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Cationic Ring-Opening Polymerization Of Five Membered Cyclic Dithiocarbonate Having Tertiary Amine Moiety

Suvratha Krishnamurthy[a], Yoshiaki Yoshida[a,b] and Takeshi Endo*[a]

In this work a facile route for the cationic ring-opening polymerization (**CROP**) of cylic dithiocarbonate derived from *N,N*-dibenzyl glycidylamine (**DBGA**) and carbon disulfide. The cyclic dithiocarbonate monomer, 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (**1**) can be obtained economically and easily in three steps from commercially available *N,N*-dibenzylamine. The cationic polymerization of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (**1**) was achieved by methyltriflate or ethyltriflate as an initiator. The polymerization proceeded smoothly in chlorobenzene with high monomer conversion (>90%). The polymers exibited high molar mass with narrow dispersity. The structure of the polymers were confirmed by NMR and IR analysis. Investigation of the mechanism of this polymerization by NMR studies on stoichiometric reaction of **1** with MeOTf, indicate the higher reactivity of sulfur than nitrogen for the initiator (Methyl cation, **S>N**). A strong possibility of formation of a transient aziridinium ion by neighboring group participation of the tertiary amine moiety is also seen. Finally evidence from DFT calculation also clarify the presence of more negative charge on the sulfur atom of the thiocarbonyl group compared to nitrogen.
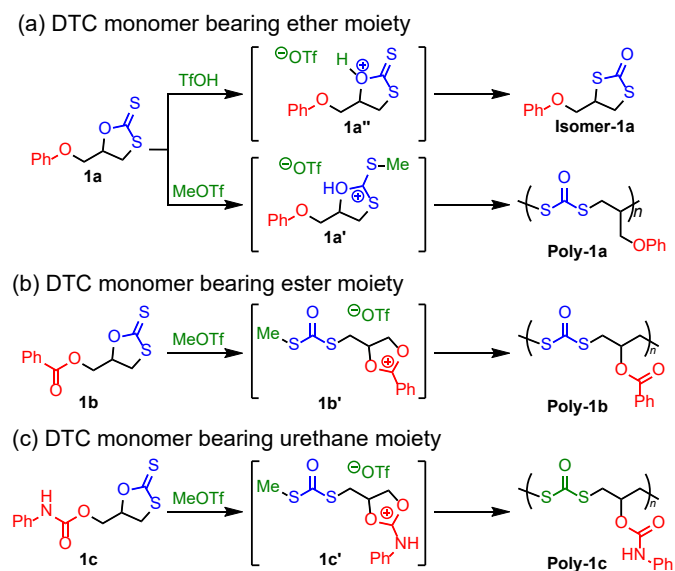
Introduction

Sulfur polymers like polysulfides, polythiourethanes, polydithio-carbonates and others are versatile polymers. Mechanical, electrical and optical properties are enhanced due to the presence of sulfur in the polymer chain.[1] Sulfur polymers often exhibit high refractive index, hence are often used to make prisms, lenses and optical materials.[2] In spite of their uses sulfur polymers are obtained by methods which involve toxic phosgene or chloroformates along with di-thiol monomers which tend to have bad odour. Hence alternative methods to obtain sulfur polymers is highly desirable.

Earlier we reported cyclic dithiocarbonate monomers can be selectively obtained by reaction of epoxide with carbon disulfide catalysed by lithium bromide.[3] Unlike cyclic carbonates, cyclic dithiocarbonates are quite reactive and polymerize at ambient temperature. This paved the way to obtain various cyclic dithiocarbonate monomers used for synthesis of sulfur polymers.[4-5]

In 1997, we found that initiators like methyltriflate (MeOTf) or ethyltriflates (EtOTf), can lead to cationic ring-opening polymerization of 5-phenoxymethyl-1,3-oxathiolane-2-thione (**1a**) [Scheme 1. (a)].[6] The initiation is triggered by attack of the exocyclic sulfur on the methyl cation to form cationic intermediate **1a'** [Scheme 1. (a)].[7] Though initiators like MeOTf led to the polymerization of **1a**, other initiators such as Brönsted/Lewis acids led to isomarization of **1a** to 5-phenoxymethyl-1,3-dithiolane-2-one (**Isomer-1a**) [Scheme 1. (a)] with trace amount of polymerization (ca. 2%).[6,7]

Previous work

(a) DTC monomer bearing ether moiety

(b) DTC monomer bearing ester moiety

(c) DTC monomer bearing urethane moiety

This work

Scheme 1. Variety of ring-opening polymerization of 5-membered cyclic dithiocarbonate (DTC) derivatives.

a. Molecular Engineering Institute, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu-shi, Fukuoka, 804-8550, Japan.

b. Faculty of Engineering, Department of Materials Science, Kyushu Institute of Technology, 1-1, Sensui-cho, Tobata-ku, Kitakyushu-shi 804-8550, Japan.

c. Address here.

