Novel Multifunctional Initiators for Polymerization of 2-Oxazolines

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Received September 3, 1991; Revised Manuscript Received January 20, 1992

ABSTRACT: Polymerization of 2-oxazolines was carried out using bifunctional and tetrafunctional initiators. Allyl-type dihalides and xylylene dihalides were used as bifunctional initiators. The allyl-type dihalides employed are 1,4-dibromo-2-butene and 3-iodo-2-(iodomethyl)-1-propene and the xylylene dihalides are *p*-xylylene diiodide and *p*-, *m*-, and *o*-xylylene dibromides. The degree of polymerization (DP) of the resulting polymer was very close to the feed ratio of the monomer to initiator. From a kinetic study, it was found that the polymerization using these bifunctional initiators for 2-oxazoline is a "fast initiation–slow propagation system". Electrophilic reactivities of allylic dibromide and allyl bromide were also evaluated by MO calculation to confirm the polymerization system. Tetrakis(bromomethyl)ethylene, an allylic tetrahalide, was used as a tetrafunctional initiator. The DP value of the polymer agreed well with the feed ratio. From ^{1}H NMR and GPC analyses the polymer was of star-shaped structure.

Introduction

2-Alkyl-2-oxazolines (ROZO) are known to polymerize by an electrophilic initiator to produce linear poly(*N*-acylethylenimine)s. The product polymers become hydrophilic or hydrophobic, depending on the nature of the acyl group.[1] In the case of polymerization using monofunctional initiators such as methyl iodide, methyl *p*-toluenesulfonate, and benzyl bromide, the initiation rate is larger than that of propagation.[2]

Telechelic polymers become increasingly important for practical use, e.g., as a prepolymer for block copolymers or a cross-linking agent. For the preparation of these telechelic polymers, a bifunctional initiator is required. Two types of bifunctional initiators for the polymerization of ROZO have been reported. One is an alkylene bis(*p*-toluenesulfonate), which gave poly(ROZO) with broad molecular weight distribution due to the slow initiation rate.[3] The other is a bis(oxazolinium salt), by which monodisperse poly(ROZO) was produced.[4,5] However, these salt-type initiators were very elaborate to prepare and inconvenient to handle due to their ease of hydrolysis.

Allylic or benzylic halides are well-known to be good electrophiles with high reactivity. Benzyl bromide is often used as a monofunctional initiator for the polymerization of ROZO, where the initiation rate is faster than that of propagation.[2c] Very recently, we have paid attention to the property of these halides and used the allylic dihalides[6] 1,4-dibromo-2-butene and 3-iodo-2-(iodomethyl)-1-propene as novel bifunctional initiators for the polymerization of ROZO. These compounds are commercially available or readily obtainable from commercial reagents and are convenient to handle because of their relatively high stability toward moisture and air. From kinetic results, the polymerization using these initiators is a fast initiation–slow propagation system. Relevant to our previous study, 1,3,5-tris(bromomethyl)benzene, a benzylic trihalide, has been used as a trifunctional initiator for the polymerization of ROZO.[7] The reactivity of the initiator compared with the propagation, however, has not been examined.

This paper deals with polymerization of ROZO using novel bi- and tetrafunctional initiators and quantitative evaluation of their reactivities. The bi- and tetrafunctional initiators used are allylic and benzylic dihalides and an allylic tetrahalide, respectively.

