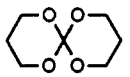
First Example of Poly(spiroorthocarbonate), a Novel Spiro Ladder Polymer

New polymer synthesis is always an important subject in the field of polymer science, which is often involved in essential processes to novel materials. Orthocarbonates, even with spirocyclic structures (e.g., spiroorthocarbonates (SOC, **1**)), are extremely susceptible toward electrophilic agents, although they are thermally stable and almost unreactive to alkali. SOC is known to be a potential monomer which readily undergoes cationic polymerization with expansion in volume.[1] In contrast to **1**, we have noticed that aromatic SOC (**2**) is much less reactive toward electrophilic agents such as BF_3OEt_2 under severe conditions.[2]



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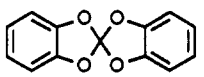
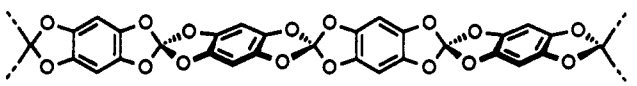


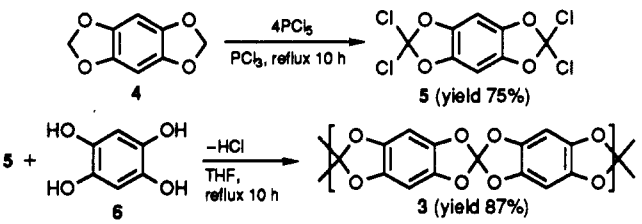
2

If such an aromatic SOC structure can be incorporated into the polymer main chain,[3] a very characteristic new polymer in both structure and property is expected from the viewpoint of a promising acid-stability, rigid spirocyclic structure consisting of successive intercrossing moieties at an angle of 90°, good crystallinity due to high molecular symmetry, etc. In this paper the first example of poly(spiroorthocarbonate) (poly SOC), a novel spiro ladder polymer, is demonstrated.



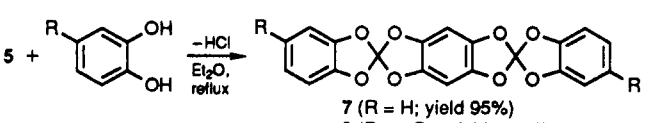
3

Preparation of poly(SOC) (**3**) was carried out by the polycondensation of 2,2,6,6-tetrachlorobenzo[1,2-*d*:4,5-*d'*]bis[1,3]dioxole (**5**) with 1,2,4,5-tetrahydroxybenzene (**6**)[4]



with reference to the synthetic procedure for **2**.[5] Tetrachloride **5** was synthesized by chlorination of benzo[1,2-*d*:4,5-*d'*]bis[1,3]dioxole (**4**)[6] with phosphorus pentachloride.

When **5** and **6** were mixed and refluxed in tetrahydrofuran (THF),[7] a white precipitate was isolated. The precipitate was insoluble in any ordinary solvents. The IR spectrum of the polymer (**3**) showed characteristic absorptions attributable to CO (1100 cm^{-1}) and five-membered aromatic carbonate (1859 and 1834 cm^{-1}) but no phenolic OH absorption. This result clearly indicates the end group of the polymer should be a cyclic carbonate but not a hydroxy group. Model compounds **7** and **8** were synthesized by the reaction of **5** and corresponding catechols. The IR spectrum of **7** was well consistent with that of **3** except for the carbonate absorption.



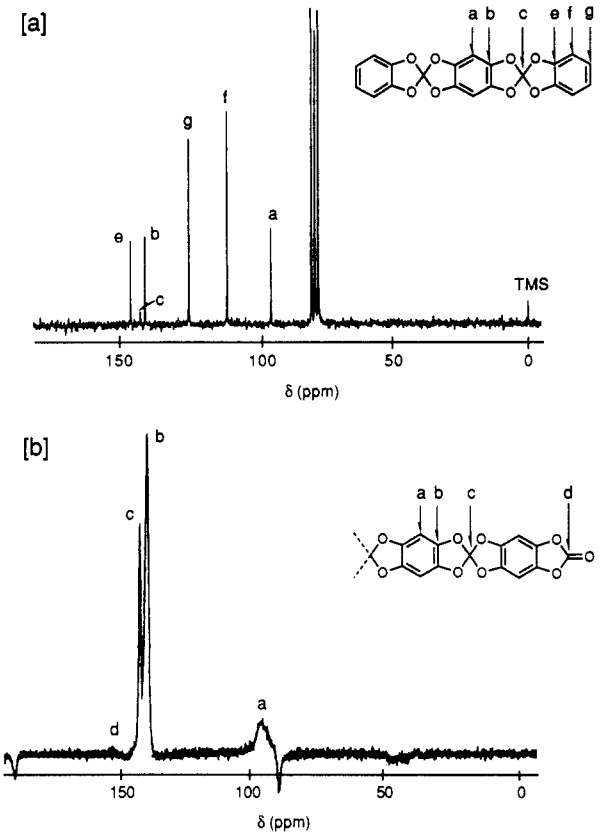
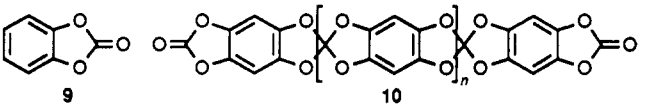


