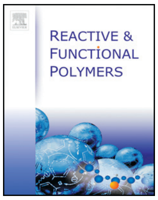
Reactive and Functional Polymers 100 (2016) 37–43

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react



Anionic ring-opening polymerization of cyclic 1,3-dithiocarbonate and thermal depolymerization

Su Jin Jeon, Min-young Jung, Jung Yun Do *

Department of Chemistry Education, Pusan National University, Pusan 609-735, South Korea

ARTICLE INFO

Article history:
Received 18 November 2015
Received in revised form 4 January 2016
Accepted 4 January 2016
Available online 8 January 2016

Keywords:
Poly(dithiocarbonate)
Cyclic 1,3-dithiocarbonate
Anionic ROP
Depolymerization
Back-biting

ABSTRACT

A new anionic ring-opening polymerization (ROP) was used to synthesize polydithiocarbonates from cyclic dithiocarbonates. The polymerization was optimized in the presence of dibenzo-18-C-6 and NaH/EtOH, and carried out at 50 °C to suppress any retropolymerization. Six- and seven-membered cyclic dithiocarbonates underwent ROP to afford the corresponding polymers. Thermal depolymerization of the prepared polymers generated a dimer, which was found to be a back-biting mechanism according to ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The characteristic structure of the linear polymer was defined by ^{1}H NMR and ^{13}C NMR spectroscopy, and compared with the monomer. The ROP at 80 °C exhibited the formation of a polymer contaminated by a dimer. Thermal analysis of the polymers by differential scanning calorimetry and thermogravimetric analysis revealed a melting process at 85–110 °C and thermal instability accompanying a 5% weight loss at 150–230 °C.

1. Introduction

The driving force of ring-opening polymerization (ROP) is the ring strain of a cyclic monomer that is dependent on the ring size and steric hindrance of the constituent atoms or groups [1]. The negative Gibb's free energy (ΔG) of ROP is the sum of the enthalpy (ΔH) factor, including strain relief, and negative entropy change (ΔS) during polymerization [2–3]. Polymerization is accompanied by a decrease of entropy due to the loss of translational freedom of the monomers. The contribution of entropy to the free energy is associated with temperature ($\Delta G = \Delta H - T\Delta S$). Hence, a reverse polymerization, retropolymerization, can occur at higher temperatures [4]. Various cyclic monomers have been developed for polycarbonates, polyamides, polyesters, and polyolefins [5–7]. For example, the ROP of an epoxide is initiated by anionic or cationic reagents [8]. Nylon 6 is produced by the thermal ROP of ε-caprolactam. Five- and six-membered cyclic carbonates are polymerized to polycarbonates under ionic initiators [3,9]. Sulfur analogs of the cyclic carbonates have attracted attention for sulfur-containing polycarbonates, which exhibit good thermal and optical properties as well as chemical and biological resistance [10–11]. Several types of cyclic thiocarbonates were proposed for the formation of poly(thiocarbonate)s through ROP, such as cyclic trithiocarbonate (–S–CS–S–), cyclic 1,3-oxathiolane-2-thione (–S–CS–O–), and cyclic thione carbonate (–O–CSO–) [12–15], whose polymerization was initiated by cationic reagents. On the contrary, there is no report related to the ROP of cyclic dithiocarbonates (–S–CO–S–), such as 1,3-dithiolan-2-one and 1,3-dithian-2-one. T. Endo's group reported the synthesis of a poly(dithiocarbonate) from the cationic ROP of 1,3-oxathiolane-2-thione (–S–CS–O–) and polymer instability caused by a back-biting reaction [16–18]. The isomeric transformation of 1,3-oxathiolane-2-thione to 1,3-dithiolan-2-one was irreversible under cationic ROP conditions, where the formed cyclic dithiocarbonate was unreactive. Anionic polymerization of a six-membered cyclic monothiocarbonate (–O–CO–S–) was previously reported to occur via the carbonyl–sulfur bond cleavage [19]. Therefore, a similar polymerization reaction is expected from the cyclic dithiocarbonate. The anionic ROP might involve several steps, such as nucleophilic attack on a carbonyl, ring cleavage, and reproduction of a sulfur anion for polymer growth. The anionic ROP should be initiated at a certain temperature because of the possible depolymerization at higher temperatures. The ring size of a cyclic dithiocarbonate monomer will contribute to both polymerization and depolymerization.

2. Experimental

2.1. Materials and characterization

All reagents were purchased from Sigma-Aldrich Corporation, and the reagent-grade solvents were dried when necessary and purified by vacuum distillation. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectroscopy experiments (Bruker AM-300 spectrometer) were conducted to characterize their molecular structure. The mass spectra were recorded on an Agilent 1200LC/1100 MSD SL mass spectrometer. A Magna-IR 750 spectrometer (Nicolet Instrument Co., USA) recorded the Fourier transform infrared (FTIR) spectra. Thermal analysis was performed on a Mettler Toledo DSC 822e and TAG/SDTA 851e, with a

---

* Corresponding author.
E-mail address: jydo@pusan.ac.kr (J.Y. Do).

http://dx.doi.org/10.1016/j.reactfunctpolym.2016.01.005

heating rate of 10 °C/min under nitrogen atmosphere. Molecular weights of polymers were determined by Agilent PL-20 using a polystyrene standard. Elemental analysis was run on a Vario EL elemental analyzer.

