Optically Active Poly- and Oligo(biphenyl carbonate)s as Stable Helical Molecules

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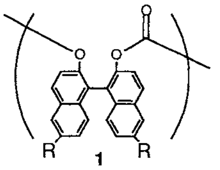
Low molecular weight polycarbonate ((*R*)-**2**) derived from polycondensation of (*R*)-4,4',6,6'-tetramethyl-2,2'-dihydroxybiphenyl ((*R*)-**3**) showed large Cotton effect at 210 nm compared with its unit model. CD spectra of model oligomers of (*R*)-**2** (2-8mers) obtained by stepwise synthesis and their structure simulation suggested that (*R*)-**2** and higher oligomers can hold a stable left-handed helix.

Many naturally occurring polymers such as polypeptides, amylose, and DNA adopt helical structures, which are essential to their characteristic functions such as catalytic activity and preservation or transmission of genetic information. Their helical structures are induced by asymmetric carbon atoms on the main chain. On the other hand, a few artificial polymers with stable helical conformations have been synthesized to date by either asymmetric polymerization of a prochiral monomer and enantioselective polymerization of a racemic monomer mixture.[1, 2] Meanwhile, optically active polymers consisting of the units with atropisomerism such as binaphthyl group,[3] have recently attracted much attention.[4] As part of our program to construct artificial helical polymers, we have started synthesizing poly(aryl carbonate)s involving C_2-chiral units with atropisomerism.[5] Recently, we have reported poly(binaphthyl carbonate)s (**1**) with a helical conformation and their helicity.[6] To investigate the scope and limitation of C_2-chiral aryl unit for polymer helicity, 4,4',6,6'-tetrasubstituted-2,2'-dioxybiphenyl unit was chosen. In this paper, we report the synthesis and structure of poly(biphenyl carbonate)s (**2**) and their model oligomers.



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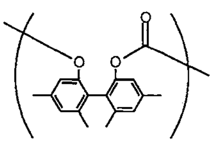

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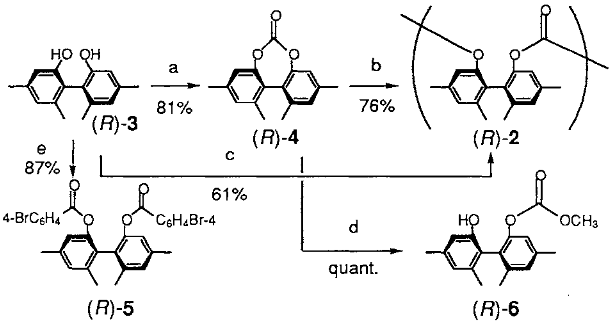
(+)-4,4',6,6'-Tetramethyl-2,2'-dihydroxybiphenyl ((+)-**3**) was prepared by the procedure reported by Toda *et al.*[7] The (*R*)-configuration for (+)-**3** was established by applying the CD exciton coupling method to the corresponding bis(4-bromobenzoyl) ester ((+)-**5**) derived from (+)-**3**.[8,9] Cyclic carbonate ((*R*)-**4**) was prepared by treating (*R*)-**3** with triphosgene.[10] Anionic ring-opening polymerizations of (*R*)-**4** with 20-50 mol% *t*-BuOK in THF under various conditions always gave thoroughly insoluble materials quantitatively in ordinary solvents such as chloroform, DMF, DMSO etc.,[11] similarly to the case of **1** (R = H).[6] To prepare soluble polymer, polycondensation of (*R*)-**3** with bis(4-nitrophenyl) carbonate in refluxing toluene was conducted. Although most of the products were still insoluble, a dichloromethane-soluble low molecular weight part (M_n = 200, M_w/M_n = 1.10 (PSt standards),[12] $[\alpha]_D^{26}$ +27.4° (*c* 0.1, THF)) could be collected in *ca.* 1% yield. The identical IR spectra of the two parts indicated that they were the same polycarbonates assigned as (*R*)-**2**.



Scheme 1. Reagents and Conditions: (a) triphosgene, pyridine, THF, rt. (b) *t*-BuOK, THF rt, 20 min. (c) bis (4-nitrophenyl) carbonate, DMAP, toluene, reflux. (d) MeOH, rt. (e) 4-BrC$_6$H$_4$COCl, pyridine, CH$_2$Cl$_2$.

