Nonproportional Effects of Optical Purity of Chiral Aryl Isocyanide Monomers Possessing (d) or (l)- Menthoxycarbonyl Groups on Induction of Screw-Sense in Poly(aryl isocyanide)s

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ABSTRACT: Polymerization of p- and m-menthoxycarbonylphenyl isocyanides having various optical purities has been performed by use of a Pd-Pt μ-ethynediyl dinuclear complex as an initiator and the induction of the screw-sense of the resulting helical polymers has been examined. The absolute value of optical rotations and the Cotton effect at about 365 nm in CD spectrum nonproportionally increase with increase in the optical purity of menthoxycarbonylphenyl isocyanides. In the polymers of p-menthyloxycarbonylphenyl isocyanide a positive nonlinear effect is observed while m-substituted analogs show a negative one.

KEY WORDS   Poly(isocyanide)s / Helical Polymer / Optical Rotation / Circular Dichroism / Transition Metal Complex /

Macromolecular asymmetry arisen from the helical structure of a polymer main chain receives much attention since it is closely related to the function of polymers.[1-3] Although many stereoregular macromolecules take a helical conformation in the solid state, they exist as short-range helices in solution.[4] To date limited numbers of synthetic polymers that keep a stable helical structure are known; for example ploy(isocyanate)s,[5-7] poly(chloral)s,[8,9] and poly(triarylmethyl methacrylate)s.[10-12]

P (right handed)   M (left handed)
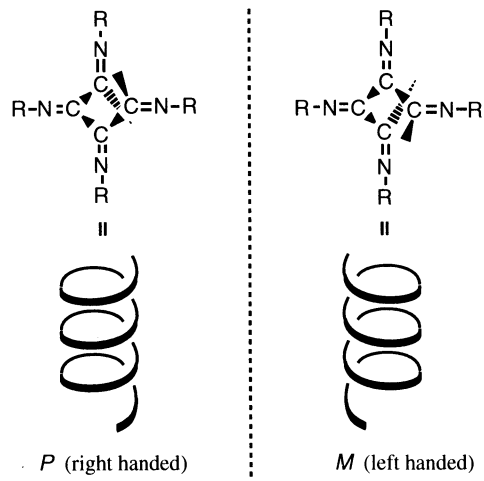
Poly(isocyanide)s having bulky substituents also adopt a stable helical conformation even in solution.[13-16] The helicity in poly(isocyanide)s is determined by the torsion angle of the N=C–C=N bonds and the steric interaction of substituents on the nitrogen atoms. One turn of the helix in poly(isocyanide)s is composed by four monomers. The first example of single-handed helical poly(isocyanide)s has been reported by Drenth and Nolte.[17] They have separated a racemic poly(t-butyl isocyanide)s into a pair of right handed (P) and left handed (M) helical polymers by chromatography using a chiral stationary phase. The helical sense of polymers can be controlled by including chirality in the side group since chiral polymers with P and M helices become diastereomers and are

no longer thermodynamically equivalent.[18-22] Indeed, the polymerization of (R)-(CH₃)₂CHCH₂CH(CH₃)NC gives a left-handed helix preferentially, whereas (S)-PhCH(CH₃)NC produces a right-handed helix. As amino functions of amino acids and peptides can be easily converted in isocyano groups through formamide, some biomimic polymers with helical chirality have been prepared and their properties have been explored extensively.[23,24]

Since chromatographic resolution by an optically active column is less applicable to poly(isocyanide)s other than poly(t-butyl isocyanide)s, some attempts have been made for the selective synthesis of single-handed helical polymers of achiral isocyanides. Addition of optically active amines into the polymerization system of t-butyl isocyanide by a Ni(II) salt generates optical active polymers, which display %ee values up to 85%.[25] Polymerization of achiral isocyanides with bulky chiral co-monomers yielded polymers with a large optical rotation. It is of interest that the helical sense of copolymers of chiral and achiral isocyanides is opposite to that of the homopolymer of a chiral isocyanide.[26] This unusual phenomenon has been explained as follows. The bulky chiral isocyanide polymerizes slowly to give a polymer with an M helix, while the fast polymerization of achiral monomer yields a racemic mixture of P and M helices. In the copolymerization between chiral and achiral isocyanides, the former is preferably included into M helices and results in retarding the growth of M helices relative to P helices which are mainly formed by the achiral monomer. Screw-sense selective (SSS) polymerization of achiral isocyanide by an optically active initiator has been reported by Novak.[27,28] Polymerization of t-butyl isocyanide by nickel initiators possessing chiral acetate ligands gave helical poly(isocyanide)s with predominant one screw-sense while less sterically hindered isocyanide produced optically inactive polymers. However, the molecular weights of the resulting polymers are very low ($M_n < 1,000$). SSS polymerization of 1,2-diisocyanoarene has been achieved by Ito and coworkers using chiral palladium initiators which are obtained by means of the resolution of a diastereomeric mixture using HPLC.[29] Recently they showed that the palladium complex having a 1,1'-binaphthyl group is also effective to SSS polymerization of 1,2-diisocyanoarene.[30,31]

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Previously we reported a novel living polymerization of aryl isocyanides using a μ-ethynediyl Pd–Pt dinuclear complex **1** to give poly(isocyanide)s with a narrow polydispersity index in a quantitative yield.[32,33] This living polymerization has been successfully applied to a novel SSS polymerization system using a block-copolymerization technique.[34] Thus, chiral oligomer complexes prepared from complex **1** and 30 equivalents of optically pure menthoxycarbonylphenyl isocyanide effectively initiate SSS polymerization of achiral isocyanides possessing bulky substituents to give single-handed helical polymers predominantly. The characteristic of this method is that no special operations other than those in usual block copolymer synthesis are needed. Since the oligomeric complexes having an active palladium end group are very stable even in air at room temperature for several months, the oligomeric complexes may be suitable for a practical initiator for the SSS polymerization of aryl isocyanides.

As described above, optically pure menthoxycarbonyl-phenyl isocyanide gave single-handed helical polymers selectively. We were interested in the relationship between the enantiomeric excess (ee) of the chiral monomers and the optical activities of the resulting polymers because poly(isocyanate)s prepared from monomers with low %ee often exhibited a large optical activity similar to those of enantiomerically pure samples and such studies have never been performed on poly(isocyanide)s.[35] Living nature in the polymerization of aryl isocyanides by complex **1** enables the precise synthesis of poly(isocyanide)s from chiral monomers with various ee values. Thus, our polymerization system seems to be suitable to estimate such relationship. We wish to present here the nonproportional effect of the optical purity of isocyanides on the optical activities of the resulting polymers, which is strongly depend on the substituent of the aryl isocyanide monomers.

EXPERIMENTAL

Materials

Aryl isocyanides possessing (*l*)- and (*d*)-menthoxycarbonyl groups were prepared from the corresponding formamide by dehydration.[36] μ-Ethynediyl Pt-Pd complex **1** was prepared by the reaction of Pt(PEt₃)₂(C≡CH)Cl and Pd(PEt₃)₂Cl₂ using a CuCl catalyst as previously reported.[37]

Polymerization

A typical procedure is as follows. To a solution of menthoxycarbonylphenyl isocyanide (246 mg, 0.86 mmol) in 10 mL of THF was added complex **1** (7.5 mg, 8.6 mmol) under an argon atmosphere. The reaction mixture was stirred for 15 h under reflux, and concentrated into about 2 mL under reduced pressure. The resulting solution was poured into 100 mL of methanol. The precipitate was collected and washed with methanol to give yellow solid.

3d: 92% Yield; IR (KBr): v(C≡C) 2088, v(C=O) 1715, v(C=N) 1650 cm⁻¹; ¹³C NMR: δ 164.1 (br, Ar*C*OOC), 160.6 (br, *C*N), 150.8 (br, Ar–*C*), 129.9 (br, Ar–*C*), 127.9 (br, Ar–*C*), 117.0. (br, Ar–*C*), 74.3 (br, menthyl–*C*H), 47.3 (br, menthyl–*C*H), 41.2(br, menthyl–*C*H₂), 34.4 (br, menthyl–*C*H₂), 31.4 (br, menthyl–*C*H), 26.5 (br, menthyl–*C*H), 23.8 (br, menthyl–*C*H₂), 22.1 (br, menthyl–*C*H₃), 20.8 (br, menthyl–*C*H₃), 16.6 (br, menthyl–*C*H₃). Anal. Calcd for C₁₈₂₆H₂₃₆₀N₁₀₀Cl₂O₂₀₀P₄PdPt: C, 74.58; H, 8.09; N, 4.76. Found: C, 74.21; H, 7.81; N, 4.80.

5d: 83% Yield; IR (KBr): v(C≡C) 2088, v(C=O) 1715,

1650 cm⁻¹; ¹³C NMR: δ 164.4 (br, Ar*C*OOC), 162.2 (br, *C*N), 147.5 (br, Ar–*C*), 130.4 (br, Ar–*C*), 128.0 (br, Ar–*C*), 125.7 (br, Ar–*C*), 120.9 (br, Ar–*C*), 119.0 (br, Ar–*C*), 73.8 (br, menthyl–*C*H), 47.1 (br, menthyl–*C*H), 40.8 (br, menthyl–*C*H₂), 34.4 (br, menthyl–*C*H₂), 31.5 (br, menthyl–*C*H), 26.3 (br, menthyl–*C*H), 23.5 (br, menthyl–*C*H₂), 22.1 (br, menthyl–*C*H₃), 21.0 (br, menthyl–*C*H₃), 16.5 (br, menthyl–*C*H₃); Anal. Calcd for C₁₈₂₆H₂₃₆₀N₁₀₀Cl₂O₂₀₀P₄PdPt: C, 74.58; H, 8.09; N, 4.76. Found: C, 74.56; H, 7.82; N, 4.83.

Measurements

¹H and ¹³C NMR spectra were measured in CDCl₃ on JEOL JNM-LA400 spectrometers using SiMe₄ as an internal standard. IR spectra were recorded on Perkin-Elmer System 2000 FT-IR. Optical rotations and CD spectra were measured on JASCO DIP-1000 and JASCO J-725, respectively. Molecular weight measurements were performed by a Shimadzu LC-6AD liquid chromatograph equipped with Shimadzu GPC-805, -804 and -8025 columns using THF as an eluent. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

RESULTS AND DISCUSSION
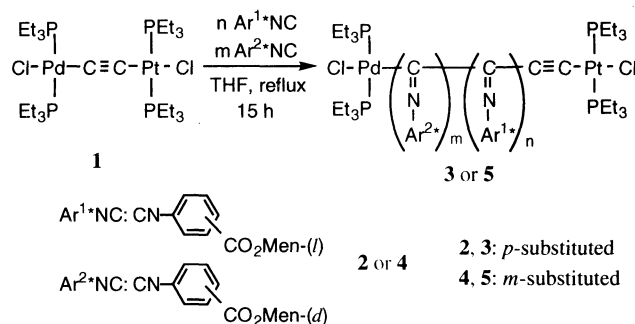
Living polymerization of *p*-(*d*)-menthoxycarbonylphenyl isocyanide (*d*)-**2** with **1** gave a polymer (**3a**) with a large negative optical rotation while the polymer of (*l*)-**2** showed a large positive one.[34] In contrast, polymer **3d** prepared from a racemic mixture of (*d*)- and (*l*)-**2** was almost optically inactive. Polymerization of a mixture of (*d*)- and (*l*)-**2** with several ratios has been performed using 1 mol% of complex **1**. As shown in Table I, all reactions proceeded smoothly to give polymers with a narrow polydispersity index in quantitative yields. Even in the reaction using a chiral initiator no significant difference was found in the polymerization rate between (*d*)- and (*l*)-**2**. Therefore, polymers **3b-3f** would be a random copolymer between (*d*)- and (*l*)-**2**. Broadening of the signals attributed to the imino carbons in the ¹³C NMR spectra of **3b-3f** relative to those of **3a** and **3g** may support the random structure of **3b-3f**. It is of interest that polymer **3b** prepared from 75 mol% of (*d*)-**2** and 25 mol% of (*l*)-**2** exhibited a large negative optical rotation. Thus, the relationship between [α]D values of polymer **3** and %ee of isocyanide monomer **2** are plotted in Figure 1. Optical rotations of these polymers are out of proportion to the %ee of **2** with a convex deviation from the linearity through a wide range of ee values. The CD spectra of these polymers **3** are shown in Figure 2. It should be noted that the intensity of Cotton effect at 364 nm, which is characteristic to poly(aryl isocyanide)s,[26] is proprtional to optical rotation. Hence, the CD intensity also displays a positive nonlinear effect upon %ee of isocyanide monomer **2**. The optical rotation and the CD

1030

Polym. J., Vol. 31, No. 11-2, 1999

Table I. Polymerization of p-menthoxycarbonylphenyl isocyanide (**2**) and m-menthoxycarbonylphenyl isocyanide (**4**)

polymers	monomer			Yield	M_n [a]	M_w/M_n [a]	$[\alpha]_D^{20}$ [b]	$\Delta\varepsilon_{364}$ [c]
	Ar^1*NC (mol%)	Ar^2*NC (mol%)	ee / %	/ %			/ deg	/ $dm^3 \cdot cm^{-1} \cdot mol^{-1}$
3a	(l)-**2** 0	(d)-**2** 100	100	90	13,300	1.12	−1054	−11.98
3b	(l)-**2** 25	(d)-**2** 75	50	94	11,200	1.09	−877	−9.05
3c	(l)-**2** 40	(d)-**2** 60	20	91	12,700	1.09	−470	−4.24
3d	(l)-**2** 50	(d)-**2** 50	0	92	12,600	1.09	9	0.27
3e	(l)-**2** 60	(d)-**2** 40	20	91	12,100	1.10	479	4.84
3f	(l)-**2** 75	(d)-**2** 25	50	89	11,900	1.10	886	10.09
3g	(l)-**2** 100	(d)-**2** 0	100	95	13,200	1.13	1070	13.01
5a	(l)-**4** 0	(d)-**4** 100	100	87	11,900	1.08	−260	−2.89
5b	(l)-**4** 25	(d)-**4** 75	50	89	11,500	1.06	−68	−0.98
5c	(l)-**4** 40	(d)-**4** 60	20	92	12,600	1.07	−29	−0.33
5d	(l)-**4** 50	(d)-**4** 50	0	83	12,000	1.07	0	0
5e	(l)-**4** 60	(d)-**4** 40	20	85	11,800	1.07	29	0.34
5f	(l)-**4** 75	(d)-**4** 25	50	91	11,800	1.07	67	0.94
5g	(l)-**4** 100	(d)-**4** 0	100	85	11,500	1.06	270	2.81

[a] M_n and M_w/M_n were determined by a GPC analysis based on the calibration of polystyrene standards. [b] $c = 0.1$, $CHCl_3$. [c] CD spectra were measured in $CHCl_3$ at ambient temperature. The $\Delta\varepsilon$ values are based on the molecular mass of an isocyanide monomer unit.

intensity correspond to the helical sense excess of the polymer. Similar phenomenon was observed not only in the copolymers of (R)- and (S)-2,6-dimethylheptyl isocyanates[35] but also in the acid-base complex formation of poly((4-carboxylphenyl)-acetylene).[38] On the other hand, the $[\alpha]_D$ values of the block copolymers between (d)- and (l)-**2** are proportional to the molar ratio of (d)- and (l)-**2** and optical rotations of mixtures of polymers **3a** and **3g** also lie on the proportional line, suggesting that such nonlinear effect is characteristic to random copolymers **3b-3f**.
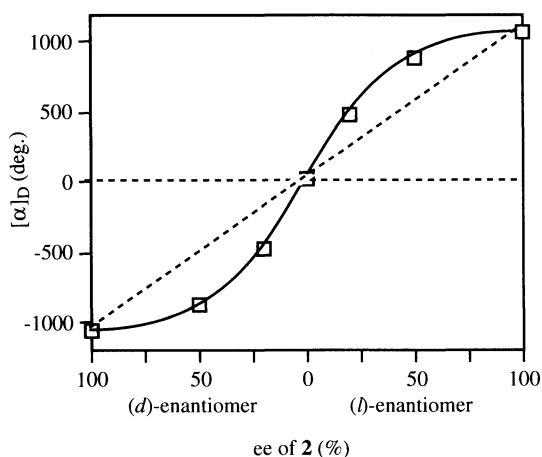

Figure 1. Optical rotation vs enantiomeric excess in the copolymers prepared from p-(d)- and (l)-menthoxycabonylphenyl isocyanides (**2**).

Copolymerization of m-substituted analogs (d)- and (l)-**4** were also carried out to yield polymers **5b-5f** in good yields, and their data including $[\alpha]_D$ and $\Delta\varepsilon$ values are summarized in Table I. The CD intensity at 364 nm is also proprtional to optical rotation in polymer **5**. To our surprise, the absolute values of $[\alpha]_D$ and $\Delta\varepsilon$ of polymer **5b** prepared from 75 mol% of (d)-**4** and 25 mol% of (l)-**4** are much smaller than those of **5a** which is a homopolymer of (d)-**4**. The plots of optical rotations of **5** against %ee of monomer **4** are represented in Figure 3, exhibiting a negative nonlinear effect. These results suggest that the optical properties of the random copolymers prepared from a pair of enantiomers depend on the pendant groups.
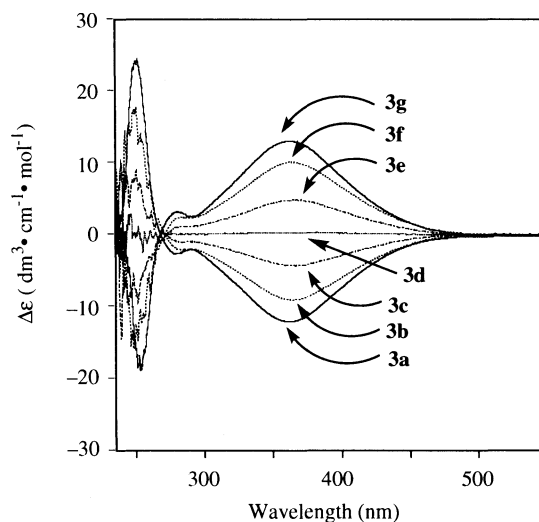

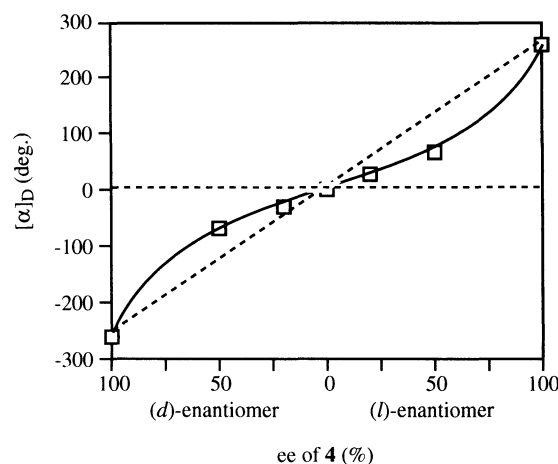**Figure 2.** CD spectra of polymers **3** in $CHCl_3$ at ambient temperature.

Figure 3. Optical rotation vs enantiomeric excess in the copolymers prepared from m-(d)- and (l)-menthoxycabonylphenyl isocyanides (**4**).

Et₃P ... PEt₃   n Ar¹*NC
Cl–Pd ... C≡C–Pt–Cl   n Ar²*NC
Et₃P ... PEt₃   THF, reflux
          15 h

6

Et₃P ... PEt₃
Cl–Pd ... C≡C–Pt–Cl
Et₃P ... PEt₃

7

Ar¹*NC: CN—⟨⟩—CO₂Men-(*l*)   (*l*)-**2**
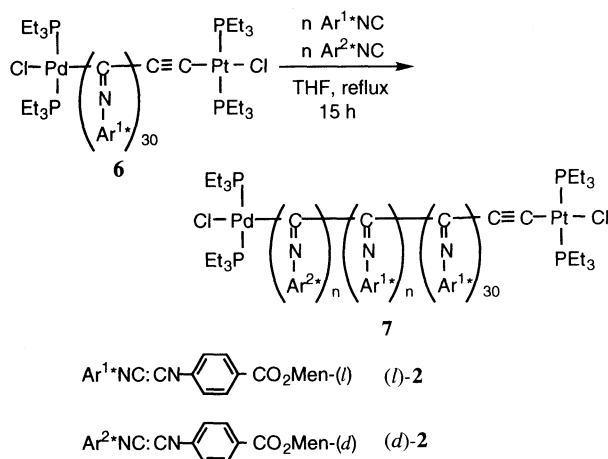
Ar²*NC: CN—⟨⟩—CO₂Men-(*d*)   (*d*)-**2**

Table II. Polymerization of a racemic mixture of *p*-(*l*)- and (*d*)-menthoxycarbonylphenyl isocyanide (**2**) by a chiral oligomeric complex (**6**)

polymers	2 (racemic mixture) n	M_n [a]	M_w/M_n [a]	$[\alpha]_D^{20}$ [b] / deg
6	0	5,200	1.10	829
7a	30	8,800	1.12	638
7b	50	11,400	1.12	475
7c	70	14,000	1.11	387

[a] M_n and M_w/M_n were determined by a GPC analysis based on the calibration of polystyrene standards. [b] $c = 0.1$, CHCl₃.

In order to obtain information on the structure of polymer **3d**, we examined copolymerization of a racemic mixture of (*d*)- and (*l*)-**2** initiated by an oligomeric complex (**6**) prepared from **1** with 30 equivalents of (*l*)-**2**.[34] In our previous work sterically hindered isocyanides like 3,5-di(propoxycarbonyl)-phenyl isocyanide, which form a rigid helix, polymerized keeping a helical sense of chiral oligomeric complexes. In contrast, screw-sense selective polymerization of less hindered isocyanides such as *p*-(cyclohexyloxycarbonyl)phenyl isocyanide was not achieved by a block copolymerization method since they do not keep a stiff helical structure.[39,40] The results obtained here are shown in Table II. Although the polymerization proceeded smoothly to give copolymers **7** with a narrow polydispersity index, the value of optical rotation of resulting polymers **7** remarkably falls down with increase of M_n, suggesting that the copolymers of (*d*)- and (*l*)-**2** do not keep a stiff helical structure in solution. As described above, homopolymers of (*d*)- and (*l*)-**2** form one-handed helices predominately. Since there is a small difference in the structures between homopolymer and copolymer of (*d*)- and (*l*)-**2**, the molecule of homopolymers of (*d*)- and (*l*)-**2** may not have a perfectly rigid helix like poly(*t*-butyl isocyanide)s but a dynamic one such poly(isocyanate)s[5–7,35] and poly(phenyl-acetylene)s.[38,41,42]

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1032

Polym. J., Vol. 31, No. 11-2, 1999