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Racemization and Deracemization of Poly(quinoxaline-2,3-diyl)s

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Racemization of optically active oligo- and poly(quinoxaline-2,3-diyl) derivatives with a single screw-sense, prepared by the polymerization of 3,6-diaryl-1,2-diisocyanobenzenes catalyzed by methylpalladium(II) initiator, was investigated. Pentameric and hexameric oligomers with a living palladium terminus were reluctant to undergo racemization in solution at room temperature. However, the (oligoquinoxalinyl)bis(phosphine)palladium(II) complexes underwent a phosphine exchange reaction in the presence of an excess of phosphine ligand with partial racemization at room temperature. Oligomers without palladium terminus, prepared by a treatment of the corresponding palladium derivatives with methylmagnesium bromide, underwent racemization more rapidly, the rate of which depended upon the bulkiness of the substituents at the 5,8-positions of the quinoxaline rings and oligomerization degree, i.e., the number of the quinoxaline units in the oligomer chain. Starting from the racemic polymers with a living palladium terminus, substantial deracemization of the helical poly(quinoxaline-2,3-diyl) was induced by means of optically active 2,3-O-isopropylidenedioxy-1,4-bis(diphenylphosphino)butane ligand, which coordinated to the palladium terminus.

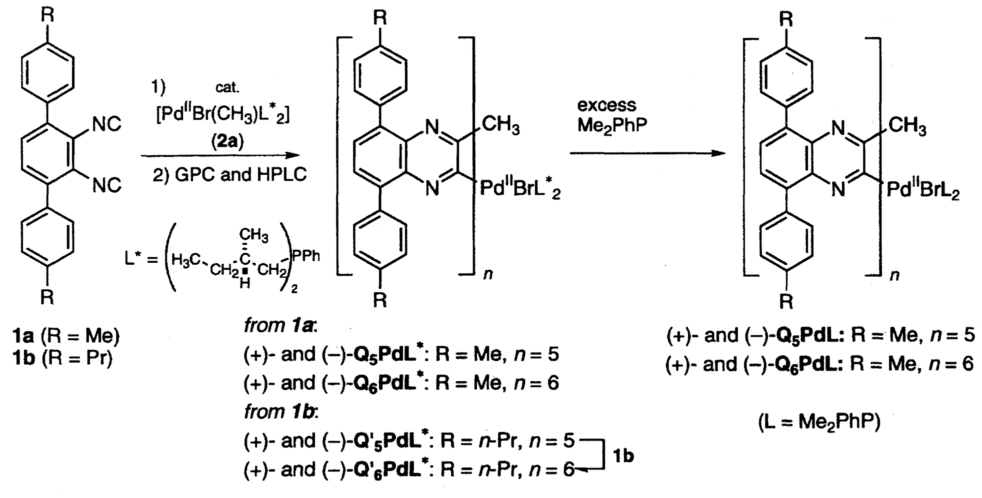
Poly(quinoxaline-2,3-diyl)s, which are successfully synthesized by selective, successive insertion of diisocyanobenzenes into the carbon–palladium bond of organopalladium(II) complex catalyst, adopt a helical structure, as revealed by X-ray analyses of some oligo(quinoxaline-2,3-diyl)s.[1—4] The new polymerization provided optically active helical poly(quinoxaline-2,3-diyl)s which feature a single screw-sense structure. Noteworthy is that the helical structure consists of axial chirality, i.e., atropisomerism at the main-chain,[5] unlike many other optically active polymers of helical structures, which are maintained by a number of stereogenic centers at the main-chains and/or side-chains.[6] For the synthesis and molecular design of new classes of optically active polymers, it may be important to gain insight into the structural facters which determine the helical stabilities. Herein, we report on an investigation of the stability of the helical structure of the poly(quinoxaline-2,3-diyl)s through their racemization.

The screw-sense selective synthesis of poly(quinoxaline-2,3-diyl)s has been approached by two strategies. One is the use of enantiopure helical (oligoquinoxalinyl)palladium complexes, which were obtained by resolution of the racemate by HPLC with an aid of optically active phosphine ligand, as initiators;[2,3] the other is the use of optically active binaphthylpalladium initiators.[4] To investigate the stabilities of the helical structure, the former method was chosen, because the former has advantages of having only helical chirality in the produced polymers, while the latter method provides polymers with additional axial chirality at the terminal group.

