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Cationic Ring-Opening Polymerization of Five-Membered Cyclic Thiocarbonate Bearing an Adamantane Moiety via Selective Ring-Opening Direction

Hisamitsu Kameshima,^{†,§} Nobukatsu Nemoto,^{†,‡} Fumio Sanda,[‡] and Takeshi Endo^{*,†}

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan, and Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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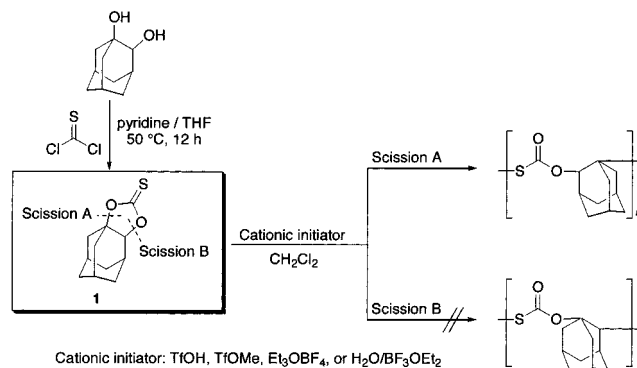
ABSTRACT: A novel five-membered cyclic thiocarbonate bearing adamantane moiety, 4,6-dioxatetracyclo[6.3.1.1.^{3,10}3.7]tridecane-5-thione (**1**), was synthesized from 1,2-adamantanediol and thiophosgene in the presence of pyridine. Monomer **1** underwent cationic ring-opening polymerization initiated by triethyl-oxonium tetrafluoroborate (Et₃OBF₄), methyl trifluoromethanesulfonate (TfOMe), trifluoromethanesulfonic acid (TfOH), and H₂O with 2 mol % of boron trifluoride etherate (BF₃OEt₂) in CH₂Cl₂ at 30 °C to afford the polythiocarbonate by isomerization of the thiocarbonyl group into a carbonyl group with selective ring-opening direction. The number-average molecular weight and polydispersity of the polymer obtained by polymerization with H₂O/BF₃OEt₂ were 10 600 and 1.44, respectively. The temperature with 5% weight loss of the obtained polymer was 338 °C. Monomer **1** expanded as large as 14% during the polymerization.

Introduction

Adamantane (tricyclo[3.3.1.1.^{3,7}]decane), a highly symmetrical tricyclic hydrocarbon consisting of fused chair-form cyclohexane rings,¹ has been inserted into the backbone of many polymers including polysulfones, polyesters, polyamides, and polyimides.² These polymers exhibit high glass transition temperatures and chain stiffness with reduced crystallinity and enhanced solubility. The increased stability of these polymers is attributable to the unique diamond-like cage structure of adamantane. In addition, the UV–vis transparency of adamantane attracts much attention for incorporating into polymeric materials for short wavelength micro-lithography.³

On the other hand, monomers that expand or do not shrink during polymerization are important in material science.^{4,5} Cyclic carbonates undergo cationic and anionic ring-opening polymerizations with volume expansion, which can be accounted for by the different strengths of intermolecular interactions of the monomers and polymers.⁴ Cyclic carbonates linked to aliphatic cyclic moieties especially exhibit large volume expansion on polymerization; e.g., a six-membered cyclic carbonate having a norbornene moiety undergoes volume expansion as large as 8.2% during anionic polymerization.⁶ In addition, sulfur-containing polymers are gaining importance due to their excellent optical and thermal properties.⁷ In the course of studying ring-opening polymerizations of cyclic carbonates, we have designed a sulfur analogue of cyclic carbonate, i.e., cyclic

Scheme 1



monothiocarbonate. We have reported that the anionic ring-opening polymerization of a six-membered cyclic monothiocarbonate⁸ proceeds via selective ring-opening with C–S bond cleavage. We have also reported the controlled cationic ring-opening polymerization of a six-membered cyclic monothiocarbonate⁹ and the cationic ring-opening polymerization of a five-membered cyclic monothiocarbonate¹⁰ with an ester group, which has unique polymerization behavior presumably due to the neighboring group participation at the propagating polymer end.

