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Enantiomer-selective Living Polymerization of *rac*-Phenyl Isocyanide Using Chiral Palladium Catalyst

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Electronic Supplementary Information

Abstract We report the polymerization of phenyl isocyanides with the chiral palladium(II) initiating system. The resulting polymers with optically active properties were obtained by polymerization of the racemic isocyanide monomer (*rac*-1), and enantiomerically unbalanced polymerization of the monomer was found, providing substantial evidence for the enantiomer-selective polymerization of *rac*-1 mediated through chiral catalyst. A comparison between the enantiomerically pure monomers, 4-isocyanobenzoyl-L-alanine decyl ester (1s) and 4-isocyanobenzoyl-D-alanine decyl ester (1r), revealed a drastic discrepancy in the reactivity ratio of their homopolymerizations. It turned out that the monomer reactivity ratio of 1s was higher than that of 1r with chiral ligands. The results clearly demonstrated the inclination for incorporation of the 1s enantiomer during the polymerization process and thus resulted in the enantiomer-selective polymerization in this system. The effects of the catalyst chirality on the optically active properties of polymerization were investigated, and it was concluded that the formation of higher-ordered conformation with a handed helicity might be attributed to the chiral induction of chiral palladium(II) catalyst. Moreover, the polymers obtained through the enantiomer-selective polymerization of the enantiomerically pure monomer were with a significant improvement of the optical activity if the chirality of the monomer and the catalyst matched with each other.

Keywords Enantiomer-selective polymerization; Kinetic resolution; Chiral sulfinamide bisphosphine; Polyisocyanides; Living polymerization

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Stimulated by the discovery of helical structures in biopolymers, a considerable number of studies have been conducted on artificial helical polymers in recent years, such as steric restricted polyacrylates[1, 2] and poly(arylvinyl)s[3−5], polyisocyanides[6−10], polyisocyanate[11−14], polycarbodiimide[15−18], and polyacetylenes[19−27]. Among them, helical polyisocyanide has attracted great attention due to its unique rigid rod helical structure and various applications, such as enantiomeric separation, asymmetric catalysis, chiral recognition, as well as in material sciences. Thus, the development of a novel synthetic method for facile synthesis of optically active helical polyisocyanides becomes much more urgent.

Among the methods for synthesizing chiral molecules, enantiomer-selective polymerization is a unique one in which an enantioenriched monomer and an optically active polymer are generated simultaneously from a racemic monomer mixture by incorporating a favored enantiomer into the backbone of polymer while leaving the unreacted enantioenriched monomer through the selection of chiral initiating systems. Considerable effort has been made on the development of enantiomer-selective polymerizations, such as the design of initiators, catalysts, and the synthesis of monomers, *etc*[28−34]. Enantiomer-selective polymerization is most commonly described by chiral metal catalysts or initiators and has been established for a variety of monomer classes, including vinyl[35−37], lactide[38−41] and cyclic monomers[39, 40]. We have reported an enantiomer-selective polymerization of phenyl isocyanides by using a single handed helical polyisocyanide bearing a living chain end as a macroinitiator. Although the enantiomer selectivity of those polymerizations could introduce chiral unit of the optically active initiators or catalysts in the generated polymers, the chiral source was lost after the polymerization and could not be reused in the further polymerizations, thus the chiral economy was low. Therefore, the development of new strategies for enantiomer-selective polymerization of racemic monomers to afford optically active helical polymers is of great significance.

Recently, the controlled/living polymerization of isocyanides has been achieved using a series of novel organo-palladium complexes by our group, which could