† Correspondence to: T. Endo (E - mail: endo.takeshi328@mail.kyutech.jp)
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Later an ester derived monomer, 5-benzoyloxymethyl-1,3-oxathiolane-2-thione (**1b**) also underwent cationic ring-opening polymerization. For **1b** initiation begins by attack of exocylic thiocarbonyl with the methyl cation rather than the carbonyl group of ester [Scheme 1. (**b**)]. However, the ester functional group in **1b** had a beneficial neighboring group participation (**NGP**) which leads to intermediate **1b'** confirmed by NMR.[8] Similarly, a urethane derived monomer 5-[(Phenylamino)-carbonylmeth-oxy]-1,3-oxathiolane-2-thione (**1c**) also proceeds through an intermediate **1c'**, which is stabilized by **NGP**.[9] Monomers like **1a** that are unable to stabilize the carbenium ion by **NGP** polymerize to include two carbon subunit into the polymer main chain. However, monomers like **1b** and **1c** which can stabilize the carbenium ion by **NGP** leads to polymer with three carbon subunits in the main chain along with a shift in the heteroatom.   Do and coworkers have also reported ring-opening polymerization of cyclic dithiocarbonate with a **NGP** through thiirane ring formation.[10]

In this present work, we report the synthesis of a new tertiary amine containing dithiocarbonate monomer, 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (**1**) which is obtained from dibenzylamine (**DBA**). This new monomer, (**1**) was subjected to cationic ring-opening polymerization with methyl triflate as the cationic initiator. Since the monomer (**1**) contains two competitive atoms for the methyl cation i.e., sulfur and nitrogen, the outcome of the reaction can be two ways. If reactivity for methyl cation is higher for sulfur than nitrogen (**S>N**), this leads to initiation of the polymerization. However, a higher reactivity of nitrogen (**N>S**) leads to neutralization of the methyl cation by formation of *N*,*N*-dibenzyl-*N*-methyl-1-(2-thioxo-1,3-oxathiolan-5-yl)methanaminium triflate (**3**), which inhibits the polymerization. Based on our previous results we hypothesized reaction of **1** proceeds through intermediate 5-((dibenzylamino)methyl)-2-(methylthio)-1,3-oxasulfonium triflate (**2**), through the exocyclic sulfur rather than nitrogen with MeOTf, because the basicity of the nitrogen is reduced due to the presence of two bulky benzyl group. Here we study the polymerization behavior of **1** with the initiator methyl trifluoromethanesulfonate.

Experimental

Materials

n-hexane, tetrahydrofuran (THF), methanol, dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF) and carbon disulfide (CS$_2$) were purchased from Wako Pure Chemical Industry. Dibenzylamine, tribenzylamine, epichlorohydrin, lithium bromide (LiBr), methyl trifluoromethanesulfonate (MeOTf), ethyl trifluoromethanesulfonate (EtOTf), and trifluoromethanesulfonic acid (TfOH) were from Tokyo Chemical Industry. Anhydrous chlorobenzene was used as received from Sigma Aldrich with Sure/Seal™.

Measurements

Size exclusion chromatography (SEC) was carried out on TOSOH HLC-8220 system equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion limited molar mass); super-AW4000 (6 μm, >4 x 105), super-AW3000 (4 μm, >6 x 104) and super-AW2500 (4 μm, >2 x 103)] with refractive index and ultraviolet detectors at 40 °C. The system was operated using 10 mM LiBr in DMF as eluent at a flow rate of 0.5 mL/min. Polystyrene standards were employed for calibration. ^{1}H and ^{13}C NMR (nuclear magnetic resonance) spectroscopy was performed with a JEOL ECS-400 NMR spectrometer operating at 400 MHz with tetramethyl silane (TMS) as an internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Fisher Scientific Nicolet iS10 spectrometer by ATR method over a range from 650 to 4000 cm^{-1}. The X-ray crystallography (XRC) of the single crystal were collected on a Rigaku XtaLAB Synergy-R/DW system equipped with HyPix detector using Cu-Kα radiation (λ=1.54184 Å). The detail of crystal data and structure refinement is shown in supporting information. Geometry optimized structure was estimated by using density functional theory (DFT) calculation with B3LYP/6-31+G(d) method (Gaussian 16). Differential scanning calorimetry (DSC) was performed on a Seiko Instrument DSC-6200R with an aluminium pan under a 50 mL/min N$_2$ flow at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a Seiko Instrument Inc. TG-DTA 6200 with an aluminium pan under a 200 mL/min N$_2$ flow at a heating rate of 10 °C/min.

Synthetic procedures

Synthesis of the DBGA

Epichlorohydrin (2.0 mL, 25.5 mmol) was added to a solution of **DBA** (2.0 g, 18.67 mmol) in MeOH (10 mL) at room temperature and stirred. After 5 h, to this solution aq. NaOH (2.0 g in 10 mL) was added dropwise at 0 °C, the heterogeneous solution was then warmed to room temperature and stirred overnight. The resulting solution was then diluted and extracted with EtOAc, dried (MgSO$_4$), filtered, concentrated and then purified by SiO$_2$ (Hexane:EtOAc 95:5 to 90:10, v/v) to obtain **DBGA**[11] as an oil.(2.27 g, 48 %); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.36 (d, *J* = 7.3 Hz, 4H), 7.28 (dd, *J* = 10.2, 4.6 Hz, 4H), 7.19 (dd, *J* = 8.3, 6.2 Hz, 2H), 3.65 (dd, *J* = 97.6, 13.7 Hz, 4H), 3.03 (td, *J* = 6.4, 3.7 Hz, 1H), 2.74 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.65-2.56 (m, 1H), 2.37 (ddd, *J* = 9.4, 7.8, 4.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 139.2, 128.6, 128.1, 126.8, 58.7, 55.6, 50.8, 44.5.

