

Optically Active Helical Polyisocyanides Bearing Chiral Phosphine Pendants: Facile Synthesis and Application in Enantioselective Rauhut-Currier Reaction

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Electronic Supplementary Information

Abstract Three novel enantiopure phenyl isocyanide monomers with BH₃-protected phosphine functional group were designed and synthesized. Polymerization of these monomers using an alkyne-Pd(II) complex as a catalyst led to the formation of respective helical polyisocyanides in high yields with controlled molecular weights (M_n s) and narrow molecular weight distributions (M_w/M_n s). Removing the protecting BH₃ groups afforded helical poly(phenyl isocyanide)s bearing phosphine pendants. Thanks to the chiral induction of monomer, the isolated helical polyisocyanides showed high optical activity, as revealed by circular dichroism (CD) and absorption spectroscopies and polarimetry. The helical structures of these polymers were quite stable in various organic solvents with different polarities and in a wide temperature range. Moreover, these helical polymers could be used as organocatalysts and showed good performance in enantioselective cross Rauhut-Currier reaction. The enantiomeric excess (ee) values of the isolated products of cross Rauhut-Currier reaction could be up to 90%. The polymer organocatalysts could be easily recovered from the reaction mixtures and reused at least five times in the reaction without significant loss of their enantioselectivities and catalytic activities.

Keywords Helical polymer; Polyisocyanide; Coordination polymerization; Polymer catalyst

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INTRODUCTION

Helix is one of the central structural motifs in biomacromolecules such as α -helix in proteins and double helix in DNA. It also plays an important role in realizing marvellous biological activities in living systems^[1–3]. Stimulated by helical structure in Mother Nature, studies on artificial helical polymers and oligomers have attracted great research attention over the past decades^[4–6]. The objective of this research is not only to deepen the understanding on the structure-property relationships of biomacromolecules but also to develop new functional materials with novel properties and applications. In this context, polyisocyanides are of particular interest owing to their stable helical conformations and wide applications^[7–9]. Optically active helical polyisocyanides can be used in chiral recognition^[10, 11], enantiomer separation^[12, 13], asymmetric catalysis^[14, 15], liquid crystal^[16, 17], and so on. Incorporation of helical

polyisocyanides into conjugated polythiophenes yielded block copolymers with controllable self-assembly morphologies and light emission properties^[18–20]. Introduction of novel functional groups into the pendants or the ends of polyisocyanides would generate new materials with novel properties and functions. Although many functional polyisocyanides have been reported, chiral polymer catalysts based on helical polyisocyanide for asymmetric reaction are very limited. Nevertheless, such polymer catalysts have many advantages: (1) the chiral microenvironment of helical main chains can be used to tune the enantioselectivity of an organic reaction; (2) the helicities of polyisocyanides can significantly enhance the enantioselectivity of an asymmetric organic reaction; (3) the relatively high molecular weights of polymer catalysts can facilitate the catalysts recovery and recycle use in further reactions^[21–23]. However, to the best of our knowledge, reports on organocatalyst based on optically active helical polymers are very rare, probably due to lack of theory for catalyst design^[24]. Thus, to develop novel helical polymer-supported catalysts for asymmetric reaction is of great desire.