Figure 1. ^{13}C NMR spectra: (a) Model compound **7** ($CDCl_3$, 90 MHz); (b) polymer **3** (CP/MAS, 270 MHz).

The CP/MAS high-resolution solid-state ^{13}C NMR spectrum (Figure 1b) of **3** unambiguously suggested the proposed poly(spiroorthocarbonate) structure, being supported by the ^{13}C NMR spectrum of the model compound (Figure 1a). Namely, as assigned in Figure 1, all required signals of the aromatic carbons and spirocarbons including the terminal carbonate carbons were observed. On the basis of the equal intensity of the two signals of the spirocarbon of **2** and the carbonate carbon of phenylenecarbonate (**9**) in the ^{13}C NMR spectrum of an equimolar mixture of **2** and **9**, **3** was estimated to have a degree of polymerization of ca. 26 (n = ca. 52 in **10**) and $\bar{M}_n$ 7800. Therefore, the following structure (**10**) is suggested for **3**.



9 **10**

Meanwhile, X-ray crystal structure analysis of the model compound **7**[8] clearly showed that **7** consisted only of two 90° intercrossing planes at the spirocarbon (Figure 2); hence, the polymer **3** should have a similar ordered structure. **3** was found to have 53% crystallinity by powder X-ray diffraction analysis,[9] which was an expected characteristic nature of poly(SOC).

In the thermal analysis of **3**, neither glass transition temperature nor melting point could be observed, whereas the temperature for 10% weight loss was ca. 400 °C.[10] The stability of **3** toward a few electrophilic agents was examined under various conditions. After treatment with 10 mol % of BF_3OEt_2 at 100 °C for 12 h in chlorobenzene ([C] = 0.5 M), most of the polymer (95%) was recovered. Under the same conditions **3** was completely unreactive toward acetyl chloride to give no degradation product. The acid stability of **3** was also pointed out apparently by

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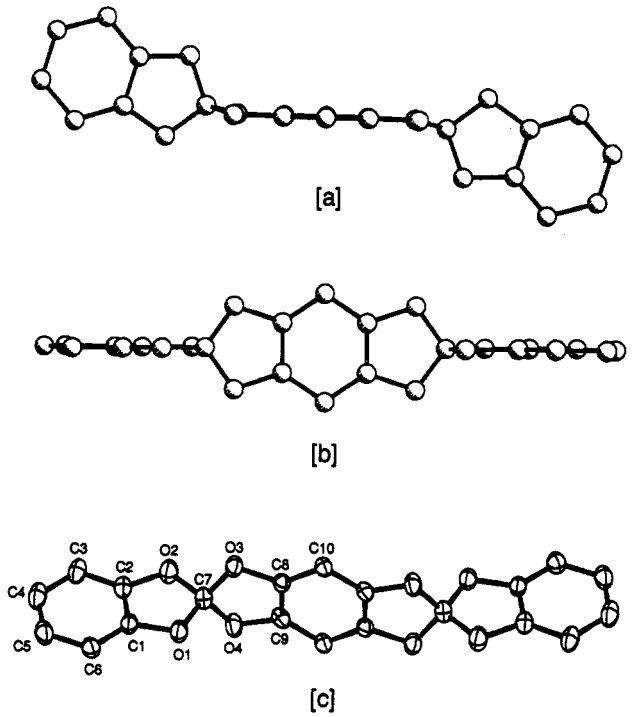
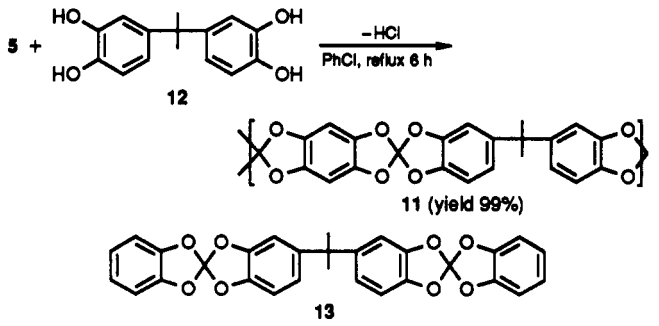


Figure 2. Molecular structure of 7 by X-ray crystal analysis:[8] (a) Perspective view from horizontal at the centered benzene ring of 7; (b) 90° rotated view of a; (c) ORTEP drawing of 7.

the model study using 7 and 8, which were entirely recovered without any change. These results demonstrate that 3 has inertness toward electrophilic agents, good thermal stability, and high crystallinity.