Synthesis of the 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1)

To a solution of **DBGA** (5 g, 23.0 mmol) in THF (100 mL) at room temperature was added LiBr (10 mol %) to this solution carbon disulfide (2.8 mL, 46 mmol) dissolved in THF (25 mL) was added dropwise over a period of 30 min. The resulting yellow solution was stirred at room temperature, after 24 h the solution was concentrated in vacuum and dissolved in dichloromethane and washed with brine, dried (MgSO$_4$), filtered and evaporated. The crude product was purified by silica gel column chromatography eluting with DCM/MeOH (100 : 0 to 98 : 2) to obtain **1** as a yellow

solid. (6.36 g, 84%); melting point 69.34 °C; IR γ (C=S) 1185 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.96-6.73 (m, 10H), 5.04-4.93 (m, 1H), 4.05-3.88 (m, 4H), 3.75-3.58 (m, 2H), 3.43-3.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 212.3, 138.7, 129.2, 128.7, 127.6, 89.5, 59.9, 54.7, 37.8; HR-FAB-MS [C$_{18}$H$_{20}$N$_1$O$_1$S$_2$]$^+$ ([M+H]$^+$): calculated = 330.0986, found 330.0984.
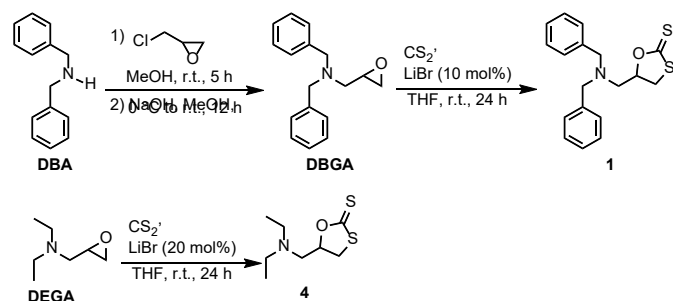
Scheme 2. Synthesis of the monomeric cyclic dithiocarbonate bearing a tertiary amine moiety (**monomer 1**).

Synthesis of the monomer 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)

To a solution of *N,N*-diethylglycidyl amine **DEGA**[12] (5.0 g, 38.7 mmol) in THF (25 mL) at room temperature was added LiBr (20.0 mol %) to this solution carbon disulfide (2.80 mL, 47.0 mmol) was added dropwise over a period of 5 min. The resulting yellow solution was stirred at room temperature, after 24 h the solution was concentrated in vacuum and dissolved in dichloromethane and washed with brine, dried (MgSO$_4$), filtered and evaporated. The crude product was purified by SiO$_2$ eluting with DCM/MeOH (100:0 to 99:1) to obtain **4** as a yellow oil. (4.30 g, 54 %); IR γ (C=S) 1183 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.18 (m, 1H), 3.65 (d, *J* = 7.4 Hz, 2H), 2.94-2.81 (m, 2H), 2.70-2.53 (m, 4H), 1.03 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 212.40, 90.16, 77.55, 77.23, 76.91, 54.26, 48.02, 37.80, 12.09; HR-FAB-MS [C$_8$H$_{16}$N$_1$O$_1$S$_2$]$^+$ ([M+H]$^+$): calculated = 206.0673, found 206.0672.

Cationic Polymerization of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) to Poly-1

To a solution of **1** (0.658 g, 2.0 mmol) in chlorobenzene (1.0 mL) was added MeOTf (1 mol%, 1 µL) and stirred at 80 °C. After 6h the homogeneous reaction mixture was allowed to cool down to room temperature, then quenched with triethylamine (0.2 mL) and to this solution was added THF (1.0 mL). This solution was added to n-hexane (200 mL) and the white powder was collected by filtration and dried under vacuum. Yield 0.58 g (88%). IR γ (C=O) 1639 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.10 ([Ph], m, 10H), 3.94 (0.2 H), 3.70-3.41 (5.2 H), 3.29 (2H), 3.08 (2H), 2.95 (1H), 2.61 (0.4 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.81, 188.23, 138.62, 128.94, 128.22, 127.12, 58.53, 57.42, 56.57, 53.15, 44.74, 32.58, 30.67. Glass transition temperature, T_g = 60.15 °C. 10% weight loss temperature, T_{d10} = 262 °C.

Cationic Polymerization 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)

To a solution of 4 (0.205 g, 1.0 mmol) in chlorobenzene (0.5 mL) was added MeOTf (2 mol%, 2 µL) at 80 °C. After 6h the polymerization solution was analysed by GPC, ^{1}H NMR and ^{13}C NMR.

The stoichiometric reaction of 1 with Methyltriflate (MeOTf).