Results and Discussion

Polymerization of 2-Oxazolines Initiated by Allylic or Xylylene Dihalides. The allylic dihalides used as novel bifunctional initiators are 1,4-dibromo-2-butene (trans) (1) and 3-iodo-2-(iodomethyl)-1-propene (3), and the xylylene dihalides are *p*-xylylene diiodide (5) and *p*-, *m*-, and *o*-xylylene dibromides (6, 8, and 9, respectively). Polymerization of ROZO using these initiators, followed by hydrolysis of terminal oxazolinium ends, gave telechelic poly(ROZO) having a hydroxyl group at both ends, 11.[8] Polymerization results are shown in Table I. Polymer 11 was obtained quantitatively in most cases. The degree of polymerization (DP) of 11 was very close to the monomer/initiator feed ratio. The molecular weight distribution evaluated by M_w/M_n was relatively narrow. In several cases, the molecular weight distribution value of the polymer was around 1.2, indicating no Poisson distribution. This may be because an impurity such as water retards the polymerization, and hence, the distribution becomes slightly broader. These results indicate that polymerization using these initiators is a "fast initiation–slow propagation system". When 1,4-dibromobutane (10) was used as a bifunctional initiator, on the other hand, the DP of 11 was larger than the feed ratio and the molecular weight distribution of 11 was broad (entry 13), indicating slow initiation followed by subsequent fast propagation.

Instead of these initiators, a mixture of a corresponding dichloride (2, 4, or 7) and sodium iodide can be used for a bifunctional initiator for the polymerization of ROZO (entries 14–16); sodium iodide was added to the mixture under stirring at 0 °C for 2 h to produce an iodide counteranion in situ during the polymerization. The yield of polymer 11 was high, and the DP of 11 agreed well with the feed ratio.

0024-9297/92/2225-3232$03.00/0

Table I
Polymerization of ROZO Using Allylic of Xylylene Dihalides as Bifunctional Initiators

	polymerization[a]			characterization of 11			
entry	R of ROZO	initiator	$[ROZO]_0/[init]_0$	yield, %	M_n[b]	DP[b]	M_w/M_n[c]
1	Me	**1**	9.0	95	960	10.2	1.19
2	Me	**1**	19.0	97	1590	17.6	1.26
3	Me	**1**	40.4	88	3040	34.6	1.19
4	Et	**1**	10.3	96	1250	11.7	1.13
5	*n*-Pr	**1**	9.9	99	1390	11.5	1.10
6	*i*-Pr	**1**	10.6	96	1270	10.4	1.19
7	Me	**3**	9.4	95	1050	11.2	1.11
8	Me	**5**	10.0	82	910	9.1	1.19
9	Me	**6**	10.0	99	1010	10.2	1.22
10	Me	**6**	19.4	86	1750	18.9	1.21
11	Me	**8**	11.0	86	1170	12.1	1.13
12	Me	**9**	10.0	87	1120	11.5	1.11
13	Me	**10**	9.6	79	1700	18.9	1.60
14	Me	**2**/NaI[d]	10.1	85	1020	10.9	1.15
15	Me	**4**/NaI[d]	10.0	82	1040	11.2	1.19
16	Me	**7**/NaI[d]	10.2	88	1090	11.1	1.24

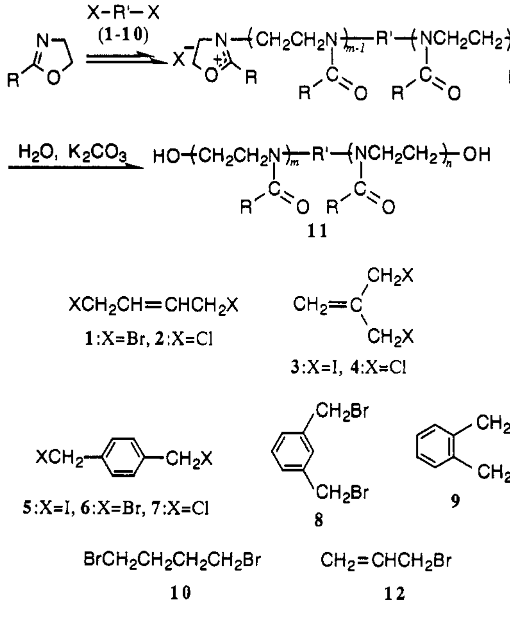
[a] Polymerization was carried out at 80 °C under argon. [b] From VPO. [c] Obtained by GPC. [d] [NaI]/[initiator] = 2.2.