In order to obtain more information on poly(SOC), we synthesized a new poly(SOC) (11) having a more soft and



flexible tetraol segment. The polymer 11 obtained from tetraol 12[11] was soluble in common organic solvents such as THF and chloroform, and its $\bar{M}_n$ of the methanol-insoluble polymer (white powder, quantitative yield) was ca. 30 000 (by gel permeation chromatography; solvent, THF). The spectral data (^1H and ^{13}C NMR and IR) completely corresponded to the proposed polymer structure, which was also supported strongly by those of the model compound 13. It was found that 11 could form a strong self-standing film by casting from a solution.

Supplementary Material Available: Spectral data for all new compounds and a table of bond lengths and bond angles of 7 (by X-ray crystal analysis) (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Bailey, W. J.; Sun, R. R.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, K.; Saigo, K.; Bitritto, M. *Ring-opening Polymerization with Expansion in Volume*; ACS Symposium Series 59; Saegusa, T., Goethals, E., Eds.; American Chemical Society: Washington, DC, 1977; p 38. (b) Endo, T.; Bailey, W. J. *J. Makromol. Chem.* **1975**, *176*, 2897. (c) Bailey, W. J.; No, K.; Pan, C.-Y.; Saigo, K.; Stansbury, J.; Tam, S.-R.; Zhou, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*, 50. (d) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416. (e) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900. (f) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1988**, *21*, 1186.

(2) (a) Amachi, K.; Takata, T.; Endo, T. *54th Annu. Meet. Chem. Soc. Jpn., Tokyo, Abstr.* **1987**, 1586. (b) There is a report on the cationic polymerization of 2 giving low molecular weight polymer, but we could not trace it. Bailey, W. J.; Amone, M. J.; Issari, B.; Lin, Y.-N.; No, K.; Pan, C.-Y.; Saigo, K.; Stansbury, J.; Tan, S.-R.; Wu, C.; Yamazaki, N.; Zhou, J. *Am. Chem. Soc., Div. Polym. Mater. Prepr.* **1986**, *54*, 23.

(3) We have already reported several polymers having alkyl SOC structure in the main chain: Tagoshi, H.; Endo, T. *Chem. Lett.* **1987**, 2363; *Macromolecules* **1989**, *22*, 3834; *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4169.

(4) Nietzki, R.; Schmidt, F. *Chem. Ber.* **1888**, *21*, 2374.

(5) Gross, H.; Rieche, A.; Hoft, E. *Chem. Ber.* **1961**, *94*, 544.

(6) Dallacker, V. F.; Edelmann, W.; Weiner, A. *Liebigs Ann. Chem.* **1968**, *719*, 112.

(7) Since 5 was highly moisture-sensitive and 6 was very air-sensitive, the polycondensation was accomplished under a stream of dry nitrogen, which efficiently removed hydrogen chloride evolved during the polymerization.

(8) Intensity data were collected on a Rigaku AFC5R four-axes diffractmeter with graphite-monochromated Mo Kα radiation. Of 2019 reflections obtained within $2\theta < 55°$, 1419 had intensities greater than $3\sigma[F_o]$ and 1323 were used for structure analysis. The structure was refined to a value of $R = 0.0698$. Crystal data of 7: $C_{20}H_{10}O_8$, triclinic space group $P\bar{1}$, $a = 8.247$ (5) Å, $b = 8.339$ (4) Å, $c = 6.555$ (3) Å, $\alpha = 109.68$ (4)°, $\beta = 91.83$ (4)°, $\gamma = 71.30$ (4)°, cell volume 400.5 (8) Å^3, $Z = 1$.

(9) By Cu Kα radiation ($\lambda = 0.1542$ nm, voltage 40 kV, current 40 mA), the X-ray diffraction pattern of 3 was recorded in the range $2\theta = 4$–60° at a scan speed 2°/min at room temperature.

(10) Differential scanning calorimetry was carried out in a heating rate 10 °C/min. Thermogravimetric analysis was performed in the same heating rate in N_2.

(11) 12 was first prepared in 69% yield by our own method consisting of acid-catalyzed condensation of catechol and acetone. 12 was reported in a patent in which a wrong compound was assigned to it.

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