To a solution of **1** (90 mg, 0.27 mmol) in CDCl$_3$ (0.6 mL) at r.t. was added MeOTf (1.2 eq, 36µL, 0.33 mmol) under argon gas. The solution was stirred for 5 minutes, and then the reaction mixture was characterized by NMR. ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.0, 131.2, 131.0, 130.8, 130.5, 130.0, 129.8, 129.6, 128.9, 128.7, 128.6, 128.3, 61.7, 53.2, 49.7, 43.0, 26.0, 13.4.

The stoichiometric reaction of Bn$_3$N with Methyltriflate (MeOTf).

To a solution of Bn$_3$N (27.0 mg, 0.10 mmol) in CDCl$_3$ (0.6 mL) at 60 °C was added MeOTf (1.0 eq, 11µL, 0.10 mmol). The solution stirred for 5 min and the reaction mixture was characterized by NMR. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53-7.34 ([Ph], m, 15H) 4.72 ([Ph-CH$_2$], s, 6H), 2.73 ([Me], s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 133.30, 130.9, 129.4, 126.5, 66.1, 44.2.

Results and discussion

1. Synthesis of the monomeric cyclic dithiocarbonate 1 and 4

The synthesis of monomer **1** and **4** was accomplished from *N,N*-dibenzylamine and *N,N*-diethylglycidylamine (**DEGA**) respectively (**Scheme 2**). *N,N*-dibenzylamine (**DBA**) was treated with epichlorohydrin followed by base to obtain **DBGA**.[11] The **DBGA** was treated with carbon disulfide in the presence of catalytic LiBr to obtain **1** as a light-yellow solid. Similarly treating **DEGA** with carbon disulfide with catalytic LiBr gave **4**. The structure of compound **1** and **4** was ascertained by FTIR (**Figs. S21 and S23**), ^{1}H NMR (**Figs. S3 and S4**) and ^{13}C NMR (**Figs. S5 and S6**). Further the high-resolution FAB mass analysis confirms the structure of **1** and **4** (**Figs. S19 and S20**). Finally the structure of **1** was unambiguously conformed by XRC analysis (**Fig 5**).

2. Study of cationic ring-opening polymerization of 1 and 4

The cationic polymerization of **1** was performed in chlorobenzene with MeOTf as the initiator (**Scheme 3**), the results of which are summarized in **Table 1**. With 5 mol% of MeOTf at ambient temperature **Poly-1** was isolated in 75 % yield with M_n = 8300 (Entry 1). To improve the molar mass, a decrease in catalyst loading (2 mol%) at ambient temperature was tried, which however led to a lower yield (Entry 2). An increase in the temperature led to complete consumption of the monomer at 60 °C with 2 mol% catalyst (Entry 5). In order to obtain the polymer with a higher molar mass the amount of initiator was decreased. However, the decrease in catalyst to 1 mol% at 60 °C decreased the yield (Entry 6). Varying the reaction time had no improvement of the yield of the polymerization (Entry 6, 7 and 8). Reaction time beyond 6h led to the decrease in the M_n value possibly due to backbiting reaction (Entry 8). Finally, a further increase in the temperature with MeOTf (1 mol%) was tried, and the conversion of **1** was 91% at 70 °C

(Entry 9) and 97% at 80 °C (Entry 10). The use of other cationic initiator like EtOTf was tried and similar results were obtained (Entry 11). However, the use of other initiator like Brönsted acid (TfOH) led to the immediate neutralization of the initiator and Poly-1 were not formed (Entry 12). The polymerization of **1** also proceeds under solvent free condition, but with lower conversion (Entry 13). Furthermore, the polymerization of 1 was performed at different concentration to investigate the concentration effect. The yield and molar mass of Poly-1 decreased in a low concentration (Entry 14), whereas the polymerization of **1** at higher concentration exhibited most desirable results of conversion, yield, M_n and M_w/M_n values (Entry 15). Cationic polymerization was also feasible in solvents like 1,4-dioxane and butyl acetate (Entry 16 and 17), but lower conversion and yield was observed in both cases. This indicates aromatic solvents are ideal for this polymerization system. The M_n values of the polymer determined by GPC based on polystyrene calibration was in good agreement with the M_n values determined by NMR based on integral value of benzyl protons and methyl protons (S-**Me**) at initiating end. Since, polymerization of 1 at room temperature (Table 1. entry 1) showed low dispersity. The evolution of molecular weight against conversion was measured for this reaction at ambient temperature and was found to reach 80% conversion after 2h with no change in the molar mass (**Fig. S26**). The living nature of the polymerization was also examined at room temperature by further monomer addition after 80% conversion. The molecular weight remains constant with no change in the molar mass (**Fig. S27**). We speculate the addition of second batch of monomer results in the neutralization of the active propagating unit by the tertiary amine on the monomer.

The cationic polymerization of **4** was performed in chlorobenzene with MeOTf. After 6 h the polymerization solution was analyzed by ^1H ^{13}C, and DEPT-135 NMR which showed the absence of polymer. However, there was an appreciable amount of thiirane and the isomerized product along with the unreacted dithiorcarbonate (4) (**Figs. S10, S11, and S12**).