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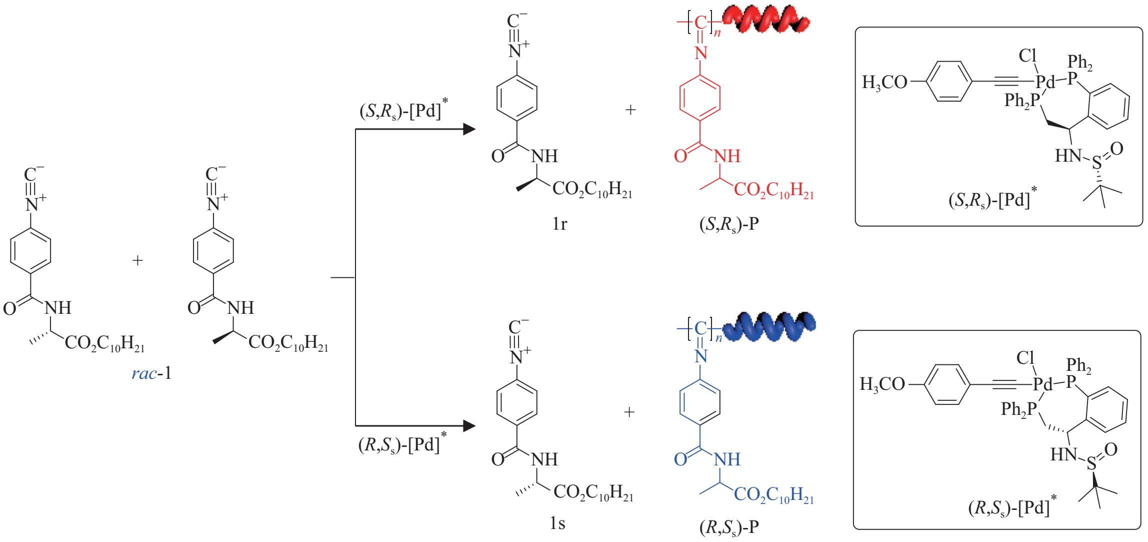
afford well-defined polyisocyanides in high yields with the controlled molecular weights and the narrow polydispersity. In this contribution, we reported the enantiomer-selective polymerization of chiral phenyl isocyanides with the achiral palladium catalyst in the presence of the chiral additive and the polymerization proceeded in highly enantiomer-selective manner with one of the enantiomers[44, 45]. To the best of our knowledge, the enantiomer-selective polymerization of racemic isocyanides has not been reported, in which one of the enantiomers is preferentially polymerized through the kinetic resolution of a racemic monomer, whereas achiral organopalladium(II) complexes produce stereo-regulated polyisocyanide through chain-end control with no enantiomer-selectivity. To achieve the enantiomer-selective polymerization, we now focused on the enantiomer-selective polymerization method using chiral initiating system.

For this study, we prepared a class of chiral palladium catalysts bearing chiral sulfinamide bisphosphine ligand (Wei-Phos)[46, 47] for the polymerization of phenyl isocyanides (Scheme 1). Monomer 1 is a phenyl isocyanide derivative that contains L-, D- or *rac*-alanine residues with a long alkyl chain as the pendants through an amide linkage. The experimental section is shown in the electronic supplementary information (ESI).

The number-average molecular weights (M_n) of the obtained polymers from racemic monomers could reach 5×10^4 g/mol, and the molecular weight distributions (M_w/M_n) were quite narrow. The enantiomeric excess (*ee*) of the unreacted monomer was 54.9%. In addition, the chiral sulfinamide bisphosphine ligand could affect the enantiomer selectivity, and the enantiomer selectivity changed when the chirality of the used phosphorus ligands altered. It has been found that the enantiomer bearing an *S*-alanine pendant with a long decyl chain was predominantly polymerized when using (S,R_s)-[Pd]*, while the enantiomer bearing an *R*-alanine pendant with a long decyl chain was predominantly polymerized when using (R,S_s)-[Pd]*. The obtained polymers possessed an optical activity, and the molar CD intensity at 364 nm ($\Delta\varepsilon_{364}$, in THF, at 25 °C) of the polymers could achieve −11.9 and +11.8, respectively.

We explored the enantiomer-selective polymerization of *rac*-1 using (S,R_s)-[Pd]* and conducted the kinetic studies of this system. The relationship among M_n, M_w/M_n, and the monomer conversion for the polymerization of *rac*-1 using the chiral palladium(II) initiating system is shown in Fig. 1(a) and Fig. S1 (in ESI). The M_n values of the resulting polymers increased with the increase of the monomer conversion, and the M_w/M_n values of the obtained polymers



Scheme 1 Enantiomer-selective polymerization of *rac*-phenyl isocyanide by using chiral palladium(II) catalyst

