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Notes

Synthesis and Chirality Sensing Properties of Poly[(phenyleneethynylene)-*alt*-(carboxybiphenyleneethynylene)]s

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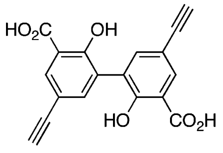
Living organisms consist of a variety of optically active substances including biological polymers, such as nucleic acids and proteins, and often show quite different biological responses toward a pair of enantiomers, such as chiral drugs and chemicals.[1] Therefore, the development of useful and sensitive methods of the detection and assignment of chirality of molecules has recently aroused great interest. To date, a large number of artificial receptor molecules (hosts) have been developed for these purposes.[2,3] Among them, achiral or dynamically racemic molecules[4] and supramolecules[5] bearing chromophoric units and π-conjugated macromolecular helical systems[2a,b,6,7] are particularly interesting because upon noncovalent binding to a nonracemic guest, the chirality is transferred to the receptors, resulting in the generation of one of the enantiomeric or diastereomeric twisted or helical conformers, thus producing a characteristic induced circular dichroism (ICD) in the chromophore region of the receptors.[2] The ICDs can be utilized as a novel chirality-sensing probe to determine the absolute configuration and enantiomeric excess (ee) of the guest molecules. In sharp contrast to achiral or dynamically racemic chromophoric small molecular systems, chirality is significantly amplified in dynamic helical polymers due to the high cooperativity,[2a,b,8] which enables the detection of chirality of the nonracemic guests with a high sensitivity.



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Recently, we reported that the C_2-symmetric carboxybiphenol **1** with a dynamic axial chirality could respond to the chirality of optically active diamines, thus showing an ICD due to an excess single-handed, axially twisted conformation.[9] We anticipated that **1** might be used as a versatile building block for the synthesis of more sensitive chirality-responsive, π-conjugated polymers because **1** possesses polymerizable ethynyl groups at the *meta* positions on the phenyl moieties, and the resulting π-conjugated polymers may form a dynamic helical conformation; the chiral information of the guest first transfers to the carboxybiphenol moieties through noncovalent acid−base interactions, and subsequently, the induced axial chirality may be further amplified in the π-conjugated polymer backbone as an excess of a single-handed helix. To explore this possibility, three novel poly[(phenyleneethynylene)-*alt*-(carboxybiphenyleneethynylene)]s (poly-**5a**−poly-**5c**) were synthesized by the palladium(0)−copper(I)-catalyzed cross-coupling polymerization of the fully protected carboxybiphenol derivative **2** with *o*-, *m*-, and *p*-diiodobenzene derivatives **3a**−**3c**, followed by alkaline hydrolysis of the ester protecting groups (Scheme 1). Their chirality sensing properties were then investigated by CD spectroscopy, and the results were compared to that of **1**.

The carboxybiphenol derivative **2** bearing two protected hydroxy and carboxy groups as acetates and methyl esters, respectively, was synthesized by the reaction of 3,3′-bis(methoxycarbonyl)-5,5′-diethynyl-2,2′-biphenol, which had been prepared according to the previously reported method,[9a] with acetyl chloride, and was copolymerized with three regioisomers of the diiodobenzene derivative bearing two triethylene glycol substituents (**3a**, **3b**, **3c**) (Scheme 1). The copolymerization was carried out using a Pd-catalyzed, CuI-modified cross-coupling reaction in the presence of diisopropylamine in toluene at 60 °C, affording the corresponding polymers (poly-**4a**−poly-**4c**) in high yield (>73%) (Table 1). This method is well-known to be effective for the synthesis of poly(aryleneethynylene)s.[10] The number-average molecular weights (M_ns) of poly-**4a**−poly-**4c** were relatively high ($(1.0-1.3) \times 10^4$), as determined by size exclusion chromatography (SEC). The polymers were then converted to poly-**5a**−poly-**5c** by alkaline hydrolysis of the ester groups (Scheme 1). Complete removal of the acetyl and methyl protecting groups of poly-**4a**−poly-**4c** was confirmed by IR, ^{1}H NMR, and elemental analyses. The obtained poly-**5a**−poly-**5c** were soluble in tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF).