3. Structural analysis of Poly-1

The characterization of polymer structure, **Poly-1** (Table 1. Entry 10) was accomplished by ^1H NMR, ^{13}C NMR and FTIR measurements. The polymer chain contains a major three carbon dithiocarbonate unit (85%) along with a minor amount of two carbon dithiocarbonate unit (15%). The cationic intermediate is stabilized by the aziridine ring formation which results in formation of the copolymer. Previous reports by Do and co-workers also indicate the stabilization of the cationic intermediate by neighbouring sulfur atom by thiirane formation which results in formation of copolymers of two and three carbon subunits.[10c] Its interesting to note that, when **NGP** leads to formation of larger five membered cyclic intermediates during chain propagation (Scheme 1. 1b' and 1c') polymerization mainly leads to homopolymer (Scheme 1. Poly-1b and Poly-1c). Whereas, when **NGP** results in smaller three membered cyclic intermediates aziridinium ion (**2**, Scheme 1) or thiirane[10c] during chain propagation, leads to copolymer with major and minor unit.

The ^1H NMR spectra of monomer **1** and **Poly-1** is illustrated in **Fig. 1**. The full-scale ^1H, ^{13}C, and DEPT-135 NMR spectra are also illustrated in **Fig. S7, S8, and S9**. The aromatic proton of the phenyl ring appears between 7.2 to 7.4 ppm in the spectra of monomer and polymer. The benzyl protons of monomer appeared as a quintet peak around 3.69 ppm, whereas that of polymer appeared as a strong singlet at 3.63 ppm. The methylene protons attached to nitrogen atom of monomer appeared as a multiplet peak around 3.27 to 3.43 ppm, whereas methylene protons attached to nitrogen that of polymer was seen around 3.43 ppm as the minor unit. The methylene proton attached to the sulfur of the major dithiocarbonate unit appeared at 3.28 and 3.08 and the methylene protons attached to sulfur of the minor dithiocarbonate unit appeared at 2.61. The methine protons of the major and minor dithiocarbonate units appeared at 2.95 and 3.94 ppm, respectively.

Table 1. Cationic ring-opening polymerization of **1**.

entry	Initiator (mol%)	Solvent (M)[a]	$[1]_o/[I]_o$	Temp. (°C)	Time (h)	Conv. (%)[b]	Yield (%)[c]	M_n (calulated)[d]	M_n (SEC) (g/mol)[e]	M_n (NMR) (g/mol)[f]	M_w/M_n [e]
1	MeOTf (5)	PhCl (1)	20	r.t.	2	88	75	6940	8300	7400	1.29
2	MeOTf (2)	PhCl (1)	50	r.t.	2	35	24	16820	8200	7250	1.34
3	MeOTf (2)	PhCl (1)	50	40	2	59	39	16820	13000	11530	1.38
4	MeOTf (2)	PhCl (1)	50	50	2	79	78	16820	15800	14660	1.40
5	MeOTf (2)	PhCl (1)	50	60	2	≥99	≥99	16820	16200	16630	1.39
6	MeOTf (1)	PhCl (1)	100	60	2	40	30	33300	16000	16475	1.42
7	MeOTf (1)	PhCl (1)	100	60	6	63	42	33300	17700	19911	1.46
8	MeOTf (1)	PhCl (1)	100	60	12	65	55	33300	10000	12020	2.27
9	MeOTf (1)	PhCl (1)	100	70	6	91	85	33300	22300	22400	1.47
10	MeOTf (1)	PhCl (1)	100	80	6	97	86	33300	24000	23000	1.39
11	EtOTf (1)	PhCl (1)	100	80	6	90	87	33300	23000	21500	1.52
12	TfOH (1)	PhCl (1)	100	80	6	-	n.r.[g]	-	-	-	-
13	MeOTf (1)	Neat	100	80	6	66	62	33300	36000	33600	2.23
14	MeOTf (1)	PhCl (0.5)[h]	100	80	6	77	73	33300	13300	11532	1.99

15	MeOTf (1)	PhCl (2)	100	80	6	95	88	33300	25600	25744	1.40
16	MeOTf (1)	Dioxane[i]	100	80	6	50	40	33300	15700	14000	1.49
17	MeOTf (1)	BuOAc (2)[j]	100	80	6	76	69	33300	19947	19740	1.52

