overline{M}_n$ 54000, $\overline{M}_w/\overline{M}_n$ 2.21.

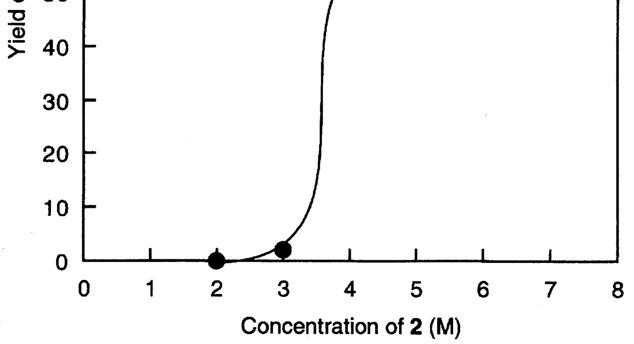


Fig. 3. Effect of concentration of **2** ($\overline{M}_n$ 38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : AN = 44 : 56) on the crosslinking reaction of **2** in the presence of TFA (5 mol%) in CH_2Cl_2 at 0 °C for 1 h.

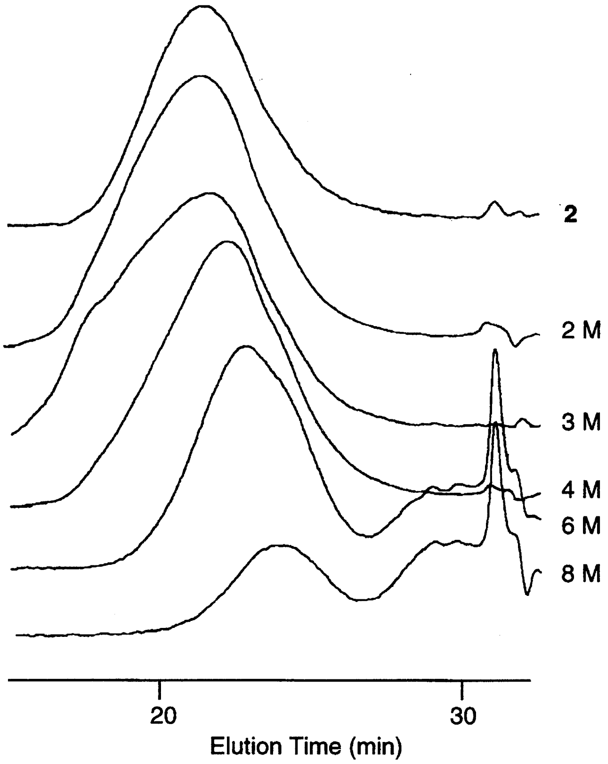


Fig. 4. GPC profiles of CH_2Cl_2-soluble part obtained in the crosslinking of **2** ($\overline{M}_n$ 38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : AN=44 : 56) in the presence of TFA (5 mol%) in CH_2Cl_2 at 0 °C for 1 h.

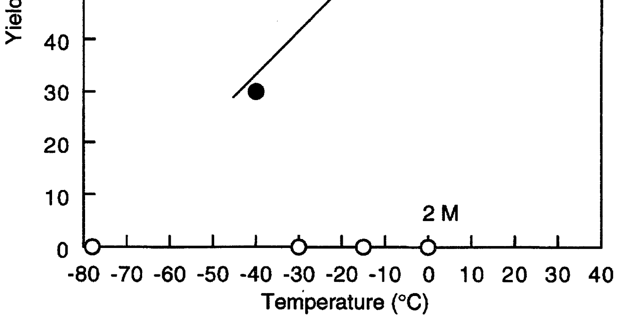


Fig. 5. Effect of temperature on the crosslinking of **2** ($\overline{M}_n$ 38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : An = 44 : 56) in the presence of TFA (5 mol%) in CH_2Cl_2 for 1 h. ●; 6 M, ○; 2 M.

38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : AN = 44 : 56) in 2 and 6 M concentrations. No crosslinked polymer was obtained in the reaction in 2 M even at −78 °C. In 6 M, the yield of **3** increased as the reaction temperature increased, which was different from the result reported in the cationic polymerization of a bicyclic orthoester.[7] The conflict may be caused by the lower initiation efficiency of the catalyst, namely, the lower degree of dissociation of proton from TFA at lower reaction temperature. The higher viscosity of the reaction mixture at lower temperature should also decrease the yield of the crosslinked polymer at lower temperature. An irreversible reaction to form an ester structure was confirmed by the IR spectrum of the crosslinked polymer obtained in the reaction at 30 °C. Moreover, the temperature effect on the crosslinking of **2** in the presence of $SnCl_4$ was examined (Fig. 6). At −10— −78 °C, the yield of **3** increased as the temperature decreased, while the trend reversed above 0 °C. Thus, we can explain the temperature effect on the crosslinking of **2** as follows.