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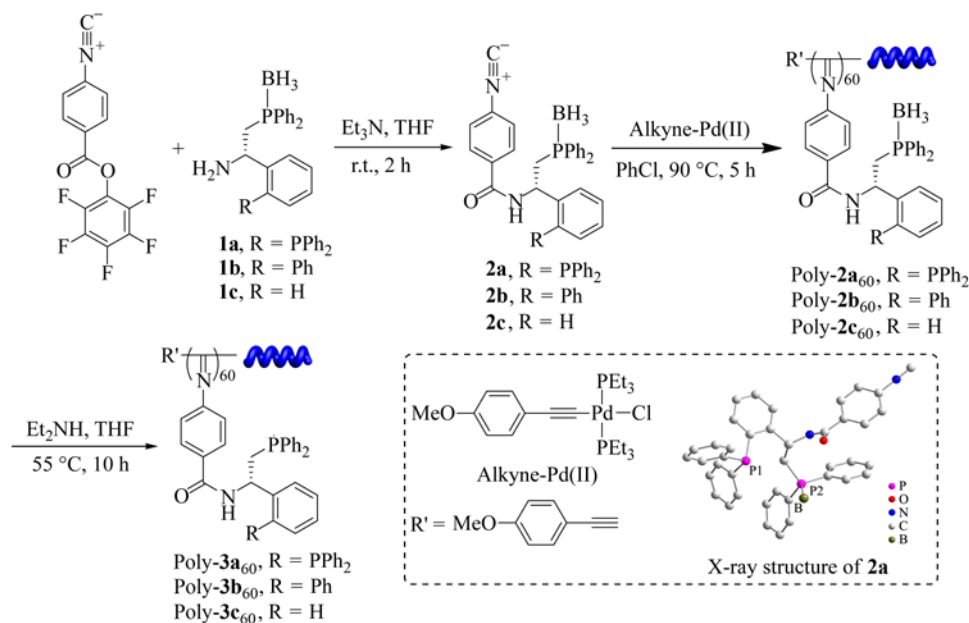
Over the last few years, great progress on asymmetric organocatalysts based on chiral phosphine has been achieved, which has been developed to be an attractive synthetic strategy for syntheses of optically active materials^[25–27]. The advantages of chiral phosphine catalysts include mild reaction conditions, wide functional group tolerance and free of transition metals^[28–30]. Among the phosphine-catalyzed reactions, Rauhut-Currier reaction of two active olefins is an effective strategy for constructing carbon-carbon bonds and increasing the densities of vinyl functionalized organic building blocks^[31, 32]. Therefore, a large number of studies have been devoted to the design and synthesis of chiral catalysts to promote the enantioselective Rauhut-Currier reaction^[33, 34]. However, the catalytic activity of the chiral phosphine is usually low and thus a relatively high catalyst loading (often 10 mol%–20 mol%) is required to assure an satisfied yield and enantioselectivity^[35, 36]. An effective solution to overcome these drawbacks is to design and synthesize chiral polymer-supported phosphine catalysts, which may enhance the enantioselectivity and facilitate the catalyst recovery and recycle use^[37, 38]. Probably due to the limited synthetic methods, this kind of functional polymers have rarely been reported to date.

In this contribution, we design and synthesize three novel enantiopure phenyl isocyanide monomers with BH_3 -protected phosphine groups. Polymerizations of these monomers using an alkyne-Pd(II) catalyst afforded a family of optically active poly(phenyl isocyanide)s in high yields with controlled number-average molecular weights (M_n s) and narrow molecular weight distributions (M_w/M_n s). Because of the chiral induction of the monomer, the isolated helical polyisocyanides showed high optical activities, as revealed by circular dichroism (CD) and polarimetry studies. Interestingly, after the protecting BH_3 groups were removed, such polymers bearing phosphine pendants could be used as asymmetric organocatalysts in cross Rauhut-Currier reaction. The enantiomeric excess (*ee*) of the products could be as high as

90%. Moreover, thanks to the higher M_n of the polymer catalysts, they could be facilely recovered and reused in the reaction for at least five cycles without significantly losing their activities and enantioselectivities.

RESULTS AND DISCUSSION

As outlined in Scheme 1, three phenyl isocyanide monomers bearing single and dual chiral phosphine substituents were designed and synthesized following the procedure reported previously by our group (see electronic supplementary information (ESI) for details). Firstly, three amines **1a**, **1b** and **1c** were prepared according to the reported literature with slight modifications. Their structures were confirmed by ^1H -NMR^[39]. Because the alkyl phosphine group was sensitive to air, the phosphine connecting with an alkyl group of the three amines was protected by BH_3 ^[39]. The amines were then reacted with perfluorophenyl 4-isocyanobenzoate respectively in THF at room temperature, affording the expected isocyanide monomers in high yields (> 87%). The structures of these isocyanide monomers were confirmed by ^1H -, ^{13}C -NMR, FTIR, mass spectra and elemental analyses (Figs. S1–S12, in ESI). Comparing the three monomers, we found that monomer **2c** was less steric hindrance, while monomers **2a** and **2b** were more sterically hindered because the H atom on the *ortho*-position of **2c** was replaced by a benzene ring (**2b**) or diphenylphosphine (**2a**). Thus, the sequence of the steric hindrance for the three monomers is **2a** > **2b** > **2c**. The design principle on the different structures of monomers was just to figure out the influence of steric hindrance on the helical structures and properties of the resulting helical polyisocyanides. The structure of **2a** was further confirmed by its single crystal which was obtained by slow diffusion of hexane into solution of **2a** in 1,2-dichloroethane at room temperature. The X-ray structure of **2a** was outlined in Scheme 1^[40]; both the two phosphine groups were clearly observed, and the alkyl phosphine was



Scheme 1 Synthesis of poly(phenyl isocyanide)s bearing phosphine pendants

coordinated with BH_3 .