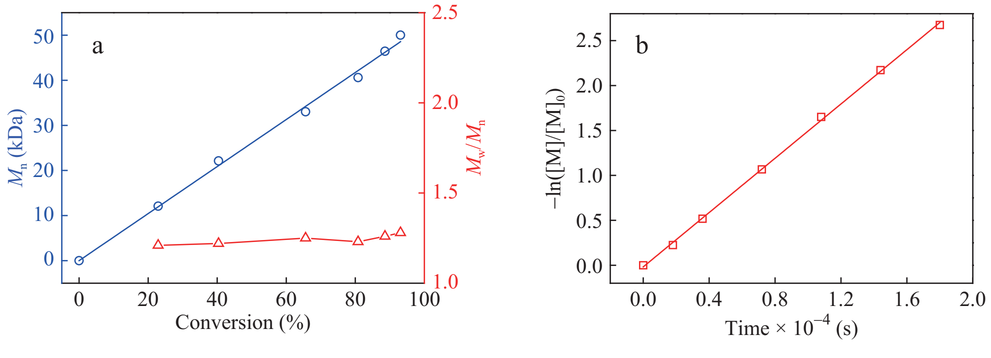


Fig. 1 (a) Dependence of M_n and M_w/M_n on the monomer conversion for the polymerization of *rac*-1 using the (S,R_s)-[Pd]* initiating system; (b) Kinetic plots for the polymerization of *rac*-1 using the (S,R_s)-[Pd]* initiating system

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were relatively narrow (1.21−1.28), suggesting that the polymerization proceeded in a controlled/living manner. Further studies revealed that the apparent polymerization rates of *rac*-1 using the chiral palladium(II) initiating complex were first-order with respect to the monomer concentration because a linear correlation could be clearly observed between $-\ln([M]/[M]_0)$ with the polymerization time, indicating that the polymerization of *rac*-1 using chiral palladium(II) initiating system was living-like (Fig. 1b). Meanwhile, as expected, the 1s enantiomer was polymerized faster than the 1r enantiomer as shown in Fig. S2 (in ESI). In order to further classify the living property of this polymerization, the freshly generated Pd(II)-terminated (S,R_S)-P_{100} was used to initiate the *rac*-1 monomer in $CHCl_3$ at 50 °C under the similar conditions described in ESI. As shown in Fig. S3 (in ESI), the SEC trace of the afforded block copolymer (S,R_S)-$P_{100\text{-}b\text{-}50}$ shifted to the higher molecular weight region as compared to that of the (S,R_S)-P macroinitiator precursor. This result further confirmed that the polymerization of *rac*-1 using the chiral palladium(II) catalyst indeed proceeded in a living/controlled chain-growth manner, affording well-defined polymers with an active living chain end.

Moreover, an enantioenriched polymer could lead to higher ordered conformations. The UV-Vis absorption and CD spectra of *rac*-P, (S,R_S)-P and (R,S_S)-P in solution are depicted in Fig. 2(a). It can be found that the racemic polymer *rac*-P polymerized with the achiral palladium(II) catalyst showed no CD signals in solution, and no obvious absorption and cotton effects were observed around 364 nm, suggesting that equivalent left- and right-handed helices were simultaneously produced as expected. For comparison, after polymerization under the same experimental condition using the chiral catalyst, the chiroptical properties of the isolated polymers were investigated. (S,R_S)-P showed a negative cotton effect around 364 nm that corresponds to the n-π^* transition of imino groups of polyisocyanide backbone. The molar CD intensity at 364 nm ($\Delta\varepsilon_{364}$) of (S,R_S)-P was estimated to be −11.9, suggesting that the polymer adopted a higher ordered chiral conformation, a left-handed helicity. The CD spectrum of the afforded (R,S_S)-P is also shown in Fig. 2(a). As expected, the polymer showed a mirror image to that of the (S,R_S)-P. The $\Delta\varepsilon_{364}$ was estimated to be +11.86, almost the same absolute value to that of the (S,R_S)-P but opposite in the sign, suggesting that the right-handed helix was preferentially yielded. This result further confirmed that the enantiomer-selective polymerization of the racemic phenyl isocyanides was ascribed to the asymmetric induction of the chiral catalyst, and the helicity of the afforded polymer was controlled by the phosphorus ligand. What is more, the helical structures of the afforded polymers were quite stable; no helix inversion was observed in the toluene solution of (S,R_S)-P at 100 °C for even 24 h (Fig. S4 in ESI). Additionally, the intensity of this cotton effect depended on the molecular weight, which increased with the molecular weight. This is because the helix became more-developed with the increase of the molecular weight to reach a single-handed helicity, resulting in the increase of the optical activity. Meanwhile, it should be noted that after reaching the maximum value, CD signal no longer increased even though the molecular weight of the polymer still increased largely.