Results and Discussion

Ligand Exchange Reactions of (Oligoquinoxalinyl)palladium(II) Complexes.

Synthesis of Highly Enantio-Enriched Helical Oligomers with Living Palladium Terminus. In the previous paper, we demonstrated the oligomerization of 3,6-di-*p*-tolyl-1,2-diisocyanobenzenes **1** catalyzed by a bromo(methyl)palladium(II) complex **2a** with optically active phosphine ligands (Scheme 1).[2c] The reaction provided diastereomeric pairs of oligomers in a nearly 1 : 1 ratio, each of which was separated into pure diastereomers by preparative HPLC. (Oligoquinoxalinyl)palladium complex (+)- and (−)-$\mathbf{Q_5PdL^*}$, and (+)- and (−)-$\mathbf{Q_6PdL^*}$ thus isolated were stable in solution at room temperature for several days without any detectable decrease in diastereomeric excesses. To have (oligoquinoxalinyl)palladium complexes only with helical chirality, ligand-exchange reactions of the diastereomerically pure complexes with excess achiral Me_2PhP were attempted. The ligand-exchange reaction of (+)- and (−)-$\mathbf{Q_6PdL^*}$provided optically active (+)- and (−)-$\mathbf{Q_6PdL}$ in moderate-to-good yields (Table 1). However, a decrease in the optical rotation was observed for a reaction at room temperature, indicating that racemization took place in the presence of excess phosphine (Entries 1 and 2). In the case of (−)-$\mathbf{Q_5PdL^*}$, a reaction for 36 h at room temperature resulted in a complete loss of the optical activity (Entry 7). The racemization may be attributed to the destruction of intramolecular coordination of the proximal quinoxaline nitrogen (Fig. 1), which may stabilize the helices, by excess phosphine, as revealed by X-ray analyses of some (oligoquinoxalinyl)palladium complexes.[1b,2b,4] The racemization was, however, completely suppressed by carrying out the reaction at −78 °C (Entries 3 and 4). When (+)-$\mathbf{Q_6PdL^*}$ ($[\alpha]_D^{20} = +219°$, $CHCl_3$) was treated with a large excess of achiral dimethyl(phenyl)phosphine in THF at −78 °C for



Scheme 1.

Table 1. Ligand Exchange Reactions of (Oligoquinoxalinyl)palladium Complexes

Entry	Compounds	Conditions temp/time	Products	Yield (%)	$[\alpha]_D^{20}$ ($CHCl_3$)
1	(+)-Q_6PdL*	r.t./2 h	(+)-Q_6PdL	67	+427°
2	(+)-Q_6PdL*	r.t./62 h	(+)-Q_6PdL	33	+185°
3	(+)-Q_6PdL*	−78 °C/10 min	(+)-Q_6PdL	60	+442°
4	(+)-Q_6PdL*	−78 °C/30 min	(+)-Q_6PdL	78	+451°
5	(−)-Q_6PdL*	r.t./2 h	(−)-Q_6PdL	74	−406°
6	(−)-Q_6PdL*	−78 °C/10 min	(−)-Q_6PdL	90	−459°
7	(−)-Q_5PdL*	r.t./36 h	Q_5PdL	72	0°

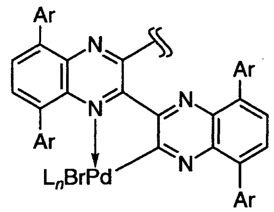


Fig. 1. Intramolecular coordination of the proxymal quinoxaline nitrogen in (oligoquinoxalinyl)palladium(II) complexes.

10 min, ligand-exchange took place, giving the corresponding (hexaquinoxalinyl)palladium(II) bromide bis[dimethyl(phenyl)phosphine] complex (+)-**Q_6PdL** ($[\alpha]_D^{20}$ = +442°, $CHCl_3$) without significant racemization. Similarly, (−)-**Q_6PdL*** ($[\alpha]_D^{20}$ = −468°, $CHCl_3$) was converted to (−)-**Q_6PdL** ($[\alpha]_D^{20}$ = −459°, $CHCl_3$) at −78 °C (Entry 6).

