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Free Radical Polymerization of Volume Expandable Vinylcyclopropane

Jun-ichi Sugiyama,* Keiko Ohashi, and Mitsuru Ueda

Department of Materials Science and Engineering, Yamagata University, 4-3-16 Jounan, Yonezawa, Yamagata 992, Japan

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ABSTRACT: Synthesis and polymerization of 1,1-bis(phenoxycarbonyl)-2-vinylcyclopropane (**2**) were carried out. The new monomer **2** afforded a 1,5-addition polymer in good conversion by radical initiation. The polymers exhibit T_g as 76-84 °C and T_d as 361-377 °C. **2** showed a positive volume change (+6.77%) on polymerization. This could be explained by the facts that the molecular weight of **2** is relatively large and **2** is crystalline at ambient temperature, which means the monomer is already compressed. The compositions of the 1,5-adduct, molecular weights, and volume expansion ratios decreased with increasing reaction temperature or by using solvent in the polymerization. An unknown unit from a side reaction in the polymer might consist of a cyclobutane skeleton.

Introduction

The monomers currently used in the manufacture of all the commercial potting and casting resins, molding resins, film coatings, etc. exhibit some degree of shrinkage during polymerization.[1] We are interested in an expanding monomer for dental materials, which require a no shrinkage monomer and a relatively high glass transition temperature (T_g) (above 70 °C) of the resulting polymer. In general, cyclic monomers show a smaller degree of shrinkage than vinyl monomers, but polymerizable cyclic monomers affording polymers with high molecular weights by radical initiation are few. Vinylcyclopropane (**1**) having radical stabilization groups on the cyclopropane ring is one of the monomers affording relatively high molecular weight polymers and low shrinkage in volume through the radical ring-opening polymerization (Scheme 1).[2-7] Cho et al. reported the T_g's of the polymers obtained from 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (**1a**) and 1,1-dicyano-2-vinylcyclopropane (**1b**) were 40 and 25 °C, respectively.[5b] These T_g's are low for dental materials.

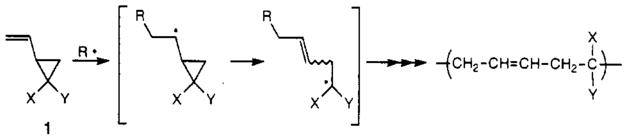
In general, the T_g could be raised by the introduction of large side groups because the repulsion or the attraction of these groups could appreciably lower the chain mobility. Therefore we prepared a novel monomer, 1,1-bis(phenoxycarbonyl)-2-vinyl-cyclopropane (**2**), with introduced phenyl groups to improve the T_g. This article describes the polymerization of **2** and the properties of the resulting polymers.

Experimental Section

Materials. Methylene chloride was purified by distillation over phosphorus pentoxide. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone until the blue color of the ketyl of benzophenone was well established and then distilled. Sodium hydride (60% in oil) was washed with *n*-hexane to remove oil and then dried *in vacuo*. Other reagents were obtained commercially and used as received.

Measurements. IR spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. NMR spectra were obtained on a JEOL JNM-EX270 (270 MHz) spectrometer. Molecular weights were determined by a gel permeation chromatograph (GPC) based on standard polystyrenes using a JASCO PU-980 intelligent HPLC pump equipped with Shodex KD-800P and KD-80M columns at 40 °C in *N,N*-dimethylformamide. Thermal properties were measured by a Seiko SSC 5000 thermal analyzer at a heating rate 10 °C/min for thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) of the samples was performed by use of a Seiko SSC 5200 at a heating rate of 10 °C/min under an N_2 purge using preheated samples (200-300 °C).

Scheme 1



X, Y = H, Cl, COOEt, CN, Ph

Measurement of Density. Densities of the monomer and polymers were measured by the sink and float test at 25 °C employing standard hydrometers. The samples of monomer were crystallized from cyclohexane or pressed at 300 kg/cm^2 for 1 min *in vacuo*. The samples of polymers were as-cast films from chloroform solution.

