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Optically Active Poly(aryl carbonates) Consisting of Axially Chiral Units. Chiral Binaphthyl Group Induced Helical Polymer

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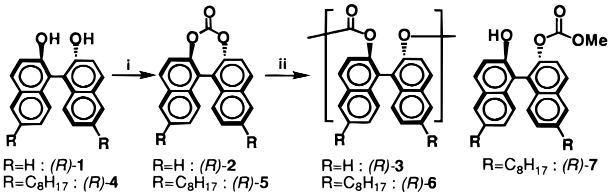
Precise control of architecture of macromolecules is one of the major subjects in polymer science. Optically active polymers often play important roles as key fundamental materials for well-defined polymers with specific secondary and/or tertiary structures.[1,2] In a few synthetic methodologies for optically active polymers, chiral monomer polymerization has essential advantages in applicability of monomer, apart from both asymmetric polymerization of achiral or prochiral monomers and enantioselective polymerization of a racemic monomer mixture.[2,3] Higher structures such as helix are originated by central chirality on carbon atom of the main chain unit as exemplified by proteins and genes. Meanwhile, optically active polymers based on molecular dissymmetry such as atropisomerism are of special interest as structurally fascinating polymers. From viewpoint of synthesis of polymers with C_2 chiral units in their backbones, we have already reported the synthesis and ring-opening polymerization of a racemic cyclic carbonate composed of 1,1′-binaphthyl moiety, a typical molecular dissymmetry unit,[4] as part of our research on polycarbonates.[5] Successive studies using optically active ones have suggested that corresponding optically active polycarbonates can take helix structures.[6] Recent increasing studies concerning with binaphthyl group containing polymers[7,8] have prompted us to report preliminary results on the synthesis and structure of the chiral binaphthyl group based optically active polycarbonates.

Scheme 1[a]



[a] Key: (i) 4-nitrophenyl chloroformate (2 equiv), diisopropylethylamine (2 equiv), CH_2Cl_2, 0 °C, 1 h; yield 79% ((*R*)-**2**) and 86% ((*R*)-**5**); (ii) *t*-BuOK (1 mol %), THF (0.1 M), 20 °C, 15 min; yield 96% ((*R*)-**3**) and 81% ((*R*)-**4**).

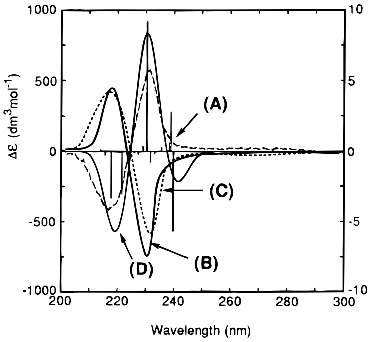


Figure 1. CD Spectra (A) observed for (*R*)-**6** in c-Hex, (B) observed for (*R*)-**7** in c-Hex, (C) observed for (*S*)-**6** in c-Hex, and (D) calculated for corrected helix of model 10-mer (*R*)-**8**.

Optically active binaphthyl group based cyclic carbonates ((*R*)-**2** and (*S*)-**2**, $[\alpha]^{24}_{\mathrm{D}}$ −440° and +442° (*c* 1.00, THF)) were prepared in 79% yield from corresponding 1,1′-bi-2-naphthols **1** (Scheme 1 for the *R*-form) as reported for racemic one.[4] Anionic ring-opening polymerization of **2** with *t*-BuOK afforded thoroughly insoluble materials (**3**)[9] in ordinary organic solvents such as chloroform, DMF, DMSO, ethylene carbonate, and so on, unlike the corresponding polycarbonate from racemic **2** which was readily soluble in typical organic solvents such as THF, chloroform, benzene, etc. To enhance the solubility of **3**, long alkyl chain containing polymers (**6**) were designed and synthesized. Carbonate cyclization of two octyl group containing binaphthol **4**, derived from **1** through four steps in 63% overall yield, was similarly[4] carried out to afford cyclic carbonates (**5**, $[\alpha]^{23}_{\mathrm{D}}$ −280° (*c* 0.15, THF)) in 86% yield. Anionic polymerization of **5** with *t*-BuOK yielded polycarbonate **6**[10] (for the *R*-form, $[\alpha]^{24}_{\mathrm{D}}$ + 530° (*c* 0.15, THF) as methanol-insoluble polymer (Scheme 1). The identical IR spectrum of **6** to **3** indicated that the insoluble product **3** can be a similar polycarbonate.[9]

