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Highly Effective, Easily Accessible Screw-Sense-Determining End Group in the Asymmetric Polymerization of 1,2-Diisocyanobenzenes

Michinori Suginome,* Sylvain Collet,† and Yoshihiko Ito*,‡

Department of Synthetic Chemistry and Biological Chemistry,
Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

suginome@sbchem.kyoto-u.ac.jp

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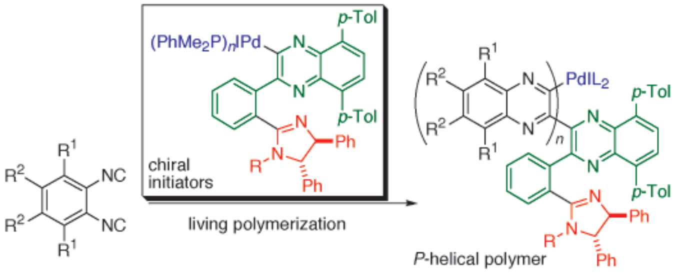
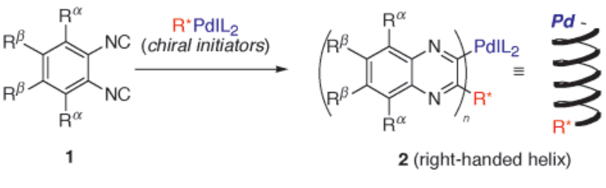
ABSTRACT



Enantiopure helical poly(quinoxaline-2,3-diyl) was formed stereoselectively in the polymerization of 1,2-diisocyanobenzene using a new organopalladium initiator bearing the (4*S*,5*S*)-*N*-acyl-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl group as the polymer-end screw-sense-determinant.

Increasing attention has been paid to the exploration of structurally well-defined helical polymers with a single screw-sense.[1] Such polymers are expected to serve as functional materials, of which functions may be derived from their helical structures. However, the synthetic polymers of stable single-handed screw-sense, which do not undergo significant racemization of the helical structure, have not been well exploited to date. Recently, we reported highly screw-sense selective living polymerization of 1,2-diisocyanobenzenes **1** using optically pure initiator **3** derived from (7′-methoxy-1,1′-binaphth-2-yl)palladium(II) complex (Scheme 1, Figure 1).[2] It is noted that the chiral binaphthyl group, which remains at the polymer-end opposite to the propagating palladium end, induces the helical screw-sense to a growing poly(quinoxaline) backbone, giving optically active poly(quinoxaline)s **2**, whose helical structures were quite stable even at elevated temperatures (ca. 100 °C). The results

Scheme 1



[†] JSPS postdoctoral fellow (1999−2000). Present address: Faculty of Sciences and Technics, University of Nantes, 2 rue de la Houssiniére BP92208, 44322 Nantes Cedex 3, France.

[‡] Present address: Faculty of Pharmaceutical Science, Kyoto Pharmaceutical University, Yamashina-ku, Kyoto 607-8412, Japan.

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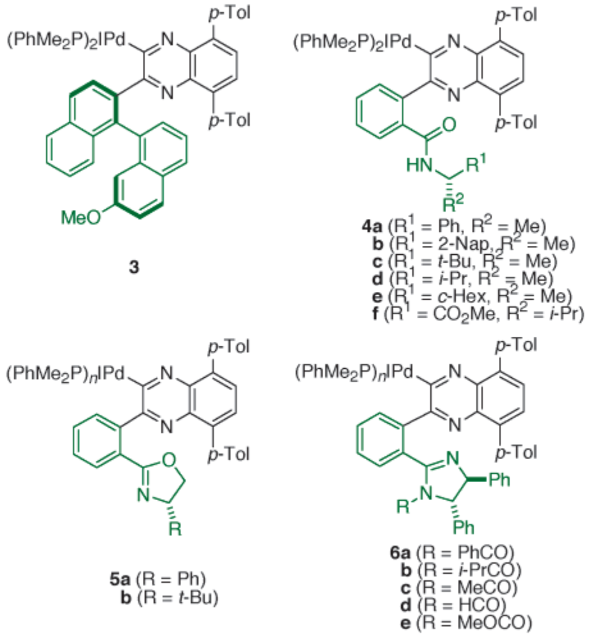