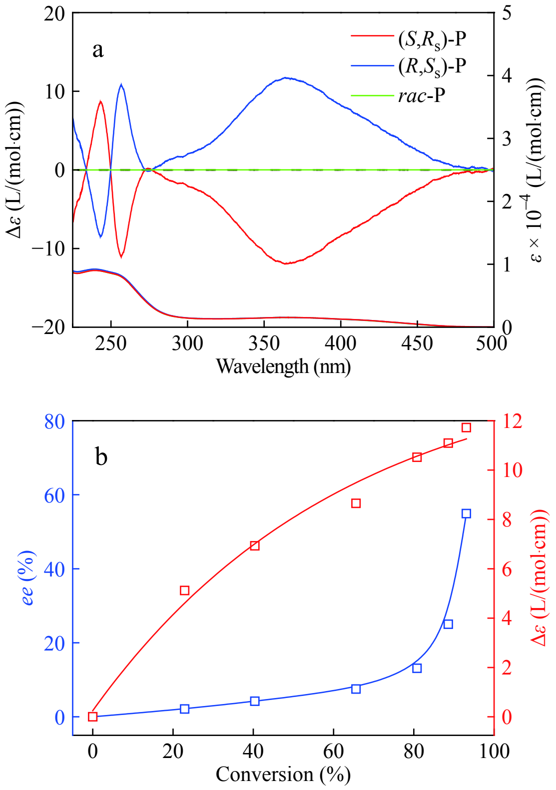

Fig. 2 (a) CD and UV-Vis absorption spectra of (S,R_S)-P, (R,S_S)-P, *rac*-P in THF at 25 °C; (b) Relationship between *ee* of unreacted monomer, $\Delta\varepsilon_{364}$ of polymer (S,R_S)-P, and monomer conversion of polymerization of *rac*-1 using the (S,R_S)-$[Pd]^*$ initiating system

The enantiomeric imbalance of the left-over monomers and chiroptical activity of the resulting polymers showed that the chiral catalyst could be applied to promote the enantiomer-selective polymerization of the racemic phenyl isocyanides. For the (S,R_S)-$[Pd]^*$ initiating system, the 1s enantiomer was preferentially polymerized with the unreacted monomer of 13.1% *ee* at the 80% monomer conversion, and the resulting polymer showed the $\Delta\varepsilon_{364}$ of −10.52 (Fig. 2b). The reaction rate of the 1s enantiomer was faster than that of the 1r enantiomer. Fig. 2(b) shows the change in *ee* of the unreacted monomer and the chiroptical properties of the isolated polymers as a function of monomer conversion in the polymerization of *rac*-1 using chiral palladium catalyst. The *ee* value of the unreaction monomer increased with increasing monomer conversion, and the optical purity (*o.p.*) of the resulting polymers increased with increasing monomer conversion. The *o.p.* value of the resulting polymer is given by *ee*/conv − *ee*[45, 46], and the *o.p.* value of resulting polymer was 3.11% at the 80.8% monomer conversion. This indicated that the chiroptical properties of the polymer were due to the excess of the 1s enantiomer in the obtained polymer. These results showed that the chiral palladium(II) complex could affect the addition of *rac*-1 to the growing end, where the 1s enantiomer of racemic

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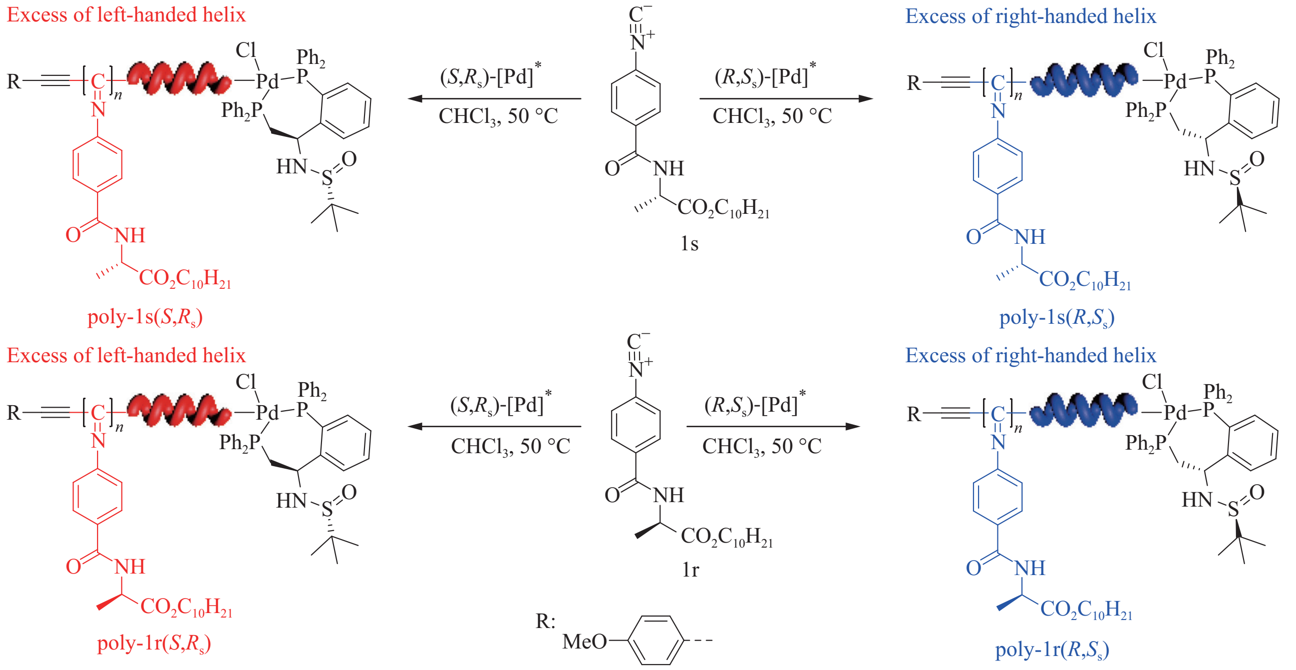
monomers was predominantly polymerized, *i.e.*, an enantiomer-selective polymerization.