2.2. Syntheses of cyclic 1,3-dithiocarbonates

2.2.1. Preparation of five-membered cyclic dithiocarbonate (**3**) and thiol (**4a**)

A solution of 2-methylallyloxybenzene (1.48 g, 10.0 mmol) and *meta*-chloroperoxybenzoic acid (*m*-CPBA, 77%, 2.69 g) in anhydrous CH_2Cl_2 (30 mL) was stirred for 12 h at 20 °C. The mixture was diluted with CH_2Cl_2 (100 mL) and washed with aqueous sodium bicarbonate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using ethyl acetate:hexane (1:7, *v*/*v*) as eluent to obtain epoxy product **1** with 78% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.51 (s, 3 H), 2.72 (d, 1 H, J = 4.5 Hz), 2.86 (d, 1 H, J = 4.5 Hz), 3.93 (d, 1 H, J = 10.2 Hz), 4.04 (d, 1 H, J = 10.2 Hz), 7.00 (m, 3 H), 7.30 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 18.3, 51.7, 55.4, 71.3, 114.5, 121.0, 129.4, 158.5.

To a solution of the epoxide **1** (1.64 g, 10.0 mmol) dissolved in tetrahydrofuran (THF, 30.0 mL) were successively added CS_2 (1.21 mL, 20.0 mmol) and catalytic amount of LiBr (0.09 g). After stirring for 20 h at 20 °C, the resulting mixture was diluted with CH_2Cl_2 (100 mL) and washed with water. The organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using ethyl acetate:hexane (1:4, *v*/*v*) as eluent to obtain product **2** with 50% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.72 (s, 3 H), 3.36 (d, 1 H, J = 11.1 Hz), 3.82 (d, 1 H, J = 11.1 Hz), 3.99 (d, 1 H, J = 10.2 Hz), 4.20 (d, 1 H, J = 10.2 Hz), 6.80–7.05 (m, 3 H), 7.22–7.35 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 22.9, 41.3, 70.1, 96.6, 114.7, 122.0, 129.7, 157.9, 211.1 (C = S).

A mixture of **2** (1.20 g, 5.0 mmol) and $ZnCl_2$ (0.14 g) in chlorobenzene (15 mL) was heated for 6 h at 80 °C. The cooled mixture was diluted with CH_2Cl_2 (50 mL) and washed with water. The organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated. The organic residue was purified by SiO_2 column chromatography using ethyl acetate:hexane (1:4, *v*/*v*) as eluent to obtain product **3** with 65% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.84 (s, 3 H), 3.57 (d, 1 H, J = 12.3 Hz), 3.85 (d, 1 H, J = 12.3 Hz), 4.04 (d, 1 H, J = 9.3 Hz), 4.38 (d, 1 H, J = 9.3 Hz), 6.97–7.08 (m, 3 H), 7.37 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 23.6, 42.9, 60.1, 71.3, 114.6, 121.6, 129.6, 158.0, 196.5(C = O). $C_{11}H_{12}$ S_2O_2 (240.03): C 54.97, H 5.03, S 26.68, O 13.31; Found C 54.96, H 4.99, S 26.62, O 13.43.

A solution of **3** (0.50 g, 2.1 mmol) and morpholine (0.92 g, 10.5 mmol) in ethanol (6 mL) was stirred for 2 h at 20 °C. The resulting mixture was concentrated under vacuum to remove volatile materials to yield a thiol product (**4a**).

4a: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.46 (s, 3 H), 2.31 (s, 1 H, −SH), 3.50 (s, 2 H), 3.54 (m, 4 H), 3.62 (m, 2 H), 3.94 (dd, 2 H, J = 9.3 Hz, J = 8.9 Hz), 6.89–6.99 (m, 3 H), 7.27 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 25.1, 41.0, 45 (m), 47.3, 66.6, 75.5, 114.8, 121.3, 129.6, 158.5, 166.7(C = O); IR (NaCl, cm^{-1}): 2963, 2924, 2858, 2549 (w), 1653 (s), 1596, 1500, 1404, 1239, 1206, 1113. $C_{15}H_{21}NS_2O_3$ (327.46): C 55.02, H 6.46, N 4.28, S 19.58, O 14.66; Found C 55.16, H 6.34, N 4.22, S 19.56, O 14.72.

2.2.2. Preparation of six-membered cyclic dithiocarbonates (**6**, **7a**, **7b**, **9**)

To a solution of potassium O–ethyl xanthate (1.31 g, 9.9 mmol) in water (12 mL) was slowly added 1,3-dichloroacetone (1.67 g, 10 mmol) at 0 °C. After stirring for 1 h, the obtained solid product was filtered and washed with water. It was then dissolved in CH_2Cl_2 (30 mL) and dried over anhydrous $MgSO_4$. The organic solution was filtered and concentrated to produce **5** with 65% yield, which was used for further reaction without purification. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.43 (t, 3 H, J = 7.2 Hz), 4.15 (s, 2 H), 4.32 (s, 2 H), 4.64 (q, 2 H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 13.9, 43.0, 48.2, 17.4, 195.9 (C = O), 212.9 (C = S).

A solution of **5** (1.00 g, 4.7 mmol) and KBr (2.81 g, 23.5 mmol) in acetone (14 mL) was refluxed for 24 h. The cooled mixture was filtered to remove solids and concentrated under reduced pressure. The organic residue was purified by SiO_2 column chromatography using ethyl acetate:hexane (1:4, *v*/*v*) as eluent to obtain product **6** with 77% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.85 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 39.8, 190.5 (SC = O), 198.1 (C = O); IR (NaCl, cm^{-1}): ν_{max} 1728 (C = O), 1630, 1381, 1237, 1150, 1104, 1040, 930, 878. $C_4H_4O_2S_2$ (148.21): C 32.42, H 2.72, S 43.27, O 21.59; Found C 32.42, H 2.77, S 43.19, O 21.62.

1,3-Dithiane-2,5-dione (**6**) (1.48 g, 10.0 mmol) was placed in a two-necked round-bottom flask equipped with the Dean–Stark apparatus and charged with benzene (30 mL) and molecular sieve (4 A, 1 g). To the mixture were added ethylene glycol (0.56 mL, 10.0 mmol) and *p*-toluene sulfonic acid (0.10 g, 0.5 mmol), and refluxed for 12 h. The cooled mixture was diluted with ethyl acetate (30 mL) and washed with water. The organic layer was concentrated and purified by SiO_2 column chromatography using ethyl acetate:hexane (1:4, *v*/*v*) as eluent to obtain product **7a** with 85% yield.