With these monomers in hands, our effort was directed to syntheses of helical poly(phenyl isocyanide)s bearing phosphine pendants. Initially, monomers **2a–2c** were attempted to be polymerized in THF at 55 °C using *trans*-bis(triethylphosphine)-((4-methoxyphenyl)ethynyl)palladium(II) chloride (alkyne-Pd(II)) as a catalyst, following the procedure previously reported by us^[8]. However, no polymeric products could be isolated. To our delight, the polymerizations could take place smoothly in chlorobenzene (PhCl) at 90 °C ($[\text{M}]_0 = 0.15 \text{ mol/L}$, $[\text{M}]_0/[\text{Pd}]_0 = 60$). For example, the polymerization of **2a** afforded a well-defined helical poly(phenyl isocyanide) in 85% yield. It showed a symmetric and single model elution peak in size exclusion chromatography (SEC) curves (Fig. 1a), consistent to the

living nature of the alkyne-Pd(II) initiated isocyanide polymerization^[8]. The M_n and M_w/M_n of poly-**2a**₆₀ were estimated to be 30.3 kDa and 1.20, respectively, by SEC with equivalent to polystyrene standards. Following the same polymerization procedure, monomers **2b** and **2c** could be facily polymerized. The results of the polymerizations are summarized in Table 1. All these polymers have good solubilities in most common organic solvents with different polarities including THF, CHCl_3 , toluene, PhCl, etc. The attempts to give polymers with higher M_n by increasing the initial feed ratio of monomer to the catalyst were unsuccessful, because the generated polymers had poor solubilities in PhCl and were precipitated out of the solutions during the polymerization processes. Thus, the initial feed ratio of monomer to catalyst of all the polymerizations was fixed at 60/1. Note that the monomers also contained phosphine ligand, which replaced the triethylphosphine groups on the alkyne-Pd(II) catalyst during the polymerization reactions. Thus the resulted helical polymers contained Pd(II) terminus bearing aryl phosphine ligands. Such Pd(II) complexes were unstable and decomposed during the work-up as we reported previously^[41]. The perfluorophenyl 4-isocyanobenzoate can also be polymerized by the alkyne-Pd(II) leading to polyisocyanide bearing pentafluorophenyl ester pendants. Post-modification of this polymer with amines **1a–1c** can afford the desired helical polymers. However the helicity would be a little bit lower than direct polymerizations of **2a–2c**^[42].

In addition to SEC, the structures of the polymers were further characterized by ^1H - and ^{31}P -nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopies. The peaks in the ^1H -NMR spectrum of monomer **2a** were sharp (Fig. S1, in ESI), while those of the resulting poly-**2a**₆₀ were relatively broad, especially in the aromatic region, probably due to restriction of the rotation caused by the rigid rod helical conformation of the main chain (Fig. S13, in ESI). Moreover, the $\text{C}\equiv\text{N}$ vibration band in the FTIR spectrum at 2122 cm^{-1} of **2a** completely disappeared after the polymerization, suggesting that all the isocyanides participated in the polymerization (Figs. S4 and S14, ESI). Accordingly, an intense vibration band at 1600 cm^{-1} was clearly observed in the FTIR spectrum of poly-**2a**₆₀, which corresponded to the characteristic vibration band of $\text{C}=\text{N}$ of the poly(phenyl isocyanide) backbone. ^{31}P -NMR analysis also confirmed the formation of the expected poly(phenyl isocyanide) bearing phosphine pendants. Monomer **2a** showed a resonance peak at 8.12 ppm, which was attributable to the chiral phosphine group protected by BH_3 . And another resonance peak at -20.87 ppm was attributable to triaryl phosphine atom without BH_3 group (Fig. 1b). The peaks in the ^{31}P -NMR spectrum of the resulting poly-**2a**₆₀ were very broad and the resolution was quite low. The broad signals may arise from chain rigidity and from non-uniformity of the magnetic environment in the polymer chains. However, poly-**2a**₆₀ clearly showed two resonance peaks at 8.00 and -21.95 ppm , respectively. The positive sign of the ^{31}P -NMR indicated that the BH_3 protected phosphine was maintained during the polymerization. Compared to the monomer **2a**,