To better understand the results of the polymerization of *rac*-1 (Scheme 2), we examined the homopolymerizations of phenyl isocyanides bearing *R*- or *S*-alanine pendant with a long decyl chain (1r or 1s) using the chiral palladium catalyst (*S*,*R*s)-[Pd]*. Fig. 3 shows the kinetic plots of the individual homopolymerizations. The polymerization rate for 1s was significantly faster than that of 1r, supporting the results observed from the enantiomer-selective polymeri-zation of *rac*-1 with (*S*,*R*s)-[Pd]*. The homopolymerization rates of the 1s and 1r monomers (k_{1s} and k_{1r}) were 2.37×10^{-4} s^{-1} and 0.85×10^{-4} s^{-1}, respectively.

The CD and UV-Vis spectra of the afforded polymers are



Scheme 2 Enantiomer-selective polymerization of enantiomeric pure monomers 1r and 1s using the chiral catalyst in CHCl$_3$ at 50 °C

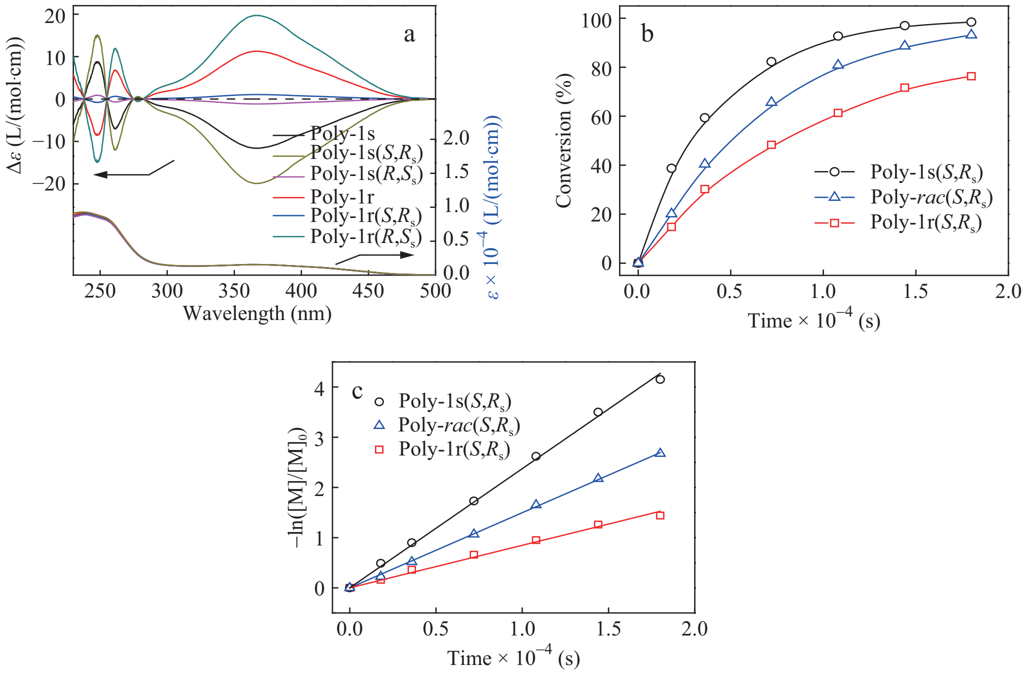


Fig. 3 (a) CD and UV-Vis absorption spectra of poly-1s, poly-1s(*S*,*R*s), poly-1s(*R*,*S*s), poly-1r, poly-1r(*S*,*R*s) and poly-1r(*R*,*S*s) prepared from the living polymerization of 1r and 1s using the chiral Pd(II) catalyst; (b) Plots of the conversions with the polymerization time of chiral monomer 1s, 1r, and *rac*-1 monomer using the chiral Pd(II) catalyst (*S*,*R*s)-[Pd]* in CHCl$_3$ at 50 °C; (c) First-order kinetic plots for the polymerization of chiral monomer 1s, 1r, and *rac*-1 monomer using the chiral Pd(II) catalyst (*S*,*R*s)-[Pd]* in CHCl$_3$ at 50 °C ($[M]_0 = 0.15$ mol/L, $[M]_0/[Pd]_0 = 150$)

depicted in Fig. 3(a). When 1s was polymerized with the chiral catalyst (S,R_{S})-[Pd]*, the isolated poly-1s(S,R_{S}) showed a strong positive CD signal at 364 nm with a value of −19.89, suggesting that a left-handed helix was predominately produced. For comparison, chiral phenyl isocyanide 1s was directly polymerized by the achiral Pd(II) catalyst. The CD and UV-Vis spectra of the isolated poly-1s are shown in Fig. 3(a). Because of the chiral induction of the monomer, the poly-1s showed a negative CD at 364 nm with the value of −11.59, much lower than that of the poly-1s(S,R_{S}) through the chiral inductions by both the chiral catalyst and the chiral monomer itself. This result indicated that the presence of chiral catalyst during the polymerization could remarkably heighten the enantiomer-sense selectivity, and almost a single left-handed helix was selectively produced. Remarkably, when 1s was polymerized with the (R,S_{S})-[Pd]*, the afforded poly-1s(R,S_{S}) exhibited a very weak negative CD at 364 