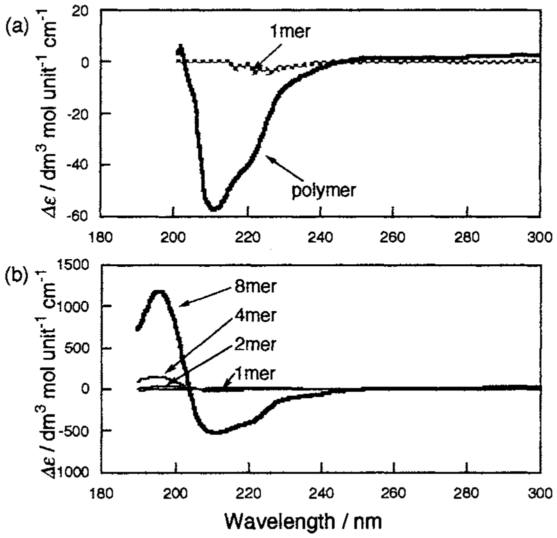
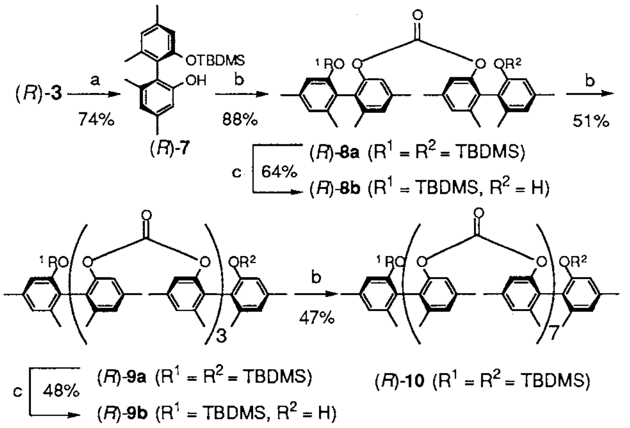


Figure 1. CD spectra of (a) polycarbonate (**2**) and 1mer model (**6**) in THF and (b) 1mer (**6**), 2mer (**8a**), 4mer (**9a**), and 8mer model (**10**) in cyclohexane.

The polymer unit model (*R*)-**6**[13] was prepared in a quantitative yield by dissolving (*R*)-**4** in methanol at room temperature. The intensity of the Cotton effect around 210 nm in the CD spectrum of the soluble (*R*)-**2** was much larger (*ca.* 10 times) than that of (*R*)-**6** as illustrated in Figure 1 (a). This result suggests that **2** adopts a regular structure such as helix like the case of **1**.[6] A structure-optimized model of 8mer is shown in Figure 2,[14] in which the main chain takes a left-handed 2_1-helix.

To investigate the dependence of the structure on degree of polymerization (DP), a number of model oligomers for (*R*)-**2** were synthesized as shown in Scheme 2.[6,15] Monosilylation of (*R*)-**3** followed by condensation with triphosgene gave disilylated 2mer ((*R*)-**8a**). Desilylation with 5 equiv of trifluoroacetic acid afforded monosilylated 2mer ((*R*)-**8b**). The same procedure for (*R*)-**8b** yielded disilylated 8mer ((*R*)-**10**). The inspection of CD spectra of some of these oligomers, shown in Figure 1 (b), indicates an extraordinarily big Cotton effect of 8mer ((*R*)-**10**) compared with those of 1mer-4mer.[16] The DP-dependent remarkable CD intensity increase in addition to the CPK model study makes us conclude that polycarbonate derived from (*R*)-**3** ((*R*)-**2**) and their higher oligomers adopts a stable helix, judging from similar behavior to those of model oligomers of **1**.[6]



Scheme 2. Reagents and Conditions: (a) TBDMSCl, Et_3N, THF, rt. (b) triphosgene, pyridine, CH_2Cl_2, rt. (c) trifluoroacetic acid (5 equiv), CH_2Cl_2, rt.

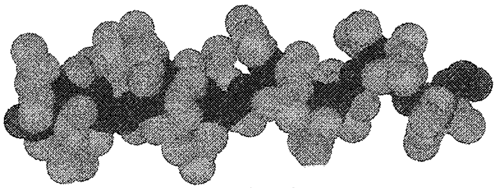


Figure 2. A model of (*R*)-**10** ($R^1 = R^2 = H$) optimized with an MM2 force field (CAChe system). The polycarbonate main chain is depicted in black. Hydrogen atoms are omitted for clarity.