This article presents the synthesis and cationic ring-opening polymerization of a novel five-membered cyclic monothiocarbonate with an adamantane moiety, i.e., 4,6-dioxatetracyclo[6.3.1.1.^{3,10}3.7]tridecane-5-thione (**1**). Monomer **1** may undergo ring-opening in two directions, which are described as scissions A and B in Scheme 1; however, it will be revealed that **1** undergoes cationic polymerization with selective ring-opening, maybe due to the difference in the stability of the carbenium ion produced. Further, the thermal behavior and the volume change during the polymerization of the obtained polymer are described.

[†] Yamagata University.

[‡] Kyoto University.

[§] Toppan Printing Co., Ltd.

[‡] Present address: Department of Materials Chemistry and Engineering, College of Engineering, Nihon University, Tamuramachi, Koriyama, Fukushima 963-8642, Japan.

* To whom all correspondence should be addressed: phone and Fax +81-238-26-3090; e-mail tendo@yz.yamagata-u.ac.jp.

Experimental Section

Materials. 1,2-Adamantanediol (tricyclo[3.3.1.1^{3,7}]decane-1,2-diol) was prepared according to the reported method.^{11,12} Thiophosgene (Tokyo Kasei Kogyo Co., Inc., 95%) and triethylxonium tetrafluoroborate (Tokyo Kasei Kogyo Co., Inc., 15% in dichloromethane) were commercially available and used as received. Triethylamine (TEA) (Tokyo Kasei Kogyo Co., Inc., >99%), pyridine (Kanto Chemical Co., Inc., >99.5%), boron trifluoride etherate (BF₃OEt₂) (Kanto Chemical Co., Inc., 95%), methyl trifluoromethanesulfonate (TfOMe) (Kanto Chemical Co., Inc., 97%), and dichloromethane were distilled over CaH₂ before use. Tetrahydrofuran (THF) was distilled from sodium. Trifluoromethanesulfonic acid (TfOH) (Tokyo Kasei Kogyo Co., Inc., 98%) was distilled just before use. Methyl trifluoromethanesulfonate (TfOMe), triethylamine, pyridine, and dichloromethane were distilled over CaH₂ before use. Other reagents were used as received.

Measurements. ¹H and ¹³C NMR spectra were recorded on a Varian INOVA-500 spectrometer in deuterated chloroform (CDCl₃) at ambient temperature. IR spectra were measured on a Horiba FT-210 spectrometer. Number-average (*M_n*) and weight-average (*M_w*) molecular weights were determined by size-exclusion chromatography (SEC) using a Tosoh DP-8020 pump, a Viscotek TDA MODEL-300 refractive index (RI) detector, and polystyrene gel columns (Tosoh TSK gels G2500H_{XL}, G3000H_{XL}, G4000H_{XL}, and GMH_{XL}, whose limitations of size exclusion are 2 × 10⁴, 6 × 10⁴, 4 × 10⁵, and 4 × 10⁸, respectively) eluted with THF at a flow rate of 1 mL/min at 30 °C using a calibration curve of polystyrene standards. Thermogravimetric analysis (TGA) was carried out using an SII TG/DTA-220 instrument at a heating rate of 10 °C/min under nitrogen. The degraded products of the polymer were analyzed by a Frontier Lab PY-2010D pyrolyzer, a Hewlett-Packard HP-5MS capillary column, and a Hewlett-Packard HP5973MSD mass spectrometer. Differential scanning calorimetric (DSC) measurement was carried out using an SII DSC-220 instrument at a heating rate of 20 °C/min under nitrogen. Densities of the monomer and polymer were measured by the density gradient tube method at 25 °C with a Shibayama Scientific Co. Ltd. model A instrument.¹³