The CD spectra of poly-**5a**−poly-**5c** were then measured in THF in the presence of optically active diamines in order to investigate whether they could respond to the chirality of the diamines, showing a characteristic ICD. When the concentration of poly-**5a** was higher than 0.0372 mM (monomer units), the polymer precipitated with the chiral diamine **6** (Chart 1), probably due to the interchain complexation of poly-**5a** with **6**. Therefore, the CD and absorption spectra of poly-**5a** were measured in THF at [poly-**5a**] = 0.0124 mM and [**6**]/[poly-**5a**] = 40 (Figure 1A). The poly-**5a** consisting of carboxybiphenol units linked by the *p*-phenylene residue exhibited a broad electronic absorption up to 410 nm with a peak at around 375 nm, and the absorbance maximum slightly shifted to a longer wavelength in the presence of the chiral diamine **6** (spectra e and f in Figure 1A). The poly-**5a** complexed with **6** exhibited an ICD in the long wavelength region of the π-conjugated polymer backbone (275−410 nm). The (1*R*,2*R*)- and (1*S*,2*S*)-**6** enantiomers induced mirror images of intense ICDs to each other (spectra a and b in Figure 1A). These results indicate that an

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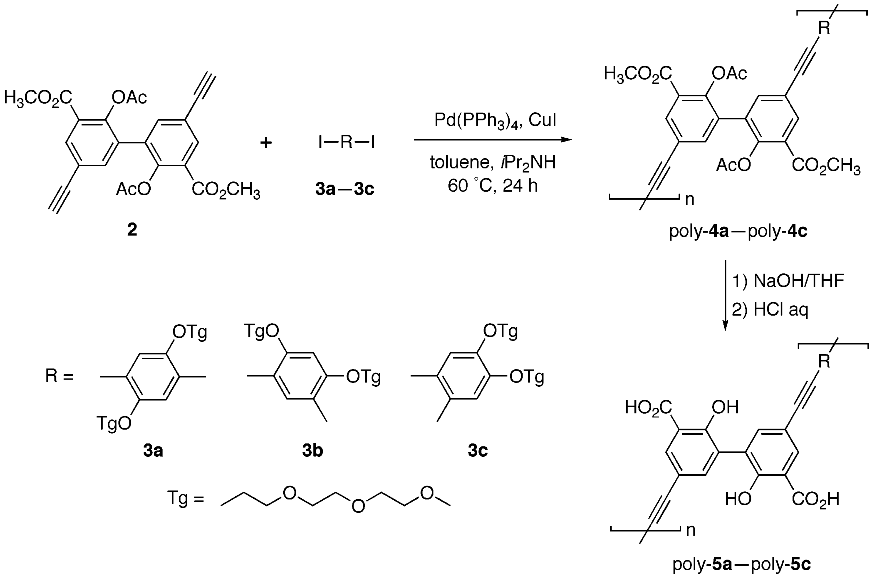
Scheme 1. Synthesis of Poly-5a−Poly-5c



excess single-handed, axially twisted conformation may be generated in the carboxybiphenol units of poly-**5a** as a result of the diastereoselective complexation with the chiral diamine **6**. The induced axial chirality may further transfer to the polymer backbone as an excess of a single-handed helical conformation, so that the polymer showed an ICD in the long wavelength region. The carboxybiphenol **1**, a model compound of poly-**5**, also showed an ICD with **6** enantiomers in THF, but at rather shorter wavelengths (275−370 nm).[9a]

Other chiral diamines, such as **7** and **8**, also exhibited ICDs with poly-**5a**, while no apparent CD was observed in the presence of chiral monoamines, such as (*R*)-**9** and (*R*)-**10** in THF and THF/$CHCl_3$ (1/9, v/v). The ICD results for various chiral diamines (**6**−**8**) with poly-**5a** are summarized in Table 2.[11] Structurally similar chiral diamines of the same configuration (**6**−**8**) afforded the same Cotton effect signs, suggesting that poly-**5a** may be utilized as a novel chirality sensor for determining the absolute configuration of the chiral diamines.

