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Notes

Polymers Capable of Undergoing Cross-Linking without Volume Shrinkage. Synthesis of Polymers Containing a Spiroorthoester Moiety by Copolymerization of Isoprene with Spiroorthoesters Having Radically Polymerizable Groups

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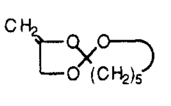
Introduction

Most monomers polymerize with considerable volume shrinkage, while spiroorthoesters (SOEs), spiroorthocarbonates, and bicycloorthoesters, so-called *expanding monomers*, can undergo polymerization without volume shrinkage or sometimes with volume expansion.[1] Introduction of such expanding monomer structures into polymers provides *expanding polymers* which show expansion in volume on cross-linking or curing. The most versatile method for the synthesis of expanding polymers is to utilize radical polymerization of corresponding vinyl monomers bearing the expanding monomer structures, partly since the expanding monomer structures are sensitive toward ionic species, especially cationic species, to result in polymerization. SOEs are the most readily available expanding monomers, because they can be prepared from epoxides and lactones in one step.[2] We have already synthesized SOE monomers with radically polymerizable groups (1 and 2) and demonstrated the introduction of the SOE group into common polymers by radical copolymerization with commercially available monomers such as methyl methacrylate, acrylonitrile, styrene, and so on.[3-6] The polymers thus obtained actually undergo efficient cross-linking with cationic catalysts without shrinkage in volume.[5,6] If these monomers are able of copolymerizing with diene monomers such as butadiene and isoprene, interesting elastic copolymers, which are cross-linked without volume shrinkage, can be obtained. In the present study, the copolymerizations of these two monomers (1 and 2) with isoprene as a representative of diene monomers and the cross-linking of the obtained polymers by cationic catalyst are disclosed.



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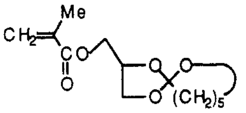

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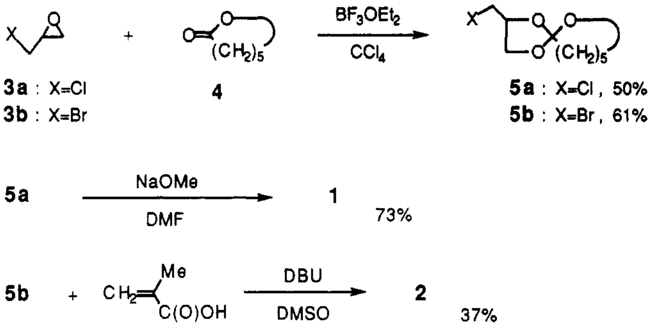
Experimental Section

Materials. Isoprene was purified by distillation after treatment with sodium. Solvents used in the polymerizations were distilled and stored over drying agents according to the conventional methods. Azobis(isobutyronitrile) (AIBN), *tert*-butylperoxy-3,5,5-trimethylhexanoate (TBP355), and di-*tert*-butyl peroxide (DTBP) were of reagent grade. Boron trifluoride etherate (BF_3OEt_2) was purified by distillation.

Scheme 1



Preparation of SOEs. Scheme 1 summarizes the synthetic routes to monomers 1 and 2. 2-Methylene-1,4,6-trioxaspiro[4.6]undecane (1) was prepared according to the reported method.[4] The overall yield from 4 was 31%. Bp: 59–61 °C (2.0 mmHg) [lit.[4] bp 89 °C (7 mmHg)]. IR (neat): 1690, 1125, 1040 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.64–1.96 (b s, 6H), 1.96–2.36 (br, 2H), 3.55–3.83 (br, 2H), 3.92 (m, 1H), 4.33 (m, 1H), 4.48 (m, 2H).

2-[(Methacryloyloxy)methyl]-1,4,6-trioxaspiro[4.6]undecane (2) was prepared similarly according to the recently reported method.[5] The overall yield from 4 was 23%. Bp: 105–110 °C (0.08 mmHg) [lit.[5] bp 101–103 °C (0.12 mmHg)]. IR (neat): 1720, 1640, 1165, 1070 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.44–1.86 (b s, 6H), 1.97 (s, 3H), 2.03–2.29 (br, 2H), 3.53–4.73 (br, 7H), 5.57 (m, 1H), 6.13 (s, 1H).