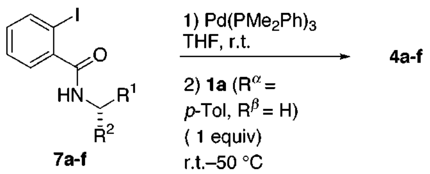
Figure 1. Chiral organopalladium initiators (R^*PdIL_2) used in the previous studies (**3**) and in this study (**4**−**6**).

demonstrate that the helical sense of polymer main-chain consisting only of sp^2-hybridized carbons can be effectively induced by a sole screw-sense determining group at the polymer end.[3,4]

The remarkable stereocontrol in the asymmetric polymerization may be largely due to the ability of the binaphthyl skeleton to create a highly effective asymmetric environment as has been established in a variety of asymmetric reactions[5] or chiral recognition processes.[6] Although some simple binaphthyl derivatives are now readily available in enantiopure forms, preparation of optically active binaphthalene derivatives with more elaborate structures often meets with synthetic difficulties. In particular, the preparation of our binaphthyl-based initiators requires several steps including the optical resolution step from commercially available starting materials.[2b] We decided to explore alternative chiral groups which are easily accessible and provide efficient chiral environments comparable to or, preferably, more effective than the binaphthyl structures. Herein, we describe highly screw-sense selective polymerization of **1** by means of chiral phenylpalladium initiators **4**−**6** (Figure 1), in which the phenyl groups are substituted with optically active *o*-substituents such as aminocarbonyl, oxazoline, and imidazoline groups derived readily from the corresponding chiral amine precursors.

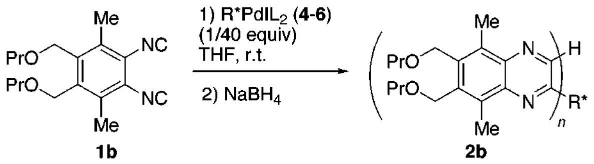
First of all, optically active *o*-(*N*-substituted aminocarbonyl)iodobenzenes **7** were prepared from *o*-iodobenzoic acid with commercially available optically active *prim*-amines and then subjected to palladation with a palladium(0)−dimethylphenylphosphine complex generated from Cp(π-allyl)-palladium with 3 equiv of the phosphine (Scheme 2). The resultant *o*-(aminocarbonyl)phenylpalladium(II) complexes were reacted with 1 molar equiv of 3,6-di-*p*-tolyl-1,2-diisocyanobenzene (**1a**) to afford quinoxalinylpalladium(II) complexes **4a**−**f** bearing *o*-(*N*-alkylaminocarbonyl)phenyl substituents.

Scheme 2



In the presence of chiral initiators **4a**−**f** (1/40 equiv) thus prepared, polymerization of 1,2-diisocyanobenzene **1b** was carried out at room temperature (Scheme 3). After consumption of 1,2-diisocyanobenzene **1b**, the polymerization was quenched by $NaBH_4$, giving **2b** in moderate-to-good isolated yields (Table 1). With initiators (*S*)-**4a-d** having *N*-(α-substituted ethyl)aminocarbonyl groups, right-handed helical polymers with low screw-sense excesses (se) (5−26%) were formed (entries 1−4). The selectivity was significantly improved by use of (*S*)-**4e** having the (*S*)-*N*-[α-(cyclohexyl)-ethyl]aminocarbonyl group, giving **2b** with 70% se (entry 5). L-Valine-derived initiator **4f** resulted in the formation of **2b** with low se (entry 6).

Scheme 3



We then turned our attention to cyclic chiral groups such as oxazoline and imidazoline for further improvement of the

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(3) The screw-sense control by a sole chiral end group was demonstrated in nickel-catalyzed polymerization of monoisonitrile. Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818.

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Table 1. Asymmetric Synthesis of **2b** by Polymerization of **1b** Using Chiral Initiators **4**[a]

entry	**4** (R^1, R^2)	% yield[b]	M_w/M_n[c]	% se (config)[d]
1	(*S*)-**4a** (Ph, Me)	46	1.31	23 (*P*)
2	(*S*)-**4b** (2-Nap, Me)	67	1.17	5 (*P*)
3	(*S*)-**4c** (*t*-Bu, Me)	71	1.15	26 (*P*)
4	(*S*)-**4d** (*i*-Pr, Me)	95	1.43	10 (*P*)
5	(*S*)-**4e** (c-Hex, Me)	81	1.10	70 (*P*)
6	(*S*)-**4f** (CO_2Me, *i*−Pr)	48	1.28	10 (*M*)