Table II
Synthesis of a BAB-Type Block Copolymer from ROZOs

	polymerization[a]			characterization of 13				
entry	initiator	$[MeOZO]_0/[init]_0$	$[n\text{-BuOZO}]_0/[init]_0$	yield, %	M_n[b]	$m + n$[b]	$p + q$[b]	M_w/M_n[c]
17	**1**	10.8	9.4	99	2350	10.9	10.5	1.16
18	**8**	9.8	10.8	99	2420	10.0	11.3	1.12

[a] Polymerization of MeOZO was carried out at 60 °C under argon, and the subsequent polymerization of *n*-BuOZO was carried out at 85 °C. [b] Determined by ^{1}H NMR. [c] Determined by GPC.

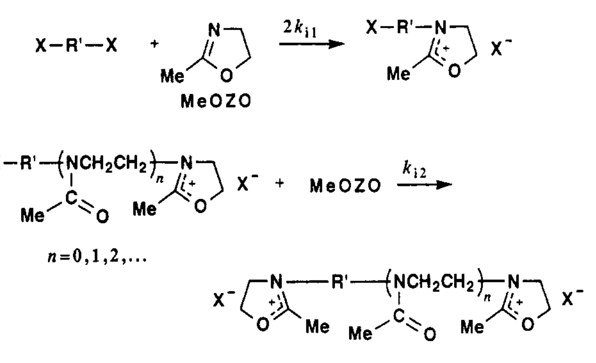
Scheme I



One of the possible applications of the present bifunctional initiator is shown by the preparation of a BAB-type telechelic block copolymer having a hydroxy group at both ends of the ROZO monomers. The preparation of the block copolymer **13** utilized a "one-pot, two-stage copolymerization" technique.[5] First, MeOZO was polymerized by using a bifunctional initiator (**1** or **8**) to give the A block (first stage), followed by the subsequent polymerization of *n*-BuOZO to produce the BAB-type block copolymer quantitatively (second stage) (Table II). The composition of MeOZO–*n*-BuOZO determined by ^{1}H NMR spectroscopy was close to the each monomer/initiator feed ratio. Furthermore, the molecular weight distribution of the block copolymer was relatively narrow.

Quantitative Evaluation of Reactivities of Novel Initiators. In order to evaluate the reaction rate quantitatively, a kinetic study of the polymerization of MeOZO initiated by these initiators was carried out by ^{1}H NMR spectroscopy,[2] where the instantaneous concentrations of monomer and initiator were determined. Figure 1 shows the time–conversion curves for MeOZO monomer and initiator **1**. **1** was consumed in a relatively early stage of polymerization. After **1** was consumed, the ratio of the integrated area of the peak at δ 2.3 due to the methyl protons of the terminal oxazolinium group and the peak at δ 5.5 due to the CH=CH group was almost 3:1, indicating that the initiation proceeded from both sites of **1**.

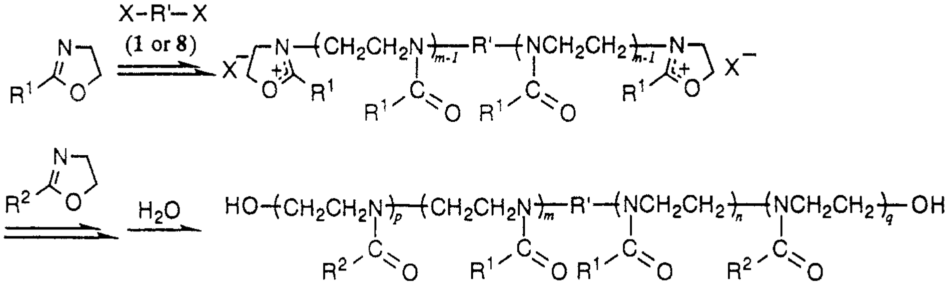
The rate constants of initiation k_{i1} and k_{i2} for the two reaction sites of the initiator are defined as follows.