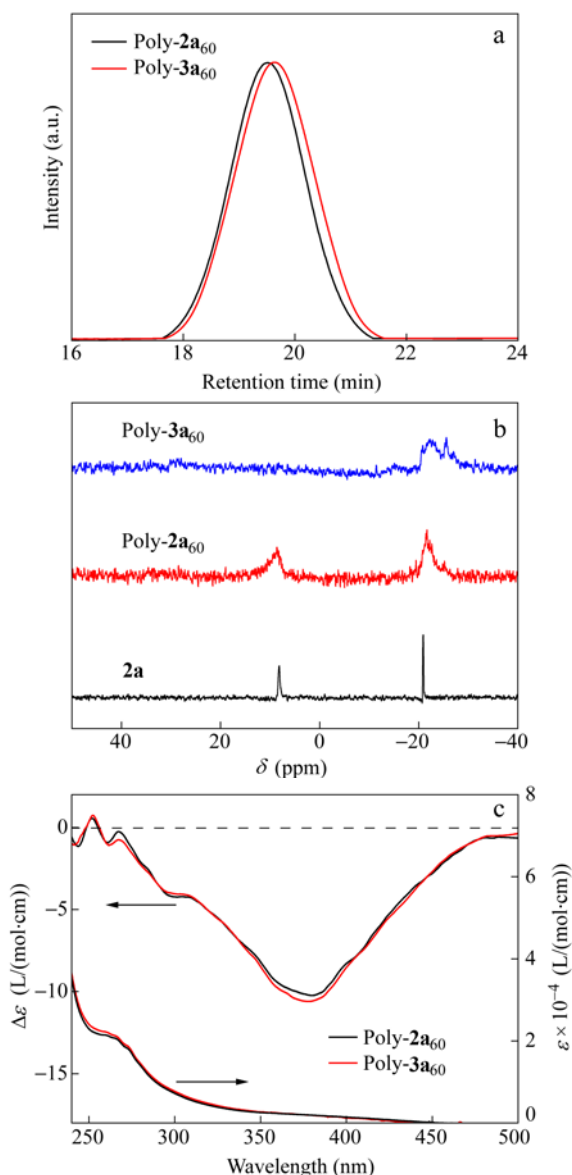


Fig. 1 (a) Size exclusion chromatograms of poly-**2a**₆₀ and poly-**3a**₆₀ (eluent = THF, temperature = 40 °C); (b) ^{31}P -NMR spectra (240 MHz) of **2a**, poly-**2a**₆₀ and poly-**3a**₆₀ recorded in CDCl_3 at 25 °C; (c) CD and UV-Vis spectra of poly-**2a**₆₀ and poly-**3a**₆₀ recorded in THF at 25 °C

Table 1 Characterization data for helical poly(phenyl isocyanide)s bearing phosphine pendants^a

Entry	Polymer	M_n^b (kDa)	M_w/M_n^b	Yield ^c (%)	$\Delta\epsilon_{374}^e$ (L/(mol·cm))	$[\alpha]_D^{25}$ ^f
1	Poly- 2a ₆₀	30.3	1.20	87 ^c	−10.11	−919.4
2	Poly- 3a ₆₀	28.8	1.27	90 ^d	−10.55	−948.3
3	Poly- 2b ₆₀	25.6	1.28	85 ^c	−9.38	−882.3
4	Poly- 3b ₆₀	24.3	1.25	91 ^d	−9.62	−898.6
5	Poly- 2c ₆₀	23.1	1.29	85 ^c	−9.63	−948.6
6	Poly- 3c ₆₀	21.9	1.24	90 ^d	−9.20	−899.1

^aThe polymers were synthesized according to Scheme 1; ^bThe M_n and M_w/M_n were determined by SEC with equivalent to polystyrene standards; ^cThe isolated yields of the polymerizations; ^dThe isolated yields of the deprotection reactions; ^eThe CD intensity at 374 nm of polymers measured in THF at 25 °C; ^fThe optical rotations of polymers measured in CHCl₃ ($c = 0.1$, 25 °C)

both the two ³¹P signals were upshifted to high field, which was ascribed to the shielding effect of the as-formed polymer (Fig. 1b). These studies confirmed formation of the expected polymers.