4,6-Dioxatetracyclo[6.3.1.1^{3,10}.0^{3,7}]tridecane-5-thione (1). Under a dry nitrogen atmosphere, 1,2-adamantanediol (3.36 g, 20.0 mmol) and pyridine (3.23 mL, 40.0 mmol) dissolved in dry THF (70 mL) and thiophosgene (1.53 mL, 20.0 mmol) dissolved in dry THF (70 mL) were added dropwise to dry THF (60 mL) at the same period at 50 °C. After the reaction mixture was stirred at 50 °C for 12 h, the reaction mixture was then filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography with a mixed solvent of ethyl acetate/hexane (volume ratio 1/1) as the eluent. Finally, the product was recrystallized from ethyl acetate/hexane to afford **1** as colorless crystals in 39.2% yield (1.65 g). The melting point could not be observed before decomposition. Temperature at 10% weight loss, 196 °C. ¹H NMR (500 MHz): δ 4.37 (d, *J* = 3.0 Hz, 1H, >CH–O–), 2.66 (d, *J* = 3.0 Hz, 1H, >CH–CH), 2.36 (s, 1H, adamantyl CH), 2.27–2.08 (m, 3H, adamantyl CH + CH₂), 1.88–1.99 (m, 4H, adamantyl CH₂), 1.63–1.78 (m, 4H, adamantyl CH₂). ¹³C NMR (125 MHz): δ 193.3 (–O–C(=S)–O–), 88.6 (>CH–O–), 85.9 (quaternary carbon), 39.1 (adamantyl carbon), 36.8 (adamantyl carbon), 35.6 (adamantyl carbon), 35.5 (adamantyl carbon), 31.5 (adamantyl carbon), 31.0 (adamantyl carbon), 29.1 (adamantyl carbon), 29.0 (adamantyl carbon). IR (NaCl, cm^{–1}): 1273 (>C=S). Anal. Calcd for C₁₁H₁₄O₂S: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.64; H, 6.75; S, 15.43.

Cationic Polymerization. A typical procedure is as follows: All glass vessels were heated in vacuo before use, filled with dry nitrogen, and handled in a dry nitrogen stream. BF₃·OEt₂ (2.84 mg, 0.020 mmol) was added to a solution of **1** (0.210 g, 1.00 mmol) in CH₂Cl₂ (1.0 mL), and the tube was evacuated and sealed off. After the reaction mixture was stirred at 30 °C for 24 h, a few drops of triethylamine were added to the reaction mixture to quench the polymerization. The polymerization mixture was evaporated under vacuum and diluted

Table 1. Cationic Ring-Opening Polymerization of **1^a**

run	initiator	temp (°C)	conv ^b (%)	<i>M_n</i> ^c	<i>M_w</i> / <i>M_n</i> ^c
1	TfOH	0	45	1600	1.60
2	TfOH	30	>99	3600	1.49
3	TfOMe	0	44	2100	1.46
4	TfOMe	30	95	3600	1.48
5	Et ₃ OBF ₄	0	28	1100	1.58
6	Et ₃ OBF ₄	30	45	2800	1.81
7	BF ₃ OEt ₂	0	trace		
8	BF ₃ OEt ₂	30	74	10 600	1.44

^a Solvent, CH₂Cl₂; monomer concentration, 1.0 mol/L; reaction time, 24 h; initiator concentration, 2 mol %. ^b Determined by comparing the integrated values of the ¹H NMR signal of the residual monomer at 4.67 ppm with those of the adamantyl protons of the monomer and polymer around 1.2–2.8 ppm. It is considered that the polymer yield is equal to the monomer conversion, because no low molecular weight compound other than the monomer was detected by SEC and NMR spectrum of the polymerization mixture. ^c Estimated from SEC eluted with THF based on polystyrene standards.

with 5 mL of CH₂Cl₂. The monomer conversion was determined by ¹H NMR spectroscopy. The mixture was poured into 200 mL of methanol to isolate the polymer. ¹H NMR (500 MHz): δ 5.7–5.5 and 5.3–5.1 (m, 1H, >CH–O–), 2.8–1.2 (m, 13H, other adamantyl protons). ¹³C NMR (125 MHz): δ 167.9 (–S–C(=O)–O–), 79.3–78.8 and 77.6–76.9 (m, >CH–O–), 52.3–51.81 (quaternary carbon), 41.4 (adamantyl carbon), 36.4 (adamantyl carbon), 36.1 (adamantyl carbon), 35.4 (adamantyl carbon), 30.6 (adamantyl carbon), 28.9 (adamantyl carbon), 28.7 (adamantyl carbon), 28.6 (adamantyl carbon). IR (NaCl, cm^{–1}): 1712 (>C=O). Anal. Calcd for C₁₁H₁₄O₂S: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.61; H, 6.68; S, 15.31.