These rate constants are listed in Table III. In all cases except for the k_{i2} value of **9**, the k_{i1} and k_{i2} values are not so much different and are larger than the k_p value. The k_{i2} value of **9** is smaller probably due to the steric hindrance. It can be seen that **1** possessed a higher initiation reactivity than allyl bromide (**12**). The k_i value of 1,4-dibromobutane (**10**) was much smaller than that of the allylic or xylylene dibromides. As seen above, polymerization using these compounds (**1**, **3**, **6**, **8**, and **9**) as bifunctional initiators provides a fast initiation–slow propagation system.

EHMO and CNDO/2 Calculations of Allylic Dibromide and Allyl Bromide. The reactivity difference

Scheme II



13 (R^1=Me, R^2=*n*-Bu)

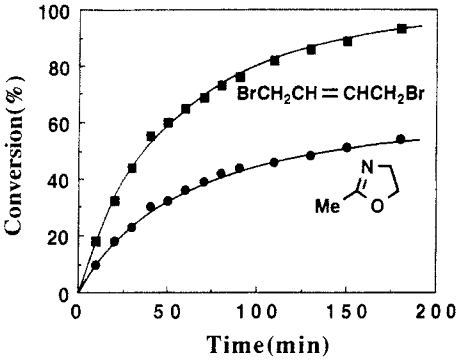


Figure 1. Time–conversion curves of the MeOZO polymerization initiated by 1,4-dibromo-2-butene (1) in CD_3CN at 35 °C: $[MeOZO]_0$ = 3.3 mol/L; $[1]_0$ = 0.55 mol/L.

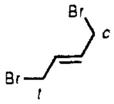
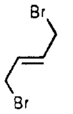
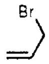
Table III
Rate Constants of the MeOZO Polymerization in CD_3CN at 35 °C

initiator	k_{i1}	k_{i2}	k_i	k_p
	rate const, $\times 10^{-4}$ L/mol·s			
1[a]	1.2	1.0		0.81[c]
3[a]	1.5	2.1		0.76
6[b]	1.1	1.1		0.81[c]
8[b]	0.90	0.89		0.81[c]
9[b]	1.2	0.47		0.81[c]
12[a]			0.38	0.81[c]
benzyl bromide			1.1[c]	0.81[c]
10[a]	0.030			0.81[c]

[a] Polymerization conditions: $[MeOZO]_0$ = 3.3 mol/L, $[initiator]_0$ = 0.55 mol/L. [b] Polymerization conditions: $[MeOZO]_0$ = 1.98 mol/L, $[initiator]_0$ = 0.33 mol/L. [c] The value was obtained with benzyl bromide initiator.[2c]

between 1,4-dibromo-2-butene (1) and allyl bromide (12) has been examined further by molecular orbital (MO) calculation. EHMO[9] (extended Hückel MO) and CNDO/2[10] calculations of 1 and 12 were carried out in order to evaluate the electronic state of the allylic carbons. Table IV shows the gross atomic population (GAP) calculated by EHMO and the total electron density (TED) by CNDO/2 of the allylic carbons for various conformations of the bromide group. The differences in GAP and TED can be calculated between the mono- and dibromide compounds from Table IV. The D_G and D_T values for 12 and 1 were calculated to be +0.006 193 to +0.007 861 by EHMO and +0.002 376 to +0.002 926 by CNDO/2, respectively (Table V). Thus, the GAP and TED of the allylic carbons of 1 are smaller than that of 12 in any conformation, indicating the stronger electrophilic (cationic) nature of the allylic carbons of 1 than that of 12. This can be taken to support the fast electrophilic attack of 1 on the nitrogen of ROZO, and these semiempirical MO calculations well explain the polymerization results using the allylic dihalide as a bifunctional initiator with the fast initiation process.