The ICD intensity was found to be significantly time dependent and steadily decreased with time when the concentration of (1*R*,2*R*)-**6** is less than [**6**]/[poly-**5a**] ≤ 10. For example, the ICD almost completely disappeared after 1 h at [**6**]/[poly-**5a**] = 4. Such a decrease in the ICD with time became slower with the increasing concentration of (1*R*,2*R*)-**6** and was negligibly small at [**6**]/[poly-**5a**] > 10. Similar time-dependent ICD intensity changes were also observed for the carboxybiphenol **1** with (1*R*,2*R*)-**6** complex.[12] The reason is not clear at present, but these concentration- and time-dependent ICD changes of the poly-**5a**−**6** complex may be closely related to the dynamic nature of the biphenol axial chirality; one of the interconverting *cisoid* and *transoid* conformers of the biphenol unit (Figure 2) may be favorably generated with an excess single-handed twist upon complexation with the chiral **6**, and this conformational change may be dependent on the concentration of **6**.

Table 1. Polymerization Results of 2 with 3a−3c under Pd(0)-Catalyzed Cross-Coupling Conditions in Toluene−Diisopropylamine (7/3, v/v) at 60 °C for 24 h[a]

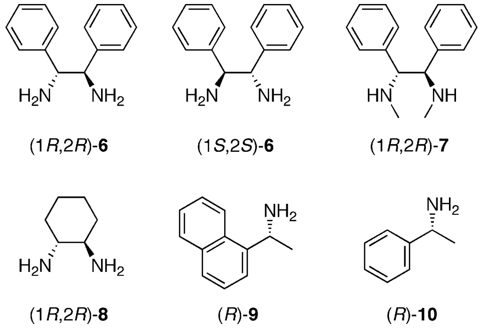
entry	monomer	polymer	yield (%)[b]	$M_n \times 10^{-3}$ (M_w/M_n)[c]
1	**2** + **3a**	poly-**4a**	94.6	13.3 (2.21)
2	**2** + **3b**	poly-**4b**	90.0	10.1 (1.59)
3	**2** + **3c**	poly-**4c**	73.4	13.4 (1.41)

[a] [**2** + **3**] = 180 mM, [$Pd(PPh_3)_4$] = 5.32 mM, [CuI] = 26.6 mM, **[2]**/**[3]** = 1.03. [b] Methanol-insoluble part. [c] Determined by SEC in $CHCl_3$ at 40 °C (polystyrene standard).

In order to explore the effect of the phenylene unit connectivity of poly-**5** on their chirality induction, the CD and absorption spectra of poly-**5b** and poly-**5c** with (1*R*,2*R*)-**6** in THF were measured. Upon complexation with the chiral diamine, these *meta*- and *ortho*-linked π-conjugated polymers also showed ICDs in the polymer backbone regions, but their ICD patterns and absorption spectra were significantly different from each other and those of the *para*-linked poly-**5a** depending on the structures of the phenylene units (spectra c and d in Figure 1A). In particular, a clear split-type Cotton effect was observed for poly-**5c**. We note that the absorption maxima (λ_{max}) of poly-**5b** and poly-**5c** noticeably shifted to shorter wavelengths by ca. 30 nm compared to that of poly-**5a**, indicating a decrease in their effective π-conjugation lengths. These differences in the ICD patterns and UV−vis spectra of poly-**5** consisting of the same carboxybiphenol and phenylene units, but the different linkage positions (*ortho*, *meta*, and *para*), suggest that these polymers may have a different chiral conformation, such as a helical conformation with a predominant screw sense depending on the structures of the phenylene units assisted by an induced dynamic axial chirality of the carboxybiphenol units through acid−base interaction.[13] The biphenol units may first take an excess single-handed axially twisted conformation upon complexation with the chiral diamine, which will further generate a different macromolecular chirality in the polymer backbones.[15]

Interestingly, these polymers exhibited different color changes in their emissions; the emission color of poly-**5b** and poly-**5c**