Preparation of 1,1-Bis(phenoxycarbonyl)-2-vinylcyclopropane (2). To a suspension of oil free sodium hydride (1.46 g, 60.8 mmol), 1,4-dibromo-2-butene (5.98 g, 27.6 mmol), and dry tetrahydrofuran (THF) (100 mL) was added dropwise diphenyl malonate (7.07 g, 27.6 mmol) in THF (100 mL) at ambient temperature under nitrogen atmosphere, and the mixture was then heated at 65 °C. After 4 h, THF was removed under reduced pressure. The residue was dissolved in ether (100 mL), washed with aqueous sodium bicarbonate, and then dried over magnesium sulfate. After the removal of ether *in vacuo*, the crude product was purified by column chromatography (benzene on silica gel) followed by recrystallization from cyclohexane. The yield of **2** was 2.37 g (32%) as colorless columns (mp 44-45 °C). IR (KBr): 1748 (C=O); 1640 (C=C), 1593, 1493, 1319, 1262, 1204, 1105, 748, 689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (dd, 1H, J = 5.1 and 8.7 Hz, *E*-H—CH< of cyclopropane), 1.98 (dd, 1H, J = 5.1 and 7.6 Hz, *Z*-H—CH< of cyclopropane), 2.87 (ddd, 1H, J = 7.6, 8.3, and 8.7 Hz, —CH< of cyclopropane), 5.30 (d, 1H, J = 9.9 Hz, *E*-H—CH=CH—), 5.44 (d, 1H, J = 17.2 Hz, *Z*-H—CH=CH—), 5.68 (ddd, 1H, J = 8.3, 9.9, and 17.2 Hz, CH_2=CH—), 7.1-7.4 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 21.2 (t), 32.2 (d), 36.0 (s), 119.7 (t, CH_2=), 121.4 (d), 126.1 (d), 129.5 (d), 132.2 (d,=CH—), 150.6 and 150.7 (s, substituted aromatic carbons), 165.9 and 168.1 (s, C=O).

Typical Procedure of the Radical Polymerization of 2. A mixture of **2** (570 mg, 1.85 mmol) and azobis(isobutyronitrile) (AIBN) (6.1 mg, 2 mol %) was heated at 60 °C in a glass tube sealed after degassing. After 48 h, the reaction mixture was dissolved in methylene chloride (5 mL) followed by pouring into a 20-fold excess of methanol. The polymer was collected by filtration as a white powder and purified by reprecipitation from methylene chloride in methanol. Yield: 462 mg (81%). IR (film): 1750 (C=O), 1591, 1493, 1196, 1165, 743, 687 cm^{-1}. ^{1}H

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Scheme 2

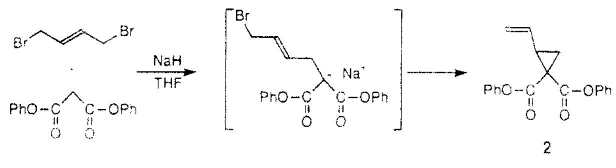


Table 1. Radical Polymerization of 2[a]

run	init[b]	temp, °C	solv[c]	yield,[d] wt %	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	inh,[f] dL/g	composition,[g] % 3	composition,[g] % 4
1	AIBN	60		81	420 000	3.1	1.59	100	0
2	BPO	80		87	120 000	3.6	0.54	61	39
3	DTBP	120		87	270 000	3.3	1.01	60	40
4	AIBN	60	PhCl	89	140 000	2.1	0.49	62	38
5	DTBP	120	PhCl	90	95 000	1.8	0.26	23	77

[a] Heated for 48 h in a sealed tube. [b] 2 mol % of AIBN (2,2′-azobis(isobutyronitrile)), BPO (benzoyl peroxide), or DTBP (di-*tert*-butyl peroxide). [c] Chlorobenzene (1 mol/L). [d] Insoluble in methanol. [e] Estimated by GPC (based on PSt). [f] Inherent viscosity; measured in chloroform (0.5 g/dL) at 30 °C. [g] Estimated by ^{1}H NMR.

NMR ($CDCl_3$): δ 2.7–3.0 (br, 4H), 5.6–5.7 (br, 2H), 6.9–7.4 (br, 10H). ^{13}C NMR ($CDCl_3$): δ 36.3 (t), 58.2 (s), 121.3 (d), 126.1 (d), 128.9 (d), 129.5 (d), 150.7 (s), 168.8 (s).

Results and Discussions

Radical Polymerization of 2. Monomer 2 was prepared from 1,4-dibromo-2-butene and diphenyl malonate (Scheme 2). Formation of the cyclopropane ring is supported by the presence of the peaks assignable to CH_2 (δ 1.83 and 1.98) and CH (δ 2.87) in the ^{1}H NMR spectrum.