Copolymerizations of 1 with Isoprene. A typical procedure for polymer I-1 is given in Table 1. A mixture of 1 (0.85 g, 5 mmol), isoprene (0.34 g, 5 mmol), TBP355 (46 mg, 0.2 mmol), and benzene (1.2 g) was heated at 100 °C for 50 h in a sealed tube. The mixture was precipitated with methanol (100 mL). The methanol-insoluble polymer was collected by decantation (gummy product, 0.28 g). IR (neat): 1665, 1640, 1130, 1040 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.59 (b s), 1.70 (b s), 2.03 (b s), 3.55–4.00 (br), 4.58–4.79 (br), 4.91–5.42 (br). Anal. Found: C, 85.90; H, 11.10 (x:y = 4:96). The results of the copolymerizations are summarized in Table 1.

Radical Homopolymerization of Isoprene. A mixture of isoprene (2.0 g, 30 mmol), AIBN (82 mg, 0.5 mmol), and benzene (1.8 g) was heated in a sealed tube at 70 °C for 50 h. The mixture was precipitated with methanol (200 mL). The methanol-insoluble polymer was collected by decantation (0.61 g, 30% yield). IR (neat): 1665, 1640, 1440, 1375, 910, 880 cm^{-1}. The ratio of four possible isomeric structures of the monomer unit was determined from the ^1H NMR integration ratio of the five signals (1.65–1.69, 1.74, 4.81, 5.02, and 5.24 ppm) of the polyisoprene obtained, according to the following four equations on the basis of Tanaka's method (eqs 1–4, I = intensity of the signal).[7]

$$\frac{[1,2]}{[cis\text{-}1,4] + [trans\text{-}1,4]} = \frac{I(5.02)}{I(5.24)} \qquad (1)$$

$$\frac{[3,4]}{[cis\text{-}1,4] + [trans\text{-}1,4]} = \frac{I(4.81)}{2I(5.24)} \qquad (2)$$

$$\frac{[\text{cis-}1,4]}{[trans\text{-}1,4] + [3,4]} = \frac{I(1.74)}{I(1.65\text{–}1.69)} \qquad (3)$$

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Table 1. Copolymerization of 1 with Isoprene[a]

	feed ratio (mol %)						copolymer				
							composition[d] (mol %)				
copolymer	1	isoprene	temp (°C)	initiator[b]	solvent (wt %)	yield (%)	x	y	$\bar{M}_w$[e]	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$
I-1	50	50	100	TBP355	PhH (100)	24	4	96	7800	4800	1.63
I-2	50	50	100	TBP355	none[c]	29	4	96	11000	5200	2.12
I-3	50	50	120	DTBP	PhCl (100)	28	11	89	24000	4900	4.90
I-4	50	50	120	DTBP	none	25	19	81	69000	9100	7.58
I-5	80	20	100	TBP355	PhH (100)	7	6	94	3900	3100	1.26
I-6	80	20	100	TBP355	none	9	12	88	5000	3400	1.47

[a] Polymerization time: 50 h. [b] 2 mol % to sum of the two monomers. [c] Bulk polymerization. [d] Determined by elemental analysis. [e] Determined by GPC based on PSt standards.

Table 2. Copolymerization of 2 with Isoprene[a]

	feed ratio (mol %)		convn[b] (%)			copolymer				
						composition[c] (mol %)				
copolymer	2	isoprene	2	isoprene	yield (%)	2	isoprene	$\bar{M}_w$[d]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
II-1	5	95	40	28	31	7	93	10 000	6 200	1.61
II-2	20	80	55	36	44	27	73	15 000	9 100	1.65
II-3	50	50	70	40	63	64	36	28 000	17 000	1.65
II-4	80	20	79	35	76	90	10	29 000	16 000	1.81

[a] Polymerization time, 50 h; solvent, benzene. [b] Calculated from the feed ratio, yield, and copolymer composition. [c] Determined by elemental analysis. [d] Estimated by GPC based on PSt standards.