Racemization of Oligo- and Poly(quinoxaline-2,3-diyl)s. The racemization during the ligand-exchange reaction suggests the importance of intramolecular coordination of the proximal quinoxaline nitrogen to the palladium atom. Next, we examined the racemization of optically active penta- and hexa(quinoxaline-2,3-diyl)s having two methyl groups at both termini, prepared by the reaction of diastereomerically pure (oligoquinoxalinyl)palladium complexes with methylmagnesium bromide (Scheme 2). In addition to p-tolyl-substituted **Q_6Me**, derived from **Q_6PdL***, p-propylphenyl-substituted optically active pentamer **Q'_5Me** and hexamer **Q'_6Me** were prepared from diastereomerically

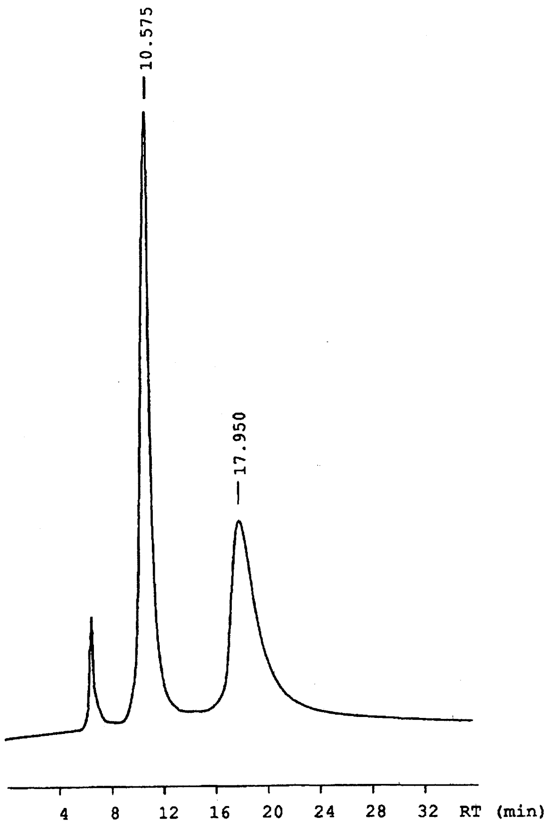
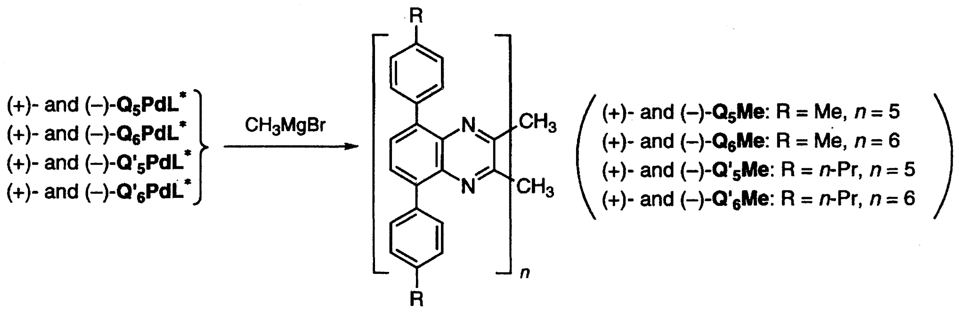


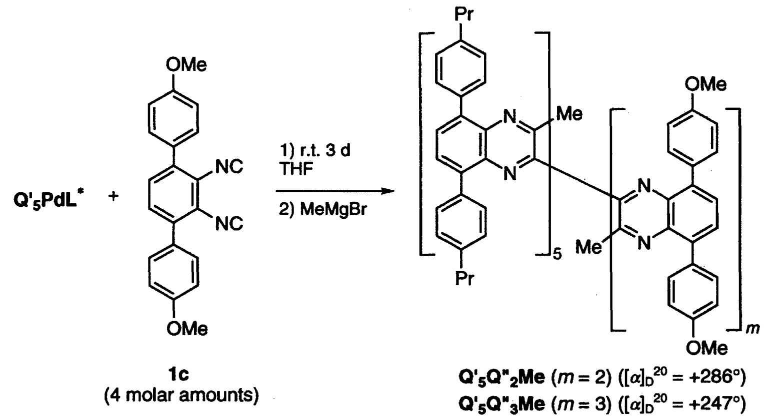
Fig. 2. HPLC analysis of racemic **Q'_5Me** using a column with chiral stationary phase. Eluent: MeOH/THF=3/1; flow rate: 0.5 mL min^{-1}; temp: 5 °C; detection: UV (254 nm).