Table IV
Calculations of Gross Atomic Population (GAP) and Total Electron Density (TED) of the Allylic Carbon in Allylic Dibromide (1) and Allyl Bromide (12)

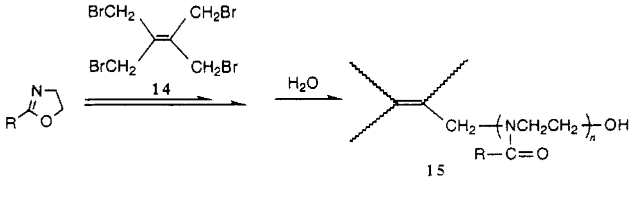
initiator[a]		EHMO GAP	CNDO/2 TED
1			
	(1*tt*)	0.627 332	3.980 114
	(1*tc*-*t*) (1*tc*-*c*)	0.626 210 0.633 887	3.980 408 3.981 915
	(1*cc*)	0.632 536	3.981 724
12			
	(12*t*)	0.634 071	3.982 781
	(12*c*)	0.640 080	3.984 650

[a] *t* indicates that Br exists in the s-trans and *c* that it exists in the s-cis conformation.

Table V
Differences in GAP and TED of the Allylic Carbons in 1 and 12

	D_G	D_T
(12*t*) − (1*tt*)	+0.006 739	+0.002 667
(12*t*) − (1*tc*-*t*)	+0.007 861	+0.002 373
(12*c*) − (1*tc*-*c*)	+0.006 193	+0.002 735
(12*c*) − (1*cc*)	+0.007 544	+0.002 926

Polymerization of 2-Oxazolines Initiated by Allylic Tetrahalide. Star-shaped telechelic polymers have been prepared by using a multifunctional initiator followed by termination with functional groups.[11] These polymers can be used for various applications such as multifunctional cross-linking agents and prepolymers for star-shaped block copolymers. As an extension of the above allylic dihalide initiator showing the fast initiation system, an allylic tetrahalide, tetrakis(bromomethyl)ethylene (14), was employed as a multifunctional initiator to give a star-shaped telechelic poly(ROZO).



The polymerization of ROZO initiated by 14 was carried out in acetonitrile at 70 °C followed by hydrolysis of

Table VI
Polymerization of ROZO Initiated by Tetrakis(bromomethyl)ethylene (14)

	polymerization[a]		characterization of 15			
entry	R of ROZO	$[\mathrm{ROZO}]_0/[14]_0$	yield, %	M_n[b]	DP[b]	M_w/M_n[c]
19	Me	21.7	99	1940	21.1	1.15
20	Me	49.9	99	3990	45.1	1.28
21	Me	98.8	99	8040	93.4	1.27
22	Et	20.0	94	1840	17.0	1.21

[a] Polymerization was carried out at 70 °C under argon. [b] From VPO. [c] By GPC.

Table VII
Comparison of Molecular Weights of Star-Shaped and Linear Poly(MeOZO) by GPC

polymer (entry)	M_n (VPO)	M_n (GPC)[a]	M_w/M_n[a]
15 (19)[b]	1940	740	1.15
15 (20)[b]	3990	1360	1.28
11 (2)[c]	1590	1260	1.26
11 (3)[c]	3040	3200	1.19

[a] The calibration curves for GPC analysis were obtained by using a polystyrene standard. [b] See Table VI. [c] See Table I.

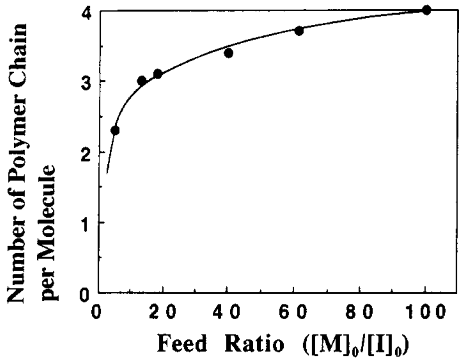


Figure 2. Relationships between the feed ratio and the number of polymer chains per molecule. The MeOZO polymerization was carried out in CD_3CN at 70 °C.

terminal ends to produce 15 quantitatively (Table VI). The DP of 15 determined by VPO was close to the monomer/initiator feed ratio. The M_w/M_n values obtained by GPC were fairly small. These data indicate that the polymerization is by a relatively fast initiation system.