a) Molar concentration. b) Conversion determined by ^{1}H NMR. c) Determined by precipitation from n-hexane. d) Using equation Mn = (formula weight of **1**) x ([**1**]$_0$/ [I]$_0$) + (formula weights of end groups), I = initiator; e) Estimated by GPC (eluent, DMF, based on polystyrene standards). f) With respect to integral value of Ph-(**CH$_2$**)$_2$ and **CH$_3$** protons g) n.r.: no reaction; h) PhCl – Chlorobenzene, i) 1,4-dioxane; j) BuOAc - n butyl acetate
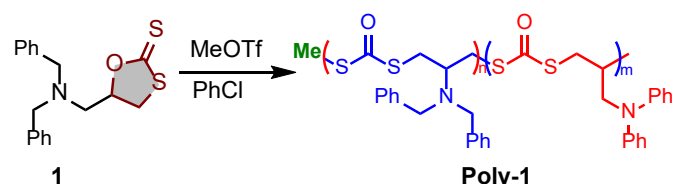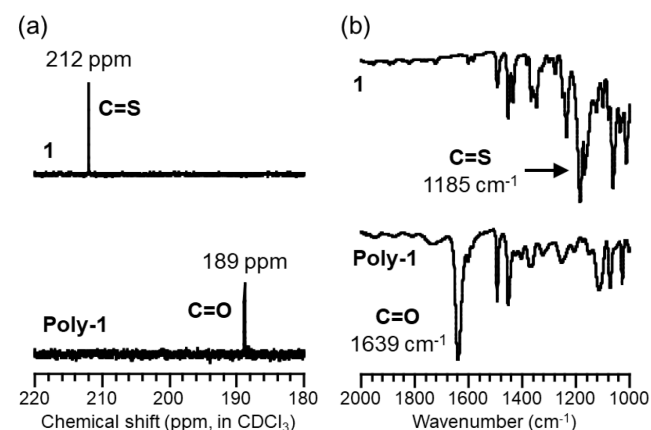

Scheme 3. Cationic ring-opening polymerization of **1** with MeOTf in PhCl to afford **Poly-1**.

To prove the ring-opening polymerization together with the isomerization of dithiocarbonate structure from S-(C=S)-O to S-(C=O)-S, we measured ^{13}C NMR and FTIR spectra of monomer and polymer (**S8, and S22**). In the ^{13}C NMR spectra, the best indication of the polymerization can be confirmed by the complete disappearance of the thiocarbonyl peak (C=S) at 212 ppm and an appearance of a single carbonyl peak (C=O) at 189 ppm (**Figs. 2a**). Further clear evidence came from the analysis of the IR spectra, the characteristic absorption of the thiocarbonyl (C=S) of the monomer **1** at 1185 cm^{-1} was completely eliminated and absorption corresponding to carbonyl (C=O) appeared at 1639 cm^{-1} (**Figs. 2b**). These results indicates that the obtained polymer had the isomerized dithiocarbonate structure in the main chain. The thermal stability of the **Poly-1** was analysed by TGA and DSC (**Figs. S24 and S25**), the polymer shows relatively high thermal stability with 10 % wight loss at 262 °C, the polymer shows glass transition temperature at 60 °C.
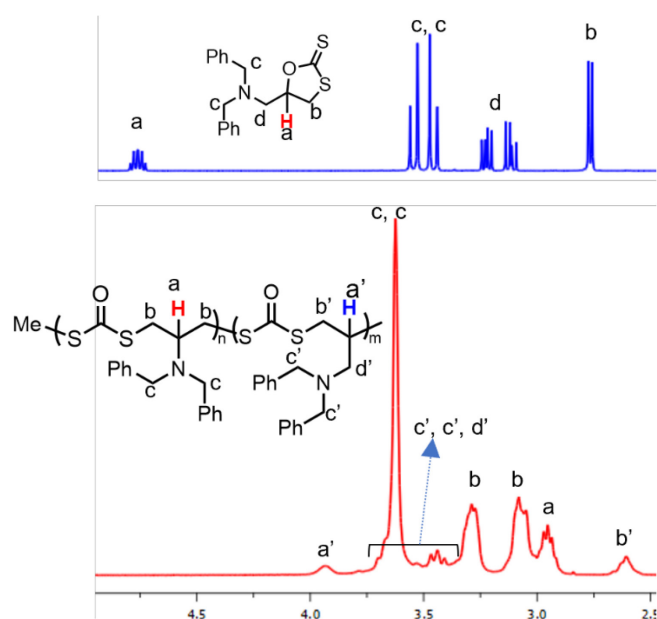
**Figure 1.** ^{1}H NMR spectra of **1** and **Poly-1** (Table 1, entry 10) observed in CDCl$_3$.

Figure 2. (a) ^{13}C NMR spectra of **1** and **Poly-1** observed in CDCl$_3$. (b) FTIR spectra of **1** and **Poly-1** measured by ATR method.

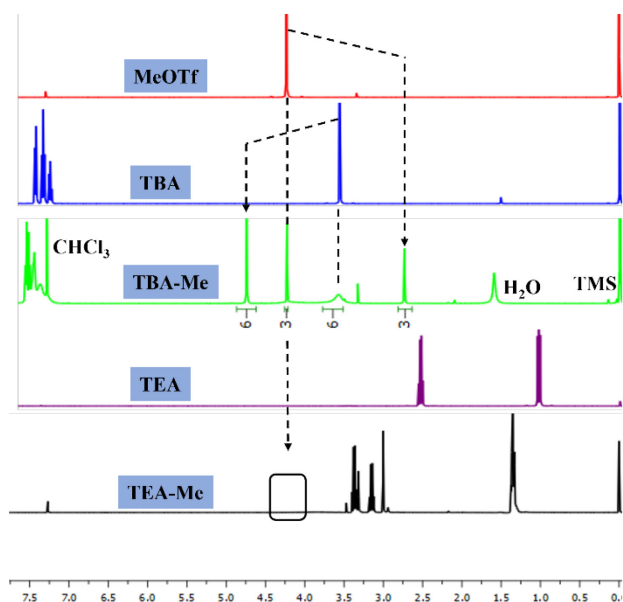### 4. Possible Mechanism of the polymerization of 1 with MeOTf