7a: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.26 (s, 4 H), 4.04 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 40.2, 65.4, 107.9, 194.7 (C = O); $C_6H_8O_3S_2$ (192.26): C 37.48, H 4.19, S 33.36, O 24.97; Found C 37.46, H 4.25, S 33.28, O 25.01.

Similarly, **7b** was prepared using propylene glycol with 65% yield.

7b: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.84 (m, 2 H), 3.40 (s, 4 H), 4.00 (t, 4 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 25.2, 38.8, 61.1, 117.3, 198.1 (C = O); $C_7H_{10}O_3S_2$ (206.28): C 40.76, H 4.89, S 31.09, O 23.27; Found C 40.75, H 4.88, S 31.18, O 23.19.

To a solution of 2-phenylthio-1,3-propanediol (1.84 g, 10.0 mmol) [20] in CH_2Cl_2 (40 mL) were added successively triethylamine (3.2 mL, 24 mmol) and methanesulfonyl chloride (3.1 mL, 22 mmol) at 0 °C. After stirring for 12 h, the reaction mixture was diluted with CH_2Cl_2 (30 mL), followed by washing with water and brine. The organic solution was dried over $MgSO_4$ and concentrated under reduced pressure to obtain a dimesylated product (2.99 g). This product and thiourea (1.9 g, 25.0 mmol) were dissolved in 2-propanol (40 mL), and refluxed for 24 h. Then, aqueous NaOH (10%, 10 mL) was added to the mixture and refluxed for additional 24 h. The reaction temperature was reduced to 25 °C and acidified to pH = 1 by adding aqueous HCl (1 M). The resulting mixture was extracted with CH_2Cl_2 and washed with brine. After drying with $MgSO_4$, the solvents were removed under reduced pressure and purified by column chromatography to produce 4-phenylthio-1,2-dithiolane (**8**) with 75% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.02 (br, 4 H), 3.63 (m, 1 H), 7.20–7.35 (m, 3 H), 7.36–7.52 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 44.2, 52.9, 125.7, 128.1, 129.5, 132.7, 133.2; IR (NaCl, cm^{-1}): ν_{max} 3629, 2955, 1586, 1479, 1434.

A mixture of 4-phenylthio-1,2-dithiolane and $NaBH_4$ (0.38 g, 10.0 mmol) in THF/methanol (30 mL, 1/1) was stirred for 2 h. The reaction mixture was acidified to pH = 1 by adding aqueous HCl (1 M), and the organic material was extracted with CH_2Cl_2 and washed with brine. The concentrated organic residue was dissolved in CH_2Cl_2 (20 mL), and N,N-carbonyl diimidazole (1.79 g, 11.0 mmol) was added at 25 °C. After stirring for 12 h, the resulting mixture was concentrated and purified by SiO_2 column chromatography using ethyl acetate:hexane (1:10, *v*/*v*) as eluent to obtain product **9** with 42% yield. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.08 (m, 2 H), 3.48 (m, 2 H), 3.95 (m, 1 H), 7.33 (m, 3 H), 7.53 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.5, 44.2, 123.7, 128.3, 128.6, 129.5, 132.1, 194.0 (C = O); IR (NaCl, cm^{-1}): ν_{max} 2931, 2854, 1643 (C = O), 1443, 876. $C_{10}H_{10}OS_3$ (242.38): C 49.55, H 4.16, S 39.69, O 6.60; Found C 49.65, H 4.43, S 39.61, O 6.31.

2.2.3. *Preparation of seven-membered cyclic dithiocarbonate (**11**)*

To a solution of potassium O–ethyl xanthate (1.30 g, 10.0 mmol) in water–THF (30 mL, 1/1, *v*/*v*) was slowly added 1,2-bis(chloromethyl)benzene (3.50 g, 20 mmol) at 0 °C. After stirring for 12 h, the mixture was diluted with ethyl acetate and washed with water.

The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using hexane as eluent to obtain epoxy product **10** with 80% yield (2.0 g). ^{1} H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.43 (t, 3 H, J = 6.9 Hz), 4.55 (s, 2 H), 4.71 (s, 2 H), 4.66–4.77 (q, 2 H, J = 6.9 Hz), 7.30–7.45 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 13.7, 37.2, 43.8, 70.1, 128.2, 129.1, 130.4, 130.8, 133.9, 135.9, 213.2 (C = S); IR (NaCl, cm^{-1}): ν_{max} 1604, 1491, 1451, 1359, 1219, 1111, 1044.

A solution of **10** (2.0 g, 7.7 mmol) and KBr (4.58 g, 38.5 mmol) in acetone (23 mL) was refluxed for 12 h. The mixture was spontaneously concentrated by heating and diluted with ethyl acetate (30 mL). After refluxing for 24 h, the cooled mixture was mixed with water (30 mL) and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using ethyl acetate:hexane (1:10, *v*/*v*) as eluent to produce cyclic dithiocarbonate (**11**) with 35% yield (0.53 g). ^{1} H NMR (300 MHz, $CDCl_3$) δ (ppm) = 4.28 (s, 4 H), 7.37 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 34.2, 128.4, 129.1, 136.5, 190.8 (C = O); IR (NaCl, cm^{-1}): ν_{max} 3026, 2972, 2919, 2850, 1698, 1605 (s), 1488, 1442, 938, 823, 763. $C_9H_8OS_2$ (196.29): C 55.07, H 4.11, S 32.67, O 8.15; Found C 55.01, H 4.11, S 32.61, O 8.27.