Polymerization of 2 was carried out in a sealed degassed tube in the presence of a radical initiator. Since the melting point of 2 was 45 °C, bulk polymerization took place above 60 °C. The results are summarized in Table 1. The polymer obtained was collected as a white powder insoluble in methanol. The polymer could dissolve in methylene chloride, chloroform, and DMF, but could not dissolve in THF. The number average molecular weight ($\bar{M}_n$) of the polymers was 95 000–420 000 estimated by GPC in DMF based on polystyrene standard.

The structure of the polymer obtained from run 1 was confirmed to be the expected ring-opening product by IR, ^{1}H NMR, and ^{13}C NMR spectra. The IR spectrum of run 1 showed the absence of an absorption at 1640 cm^{-1} assignable to a vinyl group of 2 and the presence of an absorption at 1750 cm^{-1} assignable to the carbonyl of the phenyl ester (Figure 1A). No extra peaks in the ^{1}H NMR and ^{13}C NMR spectra of the polymer were found, clearly indicating the formation of the 1,5-adduct unit 3 (Figures 2A and 3A). However, unknown signals were observed in the IR (1229 cm^{-1}), ^{1}H NMR (δ 2.5), and ^{13}C NMR (δ 121.5, 125.6, 129.3, 171.0) spectra of the polymers from runs 2–5 (Figures 1B, 2B,C, and 3B,C). The composition of 3 decreased with increasing reaction temperature and by using solvent. The unknown unit 4 in the polymers from runs 2–4 increased to 40 mol % of the whole unit and reached 77 mol % in the solution polymerization at 120 °C (run 5). Sanda et al.[7a] reported the 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane polymerized to afford cyclobutane skeletons formed by back-biting of the terminal radical. The signals of unknown 4 in the ^{1}H NMR spectra resemble the signal of the cyclobutane unit of Sanda's polymer. Thus 4 might also consist of a cyclobutane skeleton through the same mechanism (Scheme 3). If the unknown unit has a cyclobutane structure, it may be difficult to show sharp signals in the ^{1}H and ^{13}C NMR spectrum since cyclobutane will act as some stereoisomeric configuration in the polymer's main chain. This assumption could explain why the signals of the cyclobutane ring are too broad to distinguish.

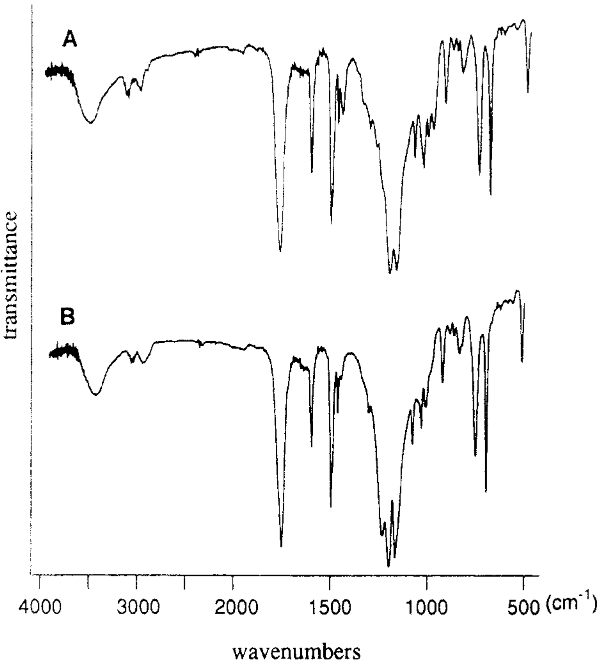


Figure 1. IR spectra of the polymers obtained from (A) run 1 and (B) run 5 (KBr).