To study the mechanism of ring-opening polymerization of **1**, we carried out the reaction with MeOTf of stoichiometric amount for **1** in CDCl$_3$ (**Figs. S13 and S14**). After reaction for 5 min, ^{13}C NMR of the reaction mixture was measured (**Fig. 3**). The carbonyl peak (C=O) appeared at 189 ppm, whereas the thiocarbonyl peak (C=S) at 212 ppm disappeared completely as mentioned above. The signal of methyl carbon attached to sulfur atom (S-CH$_3$) also appeared at 23.4 ppm, indicating that the sulfur atom of the thiocarbonyl attacked the methyl group of MeOTf. Furthermore, the appearance of the new peaks suggested the formation of aziridinium salt containing the dibenzyl amine moiety according to the literature.[13] This result indicated that the generated cation might be stabilized as a dibenzyl aziridinium cation in the propagating terminal. The formation of aziridine ring through **NGP** was reported earlier for similar substrates (xanthates), confirmed through kinetic data and computational studies.[14]

We speculated that, approach of methyl cation towards the tertiary amine is hindered due to the bulky dibenzyl groups. To prove this hypothesis, we carried out a stoichiometric reaction of MeOTf with two tertiary amines tribenzylamine (**TBA**) (**Figs. S15 and S16**) and triethylamine (**TEA**) (**Figs. S17 and S18**) in CDCl$_3$ at 60 °C. The comparison ^{1}H NMR spectra of these individual reaction mixture clearly suggest tribenzyl methyl ammonium salt (**TBA-Me**) is formed to a lesser extent than triethyl methyl ammonium salt (**TEA-Me**). In the former ca. 50% of the **TBA** remains unreacted whereas **TEA** completely reacts

with the MeOTf. This is a clear indication that, ability of the amine to attack the Methyl cation is decreased in **TBA** due to the presence of bulky benzyl groups (**Fig. 4**).
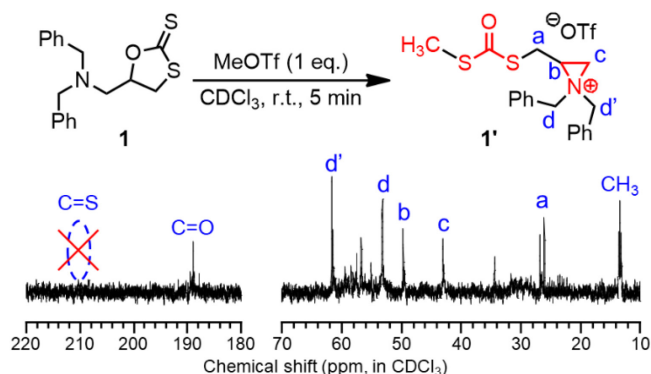
Figure 3. ^{13}C NMR spectrum of the reaction mixture with MeOTf of stoichiometric amount for **1** in CDCl$_3$.

Figure 4. ^{1}H NMR spectra of MeOTf, TBA, and the reaction mixture with MeOTf of stoichiometric amount for tribenzylamine in CDCl$_3$.

5. Polymerization of 1 in presence of external base

In order to probe the possible higher reactivity of the sulfur than nitrogen in **1** we carried out the polymerization of in presence of external base. For these two external bases i.e. tribenzylamine (**TBA**) and triethylamine (**TEA**) were tested. Polymerization of **1** with MeOTf (2 mol%) at 60 °C in presence of **TBA** (0.2 eq.) proceeds with lower conversion and yield but with no change in the molar mass of **Poly-1** (Table 2, entry 2 vs entry 1). On the other hand, **TEA** (0.2 eq.) completely inhibits the polymerization of **1** (Table 2, entry 3). Finally, we found that polymerization proceeds even with a higher amount of TBA (Table 2, entry 4). Hence the exocyclic sulfur has higher reactivity

for the methyl ion compared to the amine substituted with bulky dibenzyl group. The presence of bulkier benzyl group on the nitrogen hampers it attack on the methyl ion whereas less bulkier ethyl group on the nitrogen can easily neutralize the methyl ion.