[a] A mixture of **4** and **1** (40 equiv) was stirred for 18−24 h at room temperature. [b] Isolated yield (preparative GPC). [c] Determined by GPC using polystyrene standard. [d] Screw-sense excess determined by CD spectroscopy. The *P* configuration denotes right-handed helix.

selectivity. Initiators **5** and **6** were prepared from the corresponding *o*-(4-substituted 4,5-dihydrooxazol-2-yl)iodobenzenes or *o*-(*N*-acyl-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl)iodobenzenes, which were easily available from the corresponding optically active *β*-amino alcohols or (*S*,*S*)-1,2-diphenylethylenediamine, respectively.[7,8] As for the synthesis of imidazoline derivative **6**, *N*-acyl- and *N*-methoxycarbonyl-substituted **6a**−**e** were obtained in high yields under the reaction conditions employed for the preparation of **4**, whereas the N-H or N-Me derivatives (R = H or Me) could not be isolated due to their instability.

Use of the oxazoline initiators **5a** and **5b** in the polymerization, however, resulted in moderate selectivities (Table 2, entries 1 and 2). On the other hand, the imidazoline initiators **6** provided remarkably high selectivities in the polymerization of **1b** (Table 2, entries 3−7). It should be noted that the selectivities significantly varied with the bulkiness of the *N*-acyl protecting groups (R). Thus, while the initiators bearing relatively bulky groups such as benzoyl and isobutyryl groups only resulted in moderate selectivities (entries 3 and 4), those with smaller *N*-protecting groups provided selectivities higher than 90% (entries 5−7). In particular, the formyl and acetyl derivatives **6c** and **6d** afforded right-handed helical polymers with almost perfect screw-sense selectivity.[9]

Table 2. Synthesis of **2b** by Polymerization of **1b** Using Chiral Initiators (*S*)-**5** and (*S*,*S*)-**6**[a]

entry	initiators (R)	% yield[b]	M_w/M_n[c]	% se (config)[d]
1	(*S*)-**5a** (Ph)	81	1.27	46 (*P*)
2	(*S*)-**5b** (*t*-Bu)	78	1.41	67 (*P*)
3	(*S*,*S*)-**6a** (PhCO)	84	1.27	50 (*P*)
4	(*S*,*S*)-**6b** (*i*-PrCO)	55	1.19	80 (*P*)
5	(*S*,*S*)-**6c** (MeCO)	86	1.28	98 (*P*)
6	(*S*,*S*)-**6d** (HCO)	71	1.15	>99 (*P*)
7	(*S*,*S*)-**6e** (MeOCO)	72	1.25	92 (*P*)

[a] At room temperature. Bisphosphine complexes **5** or **6** ($n = 2$), or the corresponding monophosphine complexes ($n = 1$) with an equimolar amount of additional $PhMe_2P$, were used as initiators. [b] Isolated yield (preparative GPC). [c] Determined by GPC using polystyrene standard. [d] Screw-sense excess determined by CD spectroscopy. The *P* configuration denotes right-handed helix.

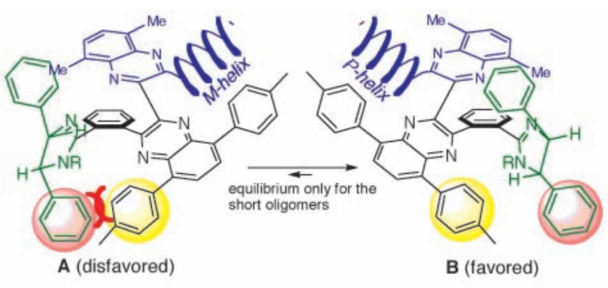

Figure 2. Possible conformation of the polymer-end in the growing polymers initiated with **6**.