(1) Below 0 °C, the yield of the crosslinked polymer was low because of the incomplete stirring efficiency of the reaction mixture. The low degree of dissociation of proton from TFA would also decrease the efficiency of crosslinking at lower temperature.

(2) Above 0 °C, the higher the polymerization temperature, the higher the yield of the crosslinked polymer was, and double ring-opening reaction of **2** also proceeded, in addition to the single ring-opening of **2**.

5. Temperature Effect on Decrosslinking. Figure 7 shows the temperature effect on the decrosslinking of **3** to **2** in CH_2Cl_2 in the presence of $SnCl_4$. The recovery of unreacted **3** increased as the reaction temperature decreased, indicating that the equilibrium between **2** and **3** might shift to **2** at higher temperature. The degree of decrosslinking of **3** by $SnCl_4$ (42%) at 10 °C was lower than that by TFA (97% as described in Section 2) at room temperature, while the degree of crosslinking of **2** by $SnCl_4$ (28% in Fig. 6) was higher than that by TFA (2% in Fig. 3, concentration of **2**; 3 M) at 0 °C. This might be caused by the lower degree of deprotonation from TFA at lower temperature. Namely, the amount of the catalytic species from proton acid TFA would be lower than that from Lewis acid $SnCl_4$ at 0 °C, and vice versa at 10 °C and room temperature.[11]

6. Crosslinking and Decrosslinking of the Copolymers

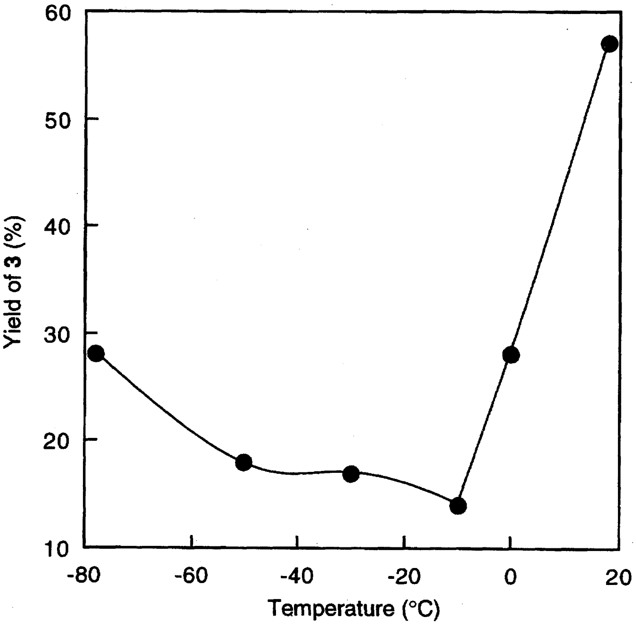


Fig. 6. Effect of temperature on the crosslinking of **2** ($\overline{M}_n$ 38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : AN = 44 : 56) in the presence of $SnCl_4$ (5 mol%) in CH_2Cl_2 (3 M) for 1 h.