The protected BH₃ groups on poly-**2a**₆₀ could be facilely removed by reaction with Et₂NH in THF at 55 °C (Scheme 1). The afforded poly-**3a**₆₀ was also confirmed by SEC, ¹H-NMR and ³¹P-NMR. As shown in Fig. 1(a), the SEC curve of poly-**3a**₆₀ was slightly shifted to shorter retention time region, as revealed by the decrease of the M_n . In the ³¹P-NMR spectrum of poly-**3a**₆₀, the resonance peak at 8.00 ppm disappeared, while a new peak at −25.52 ppm was observed, implying almost complete removal of the BH₃ groups (Fig. 1b). Under the same way, poly-**2b**₆₀ and poly-**2c**₆₀ and the deprotected poly-**3b**₆₀ and poly-**3c**₆₀ with different pendants were also prepared, and their structures were confirmed by SEC, ¹H-NMR, and ³¹P-NMR (Figs. S15–S21, in ESI).

The optical activity of the isolated poly-**2a**₆₀ and the deprotected poly-**3a**₆₀ was investigated by CD and UV-Vis spectroscopies. Because the monomer was enantiopure, the isolated poly-**2a**₆₀ showed intensely negative CD around 374 nm which was attributed to the $n\text{--}\pi^*$ transition of the C=N of the poly(phenyl isocyanide) backbone (Fig. 1c). The molar CD intensity at 374 nm ($\Delta\epsilon_{374}$) was estimated to be −10.11 L/(mol·cm), which was further confirmed by polarimetry. A $[\alpha]_D^{25}$ value of −919.4 ($c = 0.1$, CHCl₃, 25 °C) was reported, indicating formation of an excess of left-handed helix. The CD and UV-Vis profiles of deprotected poly-**3a**₆₀ are very similar to those of poly-**2a**₆₀ precursor, suggesting that the helical conformation was maintained during the deprotection reaction. The removal of the BH₃ groups had no significant effect on the helical structure and the optical activity. The $\Delta\epsilon_{374}$ of poly-**3a**₆₀ was determined to be −10.55 L/(mol·cm), consistent with the value of optical rotation which is −948.3 ($c = 0.1$, CHCl₃, 25 °C). The optical activities of poly-**3b**₆₀ and poly-**3c**₆₀ were also investigated by CD and UV-Vis spectroscopies. Although the steric hindrances of these two polymers were smaller than that of poly-**3a**₆₀, the CD intensity are almost the same, implying that an excess of left-handed helix was induced (Figs. S22 and S23, in ESI).

To further confirm the helical conformations of the synthetic polymers, concentration-dependent CD and UV-Vis spectra of poly-**3a**₆₀ were recorded. As displayed in Fig. 2(a), both CD and UV intensities increase with the increase of the polymer concentration in THF at 25 °C. Plots of CD and UV

intensities at 374 nm with the concentration reveal that the intensities are linearly correlated to the concentrations (Fig. 2b). Moreover, the asymmetric factor ($\Delta\epsilon/\epsilon$) at 374 nm keeps constant (Fig. S24, in ESI), indicating that the CD