The polymer unit model (*R*)-**7** ($[\alpha]^{24}_{\mathrm{D}}$ − 21° (*c* 0.15, THF)) was prepared quantitatively by dissolving (*R*)-**5** in methanol at room temperature. The sign of specific rotation of (*R*)-**6** was opposite to that of (*R*)-**7**, whereas its value was much larger than that of (*R*)-**7**. The same relation could be observed in the CD spectra of (*R*)-**6** and (*R*)-**7** where clear opposite Cotton effect was confirmed (Figure 1). The CD spectrum of (*R*)-**6** exhibited intense bisignate Cotton effects of positive first and negative second signs around 200−400 nm. No solvent effect was confirmed: the CD curve was little changed by changing solvent (THF, ether, and cyclohexane) in each case. The CD curve of (*R*)-**6** was mirror image with that of (*S*)-**6** (Figure 1), suggesting perfectly opposite

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(9) IR of **3**: (KBr) $\nu_{\mathrm{C=O}}$ 1777, $\nu_{\mathrm{C-O}}$ 1300−1100 cm^{-1}.

(10) To a solution of (*R*)-**5** (171 mg, 0.32 mmol) in THF (3.2 mL) was added 7.16 μL of a solution of *t*-BuOK (0.477 M) in THF in one portion at 0 °C. The mixture was stirred for 15 min at 0 °C. Polymer **6** was obtained as methanol-insoluble product (white powder, yield 80−81%, M_n 4700−5800, M_w/M_n 1.3, IR(KBr)$\nu_{\mathrm{C=O}}$ 1767, $\nu_{\mathrm{C-O}}$ 1250, 1188 cm^{-1}).

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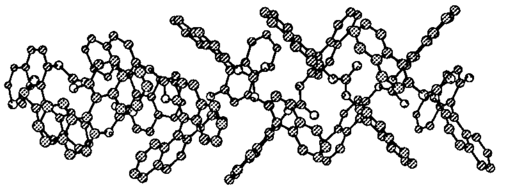
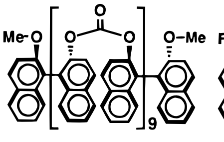


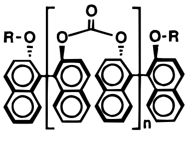
Figure 2. Side view of optimized structure of the model decamer (*R*)-**8** (dihedral angle between the two naphthalene rings: $\tau = 73°$) obtained by empirical conformational analysis (MM2 calculations).

Cotton effect depending on the monomer chirality. Such clear difference in Cotton effect between (*R*)-**6** and (*R*)-**7** suggests that some special conformational effect of (*R*)-**6** exerts considerable influence on the CD.

Empirical conformational analysis of a model decamer of (*R*)-**3** ((*R*)-**8**) by MM2 calculation indicated a slightly distorted helix (Figure 2), revealing a possible helical structure of (*R*)-**3**.[11] To confirm it, the CD spectrum calculation[12] was carried out for the modified structure of (*R*)-**8** which was corrected as a straightforward 4_1-helix molecule. The calculated CD spectrum of (*R*)-**8** nearly coincided with the observed CD spectrum of (*R*)-**6** (Figure 1), strongly suggesting stable helix structure of **6** in solution and the insolubility of **3** probably due to such regular structure.



(*R*)-**8**



(*S*)-**9**, n=0, R=H, SiMe$_2$Bu^t (1 merSi)
(*S*)-**10**, n=1, R=SiMe$_2$Bu^t (2 merSi2)
(*S*)-**10'**, n=1, R=H (2 merOH2)
(*S*)-**11**, n=1, R=H, SiMe$_2$Bu^t (2 mer Si)
(*S*)-**12**, n=3, R=SiMe$_2$Bu^t (4 merSi2)
(*S*)-**12'**, n=3, R=H (4 merOH2)
(*S*)-**13**, n=3, R=H, SiMe$_2$Bu^t (4 mer Si)
(*S*)-**14**, n=4, R=SiMe$_2$Bu^t (8 merSI2)
(*S*)-**14'**, n=4, R=H (8 merOH2)
(*S*)-**15**, n=2, R=SiMe$_2$Bu^t (3 merSi2)
(*S*)-**15'**, n=2, R=H (3 merOH2)

To clarify the origin of the CD spectral change from **8** to **3** or **6**, a number of silylated and unsilylated oligomeric terminal diphenols (2−8-mers (*S*)-**9**−(*S*)-**15**) as model oligomers for **3** were synthesized. The CD spectra of several oligomers are shown in Figure 3 in which a dramatic change of Cotton effect around 3-mer from (−) to (+) occurs while a pronounced big increase in intensity takes place from 4-mer. Specially noteworthy is unambiguously different Cotton effect of dihydroxy trimer (**15′**) from that of disilylated trimer (**15**): this would be due to a certain structural change by some interaction between the two silyl groups.