Chart 1. Structures of Optically Active Amines



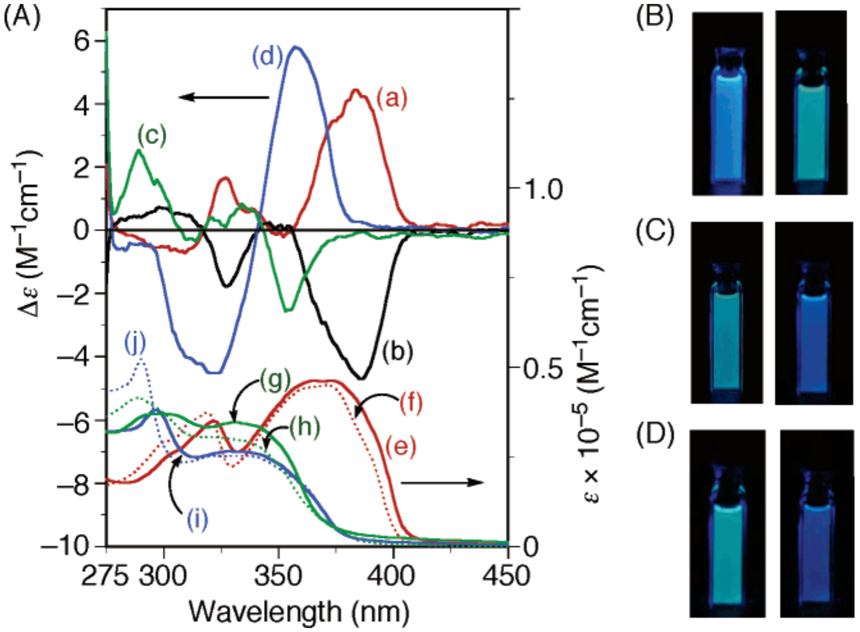


Figure 1. (A) CD spectra of poly-**5a** with (1*R*,2*R*)-**6** (a, red line) and (1*S*,2*S*)-**6** (b, black line) and poly-**5b** (c, green line) and poly-**5c** (d, blue line) with (1*R*,2*R*)-**6** in THF at room temperature. Absorption spectra of poly-**5a** (e, f), poly-**5b** (g, h), and poly-**5c** (i, j) with (e, g, i; solid lines) and without (1*R*,2*R*)-**6** (f, h, j; dotted lines) in THF at room temperature are also shown. [**6**]/[polymer] = 40 and [polymer] = 0.0124 mM. (B−D) Photographs of the visible difference of poly-**5a** (B), poly-**5b** (C), and poly-**5c** (D) in the absence (left) and presence (right) of (1*R*,2*R*)-**6** in THF under UV light at 365 nm.

Table 2. CD Data of Poly-5a−Poly-5b−Chiral Diamine Complexes at Room Temperature[a]

				first Cotton effect	
entry	polymer	solvent	diamine	sign	Δε (λ)
1	poly-**5a**	THF	(1*R*,2*R*)-**6**	+	4.46 (383)
2		THF	(1*S*,2*S*)-**6**	−	4.67 (383)
3		THF	(1*R*,2*R*)-**7**	+	6.66 (392)
4		THF/CHCl$_3$ (1/1, v/v)	(1*R*,2*R*)-**8**	+	1.43 (380)
5	poly-**5b**	THF	(1*R*,2*R*)-**6**	−	2.56 (353)
6		THF	(1*R*,2*R*)-**7**	−	7.16 (352)
7		THF/CHCl$_3$ (1/1, v/v)	(1*R*,2*R*)-**8**		ca. 0

[a] [Diamine]/[polymer] = 40 and [polymer] = 0.0124 mM; Δε (M^{-1} cm^{-1}) and λ (nm).

changed from green to blue upon complexation with the mono- and diamines, while that of poly-**5a** changed from blue to green (Figure 1B−D). Poly-**5b** and poly-**5c** also exhibited ICDs upon complexation with other chiral diamines. Although the poly-**5b**−chiral diamine complexes showed a similar ICD pattern (Table 2), the poly-**5c** complexed with the same chiral diamines exhibited significantly different ICDs in their patterns depending on the structures of the diamines (Figure S-2 in the Supporting Information), probably due to a difference in the conformations of poly-**5c** induced by the chiral diamines. Moreover, it should be noted that poly-**5c** exhibited intense ICDs upon complexation with chiral monoamines, such as (*R*)-**9** and (*R*)-**10** (Figure S-2 in the Supporting Information), whereas poly-**5b** as well as poly-**5a** and the model compound **1** did not show any ICD in the presence of the chiral monoamines in their π-conjugated chromophore regions (>275 nm).