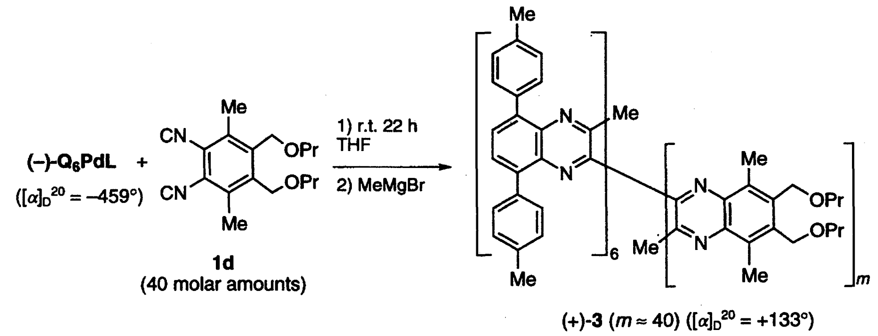
Scheme 2.

Table 2. Racemization Kinetics of $\mathbf{Q_6Me}$, $\mathbf{Q'_5Me}$, and $\mathbf{Q'_6Me}$

Compound	Temp K	Rotation α (deg) initial/final	Length of run s	Rate constant s^{-1}	Activation energy E_a/kJ mol^{-1}
Q_6Me	295	+0.157/+0.093	5.18×10^5	1.06×10^{-6}	100
	317	−0.414/−0.147	5.76×10^4	1.83×10^{-5}	
	334	+0.535/+0.141	1.08×10^4	1.26×10^{-4}	
Q'_5Me	295	+0.638/+0.612	6.91×10^5	6.28×10^{-8}	106
	317	+1.857/+1.374	2.23×10^5	1.36×10^{-6}	
	334	+1.067/+0.960	1.08×10^4	1.01×10^{-5}	
Q'_6Me	326	−0.751/−0.693	8.64×10^4	9.17×10^{-7}	133
	348	−0.766/−0.594	1.44×10^4	1.81×10^{-5}	
	363	−0.859/−0.323	7.20×10^3	1.34×10^{-4}	