In order to confirm that the polymerization proceeds from four sites of 14, the average number of polymer chains per molecule 15 was determined under various monomer/initiator feed ratios by ^1H NMR spectroscopy (Figure 2). The average number increased with increasing feed ratio. When the feed ratio was more than 10, the number was beyond 3, indicating that the polymer was of star shape. Polymerization under the feed ratio of 100 gave a polymer having four chains per molecule, implying that all initiating sites of 14 were consumed.

Star-shaped polymers are known to be of spherical conformation in solution.[11] The molecular weight of a star-shaped polymer (by GPC) is smaller than that of a linear polymer. Table VII shows the results of GPC measurement of 15 and linear poly(ROZO) 11 having a hydroxyl group at both ends. The molecular weight of a linear-type polymer by GPC is almost the same as that by VPO. On the other hand, the molecular weight of 15 was much smaller than that by VPO. From these results, the conformation of 15 in solution was spherical, and hence, polymer 15 was of multiarmed structure.

Conclusions

The present study provides several novel multifunctional initiators for the polymerization of 2-oxazolines. The polymerization using allylic dihalide or benzylic dihalide gave molecular weight-controlled poly(ROZO) in high yield. All the bifunctional initiators 1–9 used in this study are good initiators for the preparation of telechelic and block poly(ROZOs) having relatively narrow molecular weight distribution. From a kinetic study, the polymerization using these initiators is a fast initiation and slow propagation system. The allylic tetrahalide tetrakis(bromomethyl)ethylene is a good initiator for the preparation of a star-shaped telechelic poly(ROZO).

Experimental Section

Materials. The solvent acetonitrile was purified by distillation over calcium hydride. Commercial reagents MeOZO and EtOZO were purified by distillation over potassium hydroxide. *n*- and *i*-PrOZOs, 3-iodo-2-(iodomethyl)-1-propene (3), *p*-xylylene diiodide (5), and tetrakis(bromomethyl)ethylene (14) were prepared according to the literature.[12-15] Other reagents and solvents were purified in the usual manner. All operations were carried out under argon.

Polymerization Using Allylic or Xylylene Dibromide as a Bifunctional Initiator. A typical run was as follows (entry 1). 0.213 g (0.996 mmol) of 1,4-dibromo-2-butene (1) was placed in a glass tube, and the atmosphere was replaced with argon. Five milliliters of acetonitrile and 0.759 g (8.92 mmol) of MeOZO were added, in order, to the tube by using a syringe. The tube was sealed and the mixture was heated at 80 °C for 7 h. After being cooled at room temperature, the tube was opened and 0.54 g (30 mmol) of water and 1.66 g (12 mmol) of potassium carbonate were added to the mixture. The tube was again sealed and the mixture was heated at 80 °C for 20 h. The tube was opened and the solvent was evaporated. Then the residue was extracted with 30 mL of chloroform, and the organic layer was separated. After evaporation of the solvent and reprecipitation (acetonitrile–diethyl ether), the polymer material was collected and dried in vacuo to give 0.803 g of 11 (yield 94%): ^1H NMR ($CDCl_3$) δ 2.1 (s, $CH_3C{=}O$), 2.9–3.9 (br, CH_2N and CH_2O), 5.4–5.6 (m, $CH{=}CH$); IR (neat) 3400 (ν_{O-H}), 1630 cm^{-1} ($\nu_{C=O}$).