2.3. *Polymerization of cyclic dithiocarbonates*

General procedure: All glassware were dried and washed with N_2 flow before use. A catalyst solution (NaOEt, 0.025 M) was prepared. NaH (60% in mineral oil, 120 mg, 3.0 mmol) was placed in a 250-mL round-bottom flask under N_2 condition and charged with anhydrous benzene (20 mL). Ethanol (175 μL, 3.0 mmol) was slowly added at room temperature and diluted with additional benzene (100 mL) to yield 0.025 M-NaOEt stock solution. Cyclic dithiocarbonate **7a** (1.0 g, 5.2 mmol) and dibenzo-18-crown-6 (190 mg, 0.52 mmol) were placed in a 25-mL flask purged by N_2, and the catalyst solution (4.2 mL) was added at room temperature under N_2 condition. The resulting solution was stirred for 24 h at 50 °C and then cooled. The mixture was loaded on a SiO_2-packed column and treated with eluents ethyl acetate and chloroform to remove all organics except the polymer, which was isolated by passing THF. The polymer solution was concentrated and precipitated in methanol to obtain poly(dithiocarbonate) (**7P-1**) with 65% yield.

7P-1: (65% isolation) ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.38 (s, 4 H), 4.04 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 36.4, 66.7, 108.4, 188.1 (C = O).

7P-2: (75% isolation) ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.72 (m, 2 H), 3.47 (s, 4 H), 2.17 (s), 3.92 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 25.6, 36.1, 62.1, 117.3, 188.1 (C = O).

11P: (12-h polymerization, 88% isolation) ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 4.28 (s, 4 H), 7.20–7.21 (m, 2 H), 7.26–7.29 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 32.1, 128.2, 130.8, 134.8, 188.1 (C = O); IR (NaCl, cm^{-1}): ν_{max} 2926, 1712 (w), 1631 (s), 1448, 870 (s).

Sodium hydride (60%, 5 mg) was placed in a 25-mL flask and charged with anhydrous benzene (2.0 mL) and ethanol (0.10 mL). To this solution was added cyclic dithiocarbonate (**7a**, 1.0 g, 5.2 mmol) dissolved in benzene (2.0 mL). The resulting mixture was stirred for 24 h at 70 °C. The mixture was concentrated and purified by column chromatography with ethyl acetate:hexane (1:7, *v*/*v*) as eluent to afford product **12** (1.15 g) with 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.32 (t, 6 H, J = 7.1 Hz), 3.22 (d, 4 H, J = 8.1 Hz), 3.30 (d, 4 H, J = 8.1 Hz), 4.08 (s, 8 H), 4.27 (q, 4 H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 25.2, 30.1, 35.9, 66.1, 67.7, 107.8, 187.8 (C = O).); $C_{16}H_{26}O_8S_4$ (474.64): C 40.49, H 5.52, S 27.02, O 26.97; Found C 40.29, H 5.55, S 27.26, O 26.91. Liquid chromatography–mass spectrometry (LC–MS): calculated exact mass: 474.05, found 473.01 [M–H^+].

2.4. *Depolymerization of poly(dithiocarbonate) (**7P-1**)*

Sodium ethoxide (15 mg) was added to a solution of the polymer **7P-1** (0.40 g) in THF (4 mL) and refluxed for 0.5 h. The cooled mixture was concentrated and the residue was purified by column chromatography using ethyl acetate:hexane (1:7, *v*/*v*) as eluent to produce **7a** (5% yield) and **13** (55% yield).

13: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.28 (s, 8 H), 4.08 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 40.4, 65.5, 108.2, 195.0 (SC = O); $C_{12}H_{16}O_6S_4$ (384.52): C 37.48, H 4.19, S 33.36, O 24.97; Found C 37.51, H 4.25, S 33.11, O 25.13. LC–MS: calculated exact mass: 383.98, found 382.95 [M–H^+].