Molecular Orbital Calculation. All calculations were done on an Apple Power Macintosh G4 using the Mac GAMESS ab initio program.¹⁴ Geometries of molecules were optimized by the 3-21G basis set.

Results and Discussion

The novel cyclic monothiocarbonate bearing adamantane moiety **1** was synthesized by the reaction of 1,2-adamantanediol with thiophosgene in the presence of pyridine in THF. 1,2-Adamantanediol was prepared from 1-adamantanol in five steps according to a reported method.^{11,12}

The cationic ring-opening polymerization of **1** was carried out using TfOH, TfOMe, Et₃OBF₄, or H₂O/BF₃·OEt₂ as the initiator, summarized in Table 1. Polymerization of **1** proceeded in all cases in Table 1 except run 7. It is considered that the polymer yields are equal to the monomer conversion, because no low molecular weight compound other than the monomer was detected by SEC (Figure 1) and NMR spectrum of the polymerization mixture. The molecular weight distributions of the polymers were somewhat broad (1.44–1.81). BF₃·OEt₂ afforded the polymers with the *M_n*'s higher than TfOMe and TfOH did, presumably due to the low initiator efficiency. At 0 °C with BF₃·OEt₂ (run 7 in Table 1), no polymerization of **1** took place, supporting this assumption. In the polymerization with BF₃·OEt₂, the initiating species should be H⁺ formed from a trace amount of H₂O contaminated in the polymerization mixture. The difference in initiator efficiency between TfOMe and TfOH was unclear. Et₃OBF₄ afforded the polymer with the *M_n* larger than TfOH and TfOMe did under the conditions achieving the same monomer conversion (44–45%, runs 1, 3, and 6). Decreasing the polymerization temperature resulted in decrease of the monomer conversion and *M_n* in every case.

Figure 2 shows the time–conversion (A) and the relationship between *M_n*, *M_w*/*M_n*, and conversion (B) in

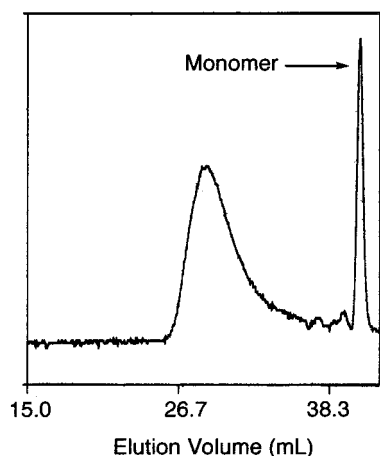


Figure 1. SEC elution curve of the polymerization mixture of **1** (run 8, Table 1): solvent, CH_2Cl_2 ; monomer concentration, 1.0 mol/L; initiator, 2 mol % of BF_3OEt_2 .