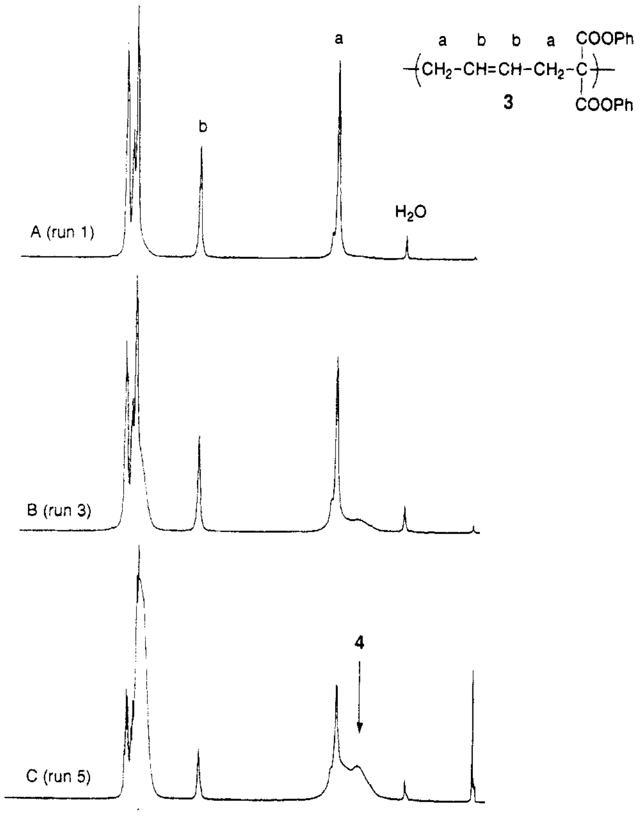


Figure 2. ^{1}H NMR spectra of the polymers obtained from (A) run 1, (B) run 3, and (C) run 5.

A high temperature and low monomer concentration might promote the intramolecular attack of the radical to form 4. Moreover, it was found that $\bar{M}_n$ and inherent viscosities decreased with the increasing formation of 4. It would be explained that the termination or chain transfer

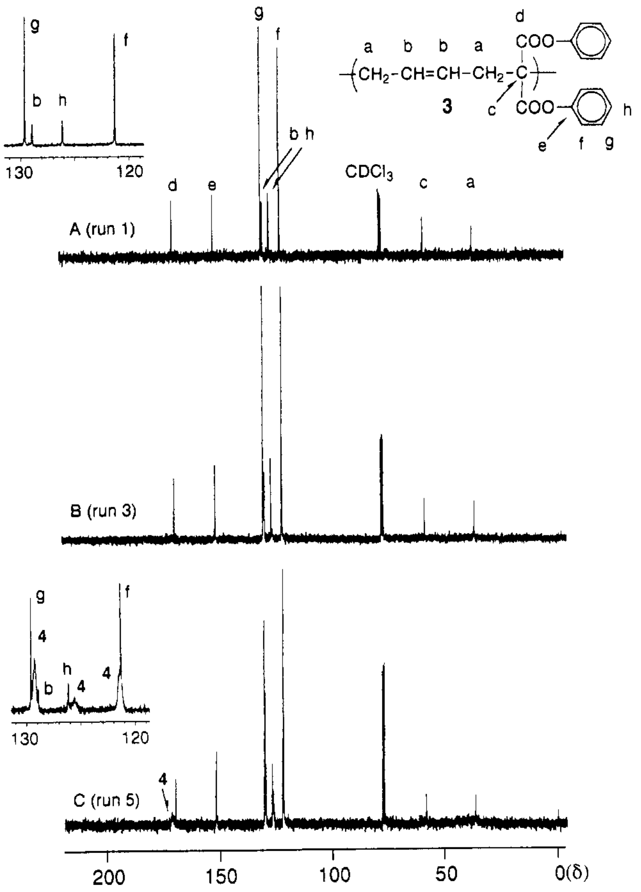
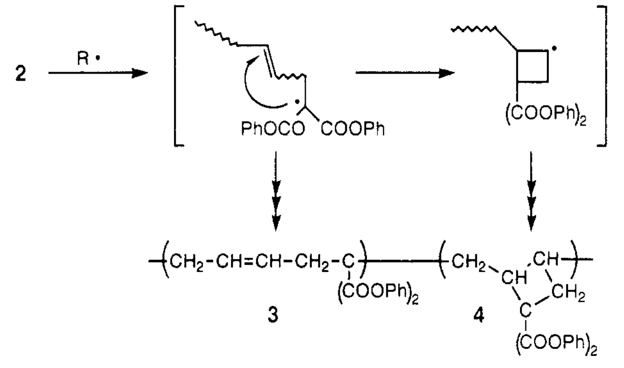


Figure 3. ^{13}C NMR spectra of the polymers obtained from (A) run 1, (B) run 3, and (C) run 5.

Scheme 3



reaction was also promoted by a high temperature and low monomer concentration.

Thermal Properties of the Polymers. The thermal stability and properties of the polymer were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA curves of the as-synthesized polymer samples are shown in Figure 4. All the polymers exhibited a degradation temperature (T_d) above 360 °C (Table 2). Glass transition temperatures (T_g) of the polymers were at 76–84 °C.