nm. The $\Delta\varepsilon_{364}$ was estimated to be −1.05, indicating that a slight excess of left-handed helix was produced. Thus, the helicity of the afforded polymers was determined by the chirality of the catalyst. When the enantiomer 1r was polymerized with the presence of (R,S_{S})-[Pd]* or (S,R_{S})-[Pd]*, similar results could be obtained. However, the CD of the resulting polymers was opposite to those polymerized from 1s due to the opposite chirality of the two monomers (Fig. 3a). The interesting chiroptical property of the afforded polymers was ascribed to the dual chiral inductions by both the monomer and the chiral catalyst used in the polymerization. When the chirality of the monomer was matched with the chiral phosphine ligand, the collaborative chiral inductions led to a better helix-sense-selectivity of the polymerization, and produced a single-handed helical polymer with strong CD intensity at 364 nm. When the chirality of the monomer and the chiral phosphine ligand was mismatched, the contradictive chiral inductions resulted in a lower helix-sense-selectivity and only a slight excess of one handed helix was produced.

In summary, the enantiomer-selective polymerization of phenylisocyanides bearing a racemic alanine (*rac*-1) or chiral alanine (1s, 1r) pendent with a long *n*-decyl chain was achieved for the first time by using a chiral initiating system. From the kinetic study for homopolymerizations of enantiomerically pure 1s and 1r, the reactivity ratio of $k_{1\mathrm{s}}/k_{1\mathrm{r}}$ was found to be 2.79. Thus, the chiral initiating system involving (S,R_{S})-W1 preferentially catalyzed the 1s polymerization into the growing ends with *rac*-1 monomers to achieve the enantiomer-selective polymerization and the *ee* of the unreacted monomers increased with the increase of monomer conversion. And the growing polymer chain adopted a higher-ordered conformation with one-handed helicity excess. In addition, for the homopolymerization of the enantiomerically pure monomer, the optical activity of the afforded polymers was significantly improved when the chirality of the monomer matched with the chiral ligand. This work on enantiomer-selective polymerization provides the beginning point for the polymerization of isocyanides. Ongoing research will focus on the isocyanide monomer and catalyst design in order to develop a high level of enantiomer-selectivity.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-018-2136-5.

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