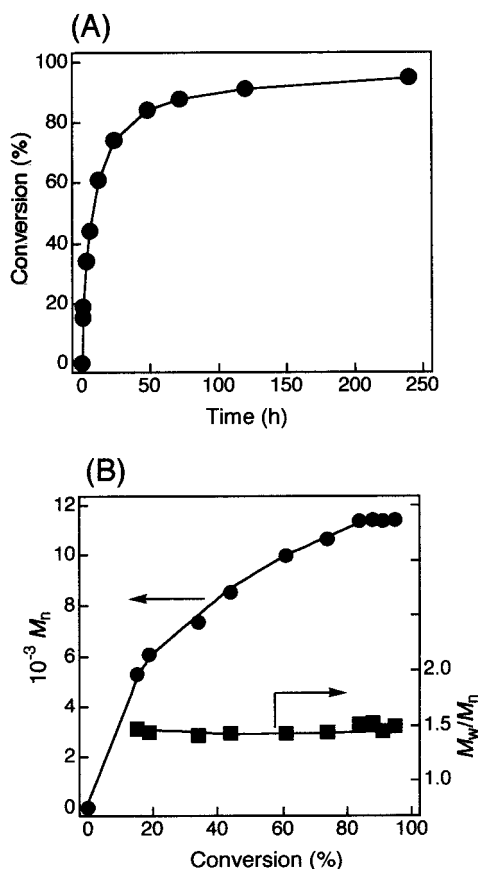


Figure 2. (A) Relationship between the time and conversion. (B) Relationship between the M_n , M_w/M_n , and conversion: solvent, CH_2Cl_2 ; monomer concentration, 1.0 mol/L; initiator, 2 mol % of BF_3OEt_2 .

the polymerization catalyzed with 2 mol % of BF_3OEt_2 in CH_2Cl_2 (monomer concentration 1.0 mol/L) at 30 °C. The relationship between the M_n and conversion was not linear. The monomer **1** was not consumed quantitatively within 240 h. The propagation rate of this polymerization is considered to be relatively slow. The polymerization may be accompanied by backbiting and/or transesterification as is often observed in cationic ring-opening polymerization.¹⁵

The polymer was isolated by precipitation with methanol and was soluble in common organic solvents such as THF, chloroform, and dichloromethane. Figure 3

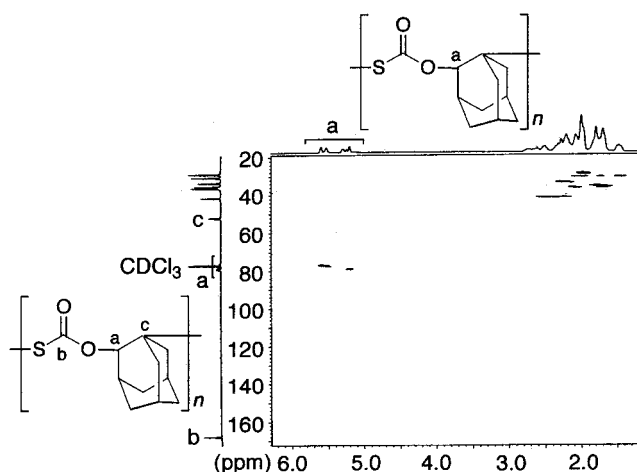


Figure 3. ^1H (top), ^{13}C (left) NMR, and ^1H – ^{13}C COSY spectra of **P1** measured in CDCl_3 . The sample was obtained by run 8 in Table 1.

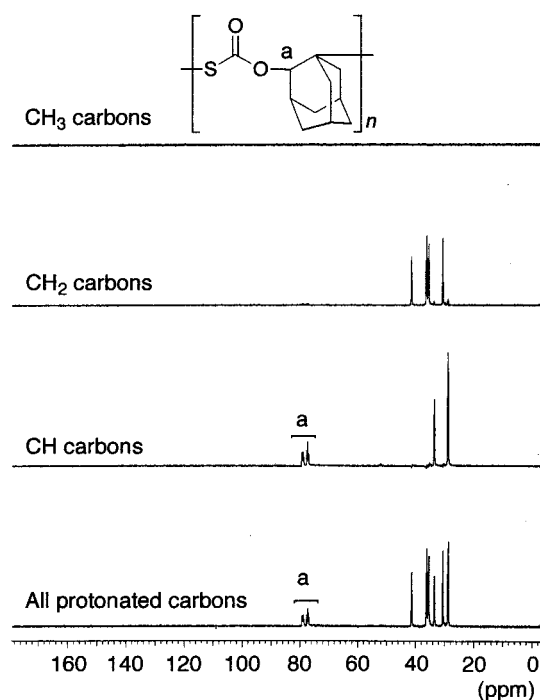
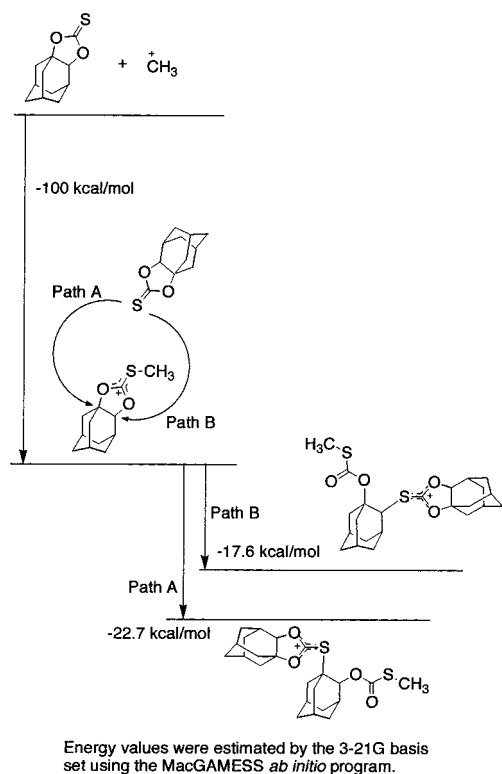