Thus, possibility of optically active biphenyl group as a C_2-chiral unit for helical polycarbonate was studied in this work, which demonstrates that the biphenyl group can be a suitable C_2-chiral unit like binaphthyl group,[6] although it appears to induce a helix slightly less stable than the binaphthyl-based one.

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References and Notes

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9 (+)- **5**: pale yellow crystals; mp 153-154 °C; IR (KBr): $\nu_{C=O}$ 1734 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.66 (4H, d, J = 9 Hz), 7.46 (4H, d, J = 9 Hz), 6.94 (4H, s), 2.29, 2.05 (s x 2, 12H); Found: C, 59.04; H, 3.96%. Calcd for $C_{30}H_{24}Br_2O_4$: C, 59.23; H, 3.98%; CD λ_{ext} (THF, 22 μM), nm ([$\Delta\varepsilon$]): 255 (-34), 238 (+12). The bisignate Cotton effects of negative first and positive second signs around 240 nm clearly show (*R*)-configuration of (+)-**5**.

10 (*R*)-**4**: colorless crystals; mp 187-188 °C; IR (KBr): $\nu_{C=O}$ 1787 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.06, 6.99 (s x 2, 4H), 2.38, 2.23 (s x 2, 12H); Found: C, 76.22; H, 6.10%. Calcd. for $C_{17}H_{16}O_3$: C; 76.10; H 6.01%.

11 This might be attributed to the fast propagation, because anionic ring-opening polymerization of cyclic carbonate to yield (*R*)-**1** (R = H) with *t*-BuOK in THF was completed within 15 sec at -78 °C: T. Takata, J. Matsuo, and T. Endo, unpublished data. When racemic **4** was used as a monomer, soluble polymer (**2**) was obtained quantitatively.

12 The averaged degree of polymerization was determined as 4 from the ^1H NMR (400 MHz, $CDCl_3$, 295 K) spectrum.

13 (*R*)-**6**: a colorless oil; $[\alpha]_D^{20}$ +4° (*c* 0.1, THF); IR (NaCl); $\nu_{O\text{-}H}$ 3500 cm^{-1}; $\nu_{C=C}$ 1759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08, 6.90, 6.68, 6.66 (s x 4, 4H), 3.67 (s, 3H), 2.38, 2.30, 1.99, 1.90 (s x 4, 12H); Found: C, 70.27; H, 6.62%. Calcd for $C_{18}H_{20}O_4 \cdot (H_2O)_{0.5}$: C, 69.89; H, 6.84%.

14 The crowdness between side chains in the optimized structures of **2** seems less than that of **1**. This weakened side chain interaction may make 4mer model (**9a**) difficult to take a stable helical structure, as presumed from much lower CD intensity of it than that of 8mer (**10**) (Figure 1 (b)) unlike the case of model oligomers of **1**.[6]

15 (*R*)-**8a**: a colorless heavy oil; $[\alpha]_D^{20}$ -29° (*c* 0.1, THF); IR (KBr) $\nu_{C=O}$ 1774 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.94, 6.74, 6.54, 6.43 (s x 4, 8H), 2.41, 2.37, 2.33, 2.01, 1.94 (s x 4, 24H), 0.68 (s, 18H), 0.09, 0.02 (s x 2, 12H); FAB-HRMS for $C_{45}H_{63}O_5Si_2$ (M + H^+): Calcd m/z 739.4214; obsd 739.4202. (*R*)-**9a**: a white amorphous solid; $[\alpha]_D^{20}$ +51° (*c* 0.1, THF); IR (KBr) $\nu_{C=O}$ 1772 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.95, 6.88, 6.69, 6.62, 6.60, 6.57 (s x 6, 16H), 2.39, 2.38, 2.27, 2.13, 1.98, 1.93, 1.84 (s x 7, 32H), 0.71 (s, 18H), 0.09, 0.04 (s, 12H); FAB-HRMS for $C_{79}H_{95}O_{11}Si_2$ (M + H^+): Calcd m/z 1275.6412; obsd 1275.6420. (*R*)-**10**: a white amorphous solid; $[\alpha]_D^{20}$ -29° (*c* 0.1, THF); IR (KBr) $\nu_{C=O}$ 1770 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.27-6.62 (m, 32H), 1.98-1.74 (m, 64H), 0.84 (s, 18H), 0.14, 0.07 (s x 2, 12H); FAB-HRMS for $C_{147}H_{159}O_{23}Si_2$ (M + H^+): Calcd m/z 2348.0810; obsd 2348.0767.

16 The CD spectra of 1mer-8mer in cyclohexane were essentially same as those in THF.