Table 3. Effects of Temperature and Concentration on the Copolymerization of 2 with Isoprene[a]

					copolymer			
run	initiator[b]	solvent (wt %)	temp (°C)	time (h)	yield (%)	$\bar{M}_w$[c]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$
1	AIBN	PhH (100)	70	50	44	15 000	9 100	1.65
2	AIBN	none[e]	70	24	56	25 000	12 000	2.08
3	TBP355	PhCl (100)	100	50	78	53 000	11 000	4.81
4	DTBP	PhCl (100)	120	7	51	77 000	21 000	3.67
5	DTBP	none	120	1[d]	25	190 000	56 000	3.39

[a] Polymerization time, 50 h; feed ratio, 2/isoprene = 2/8 (mol/mol). [b] 2 mol % to sum of the two monomers. [c] Estimated by GPC based on PSt standards. [d] The polymerization system was solidified within 1 h. [e] Bulk polymerization.

Table 4. Cross-Linking of Polymer II-4 and Volume Change on Cross-Linking[a]

					density (d^{25}, g/cm^3)		
BF_3OEt_2 (mol %)	solvent	temp (°C)	time (h)	yield (%)	before	after	volume change (%)
9	CH_2Cl_2	reflux	1.5	18	1.201	1.195	+0.5
10	PhCl	100	12	100	1.201	1.209	−0.7

[a] Determined from densities at 25 °C. [b] Calculated by the following equation: volume change (%) = [(density of cross-linked polymer) − (density of polymer **II-4**)]/(density of polymer **II-4**)] × 100.

$$[1,2] + [3,4] + [cis\text{-}1,4] + [trans\text{-}1,4] = 1 \qquad (4)$$

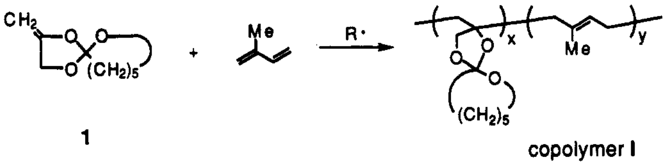
The calculation indicated 1,2 unit = 6%, 3,4 unit = 6%, *cis*-1,4 unit = 20%, and *trans*-1,4 unit = 68%.

Copolymerization of 2 with Isoprene. A typical procedure for copolymer **II-1** in Table 2. A mixture of **2** (0.27 g, 1 mmol), isoprene (1.3 g, 19 mmol), AIBN (55 mg, 0.4 mmol), and benzene (1.5 g) was heated in a sealed tube at 70 °C for 50 h. The mixture was precipitated with methanol (100 mL). The methanol-insoluble polymer was collected by decantation (gummy product, 0.48 g). IR (neat): 1730, 1665, 1640, 1180, 1040, 1020, 885 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.57 (b s), 1.68 (b s), 2.03 (b s), 3.44–4.38 (br), 4.53–4.76 (br), 4.80–5.36 (br). Anal. Found: C, 81.81; H, 9.08 (x:y = 7:93). The results of the copolymerizations are summarized in Tables 2 and 3.

Cross-Linking of Polymers I and II. A procedure for the cross-linking of polymer **I-4** is given. A mixture of polymer **I-4** (62 mg), BF_3OEt_2 (0.13 μL, 10 mol % to the SOE moiety), and chlorobenzene (1.5 mL) was heated at 100 °C for 12 h in a sealed tube. The chlorobenzene-insoluble polymer was repeatedly washed with acetone using a Soxhlet extractor to give a white solid (13 mg, 21% yield). IR (neat): 1734, 1660, 1640 cm^{-1}. Anal. Found: C, 73.75; H, 9.88 (x:y = 36:64). The results of the cross-linking of polymer **II** are given in Table 4.

Measurements. ^{1}H NMR spectra were recorded with JEOL JNM PMX-60si and JEOL FX-100 spectrometers using tetramethylsilane as the internal standard (solvent: $CDCl_3$). IR spectra were measured by a Jasco FT/IR-3 spectrometer. Gel permeation chromatography (GPC) was carried out with a Toyo Soda HPLC CCP & 8000 system equipped with three polystyrene gel columns (TSK Gel G2500, G4000, and G5000), and tetrahydrofuran (THF) was used as the solvent at 35 °C. Densities were measured by a Shibayama Kagaku density measurement apparatus Model-A.