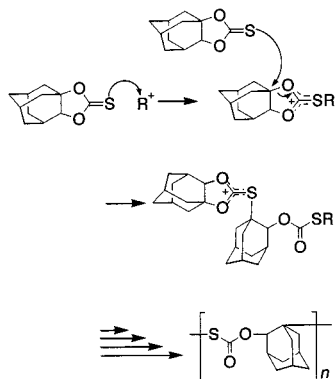
Figure 4. ^{13}C NMR-DEPT spectrum of **P1** in CDCl_3 . The sample was obtained by run 8 in Table 1.

shows the ^1H , ^{13}C NMR, and ^1H – ^{13}C COSY (correlated spectroscopy) spectra of polymer **P1** obtained by the polymerization in run 8 in Table 1. Figure 4 shows the DEPT (distortionless enhancement by polarization transfer) spectrum of **P1**. The ^{13}C NMR spectrum of **P1** showed a carbonyl carbon signal at 167.9 ppm, and the IR spectrum of **P1** showed a $\text{C}=\text{O}$ absorption peak at 1712 cm^{-1} , clearly indicating the progress of cationic ring-opening polymerization by isomerization of the thiocarbonyl group into a carbonyl group. Two ring-opening directions are possible in the polymerization as shown in Scheme 1. However, only one quaternary carbon signal was observed around 52 ppm. In addition, tertiary carbon signals adjacent to $-\text{O}(\text{C}=\text{O})\text{S}-$ were observed at around 78 ppm, and the corresponding methine proton signals were observed around 5.2 ppm. These results indicate that the tertiary carbon is connected to the ether oxygen of $-\text{O}(\text{C}=\text{O})\text{S}-$, and a quaternary carbon is connected to the sulfur atom,

Scheme 2



Scheme 3



supporting the selective ring-opening direction. The structures of the obtained polymers generated from the initiators other than BF_3OEt_2 were also elucidated by NMR and IR spectroscopies. It was confirmed that all the polymers had the same structure formed by selective ring-opening, scission A in Scheme 1.

For determining the ring-opening direction, molecular orbital calculations were carried out using the *ab initio* method. Scheme 2 shows the energy differences between methyl cation + monomer and monomeric carbenium ion formed by electrophilic attack of methyl cation to the thiocarbonyl sulfur of the monomer and between two different dimeric carbenium ions formed by electrophilic attack at quaternary (path A) and tertiary (path B) carbon atoms of the monomer. We confirmed that the dimeric carbenium ion formed by path A was more stable (5.1 kcal/mol) compared with another one formed by path B. These calculations support polymer structure mentioned above. This selectivity may be attributed to the bridgehead tertiary carbenium ion (corresponding to path A) more stable than a secondary one (path B). We present Scheme 3 as the plausible mechanism of ring-opening polymerization of **1**.