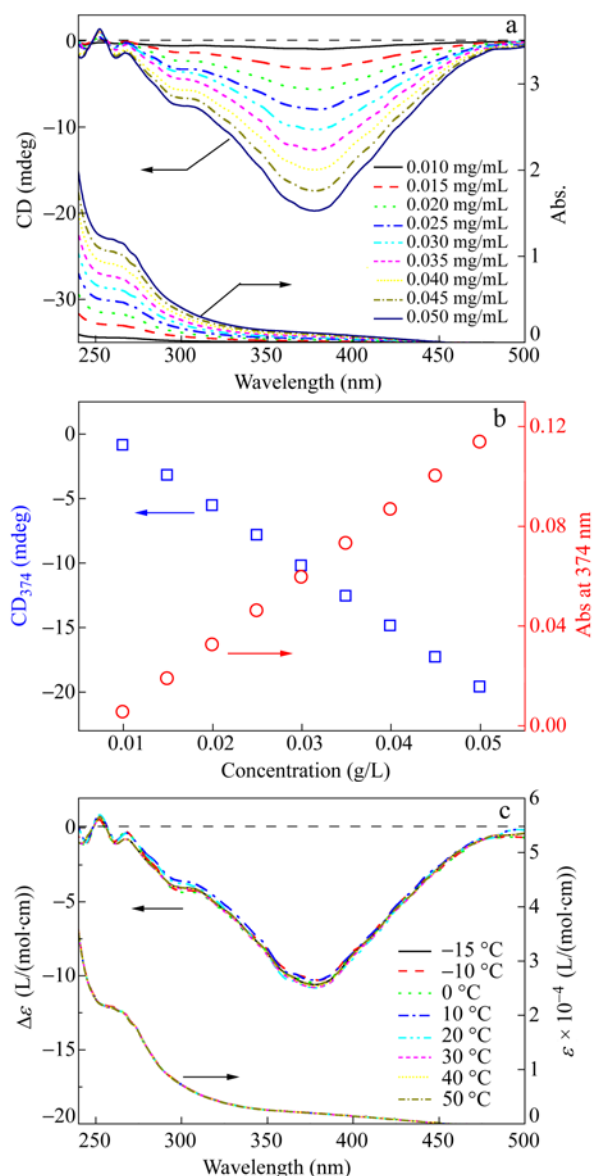


Fig. 2 (a) CD and UV-Vis spectra of poly-**3a**₆₀ measured in THF at 25 °C at various concentrations; (b) Plots of CD and UV-Vis intensities at 374 nm with the concentration of poly-**3a**₆₀ measured in THF at 25 °C; (c) CD and UV-Vis spectra of poly-**3a**₆₀ measured in THF at various temperatures

comes from the helical conformation of the polymer itself, not the aggregates of the polymers. The stabilities of the helical conformations of these polymers were then studied. It was found that the helical conformations were quite stable. There were no substantial changes in the CD and UV-Vis spectra at the temperature range from $-15\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$ in THF (Fig. 2c). Moreover, they showed the same CD and UV-Vis spectra in solvents with different polarities including THF, CH_2Cl_2 , and CHCl_3 , indicating that the solvent and temperature have no significant influences on the helical conformation and the optical activities (Fig. S25, in ESI).

It is generally accepted that some phosphines are good organocatalysts for many organic reactions, for example, cross Rauhut-Currier reaction^[28, 35]. Since all the poly-**3a**₆₀, poly-**3b**₆₀, and poly-**3c**₆₀ bear phosphine groups on the pendants, these polymers may be used as polymeric organocatalysts in organic reactions. To verify this, we have investigated their catalytic activities in the enantioselective cross Rauhut-Currier reaction by using 3-aryl acrylates (**4a**) and methyl vinyl ketone (**5a**) as the substrates. To our delight, the helical polymer poly-**3a**₆₀ displayed good performance in the enantioselective cross Rauhut-Currier reaction, yielding the desired product **6a** in 91% yield with good enantioselectivity (Table 2, entry 3). The *ee* of the isolated **6a** was determined to be 82% by high performance liquid chromatography (HPLC) using column with chiral stationary phase (see ESI for details). The results are summarized in Table 2. For comparison, the alkyne-Pd(II) was also used in the same reaction; however no desired product can be isolated. Helical poly-**3b**₆₀ and poly-**3c**₆₀ were also used in the reaction under the same reaction conditions. Although the reactions gave the expected products in good yields, the enantioselectivity was decreased (Table 2, entries 1 and 2). The *ee* values of the products were estimated to 72% for poly-**3b**₆₀ and 64% for poly-**3c**₆₀, respectively. This result is reasonable because the steric hindrance of the phosphine pendants in these two polymers are smaller than that in