In summary, novel poly[(phenyleneethynylene)-*alt*-(carboxybiphenyleneethynylene)]s poly-**5a**−poly-**5c** were synthesized by the cross-coupling polymerization of the carboxybiphenol derivative **2** with the *o*-, *m*-, and *p*-diiodobenzene derivatives **3a**−**3c**, followed by alkaline hydrolysis of the ester groups. The complexes of poly-**5a**−poly-**5c** with optically active diamines exhibited a characteristic ICD in the long wavelength regions of the π-conjugated polymer backbones in THF, probably due to a macromolecular chirality such as a helical conformation induced by an excess single-handed, axially twisted conformation of the carboxybiphenol units through chiral acid−base interactions. This concept of chirality transfer from small molecules into a dynamic axial chirality and subsequent amplification in the polymer backbone may be applicable for the design and synthesis of other novel π-conjugated polymeric receptors bearing dynamically racemic units as a building block.

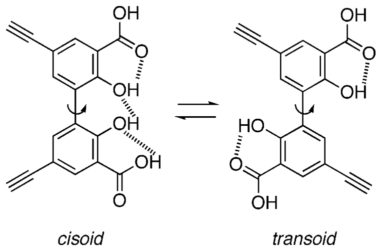


Figure 2. Interconverting *cisoid* and *transoid* conformers of the carboxybiphenol unit.

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Supporting Information Available: Experimental details of the synthesis and characterization of **2**, **3a**−**3c**, poly-**4a**−poly-**4c**, and poly-**5a**−poly-**5c**, optimized structures of poly-**5a**−poly-**5c**, CD spectra of poly-**5c** with chiral amines, and fluorescence spectra of poly-**5** with or without chiral amine. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Morioka, K.; Tamagawa, N.; Maeda, K.; Yashima, E. *Chem. Lett.* **2006**, *35*, 110. The unique feature of such axially chiral, but dynamically racemic, 2,2′-biphenols has been used for constructing asymmetric catalysts and chirality sensors. See for examples: (b) Takagi, H.; Mizutani, T.; Horiguchi, T.; Kitagawa, S.; Ogoshi, H. *Org. Biomol. Chem.* **2005**, *3*, 2091. (c) Eelkema, R.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 13480. (d) Mikami, K.; Yamanaka, M. *Chem. Rev.* **2003**, *103*, 3369. (e) Walsh, P. J.; Lurain, A. E.; Balsells, J. *Chem. Rev.* **2003**, *103*, 3297. (f) Hayashi, T.; Aya, T.; Nonoguchi, M.; Mizutani, T.; Hisaeda, Y.; Kitagawa, S.; Ogoshi, H. *Tetrahedron* **2002**, *58*, 2803. (g) Kubo, Y.; Ohno, T.; Yamanaka, J.; Tokita, S.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12700. (h) Mizutani, T.; Takagi, H.; Hara, O.; Horiguchi, T.; Ogoshi, H. *Tetrahedron Lett.* **1997**, *38*, 1991.

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(11) The optically active compounds used in this study showed no CD above 275 nm except for (*R*)-**9**.

(12) We previously proposed a 2:2 cyclic tetramer as a plausible CD active species for the **1**−**6** complex because such a tetramer formation enables the favorable *cisoid* conformation of **1** due to the intramolecular hydrogen bonds between the adjacent hydroxy groups of **1**, thus generating an excess of one of the axially twisted conformers.[9a]

(13) Molecular modeling and molecular mechanics calculations were then performed for poly-**5a**−poly-**5c** to obtain information on the possible helical conformations of the polymers. All the biphenol units were assumed to have a *cisoid* conformation because biphenols are known to favorably adopt a *cisoid* conformation due to the intramolecular hydrogen bonds between the adjacent hydroxy groups.[14] The computer-generated, optimized helical structures of poly-**5a**−poly-**5c** by a conjugate gradient method are completely different depending on the structures of the phenylene units (Figure S-1 in the Supporting Information). Therefore, these differences in their helical conformations may be correlated with the differences in their ICD patterns observed for poly-**5a**−poly-**5c** complexed with the chiral diamine **6** (Figure 1A).

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(15) Nonlinear effects between the ee of the chiral diamine **6** and observed ICD intensities of poly-**5a**−poly-**5c** were scarcely observed in the present systems. For typical nonlinear effects, see refs 2a, 2b, and 8.

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