Scheme 2

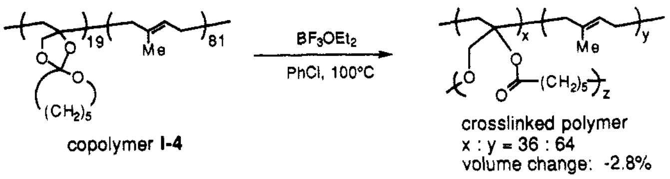


Results and Discussion

Copolymerization of 1 with Isoprene. A mixture of *exo*-methylene group-containing SOE monomer **1** and isoprene [feed ratio: **1**/isoprene = 1/1 (mol/mol)] was heated at 100 °C for 50 h in benzene in the presence of TBP355 as a radical initiator (Scheme 2).

Polymeric product was obtained in 24% yield as a methanol-insoluble viscous oil, and its molecular weight ($\bar{M}_n$) estimated by GPC was 4800. The GPC curve was

Scheme 3



unimodal. Evaporation of the methanol-soluble fraction gave only the monomer 1. The IR and ^{1}H NMR spectra of the polymer obtained clearly showed the presence of the units derived by vinyl polymerization of 1 and isoprene without the unit derived by radical ring-opening polymerization of 1. The two broad vinyl signals around 5.1 ppm in ^{1}H NMR indicated that the isoprene unit consisted of four isomeric structures based on the geometry around the C=C bond. The ratio of the isomeric structures were estimated to be *trans*-1,4/*cis*-1,4/3,4/1,2 = 68/20/6/6 from the ^{1}H NMR spectrum of homopolyisoprene prepared by the radical polymerizatiom (AIBN, 70 °C, benzene) by assuming that the ratio is the same as that of the homopolyisoprene. These results suggest that 1 is incorporated as a polymer unit into polyisoprene. However, the yield of the copolymer was low and the copolymer composition estimated by elemental analysis was x:y = 4:96.

To increase both the yield and the SOE content, the copolymerizations of 1 with isoprene were further attempted under various conditions (Table 1). However, no satisfactory copolymerization was accomplished. The results indicate that the rate of polymerization of isoprene is rather faster than that of 1. Therefore, the unit of 1 seems to be mainly bound to the polyisoprene endlike block copolymer. This would be consistent with the unimodal GPC curve. The polymer produced would involve not only copolymer with a few SOE groups but also homopolyisoprene.

Cross-Linking of Polymer I. The copolymer (copolymer **I-4**, x:y = 19:81) was treated with BF_3OEt_2 in chlorobenzene at 100 °C for 12 h. Solvent-insoluble polymer was obtained in only 21% yield (Scheme 3). The insoluble polymer was undoubtedly formed by cationic ring-opening polymerization of the SOE function, in agreement with the IR adsorptions [1734 cm^{-1} (C=O) and 1660 and 1640 cm^{-1} (C=C)].

Measurement of the density of the polymers before and after cross-linking showed 2.8% shrinkage in volume. It is noteworthy that the yield of the cross-linked polymer was very low and its composition was obviously changed before and after the cross-linking from x:y = 19:81 to x:y = 36:64. Most soluble polymer obtained as the acetone-soluble part was polyisoprene. These results can be accounted for as follows. Formation of non-cross-linkable polyisoprene and a copolymer with few SOE groups in the above copolymerization caused the low yield of the cross-linked polymer. Removal of these soluble polymers by washing certainly increased the ratio of x after the cross-linking. Further, slight volume shrinkage on the cross-linking may be attributed to the removal of a light isoprene unit (polyisoprene: d = 0.93) after the cross-linking.

Thus, the attempt to synthesize a novel SOE-containing polymer by the copolymerization of 1 with isoprene was not successful.

Copolymerization of 2 with Isoprene. It is reported that the copolymerization of methyl methacrylate (MMA, M_1) and isoprene (M_2) proceeds smoothly to give corresponding copolymer. In this case the reactivity ratios r_1 and r_2 are 0.40 and 0.78, respectively.[8] The comonomer feed ratio-copolymer composition curve of this copolymerization is shown as a dashed line in Figure 1. From this high copolymerizability, SOE-containing methacrylate (**2**) was employed as a promising candidate monomer for copolymerization with isoprene.