Polymerization Using Allylic or Xylylene Dichloride/Sodium Iodide as a Bifunctional Initiator. A typical run was as follows (entry 14). To the solution of 0.832 g (9.78 mmol) of MeOZO and 0.121 g (0.968 mmol) of 1,4-dichloro-2-butene (2) in 5 mL of acetonitrile was added 0.342 g (2.28 mmol) of sodium iodide at 0 °C under argon. The reaction mixture was stirred at 0 °C for 2 h and heated at 80 °C for 7 h. After cooling at room temperature, 0.54 g (30 mmol) of water and 1.66 g (12 mmol) of sodium carbonate were added to the mixture, followed by heating at 80 °C for 20 h. After evaporation of the solvent, the residue was extracted with chloroform and the organic layer was separated. The organic layer was dried over $MgSO_4$, followed by evaporation. The residue was dissolved in 3 mL of acetonitrile. The mixture was poured into 80 mL of diethyl ether to precipitate the polymeric materials, followed by filtration to give 0.778 g of 11 (yield 85%).

Synthesis of BAB-Type Block Copolymer from ROZOs. A typical run was as follows (entry 17): 0.957 g (11.2 mmol) of MeOZO and 0.222 g (1.04 mmol) of 1,4-dibromo-2-butene in 6 mL of acetonitrile was heated at 60 °C for 20 h under argon. After cooling to room temperature, 1.25 g (9.8 mmol) of *n*-BuOZO was added to the reaction mixture, followed by heating at 80 °C for 24 h. The reaction mixture was cooled to room temperature and 2.1 mL (2.1 mmol) of 1 N NaOH–methanol solution was added to the mixture, followed by stirring for 1 h.[4] The solvents were evaporated under reduced pressure, and the residue was extracted with chloroform. Then the separated organic layer was evaporated, and the residue was dried in vacuo to produce 2.27 g of 13 (yield 99%): ^1H NMR ($CDCl_3$) δ 0.9 (t, CH_3CH_2), 1.3 (m, $CH_3CH_2CH_2$), 1.6 (m, $CH_3CH_2CH_2$), 1.9–2.6 (m, $CH_3C{=}O$, $CH_2C{=}O$), 3.2–4.0 (br, CH_2N and CH_2O), 5.5–5.6 (m, $CH{=}CH$).

Kinetic Study. A typical run was as follows: 0.0588 g (0.275 mmol) of 1,4-dibromo-2-butene was added to 0.140 g (1.65 mmol) of MeOZO in a sample tube. Then CD_3CN was added to the total volume of 0.5 mL, and the mixture was transferred into an NMR tube. Polymerization was continued in the tube at 35 °C and monitored by recording ^{1}H NMR spectra on a Hitachi R-24A spectrometer.

EHMO and CNDO/2 Calculations. EHMO and CNDO/2 calculations were performed on IBM AT compatible Sanyo AX 16-bit microcomputer with 80287 arithmetic coprocessor and 40 MB hard disk. For EHMO and CNDO/2 calculations, the following geometrical parameters were used for each conformation: H–C(sp^3) 1.112, H–C(sp^2) 1.102, Br–C(sp^3) 1.910, C(sp^3)–C(sp^2) 1.539, C(sp^2)–C(sp^2) 1.340 (bond length in Å); H–C(sp^2)–H and H–C(sp^2)–C(sp^3) 117.8, H–C(sp^2)–C(sp^2) and C(sp^3)–C(sp^2)–C(sp^2) 121.1, 109.5 for any other carbon set (angle in degrees).

Polymerization Using Tetrakis(bromomethyl)ethylene (14) as a Multifunctional Initiator. A typical run was as follows (entry 17): 0.957 g (11.2 mmol) of MeOZO and 0.207 g (0.517 mmol) of tetrakis(bromomethyl)ethylene (**14**) were dissolved in 5 mL of acetonitrile under argon. The mixture was heated at 70 °C for 24 h. Reprecipitation (acetonitrile–diethyl ether) gave the polymeric materials (1.16 g, 99% yield). The hydrolysis of the terminal oxazolinium ends of the polymer was carried out in methanol in the presence of water and potassium carbonate to give **15** quantitatively.[8]

Measurements. ^{1}H NMR spectra were recorded on 60-MHz Hitachi R-24A, 60-MHz JEOL FX-60Q, and 250-MHz Bruker AC-250T spectrometers. IR spectra were recorded on a Shimadzu IR-27G spectrometer. Gel permeation chromatographic (GPC) analyses were performed by using Hitachi 655A with UV and RI detectors under the following conditions: Gelpack GL-A130 and GL-A120 columns with chloroform eluent at a flow rate of 1.0 mL/min. The molecular weight of the polymers was measured by a Corona 117 vapor pressure osmometer in DMF at 70 °C.