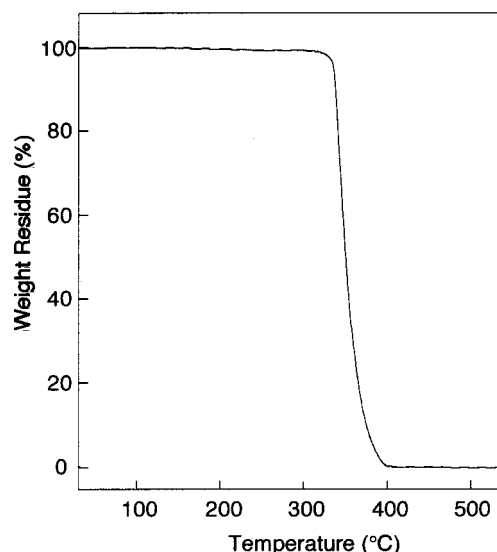


Figure 5. TGA curve of **P1** measured under nitrogen at a heating rate of 10 °C/min. The sample was obtained by run 8 in Table 1.

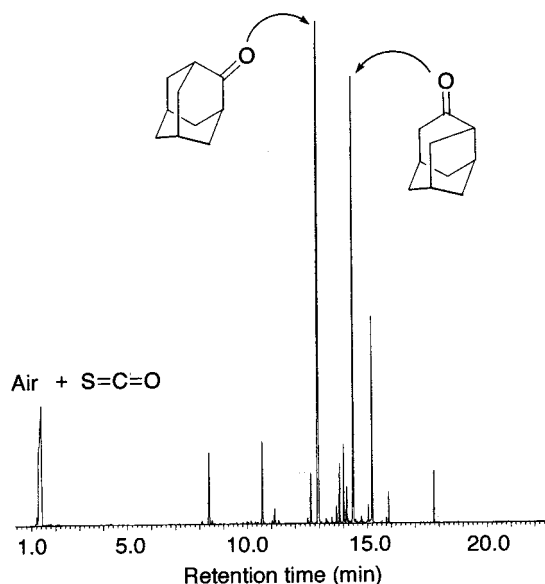


Figure 6. Gas chromatogram of decomposition products of **P1**. The sample was obtained by run 8 in Table 1. Pyrolysis conditions: temperature, 400 °C; time, 5 s; atmosphere, He. Chromatographic heating program: start, 50 °C for 5 min; heating rate 1, 10 °C/min to 120 °C; heating rate 2, 20 °C/min to 280 °C; end, 280 °C for 15 min.

The thermal behavior of **P1** was evaluated by TGA and DSC under nitrogen. Figure 5 depicts the TGA curve of **P1**. **P1** lost its 5% weight at 338 °C and then decomposed rapidly. It completely decomposed at 405 °C. The decomposed products were elucidated by gas chromatograph/mass spectrometry using an *in situ* pyrolyzer. Figure 6 shows the gas chromatogram of the products of **P1** heated at 400 °C for 5 s in helium detected by mass spectrometry. The three main peaks, whose retention times were 1.2, 12.9, and 14.4 min, can be assigned to air containing carbonyl sulfide, 2-adamantanone (tricyclo[3.3.1.1^{3,7}]decane-2-one), and 4-protoadamantanone (tricyclo[4.3.1.0^{3,8}]decane-4-one) by referring to the authentic samples. Three products are used as the starting materials of some chemical products; particularly, 4-protoadamantanone is useful as the starting material of a various 1,2-disubstituted

adamantanes¹⁶ such as 1,2-adamantanediol. No glass transition temperature was detected below the decomposition temperature (ca. 350 °C) by DSC. The high thermal stability of **P1** may be attributable to the rigid adamantane moiety and sulfur in the polymer backbone.

The densities of **P1** and **1** were 1.12 and 1.30, respectively, at 25 °C. Therefore, the polymerization of **1** proceeded with a volume expansion as large as 14%, which might be resulted from the high density of **1**.

In summary, a novel polythiocarbonate was successfully prepared by the cationic ring-opening polymerization of 4,6-dioxatetracyclo[6.3.1.1.3.¹⁰3.7]tridecane-5-thione (**1**) with selective ring-opening direction. The polymer had good solubility and high thermal stability. The monomer expanded in volume during the polymerization.

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