The fact that (*S*)-4- and -8 mers practically have CD curves resembling that of polymer (*S*)-**6** reveals that they hold similar secondary structures to **3** and **6**. The remarkable CD spectral change dependent on the degree of polymerization can be caused by the generation of some specified structure like helix, as suggested by the conformational calculation which appears to expect a possible through-space interaction between the naphthalene moieties on the helix.

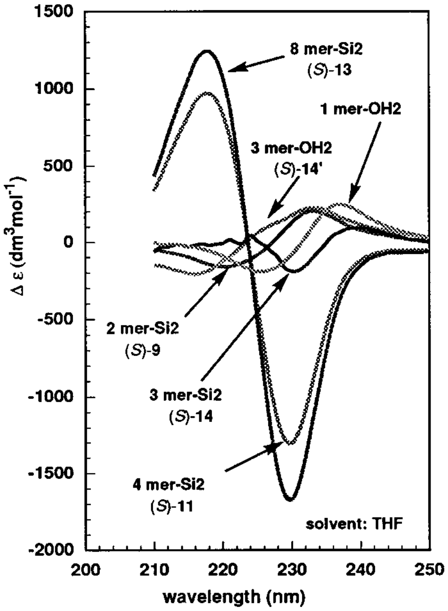


Figure 3. CD spectra of oligomers ((*S*)-**10**, (*S*)-**15**, (*S*)-**15′**, (*S*)-**12**, and (*S*)-**14**) in THF. “1 mer-OH2” denotes (*S*)-1,1′-bi-2-naphthol.

Thus, the present work describes the synthesis of optically active polycarbonates consisting of axially chiral binaphthyl groups as the main chain units, which would take a stable helix in solution. The CD behaviors of the oligomers are very interesting and suggestive of the conformational change depending on the molecular weight. Although many artificial polymers take stable helix structures in solution,[2,13,14] the number of backbone atoms of one unit (*n*) is usually limited to less than 4.[13] It is generally accepted that helix stability in non-hydrogen-bonded self-assembly molecules (i.e., typical artificial helix molecules)[15] depends on both rigidity of the main chain and appropriate interaction between the side chains.[16] Provided the helical structures of the polymers **3** and **6**, it would be quite significant that the number of backbone atoms of one unit of them ($n = 7$) is extraordinarily large enough to exceed that of DNA ($n = 6$).[13]

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Supporting Information Available: CD spectra of polycarbonate (*R*)-**6** and its unit model (*R*)-**7**, physical data of the monomers (**1**, **2**, **4**, and **5**), and synthetic schemes of alkylated binaphthol (IR)-**4** and oligomers (*S*)-**9**−**15′** (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[11] The conformational analysis of **8** was carried out by using CAChe version 3.9. The structure parameters (bond lengths and angles) for the naphthalene and carbonate groups were taken from the X-ray crystallographic data of (*R*)-**10** ($[\alpha]^{20}_{D}$ +51.7° (*c* 1.00, THF)) (unpublished data). The total energy of **8** was calculated by varying the four dihedral angles around the carbonate group from 5 to 180° with an interval of 5°. Dihedral angle between the two naphthalene rings was set at $\tau = 73°$. Generally dihedral angle of binaphthyl system is ranging from 68 to 92°: Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999 and references therein. As a result, right-handed screw sense *P* was suggested for (*S*)-**8**, while left-handed screw sense *M* was for (*R*)-**8**.

[12] Theoretical CD spectrum of the modified **8** was computed on the basis of similar exiton theory applied to the quinoxaline system: Sisido, M.; Ishikawa, Y.; Harada, M.; Ito, K. *Macromolecules* **1991**, *24*, 3999. Ito, Y.; Ihara, E.; Murakami, M.; Sisido, M. *Macromolecules* **1992**, *25*, 6810.

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