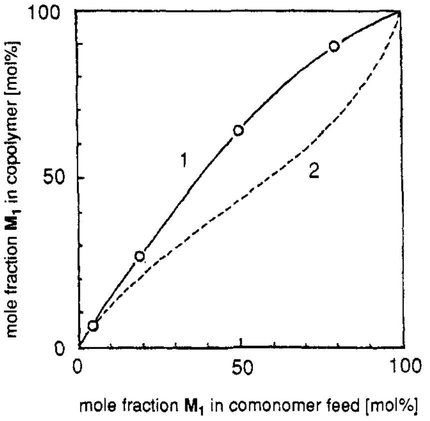


Figure 1. Comonomer feed ratio—copolymer composition curves. Curve 1 (solid line): M_1 = **2**, M_2 = isoprene, determined from data of Table 2. Curve 2 (dashed line): M_1 = MMA, M_2 = isoprene (ref 8).

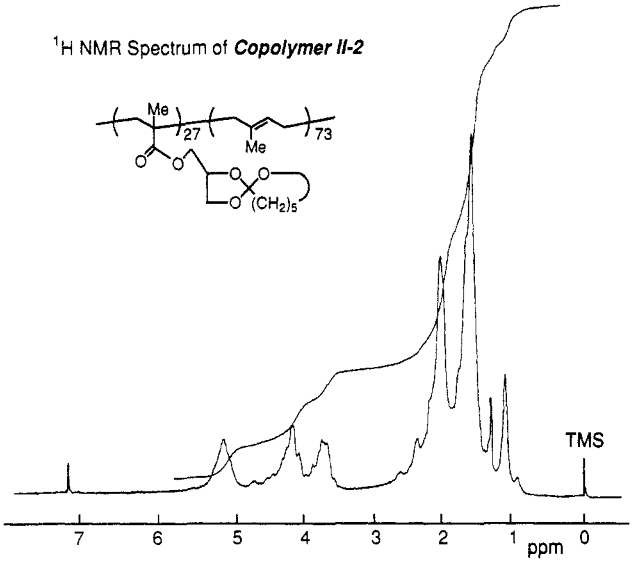


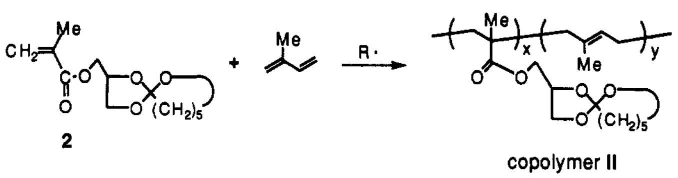
Figure 2. ^{1}H NMR spectrum of the copolymer of **2** with isoprene (copolymer **II-2**, $\bar{M}_n$ 9100) in $CDCl_3$.

The methacrylate **2** was prepared by the reaction of bromomethyl SOE and methacrylic acid according to the recently reported method (Scheme 1).[5] The radical homopolymerizability of **2** has already been reported to be slightly higher than that of MMA.[5]

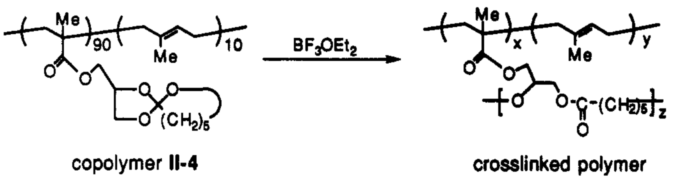
The initial copolymerizations of **2** with isoprene were carried out at 70 °C in benzene in the presence of AIBN as a radical initiator in various feed ratios (Scheme 4).

Polymeric products were obtained as methanol-insoluble parts in 31–76% yield (Table 2) and were either viscous oils (copolymers **II-1**, **II-2**, and **II-3**) or white powders (copolymer **II-4**). The structure of the products was confirmed as the corresponding copolymers by their spectral data (IR and NMR). In addition to the IR absorptions at 1730 (C=O), 1665 and 1640 (C=C), and 1180, 1040, and 1020 (C–O) cm^{-1} attributable to each structure of the two units, the ^{1}H NMR spectrum (e.g., Figure 2: copolymer **II-2**) clearly suggested the corresponding poly(isoprene-*co*-SOE methacrylate **2**) structure. Especially, the signals around 4 ppm, which were assigned to protons of the three methylenes and one methine adjacent to ester and ether oxygens of **2**, were

Scheme 4



Scheme 5



characteristic and were used for the calculation of the copolymer compositions.