The T_g's of the polymers were hardly affected by the ratio of 3 and 4. Consequently, it would be explained that disorderliness of the repeating unit in the polymer's backbone caused by 4 is hardly affected by reducing T_g because T_g of these polymers might be dominated by the aromatic–aromatic interaction of the side chain.

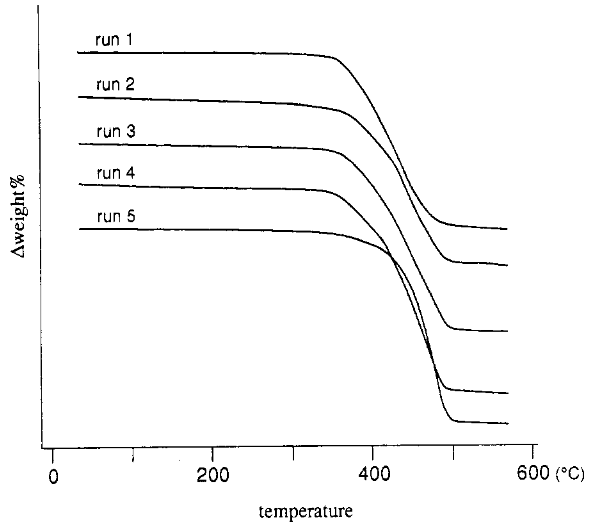


Figure 4. TGA traces for polymers (run 1–5).

Table 2. Thermal Properties of the Polymers

run	T_g,[a] °C	T_d,[b] °C	run	T_g,[a] °C	T_d,[b] °C
1	76	373	4	78	373
2	76	374	5	84	361
3	76	377			

[a] Measured by DSC. [b] Measured by TGA (temperature at 10% weight loss).

Table 3. Volume Change on Radical Polymerization[a]

run	density,[b] g/mL	vol change,[c] %	run	density,[b] g/mL	vol change,[c] %
1	1.170	+6.77	4	1.223	+2.55
2	1.216	+3.11	5	1.239	+1.28
3	1.220	+2.79			

[a] Measured by the sink and float test. [b] Density of 2: 1.255 g/mL. [c] [Density(monomer) − density(polymer)]/density(monomer) × 100.

Volume Change on Polymerization. Densities of the monomer and polymers were measured by the sink and float test. The results are summarized in Table 3. The densities of crystalline and pressed monomer were 1.264 and 1.255 g/mL, correspondingly. It showed that the pressing procedure hardly affected density, so 1.255 was used for the density of the monomer. The volume expansion ratio was decreased with the increasing formation of 4. Therefore the volume expansion might be based on the formation of 3. It could be explained because ring-opening isomerization of cyclopropane might cause the expansion of the repeating unit's free volume. Since formation of 4 meant retention of the cyclic unit, it could not contribute to the volume expansion.

On the contrary, Sanda et al. reported the volume change on polymerization of **1a** and **1b**, which is −11.18% and −13.83%, respectively.[7a] Both of them showed volume shrinkage, whereas **2** exhibited volume expansion (+6.77%). The ring-opening monomers generally show a smaller shrinkage than vinyl monomers. Endo proposed the relationship that the volume shrinkage on polymerization is proportional to the reciprocal of the monomer's molecular weight.[8] Relationships between the reciprocal of the monomer's molecular weight and the shrinkage of vinyl monomers, oxiranes which are three-membered cyclic analogs, and vinylcyclopropanes are summarized in Figure 5.[1b,7] It indicates that the shrinkage of volume decreases with increasing molecular weight. Although **1a** and **1b** showed shrinkage, monomer **2** showed an expansion larger than the usual ring-opening monomers. This could be explained by the fact that the molecular weight of **2** is larger than those of **1a** and **1b**.

Furthermore, it is known that volume expandable spiro ortho carbonate monomers exhibit the largest expansion at the temperature slightly below the melting point.[1c,9]