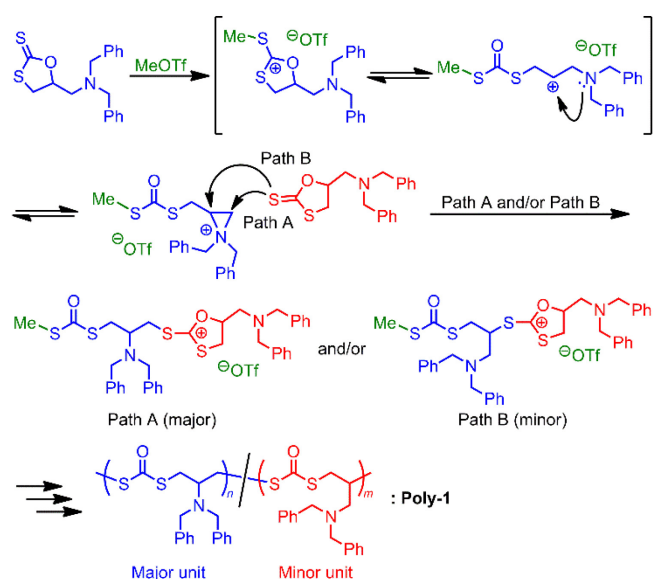**Table 2.** Cationic ring-opening polymerization of **1** with MeOTf in the presence of external base.

Entry	Base (eq.)	Conv. (%)^b	Yield (%)^c	M_n (g/mol)^d	M_w/M_n ^{d}
1	Bn$_3$N (0.2)	68	57	16657	1.43
2	Et$_3$N (0.2)	-	-	-	-
3	Bn$_3$N (1.0)	55	30	11325	1.41

6. Speculation of polymerization mechanism of 1

We also evaluated Mulliken charge of the sulfur atom of thiocarbonyl and the nitrogen atom of *N,N*-dibenzylamine moiety by DFT calculation (**Fig. 5a**). The Mulliken charge of the sulfur atom (S2) exhibited negative value, whereas that of the nitrogen atom (N13) has a positive value. This result strongly indicate that, sulfur from the thiocarbonyl group attacked the methyl group of MeOTf compared to the tertiary amine moiety on the methyl cation. Furthermore, the structure of **1** determined by XRC suggests that the nitrogen atom (N8) and methine carbon (C17) might make a bond to form the aziridine ring because the two atoms presented in the geminal position (**Fig. 5b**). According to the above results, we would like to propose a plausible mechanism of the cationic ring-opening polymerization. In the initiation step, the sulfur atom of the thiocarbonyl attacks the methyl group of the initiator. We speculate that, Lewis basicity of the nitrogen atom is reduced due to the presence of two bulky benzyl group on the nitrogen compared to the thiocarbonyl group. Hence the ability of the sulfur to attack to methyl group is more. Further the neighbouring group effect of the nitrogen atom leads to the the stabilization of the carbenium ion, which forms a moderately stable transient aziridine ring which can lead to the propagation of the polymer chain. The active aziridine ring leads to further addition of other monomers thereby leading to the polymerization of **1**. As mentioned above, the major and minor units in the polymer structure have determined by ^{1}H and ^{13}C NMR measurements. In the reaction of aziridine ring and monomer, we assume that path A maybe more favorable route than path B because of low steric hindrance. Therefore, the major unit was prepared by path A, whereas the minor unit was prepared by path B (Scheme 4).
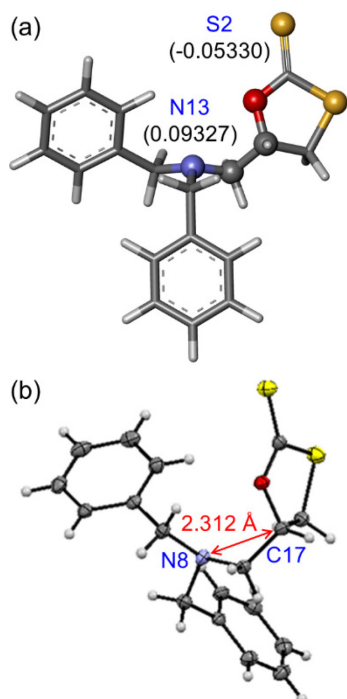
Figure 5. (a) The optimized structure of **1** by DFT calculation. (b) The structure of **1** determined by XRC. The single crystal of **1** was obtained by slow evaporation of a solution of **1** in DCM.

Scheme 4. The assumed mechanism of ring-opening polymerization of **1**.

Conclusions

In this study we have obtained a new cyclic dithiocarbonate monomer derived from *N,N*-dibenzylamine. The cationic ring opening polymerization of the cyclic dithiocarbonate derived from *N,N*-dibenzylamine was performed to obtain polydithiocarbonate. The polymerization proceeds with high monomer conversion and the resulting polymers had high molar mass and narrow dipersity. The initiation of the polymerization is achieved with catalytic MeOTf/EtOTf. The

reactivity of the exocyclic sulfur atom of the monomer towards the methyl cation from the methyltriflate is much higher than tertiary amine. This indicates the rate of initiation is higher than the rate of neutralization from the tertiary amine. The tertiary amine vicinal to the carbenium ion can lead to the stabilization of the intermediate through neighboring group participation. The tertiary amine forms a transient aziridine ring which stabilizes the carbenium ion in the propagating polymer chain. To the best of knowledge this is the first example of the cationic polymerization of cyclic dithiocarbonate monomers containing a tertiary amine moiety. The present findings indicate that the cyclic dithiocarbonate monomers containing a bulky tertiary amine can undergo cationic ring opening polymerization to yield polydithiocarbonate. In future other type of monofunctional and multifunctional dithiocarbonate monomers can be developed that can be used to synthesize linear and networked polymers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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