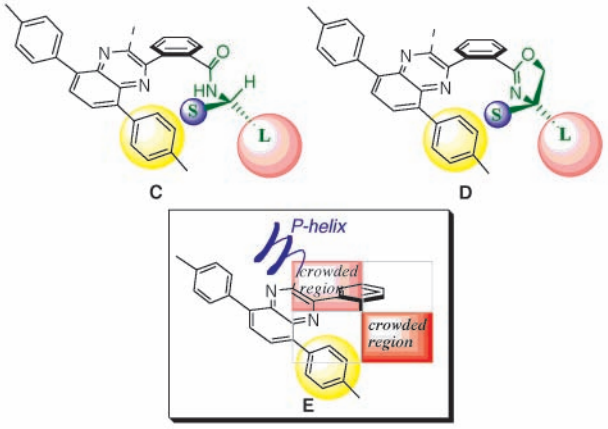

Figure 3. Possible conformation of the polymer-ends in the polymers initiated with **4** (**C**) and **5** (**D**). **E** represents general steric requirement for the generation of right-handed polymers.

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[7] The palladium complexes **5** and **6** were obtained as bisphosphine complexes ($n = 2$) and/or monophosphine complexes ($n = 1$) after isolation by preparative TLC on silica gel. The monophosphine complexes may have seven-membered ring palladacycle structures with intramolecular coordination of the oxazoline/imidazoline nitrogen onto the palladium. The monophosphine complexes were quantitatively converted to the corresponding bisphosphine complexes by addition of a molar equivalent of $PhMe_2P$ in solutions. The monophosphine complexes showed slightly lower selectivities than the corresponding bisphosphine complexes in the polymerization of **1b**. For instance, 51% se with **5b** ($n = 1$) and 93% se with **6c** ($n = 1$) were obtained. Therefore, the isolated bisphosphine complexes or the monophosphine complexes with an equimolar amount of additional $PhMe_2P$ were used in the polymerization shown in Table 2.

[8] For the ready preparation of *o*-(4,5-diphenylimidazolin-2-yl)iodobenzene from *o*-iodobenzoic acid with 1,2-diphenylethylenediamine, see Supporting Information.

[9] The screw-sense excesses of the polymers were determined by CD spectra by comparing their intensities with that of "standard polymer" obtained by polymerization of **1b** with use of diastereomerically stable and pure living pentamer as an initiator, which was isolated in the oligomerization of **1a** (4 equiv) in the presence of **6c**. The standard polymer exhibited an ca. 10% more intense CD spectrum than the corresponding polymer with the (*S*)-2′-methoxy-1,1′-binaphth-2-yl group as the end group, which we used as the standard in the previous studies.[2b] The decreased intensity for the previous poly(quinoxaline)s suggests that a little (<10%) helix inversion might have taken place during the polymer propagation by the diastereomerically pure pentameric initiator bearing an ineffective chiral end group. On the basis of the new standard, the screw-sense selectivity for the polymerization of **1b** with the 7′-methoxybinaphthyl inititor **3** is corrected to 87% in place of >95% in the previous report.

We have proposed that the screw-sense induction takes place at the oligomer stage not later than pentamer formation.[2b] As shown in Figure 2, the (*S*,*S*)-4,5-dihydro-4,5-diphenylimidazol-2-yl group selectively induces the conformation **B** leading to the right-handed helix, due to the repulsive steric interaction in the possible conformation **A** that leads to the left-handed helix.[10] The screw-sense selection with initiators **4** and **5** can be well explained by a similar steric effect, which may be generalized as Figure 3. Thus, as seen from the view along the (chiral group)−(phenyl) axis, increased steric demand at the right-lower region may lead to the selective formation of right-handed helices. The observed lower selectivities for initiators **4** and **5** may be attributed to the insufficient steric congestion at the left-upper region, which becomes equivalent to the right-lower region by rotation around the axis, allowing the minor, but significant, formation of the left-handed helix. This situation may be avoided with the imidazolyl group by virtue of its pseudo C_2 symmetry. This mechanism seems to be well suited to the helix induction for the asymmetric polymerization using binaphthylpalladium initiator **3**, in which the right-lower region is occupied by the naphthyl ring.

In summary, we achieved highly screw-sense-selective polymerization of **1b** with easily accessible chiral initiators bearing the optically active (*S*,*S*)-4,5-dihydro-4,5-diphenylimidazol-2-yl group.

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Supporting Information Available: Experimental procedures and spectral data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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[10] The proposed favorable conformation shown in Figure 2 was depicted on the basis of a preliminary single-crystal X-ray analysis of a living trimer bearing the imidazoline and $(PhMe_2P)_2PdI$ moieties at its termini, which was prepared from **6c** with 2 equiv of **1a**.