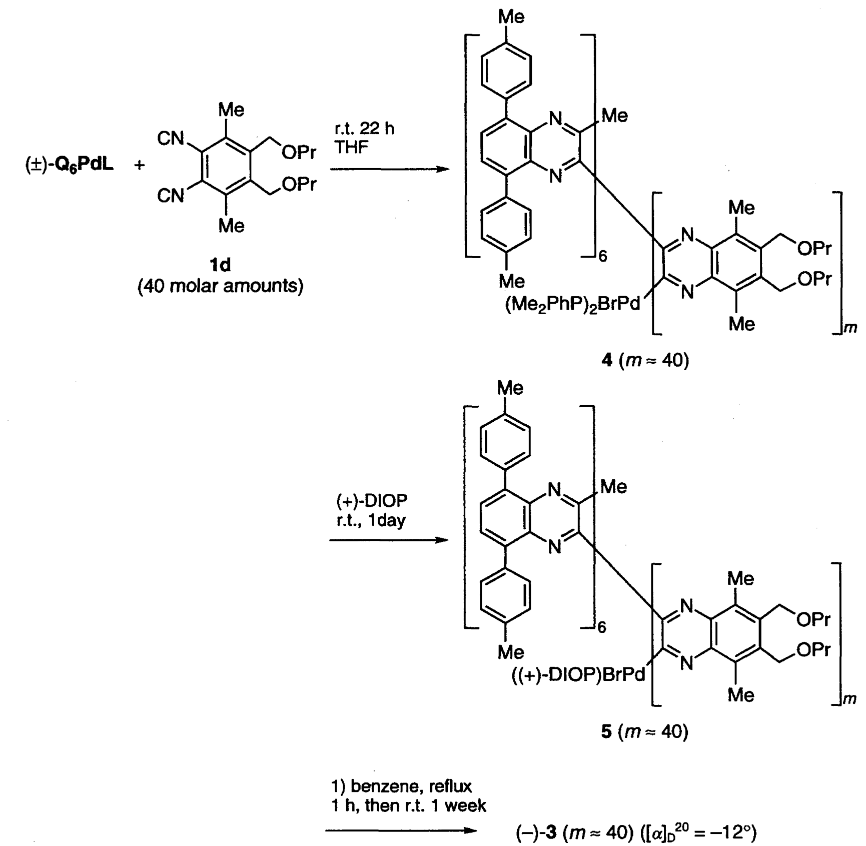


Scheme 3.



Scheme 4.

pure $\mathbf{Q'_5PdL^*}$ and $\mathbf{Q'_6PdL^*}$, respectively. It is noted that racemic $\mathbf{Q'_5Me}$ was base-line separated to both enantiomers (+)-$\mathbf{Q'_5Me}$ and (−)-$\mathbf{Q'_5Me}$ by HPLC analysis with the chiral stationary phase (Fig. 2). However, kinetic analyses showed that all oligo(quinoxaline-2,3-diyl)s ($\mathbf{Q_6Me}$, $\mathbf{Q'_5Me}$, and $\mathbf{Q'_6Me}$) slowly underwent racemization, which obeyed first-



Scheme 5.

order kinetics, though $\mathbf{Q'_6Me}$ was almost stable at room temperature (Table 2). Concerning the racemization of the oligo(quinoxaline-2,3-diyl)s, which are not anchored with the palladium(II) bis(phosphine) moiety, it is remarked that no intermediates, which are discernible by 270 MHz ^{1}H NMR from the starting (+)-$\mathbf{Q_6Me}$, were involved throughout the racemization, suggesting that the inversion of the helical structure for the racemization takes place in one step. The racemization rate constants of $\mathbf{Q_6Me}$ at 22, 44, and 61 °C were calculated to be 1.06×10^{-6} s^{-1}, 1.83×10^{-5} s^{-1}, 1.26×10^{-4} s^{-1}, respectively. The activation energy for the racemization of optically active $\mathbf{Q_6Me}$ was calculated to be 100 kJ mol^{-1} on the basis of an Arrhenius plot. Similarly, the activation energies for the racemization of optically active $\mathbf{Q'_5Me}$ and $\mathbf{Q'_6Me}$ were calculated to be 106 and 133 kJ mol^{-1}, respectively (Table 2). As may be expected, the activation energy for racemization through the inversion of the helical quinoxaline oligomers becomes larger along with an increase in the oligomerization degree ($\mathbf{Q'_5Me}$ vs. $\mathbf{Q'_6Me}$) as well as the increasing steric bulkiness of 5,8-aromatic substituents on the quinoxaline unit ($\mathbf{Q_6Me}$ vs. $\mathbf{Q'_6Me}$).

Indeed, optically active, helical quinoxaline cooligomers ($\mathbf{Q'_5Q''_2Me}$ and $\mathbf{Q'_5Q''_3Me}$), which were prepared by the reaction of $\mathbf{Q'_5PdL^*}$ and 4 molar amounts of **1c** according to the following scheme, were not racemized at all in chloroform at room temperature, although they were gradually racemized on heating at reflux in benzene (Scheme 3).

Similarly, a screw-sense selective polymerization of **1d** promoted by an initiator (−)-$\mathbf{Q_6PdL}$ provided optically active, helical poly(quinoxaline-2,3-diyl)s (**3**) after quenching with methylmagnesium bromide. However, the quinoxaline polymer (**3**) ($[\alpha]_D^{20} = +133°$, CHCl$_3$) was gradually racemized in a solvent at room temperature at a rate comparable to that of $\mathbf{Q_6Me}$, e. g., $[\alpha]_D^{20} = +109°$ (after 4 d), $[\alpha]_D^{20} = +100°$ (after 1 week) (Scheme 4). The lability of the helical structure of **3** suggests that quinoxaline rings with 5,8-dimethyl groups instead of 5,8-di-*p*-tolyl groups can not contribute to the increase in the stability of the helix.

Deracemization of (Polyquinoxalinyl)palladium Complex. These findings suggested that asymmetric induction due to the helical chirality on the racemic poly(quinoxaline-2,3-diyl)s may be achieved by introducing appropriate chiral phosphine ligand on the palladium(II) of the racemic poly(quinoxalinyl)palladium(II) bromide complex. A racemic bromobis[dimethyl(phenyl)phosphine](polyquinoxalinyl)palladium(II) (±)-**4** prepared from racemic $\mathbf{Q_6PdL}$ and 40 molar amounts of **1d** was treated with an excess of optically active 2,3-O-isopropylidenedioxy-1,4-bis(diphenylphosphino)butane ((+)-DIOP) in THF at room temperature for 1 d to afford bromo(polyquinoxalinyl)palladium(II) complex **5** ($[\alpha]_D^{20} = +4°$, CHCl$_3$), containing the DIOP ligand on the palladium(II), which was isolated with preparative GPC. After complex **5** was heated in benzene under reflux for 1 h, and then stirred at r. t. for 1 week, the reaction mixture was treated with methylmagnesium bromide in THF to provide poly(quinoxaline-2,3-diyl)s (−)-

3 with $[\alpha]_D^{20} = -12°$ ($CHCl_3$), which correspond to 9% ee (Scheme 5). The CD spectrum of (−)-**3** was weak, but characteristic of the left-handed quinoxaline helix.[2a,8,9]

Conclusion

The helical stabilities of oligo- and poly(quinoxaline-2,3-diyl) derivatives with and without the living palladium terminus were examined. (Oligoquinoxalinyl)palladium complexes were reluctant to racemization in solutions at room temperature and the methyl-terminated oligomers and polymers underwent racemization. The rate of racemization depended upon 1) the bulkiness of the substituents at the 5, 8-positions of the quinoxaline rings and 2) the oligomerization degree: number of the quinoxaline units having sufficiently bulky 5,8-disubstituents, i.e., *p*-substituted aryl groups. Accordingly, the **Q′6** unit, which consists of six 5, 8-bis(4-propylphenyl)quinoxaline rings, was the most reluctant to undergo racemization. A reversible helical inversion at elevated temperature made possible the deracemization of racemic (polyquinoxalinyl)palladium complex by using DIOP ligand as a chiral inducer, giving optically active poly(quinoxaline-2,3-diyl)s with 9%ee.

Experimental

General. All oligomerization and polymerization reactions were carried out under a nitrogen atmosphere. ^{1}H NMR spectra were measured on a Varian VXR-200 and Gemini-200 spectrometer in $CDCl_3$. The chemical shifts are reported in δ ppm. The CD spectra were measured on a JASCO J-600. HPLC analysis was carried out on a Shimadzu LC-6A. Gel-permeation chromatographic (GPC) analysis was carried out on a JASCO TRIROTAR (SHODEX AC-803) by using $CHCl_3$ as an eluent and polystyrene as the standard. Recycling GPC purification was performed with a JAI LC-908 equipped with JAIGEL-1H and 2H columns ($CHCl_3$). The mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. The optical rotation was measured with a Perkin–Elmer polarimeter 243 at 589.3 nm.

Materials. All solvents were dried over an appropriate desiccant and distilled under nitrogen. 1,2-Diisocyanobenzene derivatives **1a**—**d**,[1d,7] (+)- and (−)-(oligoquinoxalinyl)palladium complexes (**Q$_5$PdL***, **Q$_6$PdL***, **Q′$_5$PdL***, and **Q′$_6$PdL***), and methyl-terminated (+)- and (−)-oligo(quinoxaline-2,3-diyl)s (**Q$_5$Me**, **Q$_6$Me**, **Q′$_5$Me**, and **Q′$_6$Me**)[2c] were prepared according to the literature method.

Thermal Stability of the Helical Structure of (+)- and (−)-Q$_6$PdL* in Solution. Solutions of diastereomerically pure (+)- and (−)-**Q$_6$PdL*** in DMF, THF, acetonitrile, and $CHCl_3$ (0.46 M) (1 M = 1 mol dm^{-3}) were stirred at room temperature for 4 d under nitrogen. HPLC analyses of solutions with a YMC SH-045-10 column showed that no racemization took place in all of the solutions tested.