Acknowledgment. H.U. acknowledges a Grant-in-Aid for Scientific Research (No. 02750643) from the Ministry of Education, Science and Culture of Japan.

References and Notes

(1) For recent papers on 2-oxazoline polymerization, see: (a) Kobayashi, S. *Prog. Polym. Sci.* **1990**, *15*, 751. (b) Kobayashi, S.; Uyama, H. *Polym. News* **1991**, *16*, 70. (c) Cai, G.; Litt, M. H.; Krieger, I. M. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 773. (d) Chujo, Y.; Ihara, E.; Kure, S.; Suzuki, K.; Saegusa, T. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 303. (e) Miyamoto, M.; Aoi, K.; Saegusa, T. *Macromolecules* **1991**, *24*, 11. (f) Uyama, H.; Kobayashi, S. *Macromolecules* **1991**, *24*, 614.

(2) (a) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1972**, *5*, 359. (b) Saegusa, T.; Ikeda, H. *Macromolecules* **1973**, *6*, 808. (c) Saegusa, T.; Kobayashi, S.; Yamada, A. *Makromol. Chem.* **1976**, *177*, 2271.

(3) Litt, M.; Rodriguez, J.; Nava, H.; Kim, J.; McClelland, T.; Gordon, W.; Dyan, M. *New Monomers and Polymers*; Plenum: New York, 1984; p 113.

(4) (a) Swamikannu, A. X.; Hisue, G. H.; Litt, M. H.; Balasubramanian, M. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1455. (b) Hsiue, G. H.; Swamikannu, A. X.; Litt, M. H. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3043.

(5) Kobayashi, S.; Igarashi, T.; Moriuchi, Y.; Saegusa, T. *Macromolecules* **1986**, *19*, 535.

(6) Kobayashi, S.; Uyama, H.; Narita, Y. *Macromolecules* **1990**, *23*, 353.

(7) Cai, G.; Litt, M. H. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3603.

(8) Kobayashi, S.; Masuda, E.; Shoda, S.; Shimano, Y. *Macromolecules* **1989**, *22*, 2878.

(9) Hoffmann, R. *J. Chem. Phys.* **1967**, *39*, 1397.

(10) Pople, J. A.; Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, 129.

(11) (a) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 89. (b) Rempp, P.; Franta, E.; Herz, J.-E. *Adv. Polym. Sci.* **1988**, *86*, 145.

(12) Witte, H.; Seeliger, W. *Justus Liebigs Ann. Chem.* **1974**, 996.

(13) Skell, P. S.; Doerr, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 4688.

(14) Góźdź, A. S. *Polym. Bull.* **1982**, *4*, 577.

(15) Cope, A. C.; Kagan, F. *J. Am. Chem. Soc.* **1958**, *80*, 5499.

Registry No. **1**, 6974-12-5; **2**, 764-41-0; **3**, 17616-43-2; **5**, 91-13-4; **6**, 623-24-5; **8**, 626-15-3; **10**, 110-52-1; **12**, 106-95-6; **14**, 30432-16-7; MeOZO (homopolymer), 26375-28-0; EtOZO (homopolymer), 25805-17-8; *n*-PrOZO (homopolymer), 25822-74-6; *i*-PrOZO (homopolymer), 25822-68-8; (MeOZO)(*n*-BuOZO) (block copolymer), 130172-63-3; MeOZO, 1120-64-5; NaI, 7681-82-5.