poly-**3a**₆₀. Thus, the catalytic activity of poly-**3a**₆₀ in enantioselective cross Rauhut-Currier reaction was investigated in more details. Further screening of solvents, such as dichloromethane, tetrahydrofuran, ether and methyl *tert*-butyl ether (MTBE), suggested that chloroform was the best reaction medium (Table 2, entries 4–7). It was noteworthy that reducing the catalyst loading of poly-**3a**₆₀ to 10 mol% proved to be feasible and the efficiency of the cross Rauhut-Currier reaction was not impeded (Table 2, entries 8 and 9). As anticipated, higher catalyst loading brought shorter reaction time and higher yield in the cross Rauhut-Currier reaction (Table 2, entry 10). Fortunately, the *ee* of **6a** was improved to 87% when lowering the reaction temperature from $25\text{ }^{\circ}\text{C}$ to $-10\text{ }^{\circ}\text{C}$ (Table 2, entry 11). However, further lowering the reaction temperature could not improve enantioselectivity significantly and a reduced yield of **6a** was observed (Table 2, entries 12 and 13). Thus the optimized condition of Rauhut-Currier reaction is a loading of 10 wt% of poly-**3a**₆₀ in CHCl_3 at $-10\text{ }^{\circ}\text{C}$.

Under the optimized reaction conditions, we then examined the scope of the enantioselective cross Rauhut-Currier reaction. Gratifyingly, a set of 3-aryl acrylates containing functional groups of different electron nature, including F, Cl, CF_3 and CH_3 , worked well with methyl vinyl ketone to produce the corresponding cross Rauhut-Currier products **6a–6e** in 85%–90% yields with 87%–90% *ee* (Table 3, entries 1–5). Noteworthy, when **4f** and **4g** were used as the substrates, the desired **6f** and **6g** were also produced in good yields, but with a slightly decreased enantioselectivities (66%–80% *ee*) (Table 3, entries 6 and 7). Further substrate scope exploration suggested that poly-**3a**₆₀ was also an efficient catalyst for naphthyl and heteroaryl containing substrates **4h–4j** and gave the expected products **6h–6j** in good yields and enantioselectivities (Table 3, entries 8–10). For broad substrates scope, 3-aryl acrylates **4k–4m** bearing different ester groups were further synthesized and

Table 2 Optimization on enantioselective cross Rauhut-Currier reaction conditions^a

Entry	Cat.*	X (mol%)	Solvent	T (°C)	t (h)	Yield ^b (%)	<i>ee</i> ^c (%)
1	Poly- 3c ₆₀	20	CHCl_3	25	10	89	64
2	Poly- 3b ₆₀	20	CHCl_3	25	10	90	72
3	Poly- 3a ₆₀	20	CHCl_3	25	10	91	82
4	Poly- 3a ₆₀	20	CH_2Cl_2	25	10	90	74
5	Poly- 3a ₆₀	20	THF	25	10	88	75
6	Poly- 3a ₆₀	20	Et_2O	25	10	87	63
7	Poly- 3a ₆₀	20	MTBE	25	10	85	47
8	Poly- 3a ₆₀	10	CHCl_3	25	14	88	82
9	Poly- 3a ₆₀	5	CHCl_3	25	18	80	81
10	Poly- 3a ₆₀	30	CHCl_3	25	8	92	82
11	Poly- 3a ₆₀	10	CHCl_3	-10	24	88	87
12	Poly- 3a ₆₀	10	CHCl_3	-20	24	79	88
13	Poly- 3a ₆₀	10	CHCl_3	-25	24	74	88

^a Unless otherwise specified, all reactions were carried out with **4a** (0.2 mmol), **5a** (0.6 mmol) in solvent (2 mL); ^b Yield of isolated products; ^c Determined by HPLC analysis using a chiral stationary phase

Table 3 Enantioselective cross Rauhut-Currier reaction catalyzed by poly-**3a**₆₀^a

Entry	Substrate			Substrate		Product	Yield ^b (%)	ee ^c (%)
	4	R ¹	R ²	5	R ³			
1	4a	C ₆ H ₅	Et	5a	CH ₃	6a	88	87
2	4b	4-FC ₆ H ₄	Et	5a	CH ₃	6b	90	90
3	4c	4-ClC ₆ H ₄	Et	5a	CH ₃	6c	86	89
4	4d	4-CF ