Asymmetric Synthesis of Helically Stable Poly(quinoxaline-2,3-diyl)s Having Hydrophilic and/or Hydrophobic Side Chains

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Most helical polymers, natural and synthetic ones, possess multiple stereocenters in their polymer main chains, whose stereochemical control enables us to hold the helical structure of a single screw sense.[1] On the other hand, helical polymers, which maintain their whole helical chirality only by rotational (conformational) isomerism, have been scarcely known.[2−4] Recently, the synthesis of new helical polymers has attracted much interest from the viewpoint of new materials and is desired to be developed. Synthetic modification on the surface of the well-defined helical polymer structure might lead to new helical polymers of interesting physical and chemical properties. However, the successful modification of the latter helical polymers may not be feasible, because any slight structural alternation might cause a substantial change of the helical structures and stabilities.[5]

In the previous papers, we reported the synthesis of poly(quinoxaline-2,3-diyl)s, which feature the optically active helical structure, by an asymmetric living polymerization of 1,2-diisocyanobenzenes with chiral palladium catalysts.[6] Herein, we describe the asymmetric synthesis of helical poly(quinoxaline-2,3-diyl)s bearing hydrophilic and/or hydrophobic side chains on each monomer unit in the polymers. It is remarked that the helical conformation of poly(quinoxaline-2,3-diyl)s was not changed by the introduction of the hydrophilic and/or hydrophobic side chains, which may modify the surface of the rigid poly(quinoxaline-2,3-diyl)s.

Recently, we disclosed that optically active binaphthylpalladium(II) complexes (*S*)-**1a** and (*S*)-**1b** induced a screw-sense selective polymerization of 3,6-di-*p*-tolyl-1,2-diisocyanobenzene (**2**) with up to ca. 80% selectivity (Chart 1).[7] The bulky 3,6-disubstituents in **2**, which were requisite for the stabilization of the helical polymer structure in the asymmetric polymerization catalyzed by chiral methylpalladium(II) complexes,[8] however, resulted in slow polymerization (5 days for 40 molar amounts of **2** at room temperature) and low solubility of the polymers produced. Then, we examined the polymerization of 1,2-diisocyanobenzenes **3** and **4**, which have two methyl substituents at the 3,6-positions as well as two oxygenated alkyl chains at the 4,5-positions. Besides (*S*)-**1a** and (*S*)-**1b**, new optically active binaphthylpalladium(II) initiators (*S*)-**1c** and (*S*)-**1d**, which have 2′-*tert*-butyldimethylsiloxy and 7′-methoxy groups, respectively, were prepared from the corresponding optically active 2-iodo-1,1′-binaphthyls and 1.5 molar equiv of **2**. Polymerization of **3** proceeded smoothly (18−36 h) at room temperature in the presence of the binaphthylpalladium(II) initiators **1a**−**d**, providing poly(quinoxaline-2,3-diyl)s **5a**−**d**, after quenching with $CH_3MgBr/ZnCl_2$ followed by purification with GPC (eq 1).

Chart 1

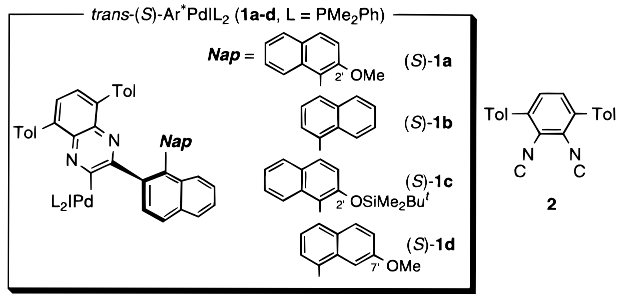
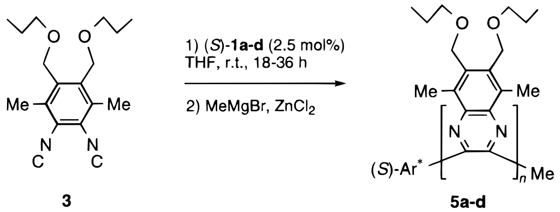


Table 1. Polymerization of 3 in the Presence of (*S*)-1a−d

entry	initiator	polymer (yield/%)	selectivity[a] (config)
1	(*S*)-**1a**	**5a** (77)	<1
2	(*S*)-**1b**	**5b** (74)	79 (*P*)
3	(*S*)-**1c**	**5c** (76)	75 (*P*)
4	(*S*)-**1d**	**5d** (79)	>95 (*P*)

[a] Assumed from the intensity of the CD spectra at 362 nm. See ref 9.



(1)

As observed in the polymerization of **2**, initiator (*S*)-**1b** produced **5b** of *P*-helices (right-handed) with high selectivity (79% ee), while (*S*)-**1a** resulted in the formation of racemate **5a** (Table 1, entries 1 and 2).[9,10] Of note is that, unlike (*S*)-**1a**, initiator (*S*)-**1c**, which has the bulkier siloxy group at the 2′-position, induced high screw-sense selectivity (entry 3). Furthermore, nearly complete screw-sense selection was achieved by use of (*S*)-**1d** having the 7′-methoxy substituent (entry 4).[11,12]

Optically active poly(quinoxaline-2,3-diyl)s **5b**−**d** having binaphthyl end groups showed remarkable helical stabilities in solutions, while the corresponding polymers having methyl end groups, which are derived from methylpalladium(II) complex catalysts, underwent racemization at room temperature.[8] Helical polymers **5b**−**d** were not racemized even at 80 °C in benzene for 60 h. Presumably, the binaphthyl end group may serve as a "wedge" to prevent rotation of the bond between the quinoxaline rings near the polymer end, which may lead to the racemization of the whole helical structure.

With the most effective, chiral binaphthylpalladium(II) catalyst **1d** in hand, screw-sense selective polymerization of 1,2-diisocyanobenzene **4**, which has two [(silyloxy)ethoxy]methyl side chains at the 4,5-positions, was carried out (eq 2). The polymer **6d** obtained after treatment with $CH_3MgBr/ZnCl_2$ was very soluble in THF, $CHCl_3$, and benzene and revealed a CD spectrum identical to that of **5d**. Desilylation of **6d** with TBAF in THF at room temperature for 3 h followed by evaporation and subsequent washing with water gave

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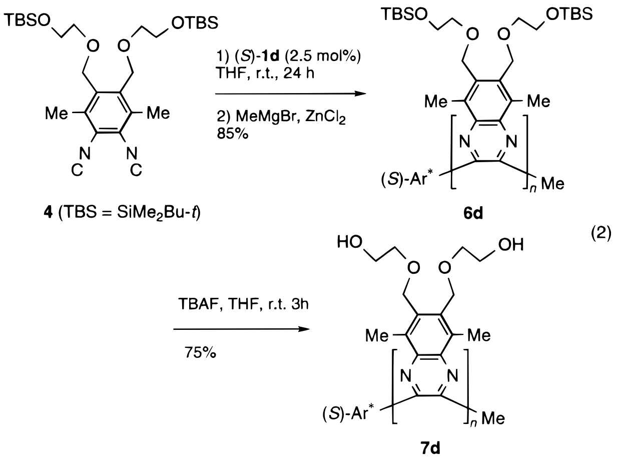
Table 2. Solubility of the Poly(quinoxaline-2,3-diyl)s with Various Side Chains[a]

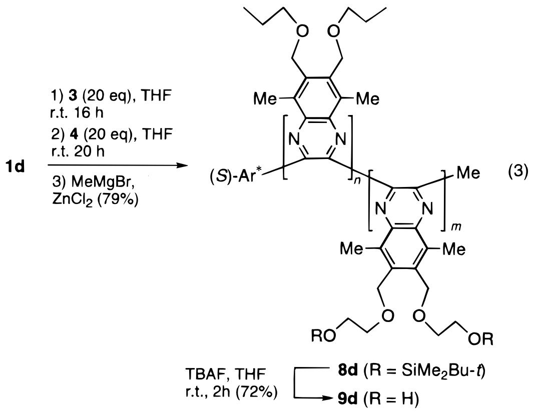
polymer	benzene	$CHCl_3$	THF	EtOH	MeOH
5d	++	++	++	−	−
6d	+++	+++	+++	−	−
7d	−	−	−	uv	++
8d	+++	+++	+++	−	−
9d	uv	+	++	++	uv

[a] The solubilities at 23 °C were classified to +++ (>300 mg/mL), ++ (300−100 mg/mL), + (100−10 mg/mL), uv (<10 mg/mL but detectable by UV), and − (not detectable by UV).



4 (TBS = SiMe₂Bu-*t*) **6d** **7d** (2)

the deprotected polymer **7d**, which was not soluble in THF, $CHCl_3$, and benzene at all, but soluble in MeOH and aqueous MeOH (80%) (Table 2). It should be noted that the CD spectrum of **7d** in EtOH exhibited a shape similar to that of **5d** in $CHCl_3$ (Figure 1) and that the helical structure of **7d** was stable in MeOH solution under reflux for at least 60 h.[13]



(3)

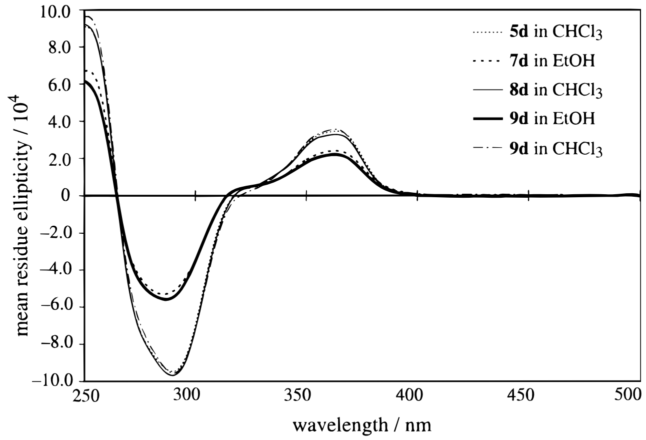


Figure 1. CD spectra of poly(quinoxaline-2,3-diyl)s **5d** ($CHCl_3$), **7d** (EtOH), **8d** ($CHCl_3$), and **9d** ($CHCl_3$ and EtOH).

Finally, applicability of the present technology to the new material synthesis is demonstrated by the synthesis of a block copolymer with hydrophobic and hydrophilic side chains on the rigid, helical poly(quinoxaline) core (eq 3). After completion of the polymerization of monomer **3** (20 molar equiv) with initiator (*S*)-**1d**, the second monomer **4** (20 equiv) was charged and subjected to the polymer propagation at room temperature, providing new polymer **8d** in good yield, which exhibited a CD spectrum characteristic of a single screw sense (Figure 1). Treatment of **8d** with TBAF furnished polymer **9d**, which showed amphiphilic solubility in that **9d** is dissolved not only in $CHCl_3$ and THF but also in alcohols (Table 2). The CD spectra of **9d** in $CHCl_3$ and EtOH exhibited nearly the same shape, indicating that the solvation did not cause any significant conformational change of the helix (Figure 1).

The successful asymmetric synthesis of poly(quinoxaline-2,3-diyl)s having the side chains on the polymer surface may find applications for preparation of new, optically active helical polymers with useful functions, whose helicity is furnished only by the rigid polymer core.

Supporting Information Available: Detailed experimental procedures and characterization of the new compounds (5 pages). Ordering and accessing information is given on any current masthead page.

References and Notes

(1) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349−372. Pu, L. *Acta Polym.* **1997**, *48*, 116−141.

(2) For optically active poly(isocyanate)s without chiral substituents, see: Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *Polym. J.* **1993**, *25*, 391−396.

(3) For optically active poly(isocyanide)s without chiral substituents, see: Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932−5933. Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818−6825. Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7926−7927. Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101−9111.

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(8) For the effect of the bulkiness of the 3,6-disubstituents on the stability of the screw sense, see: Ito, Y.; Kojima, Y.; Murakami, M.; Suginome, M. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2801−2806. See also ref 7.

(9) The selectivities were calculated on the basis of the comparison of the CD spectra with the authentic right-handed poly(quinoxaline-2,3-diyl), which was prepared by the polymerization of **3** with the well structurally defined pentamer with a living palladium terminus as a catalyst.[7] The CD spectra of these polymers were similar in shape, and their intensities at 362 nm were used for the determination of the selectivities. See Supporting Information.

(10) The helical structure of the polymers once formed may induce helices with the same screw sense without any error. This is proved by the fact that CD spectra of **5d** (M_n = 11 080) and the corresponding higher polymers (M_n = 15 530 and 22 780), which were prepared independently by the polymerization of 60 and 80 equiv of **3** in the presence of **1d**, respectively, showed the same CD intensity per quinoxaline unit.

(11) The nearly complete screw-sense selection (>95% ee) was also attained in the polymerization of **2** (40 equiv) in the presence of **1d**.

(12) The mechanism of the induction of the high screw-sense selectivity will be discussed in a forthcoming paper.

(13) Decrease in intensity of the UV spectrum of **7d** in EtOH in comparison with those for **5d** and **6d** in $CHCl_3$ was also observed. The hypochromic solvent effect may be related to the observed decrease in the CD intensity of **7d** in EtOH.

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