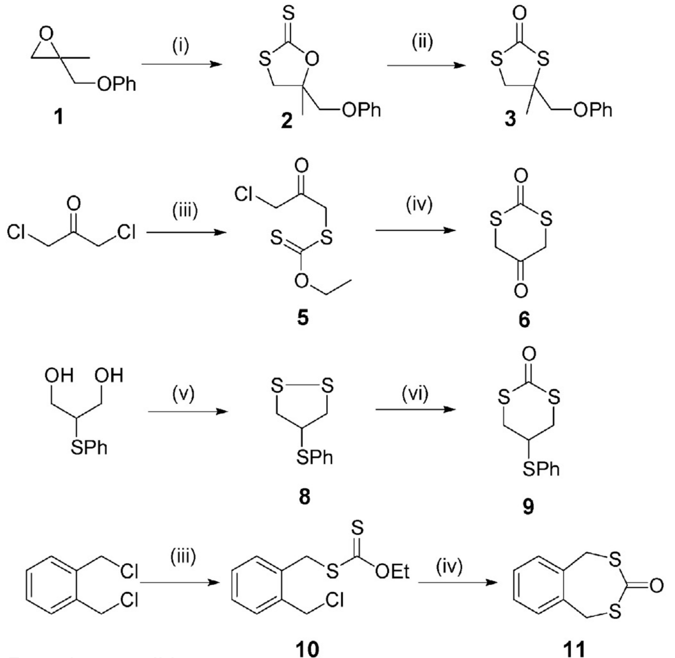
3. Results and discussion

3.1. *Synthesis of cyclic 1,3-dithiocarbonate monomers*

A five-membered cyclic dithiocarbonate **2** was prepared through the O/S isomerization of the corresponding 5-alkyl-1,3-oxathiolane-2-thione [17]. Oxidation of 2-methylallyloxybenzene with *m*-CPBA yielded an epoxide, which was coupled with CS_2 in the presence of LiBr catalyst to generate cyclic 1,3-oxathiolane-2-thione **1**. The acid-mediated isomerization of **1** using $ZnCl_2$ or trifluoromethanesulfonic acid afforded cyclic dithiocarbonate **3** with 65% yield. A six-membered cyclic dithiocarbonate (**6**) was prepared from 1,3-dichloroacetone (Fig. 1). Monoalkylation of 1,3-dichloroacetone was achieved using aqueous potassium ethyl xanthate to produce **5**, and successive intramolecular cyclization occurred accompanying elimination of chloroethane to obtain the cyclic product **6**. When KBr was added to **5** in acetone under reflux, the cyclization was accelerated to give a product with 88% yield. This was an improvement of the previous synthesis in terms of the high dilution condition and low synthetic yield [21]. Mesylation of 2-phenylthio-1,3-propanediol [20] followed by alkylation with thiourea afforded a cyclic disulfide (**8**). The formation of an S–S bond was confirmed by ^{1}H NMR and FTIR spectroscopy with no observation of a specific SH band at around 2550 cm^{-1}. Further, oxidation of 2-phenylthio-1,3-propanedithiol occurred during the reaction. The $NaBH_4$ reduction of **8** and cyclocarbonylation with N,N-carbonyl diimidazole generated a six-membered cyclic dithiocarbonate (**9**). Monoalkylation of 1,2-bis(chloromethyl)benzene with potassium ethyl xanthate, followed by thermal cyclization afforded a seven-membered cyclic dithiocarbonate (**11**). The structure of the prepared cyclic dithiocarbonates was clearly established by ^{1}H NMR spectra. The carbonyl group of S–C(O)–S was observed in the ^{13}C NMR spectrum and at 1600–1700 cm^{-1} in the FTIR absorption spectrum.

3.2. *Anionic ROP*

Anionic polymerization of a six-membered cyclic monothiocarbonate was previously reported to occur through selective carbonyl–sulfur bond cleavage and efficiently at room temperature [19]. A similar anionic polymerization was attempted with five-membered cyclic dithiocarbonates such as 1,3-dithiolane-2-one and 5,5-dialkyl-1,3-dithiolane-2-one (**3**). Polymerization was not observed and the monomer was recovered when it was attempted at various temperatures from 0 to 80 °C with anionic initiators such as NaOEt, KO^tBu, and morpholine. The reaction of **3** and an excess amount of morpholine in ethanol afforded a thiol (**4a**) as the sole product at room temperature. Nucleophilic attack of morpholine on a carbonyl and subsequent C–S bond cleavage may occur in two ways. Fast isomerization between **4a** and **4b** leads to the formation of more stable **4a**. This was deduced from a mechanistic study of an O-analog cyclic carbonate [22]. Nucleophilicity of 3°-SH is weak due to steric crowding, which is insufficient to propagate for the polymerization of **3**. 1,3-



Reaction condition:
(i) CS_2, LiBr, (ii) $ZnCl_2$ (iii)KSC(S)OEt/acetone
(iv) KBr/refluxing acetone or ethyl acetate
(v) MsCl/Et_3N and then $NH_2C(S)NH_2$ (vi)$NaBH_4$ and then N,N`-carbonyl diimidazole

Fig. 1. Synthesis of cyclic dithiocarbonates with various ring sizes.

Dithiolane-2-one, accompanying the formation of 1°-SH, was also unreactive under the anionic ROP condition. The back-biting reaction of a primary mercapto anion occurs preferentially to regenerate a cyclic dithiocarbonate (Fig. 2).

These studies of the anionic ROP were directed toward six-membered cyclic dithiocarbonates. An initial study was performed with a known cyclic dicarbonate (**7b**). On the contrary, polymer **6P-0** was not formed because of a reactive carbonyl group consuming the anionic initiator, as suggested in Fig. 3. The selective carbonyl protection of **6** produced **7a** and **7b**. Two carbonyls of **6** were protected simultaneously with excess diols under an acid catalyst. The treatment of **6** with an equivalent amount of a diol yielded a mono-protected product from selective one-site protection. The reaction of **7a** with catalyst NaOEt, which was in situ prepared from NaH and ethanol in benzene, resulted in the quantitative formation of a coupled product (**12**). The S–S bond of disulfide **12** was presumably formed through an oxidative coupling reaction of the corresponding thiols, which was driven by O_2. The result indicates that an effective carbonyl attack of the ethoxy anion and C–S bond cleavage takes place as expected. The ethoxy group of **12** was supplied by the excess ethanol. Nevertheless, no reaction occurred when solid NaOEt was used as a catalyst. Therefore, a stock solution containing NaOEt (0.025 M) was prepared from the reaction of NaH and ethanol in equivalent quantities in anhydrous benzene. Polymerization was observed when **7a** was heated in the catalyst solution, and was stopped after 12 h. Table 1 lists the conditions for the polymerization of **7a**. Polymerization progressed slowly at temperatures below 70 °C. Structural analysis of the prepared polymer was performed by ^1H NMR and ^{13}C NMR spectroscopy, and compared with **7a**. A peak at 3.26 ppm (CH_2–S) in the spectrum of **7a** shifted to 3.38 ppm of **7P-1**. The carbonyl carbon of **7a** at 194.7 ppm moved to 188.1 in the ^{13}C NMR spectrum of

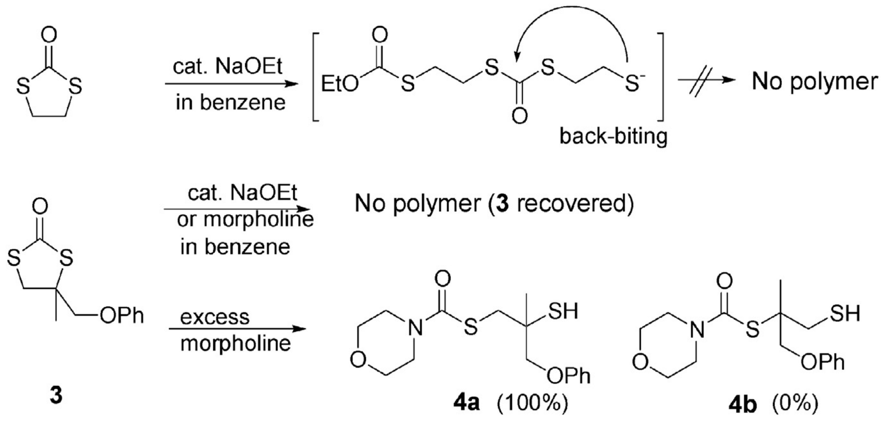


Fig. 2. Ring-opening reaction of five-membered cyclic dithiocarbonates under ROP conditions.

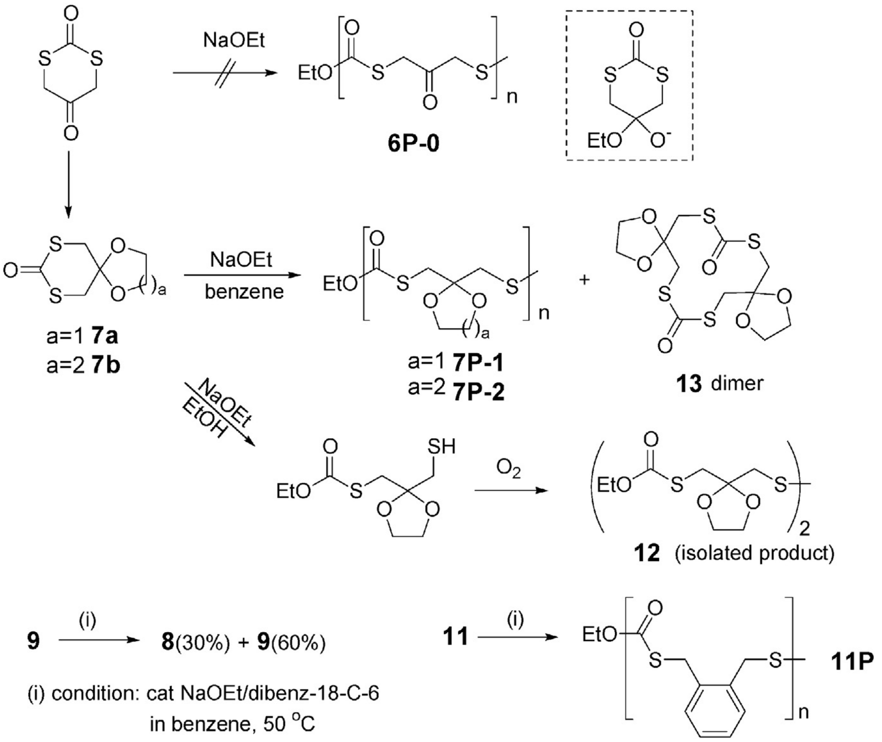


Fig. 3. Anionic ring-opening polymerization of six- and seven-membered cyclic dithiocarbonates.

the polymer **7P-1**. Methylene carbons (CH_2–S) of the monomer and polymer appeared at 40.2 and 36.4 ppm, respectively. Fig. 4 shows two strong peaks assigned to two methylene protons from a main backbone and two weak peaks at 4.25 and 1.24 ppm assigned to an ethoxy group attached to the polymer terminals.

A dimer product (**13**) was isolated together with polymer **7P-1** (Table 1, entry 4). ^{1}H NMR analysis of the crude mixture after polymerization revealed the formation of **13** and polymer with a 1:3 composition ratio. A similar result, that is, initiation of polymerization by LiOEt, was presented in entry 5 of Table 1. A back-biting reaction was considered to explain dimer **13**, which was predominant at high temperatures, and is discussed shortly. In order to suppress the side reaction, polymerization was performed a lower temperature, despite the low rate of polymerization. A phase transfer catalyst was introduced in the polymerization process to overcome the rate problem. When the polymerization exhibited a conversion of < 10% at 50 °C, the addition of dibenzo-18-C-6 improved it and the reaction was complete within 24 h. Furthermore, the polymer was isolated without the formation of **13**. Similarly, the polymerization of **7b** afforded a polymer **7P-2** under similar anionic ROP conditions using NaH/EtOH/dibenzo-18-C-6 at 50 °C and the formation of a corresponding dimer was not observed. In an attempt to polymerize 1,3-dithian-2-one, it was difficult to isolate any distinct product except for the monomer. 4-Substituted cyclic dithiocarbonate **9** with a thiophenyl group for UV detection resulted in the formation of disulfide **8** with 30% yield without a polymer. Monomer decomposition occurred through a decarbonylation under low-temperature ROP conditions. This is in contrast to the result of six-membered dithiocarbonate (**7a**,**7b**). Ring strain would contribute to ROP polymerization. The ^{13}C NMR analysis of the six-membered cyclic monomers revealed a carbonyl carbon at > 190 ppm and an upfield shift toward 188.1 ppm after the ring-opening reaction. Therefore, failure of the polymerization of monomer **9** is probably due to the rapid back-biting reaction. Moreover, steric contribution from 4,4-disubstituted cyclic dithiocarbonate (**7a**,**7b**) would retard the reaction at 50 °C. Polymerization of the seven-membered ring dithiocarbonate with a large ring size was also examined. When the ROP of monomer **11** was performed using the anionic catalysts and a crown-ether, an ROP polymer (**11P**) was obtained with 88% yield. Polymerization was completed in 12 h without dimerization and decarbonylation. Therefore, the anionic ROP of a cyclic dithiocarbonate is reversible and occurs depending on the temperature and ring size.

Table 1
Polymerization results of **7a** in various anionic ROP conditions.

Entry	Catalyst[1]	Solvent	Temp (°C)	Time (h)	Products, (%)		SM (%)[7]
1	NaOEt	EtOH/C_6H_6	70	4	12	100	0
2	NaOEt[2]	C_6H_6	25–80	24	–	0	95
3	KO^{t}Bu[2]	THF	25–70	24	–	0	92
4	NaH/EtOH[3]	C_6H_6	70	12	7P-1 + 13(3/1)[6]	85	5
5	BuLi/EtOH[4]	C_6H_6	70	12	7P-1 + 13(3/1)	77	3
6	NaH/EtOH/18-C-6[5]	C_6H_6	50	24	7P-1	65	0

[1] Polymerization was performed in solvent (ca. 20 wt./v.% of **7a**) with catalyst (2 mol%).
[2] Used as a powder.
[3] A stock solution (0.025 M–NaOEt in benzene).
[4] n-BuLi(1.0 M in hexane) was added to benzene containing ethanol to generate LiOEt in situ.
[5] Dibenzo-18-crown-6 (2 mol%) was used.
[6] The ratio was determined by ^{1}H NMR.
[7] Recovered starting material (**7a**).

3.3. Thermal properties of the prepared poly(dithiocarbonate)s

Observation of dimer **13** during the polymerization of **7a** indicates the occurrence of depolymerization, which is favorable at high temperatures. The back-biting attack of a terminal thiol group to the adjacent carbonyls in the main backbone can generate monomer **7a** and dimer **13** (Fig. 4). When polymer **7P-1** was treated with 0.1 equiv. NaOEt in THF under reflux, dimer **13** was isolated with 55% yield together with **7a** (5% yield). The structure of dimer **13** was confirmed by mass spectrometry providing the molecular weight. Thermal reaction of **7P-1** in

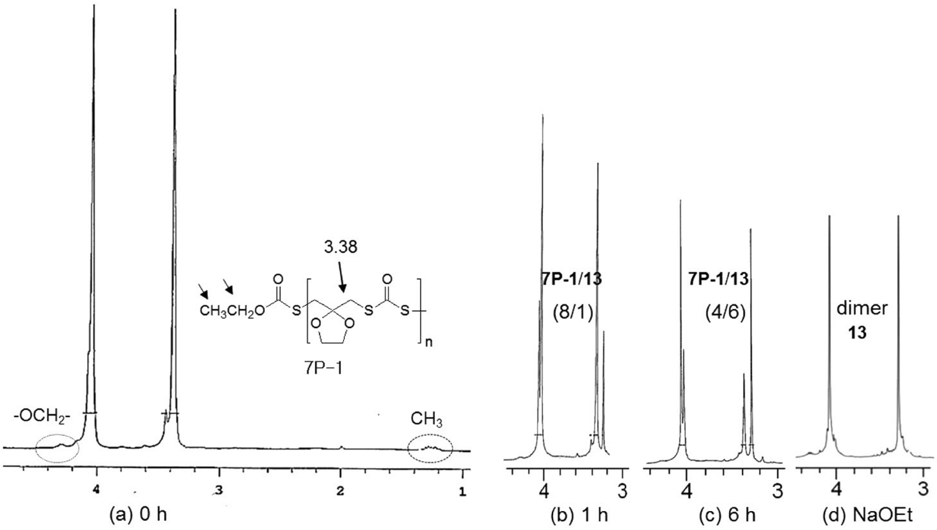


Fig. 4. ^{1}H NMR spectra of (a) the ROP polymer **7P-1** recorded during thermal depolymerization for (b) 1 h and (c) 6 h leading to the partial formation of dimer **13**, and (d) complete depolymerization using NaOEt.

benzene under reflux resulted in a gradual increase in the formation of dimer **13** with increasing reaction time. The conversion reached 60% in 6 h without NaOEt. Two peaks at 3.38 and 4.08 ppm in the ^{1} H NMR spectrum of **13** were attributed to the methylene protons bound to S and O, respectively, and separated from those of the polymer **7P-1**. The conversion was estimated from an integration ratio of **7P-1** and **13** (Fig. 4). The thermal behavior of the prepared polymers was examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC thermogram of polymer **7P-1** exhibited an endothermic shift at 103 °C due to melting. Similarly, a melting process was observed from polymers **7P-2** and **11P** at 111 and 86 °C, respectively. No crystallization accompanying an exothermic shift was observed in the first scan and in the cooling step from high temperatures. Depolymerization might be severe around the melting temperature, which prevented crystallization. The DSC curve showed no evidence of thermal depolymerization because of the rapid heating at 10 °C/min. The large endothermic shifts at 200 °C are difficult to explain and are complicated by decomposition products. Polymer decomposition was recorded from TGA (Fig. 5). The polymer **7P-1** began to lose weight at 126 °C (onset temperature) and showed 10% weight loss at 171 °C; the other polymers exhibited a higher Td (10%). Table 2 lists the thermal behavior of the prepared polymers. The better thermal stability of polymer **11P** than **7P-1** and **7P-2** is partially understood by degradation process involving a back-biting mechanism. This attack of a terminal thiol group of **11P** would occur via seven-membered cyclic approach, which is kinetically unfavorable, contributing to the thermal stability, while the other polymers (**7P-1** and **7P-2**) involve six-membered cyclic approach resulting in fast thermal degradation (Supplementary data). In addition, the polymer **7P-1** prepared at 70 °C exhibited larger molecular weights than that at 50 °C. Therefore, high temperature increased the reactivity of an intermediate mercapto anion for both polymerization and depolymerization.

4. Conclusion

ROP of cyclic dithiocarbonates was demonstrated depending on ring size. This polymerization competed with depolymerization via a back-biting reaction, which occurred predominantly at >70 °C. Dibenzo-18-C-6 was introduced to increase the reactivity of the anionic initiator, which led to successful ROP at 50 °C without depolymerization. The formation of a dimer during ROP confirmed the occurrence of depolymerization, which was verified by a thermal reaction of the prepared polydithiocarbonate. Six- and seven-membered cyclic dithiocarbonates underwent polymerization, whereas the five-membered rings failed to

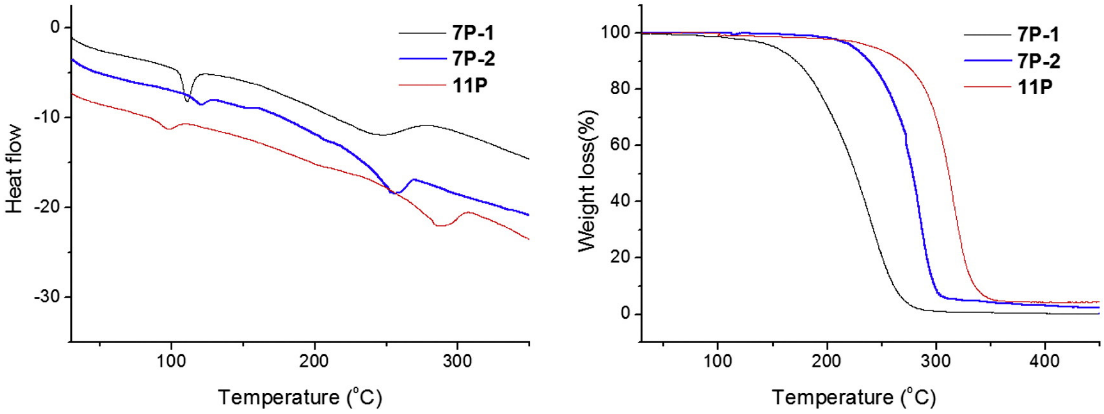


Fig. 5. Thermal properties of the prepared poly(dithiocarbonate)s by DSC (left) and TGA (right).

Table 2
Molecular weights and thermal properties of the poly(dithiocarbonate)s.

Polymers	GPC results[1]			Thermal properties (°C)			
	Mn(kDal)	Mw(kDal)	Mw/Mn	Tm	Td(onset)	Td(5%)	Td(10%)
(7P-1)[2]	10.0	11.7	1.2	–	–	–	–
7P-1	7.8	12.5	1.6	103	126	151	171
7P-2	9.3	18.0	1.9	111	205	226	240
11P	3.8	6.2	1.6	86	230	245	269

[1] The polymer was prepared at 70 °C in the anionic ROP condition without a crown ether. Other polymers were prepared at 50 °C using dibenzo-18-C6. Molecular weights were measured by a gel-permeation chromatography using THF eluent with a polystyrene standard.

provide a polymer likely due to the rapid depolymerization. Overall, anionic ROP provides an alternative way to synthesize polydithiocarbonate from stable cyclic dithiocarbonates.

Acknowledgments

This subject was supported by Korea Ministry of Environment (MOE) as “Chemical Accident Prevention Technology Development Project” and by the Technological Innovation R&D Program of SMBA (S2127285).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.reactfunctpolym.2016.01.005.

References

[1] O. Nuyken, S.D. Pask, Polymers 5 (2013) 361–403.
[2] S. Strandman, J.E. Gautrot, X.X. Zhu, Polym. Chem. 2 (2011) 791–799.
[3] J.-C. Lee, K.H. Litt, Macromolecules 33 (2000) 1618–1627.
[4] A. Duda, A. Kowalski, Thermodynamics and kinetics of ring-opening polymerization (chapter 1), in: P. Dubois, O. Coulembier, J.-M. Raquez (Eds.), Handbook of Ring-Opening Polymerization, Wiley-VCH Verlag, Weinheim, Germany 2009, pp. 1–51.
[5] T.F. Al-Azemi, K.S. Bisht, Macromolecules 32 (1999) 6536–6540.
[6] R. Jianming, X. Anguo, W. Hongwei, Y. Hailin, Des. Monomers Polym. 17 (2014) 345–355.
[7] J.M.G. Cowie, V. Arrighi, Polymers chemistry and physics of modern materials, third ed. Taylor & Francis, Boca Raton, 2007 181–183.
[8] W.R. Ashcroft, Curing agents for epoxy resins (chapter 2), in: B. Ellis (Ed.), Chemistry and Technology of Epoxy Resins, Springer, Netherlands, Chapman & Hall 1993, pp. 37–71.
[9] A. T, T. Takata, T. Endo, Macromolecules 30 (1997) 737–744.
[10] C. Bert, A. Celli, P. Marchese, E. Marianucci, C. Marega, V. Causin, A. Marigo, Polymer 48 (2007) 174–182.
[11] D.J. Darensbourg, S.J. Wilson, A.D. Yeung, Macromolecules 46 (2013) 8102–8110.
[12] C. Berti, A. Celli, E. Marianucci, M. Vannini, Eur. Polym. J. 41 (2005) 1812–1820.
[13] N. Nemoto, K. Yoshii, H. Kameshima, F. Sanda, T. Endo, J. Polym. Sci. A Polym. Chem. 41 (2003) 185–195.
[14] B. Ochiai, T. Endo, Prog. Polym. Sci. 30 (2005) 183–215.
[15] J. Hong, Q. Wang, Y. Lin, Z. Fan, Macromolecules 38 (2005) 2691–2695.
[16] W. Choi, F. Sanda, N. Kihara, T. Endo, J. Polym. Sci. A Polym. Chem. 35 (1997) 3853–3856.
[17] F. Sanda, T. Shinjo, W. Choi, T. Endo, Macromol. Rapid Commun. 22 (2001) 363–366.
[18] P. Hodge, React. Funct. Polym. 80 (2014) 21–32.
[19] F. Sanda, J. Kamatani, T. Endo, Macromolecules 32 (1999) 5715–5717.
[20] P. Štacko, P. Šebej, A.T. Veetil, P. Klán, Org. Lett. 14 (2012) 4918–4921.
[21] O. Bergeot, C. Corsi, M.E. Qacemi, S.Z. Zard, Org. Biomol. Chem. 4 (2006) 278–290.
[22] C. Sklavounos, I.M. Goldman, D.E. Kuhla, J. Org. Chem. 45 (1980) 4239–4240.