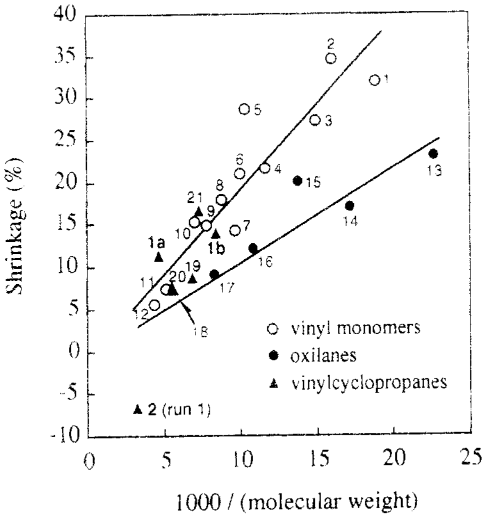


Figure 5. Relationship between shrinkage on volume and molecular weight. (1) acrylonitrile; (2) vinyl chloride; (3) methacrylonitrile; (4) vinyl acetate; (5) vinylidene chloride; (6) methyl methacrylate; (7) styrene; (8) ethyl methacrylate; (9) *n*-propyl methacrylate; (10) *n*-butyl methacrylate; (11) vinyl carbazole; (12) 1-vinylpyrene; (13) ethylene oxide; (14) propylene oxide; (15) 2,2-dimethylethylene oxide; (16) epichlorohydrin; (17) styrene oxide; (18) α-cyclopropyl-4-methoxystyrene; (19) α-cyclopropylstyrene; (20) α-cyclopropyl-4-chlorostyrene; (21) 1,1-dichloro-2-vinylcyclopropane.

This phenomenon could be explained because the crystals are considerably more dense than the amorphous liquid. Similarly, during polymerization of crystalline **2** to afford amorphous polymers, the arrangement of molecules became disordered and compression of the intermolecular distance might be released. Accordingly, the positive expansion of **2** would be also explained by the fact that **2** is a crystal, which is already compressed, whereas **1a** and **1b** are liquids at the measuring temperature (25 °C).

Summary

Radical polymerization of 1,1-bis(phenoxycarbonyl)-2-vinylcyclopropane (**2**) undergoes a 1,5-addition mode to afford a high molecular weight polymer in good yield. Selectivity in the direction of the ring-opening isomerization is quantitative at 60 °C estimated by ^{1}H NMR and ^{13}C NMR. The composition of the 1,5-adduct, molecular weight, and volume expansion rate decreased with increasing reaction temperature or decreasing monomer concentration. The unknown unit in the polymer might consist of a cyclobutane skeleton formed by back-biting of the terminal radical.

The new monomer **2** showed a positive volume change (+6.77%) on polymerization. This could be explained by the facts that the molecular weight of **2** is respectively large and **2** is crystalline at ambient temperature, which means the monomer is already compressed. The diphenyl ester **2** is a peerless high volume expanding monomer, which can be polymerized by radical initiation. Consequently, various applications for manufactures will be expected.

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References and Notes

(1) (a) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 17. (b) Luck, R. M.; Sadhir, R. K. In *Expanding Monomers: Synthesis, Characterization, and Application*; Sadhir, R. K., Ed.; CRC Press: Boca Raton, FL, 1992; Chapter 1. (c) *Ibid.* Chapter 2.

(2) (a) Takahashi, T.; Yamashita, I. *J. Polym. Sci., Part B* **1965**, *3*, 251. (b) Takahashi, T. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 403.

(3) (a) Takahashi, T.; Yamashita, I. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 131. (b) Endo, T.; Suga, K. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1831.

(4) (a) Lishanskii, I. S.; Zak, A. G.; Fedorova, E. F.; Khachaturov, A. S. *Vysokomol. Soedin., Ser. A* **1965**, *7*, 966. (b) Lishanskii, I. S.; Khachaturov, A. S. *Vysokomol. Soedin., Ser. A* **1967**, *9*, 1895. (c) Lishanskii, I. S.; Forma, O. S. *Vysokomol. Soedin., Ser. A* **1969**, *11*, 1398. (d) Endo, T.; Watanabe, M.; Suga, K.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 3039. (e) Endo, T.; Watanabe, M.; Suga, K.; Yokozawa, T. *Makromol. Chem.* **1989**, *190*, 691.

(5) (a) Cho, I.; Ahn, K. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 751. (b) Cho, I.; Ahn, K. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3169. (c) Endo, T.; Watanabe, M.; Suga, K.; Yokazawa, T. *J. Polym. Sci., Part A: Chem.* **1989**, *27*, 1435.

(6) Cho, I.; Lee, J.-Y. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 263.

(7) (a) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818. (b) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1992**, *25*, 6719.

(8) (a) Endo, T. *Sen-I Gakkaishi* **1987**, *11*, 456. (b) Endo, T. *Kobunshi* **1978**, *2*, 108.

(9) (a) Bailey, W. J. *J. Macromol. Sci.-Chem.* **1975**, *A9* (5), 858. (b) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1735.