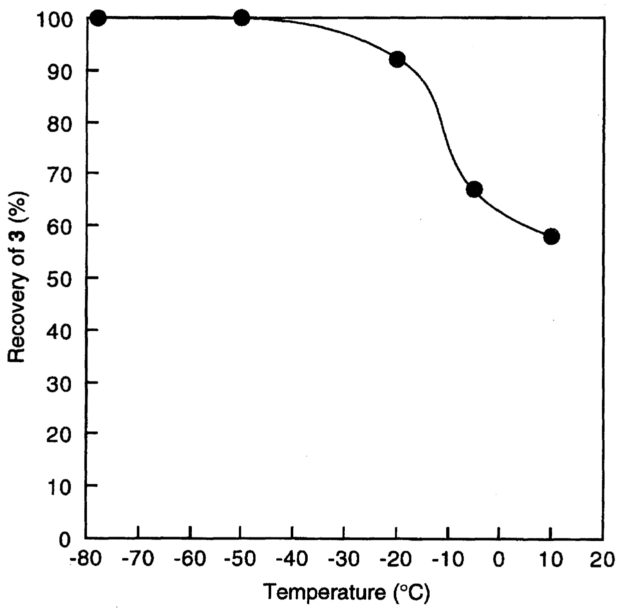
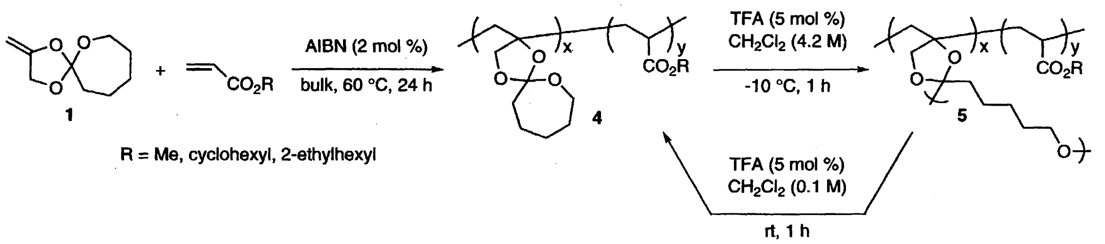
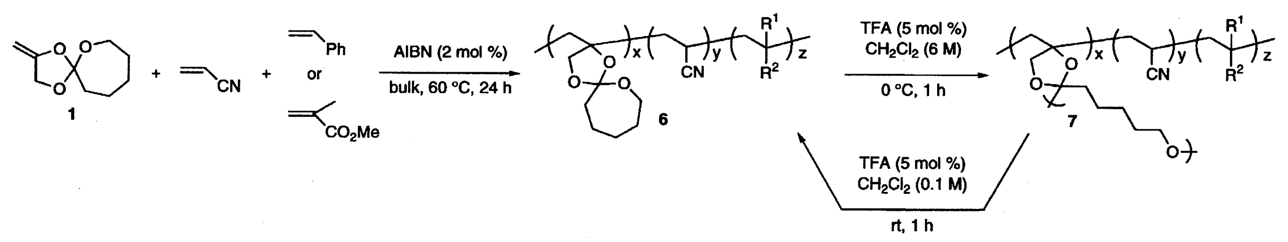


Fig. 7. Effect of temperature on the decrosslinking of **3** in the presence of $SnCl_4$ (5 mol%) in CH_2Cl_2 (0.5 M) at room temperature for 1 h. **3** was obtained in the crosslinking of **2** ($\overline{M}_n$ 38000, $\overline{M}_w/\overline{M}_n$ 2.33, unit ratio of **1** : AN = 44 : 56) in the presence of $SnCl_4$ (5 mol%) in CH_2Cl_2 (3 M) at 0 °C for 1 h.



Scheme 4.



Scheme 5.

of 1 and Acrylates. Radical copolymerizations of **1** with several acrylates such as methyl, cyclohexyl, and 2-ethylhexyl acrylates were carried out to give the corresponding copolymers (Scheme 4, Table 2). The copolymer compositions were determined by ^{1}H NMR and elemental analysis. The crosslinking and decrosslinking reactions proceeded in satisfactory yields, and no occurrence of side reaction was confirmed by GPC of the polymers before crosslinking and of the polymers recovered by decrosslinking. The two polymers showed similar ^{1}H NMR and IR spectral patterns. The crosslinked polymers were insoluble in any solvent.

7. Ternary Copolymerization. **1** has been reported not to undergo copolymerization with St and MMA.[12] On the other hand, AN can undergo the copolymerization with **1**, St, and MMA. Therefore, incorporation of St or MMA into the copolymer by copolymerization of **1**, AN, and St or MMA can be expected (Scheme 5). The results of copolymerization and equilibrium polymerization of the obtained copolymer (**6**) are summarized in Table 3. All polymers were soluble in $CHCl_3$, CH_2Cl_2, and THF. The content of **1** in the copolymerization with AN and MMA was larger than that with AN and St. The crosslinking of **6** at 0 °C for 1 h in the presence of TFA (5 mol%) proceeded to give the corresponding crosslinked polymer (**7**). The yield of **7** was smaller (ca. 50%) than that in the crosslinking of **4**, probably due to the lower content of the spiro orthoester. Decrosslinking of **7** in the presence of TFA (5 mol%) in CH_2Cl_2 (0.1 M) proceeded in quantitative conversion.

Summary

In this paper, radical copolymerizations of **1** and AN, and of **1**, AN, and St or MMA were carried out, and crosslinking and decrosslinking of the obtained polymers were examined. Although the radical homopolymerization of **1** did not proceed, the copolymerization of **1** with the comonomers proceeded satisfactorily to give the corresponding copolymers. The crosslinking of the copolymers with high concentration in CH_2Cl_2 in the presence of acid catalysts such as TFA and $SnCl_4$ at low temperature afforded the crosslinked polymers in high yields. The decrosslinking of the crosslinked polymers with low concentration in CH_2Cl_2 could efficiently regenerate the original copolymers in the presence of the acid catalysts at room temperature.

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