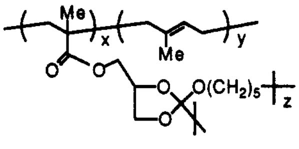
The conversion of each monomer and the yield and composition (estimated by elemental analysis) of the copolymers are summarized in Table 2. The compositions were nearly the same as those calculated from the ^{1}H NMR integration ratios.

The yield and molecular weight increased with an increase of the feed ratio of **2**. The conversion of **2** was larger than that of isoprene in any case. The comonomer feed ratio vs copolymer composition curve which was drawn based on the data of Table 2 is shown by the solid line in Figure 1. As judged from Table 2 and Figure 1, the copolymer composition was almost proportional to the feed ratio, although the conversions of the two monomers were relatively high. If the conversions are controlled sufficiently low, the solid line curve 1 probably gets near the dashed line 2.

Effects of temperature and concentration on the copolymerization [feed ratio: **2**/isoprene = 2/8 (mol/mol)] were investigated. The results are shown in Table 3.

As the polymerization temperature was raised, the molecular weight increased accordingly, but the copolymer yield appeared not to increase simply. The lower copolymer yield (25%) in the bulk polymerization at 120 °C (run 5) is presumably due to increasing viscosity owing to the formation of high molecular weight polymer ($\bar{M}_n$ 56 000). As shown in runs 1,2 and 4,5, the effect of viscosity by increasing molecular weight is remarkable. Thus, the copolymerizations of **2** proceed much more efficiently than those of **1** and afford the almost random poly(SOE methacrylate-*co*-isoprene)s in good yields.

Cross-Linking of Polymer II. Copolymer **II-4** (Table 2) was treated with BF_3OEt_2 as a cationic catalyst in dichloromethane or in chlorobenzene. As shown in Table 4, the reaction in refluxing dichloromethane resulted in a low yield of the acetone-insoluble product (18%), but in chlorobenzene at 100 °C the gelled polymer was obtained quantitatively. These solvent-insoluble polymers were found to be the cross-linked polymers containing a new poly(ether–ester) unit, from their IR spectra. The structure of the cross-linked polymer as shown in Scheme 5 is not completely correct, since a small amount of a single ring-opened unit of the SOE moiety (**6**) is unambiguously contained as reported in our recent paper.[9] The densities of the polymers before and after the cross-linking were measured (Table 4), which indicated little volume change during the cross-linking.



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As mentioned above, the copolymerization of the methacrylate monomer **2** having the SOE structure with isoprene as the representative of the diene monomers took place efficiently and gave the almost random copolymers **II**. On cross-linking of copolymer **II**, little volume change was observed. Thus, the copolymers of **2** with isoprene can be regarded as novel expanding polymers which undergo cationic cross-linking without shrinkage in volume.

References and Notes

(1) Sadhir, K.; Luck, R. M. *Expanding Monomers—Synthesis, Characterization, and Applications*; CRC Press: Boca Raton, FL, 1992.
(2) Bodenbenner, K. *Justus Liebigs Ann. Chem.* **1959**, *625*, 183.
(3) Takata, T.; Endo, T. Reference 1, Chapter 3.
(4) (a) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 25. (b) Endo, T.; Okawara, M.; Bailey, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1283.
(5) Endo, T.; Kitamura, N.; Takata, T.; Nishikubo, T. *J. Polym. Sci., Polym. Lett. Ed.* (a) **1988**, *26*, 517; (b) **1991**, *29*, 1675.
(6) Endo, T.; Mai, S.; Okawara, M. *Polym. Prepr. Jpn.* **1981**, *30*, 49.
(7) Tanaka, Y.; Takeuchi, Y.; Kobayashi, M.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 43.
(8) *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; Chapter II, p 253.
(9) Chikaoka, S.; Takata, T.; Endo, T. *Macromolecules* **1992**, *25*, 625.