Synthesis of (+)-Q$_6$PdL through Ligand Exchange Reactions. To a solution of (+)-**Q$_6$PdL*** (8.0 mg, 3.1×10^{-3} mmol) in THF (2 mL) was added dimethyl(phenyl)phosphine (22 μL, 0.16 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 10 min. Then, the mixture was subjected to preparative TLC on silica gel and GPC on polystyrene gel to give (+)-**Q$_6$PdL** in 60% yield. The structure of this compound was confirmed by a comparison with a racemic authentic sample by the use of HPLC and ^{1}H NMR. The racemic sample was prepared as follows. To a THF solution (2 mL) of *trans*-bromobis[dimethyl(phenyl)phosphine]methylpalladium(II) (14 mg, 3.0×10^{-2} mmol) was added 1,2-diisocyano-3,6-di-*p*-tolylbenzene (**1a**, 55 mg, 0.18 mmol); the mixture was stirred at room temperature for 40 h. The solvent was removed under reduced pressure, and the residue was purified by GPC on polystyrene gel (eluent: $CHCl_3$) to give (±)-**Q$_6$PdL** (21.4 mg, 31% yield). Found: C, 76.89; H, 5.25; N, 7.47%. Calcd for $C_{149}H_{121}BrN_{12}P_2Pd$: C, 76.88; H, 5.24; N, 7.22%.

Kinetic Analyses of Racemization of Q$_6$Me, Q′$_5$Me, and Q′$_6$Me. A solution of (+)- or (−)-**Q$_6$Me** (1.1×10^{-4} M) was kept in $CHCl_3$ at three temperatures (22, 44, 61 °C), and the course of the reaction kinetics were followed by measuring the optical rotation at 589.3 nm. The first-order racemization rate constants (k) were calculated from the slope of the linear plots of $\ln(\alpha^0/\alpha)$ vs. time (α^0: initial rotation; α: measured rotation). The calculated k values are collected in Table 2. The energies of activation for the racemization were estimated by an Arrhenius plot. Analyses of **Q′$_5$Me**, and **Q′$_6$Me** were carried out by a similar procedure, except for the use of toluene as a solvent and temperature used (53, 75, 90 °C) for analysis of **Q′$_6$Me**. The racemization of **Q′$_5$Me** was also monitored by an HPLC analysis with a chiral stationary phase (see below) to confirm the validity of the analyses by optical rotation.

Resolution of Racemic Q′$_5$Me by HPLC with a Chiral Column. An HPLC column (0.46×25 cm) with helically chiral poly(triphenylmethyl methacrylate) as the stationary phase was prepared according to the literature method.[10] The detailed conditions for the analysis are indicated in Fig. 2. A polarimetric detector showed that the fast-eluting peak corresponded to the (+)-enantiomer and that the slower one corresponded to the (−)-enantiomer.

Preparation of Q′$_5$Q″$_2$Me and Q′$_5$Q″$_3$Me by the Reaction of Q′$_5$PdL* with 1c. To a solution of (+)-**Q′$_5$PdL*** (50 mg, 2.0×10^{-2} mmol) in THF (10 mL) was added 1,2-diisocyano-3,6-bis(4-methoxyphenyl)benzene (**1c**, 27 mg, 7.9×10^{-2} mmol); the mixture was stirred at room temperature for 3 d. The reaction mixture was concentrated under reduced pressure, and the residue was subjected to GPC on polystyrene gel (eluent: $CHCl_3$) to afford a mixture of oligomers (61.5 mg). It was then dissolved to THF (3 mL), and a 2.8 M methylmagnesium bromide ether solution (0.7 mL) was added to this solution. The mixture was stirred at room temperature over night. After excess Grignard reagent was quenched with water, the mixture was extracted several times with $CHCl_3$. The combined extract was washed with water and dried over magnesium sulfate; the solvent was evaporated under reduced pressure. The residue was subjected to preparative TLC on silica gel (eluent: CH_2Cl_2/hexane=2/1) to afford **Q′$_5$Q″$_2$Me** (8.5 mg, 17%) and **Q′$_5$Q″$_3$Me** (10.8 mg, 19% yield). **Q′$_5$Q″$_2$Me**: $[\alpha]_D^{20} = +286°$ (*c* 0.072, $CHCl_3$). FABMS *m/z* 2532 (MH$^+$). **Q′$_5$Q″$_3$Me**: $[\alpha]_D^{20} = +247°$ (*c* 0.167, $CHCl_3$). FABMS *m/z* 2872 (MH$^+$).

Helical Stability of Q′$_5$Q″$_3$Me in Solution. **At Room Temperature.** A solution of **Q′$_5$Q″$_3$Me** ($CHCl_3$) was kept in a 10 cm cell of Perkin–Elmer polarimeter 243. No decrease in the optical rotation was observed even after 1 week.

Under Reflux in Benzene. A solution of **Q′$_5$Q″$_3$Me** (3.3 mg, 1.2×10^{-3} mmol) in benzene (5 mL) was heated at reflux for 22 h. The optical rotation was changed from +247° (*c* 0.167, $CHCl_3$) to +46° (*c* 0.167, $CHCl_3$).

Synthesis of Optically Active Polymers (+)-3 from (−)-Q$_6$PdL. To a solution of (−)-**Q$_6$PdL** (3.9 mg, 1.7×10^{-3} mmol) in THF (4.2 mL) was added 1,2-diisocyano-3,6-dimethyl-4,5-bis(propoxymethyl)benzene (**1d**) (20 mg, 6.7×10^{-2} mmol); the mixture was stirred at room temperature for 21.5 h. To the mixture was added MeMgBr (2.8 M in ether, 0.30 mL, 0.85 mmol); the mixture was stirred at room temperature for 1 h. After excess of MeMgBr was quenched with water, the mixture was extracted several times with $CHCl_3$. The combined extract was washed with water and dried over magnesium sulfate; the solvent was evaporated under reduced pressure. The residue was subjected to GPC on polystyrene gel (eluent: $CHCl_3$) to afford 13.4 mg (57% yield) of (+)-**3**. $[\alpha]_D^{20} = +133°$ (c 0.147, $CHCl_3$). $M_n = 8900$, $M_w/M_n = 1.13$.

Synthesis of Optically Active (−)-3 through Deracemization of (Polyquinoxalinyl)palladium Complex 5 with (+)-DIOP Ligand. To a solution of (±)-**Q$_6$PdL** (5.3 mg, 2.3×10^{-3} mmol), prepared from achiral *trans*-BrMePd(PMe_2Ph), in THF (5 mL) was added 4,5-bis(propoxymethyl)-1,2-diisocyano-3,6-dimethylbenzene **1d** (27 mg, 9.1×10^{-2} mmol); the mixture was stirred at room temperature for 5 d. The solvent was removed under reduced pressure and the residue was subjected to preparative GPC to afford (±)-**4** (30.3 mg). To a solution of (±)-**4** (17 mg) in THF (2 mL) was added (+)-DIOP (26 mg, 5.2×10^{-2} mmol); the mixture was stirred at room temperature for 1 d. The solution was concentrated and the residue was subjected to GPC to give 19.5 mg of **5**. After **5** was dissolved in benzene (5 mL) and heated under reflux for 1 h, the solution was allowed to stand at room temperature for 1 week. The reaction mixture was concentrated and redissolved in THF (1 mL). To the mixture was added excess methylmagnesium bromide; the mixture was stirred at room temperature for 1 h. After excess Grignard reagent was quenched with water, the mixture was extracted several times with $CHCl_3$. The combined extract was washed with water and dried over magnesium sulfate; the solvent was evaporated under reduced pressure. The residue was subjected to GPC to afford (−)-**3** (12.8 mg). The polymer showed optical rotation corresponding to 9%ee ($[\alpha]_D^{20} = -12°$ (c 0.165, $CHCl_3$)).

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8) Before heating the DIOP complex **5** in refluxing benzene, no deracemization was confirmed by a CD spectrum.

9) *Cis*-chelating ligands such as bis(diphenylphosphino)ethane, BINAP, and DIOP were ineffective for the synthesis of the helical polymers in the palladium-catalyzed polymerization of diisocyanobenzenes. For instance, use of the DIOP ligand with (cyclooctadiene)bromo(methyl)palladium(II) complex in the reaction of **1a** resulted in the fast formation of unidentifiable polymeric compound.

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