Preparation of Asymmetric Spiro Orthocarbonates via Cyclic Thionocarbonates

Chul-bae Kim, Min-Ah Park, Byungho Song,[†] and Kwangyong Park[*]

Department of Chemical Engineering, Chung-Ang University, Seoul 156-756, Korea
[†]Department of Chemistry, Sunmoon University, Asan City, Chung Nam 336-708, Korea
Received May 28, 2003

The development of monomers that show no shrinkage in volume upon polymerization is highly desirable in the field of materials such as dental fillings, high-strength composites, precision castings, and adhesives.[1] Volume shrinkage during polymerization results from the conversion of van der Waals distances between monomers to covalent bond lengths. Since the van der Waals distance separates monomer molecules approximately three times greater than a covalent bond does, the formation of new covalent bonds upon polymerization is destined to produce the substantial amount of volume contraction. A hopeful approach to prevent this shrinkage could be attained by using monomers that polymerize via the double ring-opening process, which results in two bonds breaking for each new bond formation.

Since the double ring-opening polymerization was reported in 1972,[2] various monomers based on spiro orthoester (SOE),[3] bicyclo orthoester (BOE),[4] polycyclic ketal lactone (PKL),[5] cyclic ether,[6] spiroketal,[7] and spiro orthocarbonate (SOC) skeletons[8] have been developed to show the expansion in volume upon polymerization. Among them, spiro orthocarbonates (SOCs) are the most widely investigated monomers because they show the biggest volume expansion. Moreover SOCs containing *exo*-methylene groups undergo the ring-opening polymerization not only with cationic initiators[9] but also with radical initiators.[10] Asymmetric SOCs possessing one *exo*-methylene group are more favorable than symmetric SOCs, because the extra *exo*-methylene group remained in the polymer from symmetric monomers affords the crosslinking reaction that causes the volume shrinkage.[11] Recently, N,S-[12] and S,S-analogs[13] of SOCs have been introduced as alternatives.

A variety of synthetic approaches have been reported for the preparation of SOCs. The original syntheses of SOCs consist of organotin compounds. Reactions of the cyclic thionocarbonates with cyclic tin compounds produce asymmetric SOCs.[14] Thallous alkoxide was also investigated for replacing oragnotins.[15] New synthetic route for the preparation of cyclic thionocarbonates by using the reaction of thiophosgene with diols was developed by Stansbury, *et al.*[16] Another approach involves the transesterification utilizing tetramethyl or tetraethyl orthocarbonate, which supplies the spiro carbon, with two equivalents of diols in the presence of an acid catalyst.[17] Endo developed a
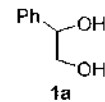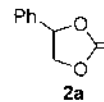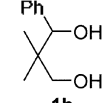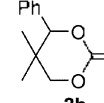
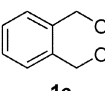[*]To whom all correspondences should be addressed. E-mail: kypark@cau.ac.kr
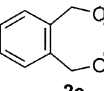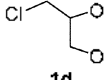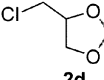
modified route using dichlorodiphenoxymethane as a suitable way for the preparation of asymmetric SOCs.[8c,10c,18] In spite of these numerous efforts, an efficient synthetic route for these monomers is still under investigation.

During a program directed toward the development of expandable monomers, we have explored various synthetic methods for the preparation of asymmetric SOCs bearing *exo*-methylene groups at α to the oxygen. The reaction of cyclic thionocarbonates with cyclic tin compounds gave the best results among those methods.

The preparation of cyclic thionocarbonate intermediates **2** was initially investigated. Even though it has been known that they could be prepared by the reaction of bis(tributyltin) alkylene glycolates with carbon disulfide,[14c] this approach did not give a good result in our case. The intermediates **2** could be prepared by the reaction of appropriate diols **1** with thiophosgene in the presence of 4-dimethylaminopyridine (DMAP) in good yields (Table 1).

Thionocarbonates **2a, 2b** and **2d** are produced in good yields (entry 1, 2 and 4). Pentagonal thionocarbonates **2a** and **2d** can be recrystallized from 10% hexane in ether, while hexagonal compound **2b** is recrystallized from ether. The desired product **2c** containing seven-membered ring was

Table 1. Preparation of Cyclic Thionocarbonates **2**

Entry	1	2	Yield (%)[a]
1	**1a**	**2a**	86
2	**1b**	**2b**	73
3	**1c**	**2c**	–
4	**1d**	**2d**	84

[a]The yields refer to isolated pure materials and based on thiophosgene.

Table 2. Preparation of Asymmetric SOCs **5**

Entry	1	4	5	Yield (%)[a]
1	**1a**	**4a**	**5a**	48
2	**1b**	**4b**	**5b**	38[b]
3	**1c**	**4c**	**5c**	52

[a]The yields refer to isolated pure materials and based on **1**. [b]GC Yield based on **1**.

not detected in this effort (entry 3). Thionocarbonates **2a**, **2b**, and **2d** were easily identified since thionocarbonyl carbons are known to display weak peaks at about 190 ppm in ^{13}C NMR spectra and strong peaks at 1240-1270 cm^{-1} in FT-IR spectra.

The consecutive coupling of **2d** with cyclic tin adducts **3**, which are freshly made by the reaction of **1** with dibutyltin oxide, give corresponding chlorine-containing asymmetric SOCs **4**. The treatment of **4** with potassium *tert*-butoxide *in situ* allows the unsaturated asymmetric SOCs **5** in good overall yields (Table 2). It is noteworthy that potassium *tert*-butoxide is necessary for the complete dehydrochlorination, while NaOEt give unsatisfactory results. Even though **5a** and **5c** were purified by the fractional distillation and recrystallization respectively, **5b** could not be isolated effectively. Structures of these SOCs can be easily identified by ^{13}C NMR spectra, because the spiro carbons of SOCs are appeared at δ 153.9 ppm for **5a**, 153.6 ppm for **5b**, and 153.5 ppm for **5c**.

The opposite synthons were adopted to investigate the best synthetic route for the preparation of SOCs. Instead of reactions between cyclic organotins **3** and chlorothionocarbonate **2d**, couplings of chlorine-containing organotin

Table 3. Preparation of **5** via Opposite Approaches

Entry	2	5	Yield (%)[a]
1	**2a**	**5a**	43
2	**2b**	**5b**	27[b]

[a]The yields refer to isolated pure materials and based on **1**. [b]GC Yield based on **1**.

with a couple of cyclic thionocarbonates **2** were performed (Table 3). Orthocarbonate **5a** was produced successfully, while the isolation of **5b** failed again. The yields in these opposite approaches are slightly lower than the cases of Table 2.

In conclusion, novel asymmetric SOCs bearing *exo*-methylene groups at a to the oxygen are produced by the reaction of cyclic thionocarbonates, which are prepared by the reaction of appropriate diols with thiophosgene in the presence of DMAP, with cyclic tin compounds.

Experimental Section

All reactions were carried out under an inert atmosphere of N$_2$. Toluene was distilled from sodium-benzophenone ketyl. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were registered in CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60 F$_{254}$ precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light (254 and 365 nm) or by iodine vapor staining. GC analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE, 30 m, 0.32 mm i.d.). Electron impact (EI, 70 eV) was used as the ionization method for the mass spectrometry. Melting points were obtained using a Barnstead/Thermolyne MEL-TEMP apparatus and are uncorrected.

General Procedure for the Preparation of Cyclic Thionocarbonates 2. To the solution of diol **1** (52.2 mmol) and DMAP (11.69 g, 95.7 mmol) in toluene (200 mL) was added thiophosgene (5.00 g, 43.5 mmol) in toluene (40.0 mL) dropwise over 15 min. After stirred for 3 h at room temperature, the reaction mixture containing lots of yellow salts was diluted with toluene (100 mL) and transferred through a sintered glass funnel containing a small pad of silica gel. The resulting organic solution was washed with 0.1 % HCl aqueous solution (60 mL), water (3 × 180 mL) and brine (60 mL); dried over MgSO$_4$; and concentrated in vacuo. The crude product **2** was purified by recrystallization.

4-Phenyl-1,3-dioxa-2-cyclopentanethione (2a) was purified by recrystallization (Et$_2$O : *n*-hexane = 9 : 1) to give a white solid (7.41 g, 86%): m.p. 35-36 °C (uncorrected); TLC R_f 0.16 (EtOAc : *n*-hexane = 1 : 1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.56 (dd, J = 8.81, 8.17 Hz, 1H), 4.99 (dd, J = 8.82, 8.48 Hz, 1H), 5.89 (t, J = 8.23 Hz, 1H), 7.35-7.48 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 75.1, 83.3, 126.5, 129.6, 130.3, 134.8, 191.9; FT-IR (KBr) 1150, 1270, 1380, 1450, 1710, 2360, 2980, 3030; HRMS (EI, 70 eV) calcd for C$_8$H$_8$O$_2$S (M$^+$) 180.0245, found 180.0312.

5,5-Dimethyl-4-phenyl-1,3-dioxa-2-cyclohexanethione (2b) was purified by recrystallization (Et$_2$O) to give a white crystalline solid (7.76 g, 73%): m.p. 119-120 °C (uncorrected); TLC R_f 0.24 (EtOAc : *n*-hexane = 1 : 1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.96 (s, 3H), 1.04 (s, 3H), 4.17 (d, J = 11.1 Hz, 1H), 4.28 (d, J = 10.8 Hz, 1H), 5.29 (s, 1H), 7.26-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.1, 22.0, 32.5, 78.6, 90.0, 127.4, 128.5, 129.3, 133.9, 189.8; FT-IR (KBr)

1200, 1240, 1290, 1370, 1450, 2350, 2880, 2960, 3420; HRMS (EI, 70 eV) calcd for $C_{12}H_{14}O_2S$ (M⁻) 222.0715. found 222.0698.

4-Chloromethyl-1,3-dioxa-2-cyclopentanethione (2d) was purified by recrystallization (Et₂O : *n*-hexane = 9 : 1) to give a white crystalline solid (6.13 g, 84%); m.p. 43-44 °C (uncorrected); TLC R_f 0.21 (EtOAc : *n*-hexane = 1 : 1); ¹H NMR (300 MHz, CDCl₃) δ 3.79-3.81 (m, 2H), 4.634 (dd, *J* = 6.22, 9.24 Hz, 1H), 4.783 (t, *J* = 8.65 Hz, 1H), 5.155-5.182 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 42.9, 71.5, 79.4, 191.1; FT-IR (KBr) 1150, 1270, 1450, 1710, 2360, 2990, 3030; LRMS *m/z* (rel abundance) 152 (M⁺, 100), 103 (7), 77 (17), 75 (51), 63 (14), 61 (17), 57 (43).

General Procedure for the Preparation of Unsaturated Asymmetric SOCs 5. To diol **1** (31.6 mmol) in toluene (132 mL) was added dibutyltin oxide (7.87 g, 31.6 mmol). The resulting solution was heated at reflux for 3 h until the theoretical amounts of water (0.57 mL, 31.6 mmol) was collected in the attached Dean-Stark trap. To the reaction mixture was added **2d** (4.00 g, 26.3 mmol) at room temperature. After stirring for 20 h at room temperature or gently heating for 4 h depending on the solubility of **3**, the resulting mixture was treated with ¹BuOK (6.50 g, 57.9 mmol) and stirred for 2 days at rt. The reaction mixture was diluted with toluene (100 mL) and transferred through a sintered glass funnel containing a small pad of silica gel in order to remove salts. The resulting organic solution was washed with water (3 × 80 mL) and brine (20 mL); dried over MgSO₄; and concentrated *in vacuo*. The crude product **5** was purified by either vacuum distillation or recrystallization.

2-Methylene-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (5a) was purified by vacuum distillation to give a colorless oil (2.60 g, 48%); TLC R_f 0.50 (EtOAc : *n*-hexane = 1 : 4); ¹H NMR (300 MHz, CDCl₃) δ 3.96-4.04 (m, 2H), 4.45-4.53 (m, 2H), 4.68-4.73 (dd, *J* = 4.03 Hz, 2H), 4.26-4.30 (dd, *J* = 7.89 Hz, 1H), 5.29 (s, 1H), 7.26-7.42 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 67.2 (1C), 72.2 (1C), 79.1 (1C), 80.7 (1C), 126.5 (1C), 129.0 (2C), 129.1 (2C), 135.6 (1C), 137.0 (1C), 153.9 (1C); HRMS (EI, 70 eV) calcd for $C_{11}H_{12}O_4$ (M⁺) 208.0736 found 208.0698.

Spiro[2,4]-benzodioxepine-4'-methylene-3,2'-[1,3]dioxolane (5c) was purified by recrystallization (*n*-hexane) to give a white solid (2.81 g, 52%); m.p. 137-138 °C (uncorrected); TLC R_f 0.53 (EtOAc : *n*-hexane = 1 : 4); ¹H NMR (300 MHz, CDCl₃) δ 4.04 (m, 1H), 4.50 (m, 1H), 4.71 (t, *J* = 1.93 Hz, 2H), 5.05 (s, 4H), 7.06-7.10 (dd, *J* = 5.54 Hz, 2H), 7.20-7.24 (dd, *J* = 5.71, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 67.17, 67.23 (2C), 81.1 (1C), 126.4 (2C), 127.5 (2C), 130.1 (1C), 136.0 (2C), 153.6 (1C); FT-IR (KBr) 1070, 1120, 1200, 1260, 1370, 1450, 1640, 2360, 2920, 3440; HRMS (EI, 70 eV) calcd for $C_{11}H_{12}O_4$ (M⁻) 208.0736 found 208.0721.

References

1. (a) Moszner, N.; Salz, U. *Prog. Polym. Sci.* **2001**, *26*, 535-576. (b) Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 265-276. (c) Kostoryz, E. L.; Tong, P. Y.; Chappelow, C. C.; Eick, J. D.; Glaros, A. G.; Yourtee, D. M. *Dental Materials* **1999**, *15*, 363-373. (d) Eick, J. D.; Robinson, S. J.; Byerley, T. J.; Chappelow, C. C. *Quintessence Int.* **1993**, *24*, 632-640.
2. Bailey, W. J.; Sun, R. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1972**, *13*, 281.
3. (a) Endo, T.; Bailey, W. J. *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 25-27. (b) Endo, T.; Okawara, M.; Yamazaki, N.; Bailey, W. J. *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 1283-1286.
4. Tanigaki, K.; Saigo, K.; Ohnishi, Y.; Kato, H.; Mizutani, K.; Ogasawara, T.; Endo, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1419-1428.
5. (a) Holder, A. J.; White, D. A.; Harris, C. D.; Eick, J. D.; Chappelow, C. C. *J. Mole. Structure (Theochem)*. **2001**, *541*, 159-169. (b) Bailey, W. J. *US Patent 4,387,215*, 1983.
6. Schaefer, R.; Heindl, D.; Schöde, D.; Nuyken, O.; Böhner, R.; Erdmann, C. *US Patent 5,750,590*. 1998.
7. Fukuchi, I.; Sanda, F.; Endo, T. *Macromolecules* **2001**, *34*, 4296-4298.
8. (a) Chappelow, C. C.; Pinzino, C. S.; Jeang, L.; Harris, C. D.; Holder, A. J.; Eick, J. D. *J. Appl. Polym. Sci.* **2000**, *76*, 1715-1724. (b) Wang, C. S. *J. Mater. Sci. Lett.* **1999**, *18*, 1259-1262. (c) Sanda, F.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 323-332. (d) Park, Y. J.; No, K. H.; Kim, J. H.; Suh, I. H. *Bull. Korean Chem. Soc.* **1992**, *13*, 375-381. (e) No, K. H. *Bull. Korean Chem. Soc.* **1988**, *9*, 183-184.
9. (a) Zhou, Z.; Jin, B.; He, P. *J. Appl. Polym. Sci.* **2002**, *84*, 1457-1464. (b) Komatsu, S.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 875-878. (c) Endo, T.; Maruoka, S.; Yokozawa, T. *Macromolecules* **1987**, *20*, 2690-2693.
10. (a) Sanda, F.; Takata, T.; Endo, T. *Macromol. Theory Simul.* **1995**, *4*, 221-231. (b) Moszner, N.; Zeuner, F.; Rheinberger, V. *Macromol. Rapid Commun.* **1995**, *16*, 667-672. (c) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 737-743.
11. Stansbury, J. W. *J. Dent. Res.* **1992**, *71*, 1408-1412.
12. Millich, F.; Eick, J. D.; Jeang, L.; Byerley, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1667-1673.
13. (a) Bromley, M. K.; Gason, S. J.; Looney, M. G.; Solomon, D. H. *Aust. J. Chem.* **1999**, *52*, 657-661. (b) Bromley, M. K.; Solomon, D. H. *Polym.* **1999**, *40*, 6539-6543. (c) Takata, T.; Kanamaru, M.; Endo, T. *Macromolecules* **1997**, *30*, 6721-6726.
14. (a) Endo, T.; Bailey, W. J. *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 2525-2530. (b) Sakai, S.; Kobayashi, Y.; Ishii, Y. *J. Org. Chem.* **1971**, *36*, 1176-1180. (c) Sakai, S.; Kiyohara, Y.; Itoh, K.; Ishii, Y. *J. Org. Chem.* **1970**, *35*, 2347-2350.
15. Sakai, S.; Kuroda, Y.; Ishii, Y. *J. Org. Chem.* **1972**, *37*, 4198-4200.
16. Stansbury, J. W. *Ph.D. Dissertation*. The University of Maryland. 1988.
17. (a) Tagishi, H.; Endo, T. *J. Polym. Sci. Polym. Chem. Ed.* **1989**, *27*, 1415-1418. (b) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900-904. (c) Endo, T.; Maruoka, S.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 2925-2929. (d) Endo, T.; Okawara, M. *Synthesis* **1984**, 837.
18. Bolln, C.; Frey, H.; Mülhaupt. *Macromolecules* **1996**, *29*, 3111-3116.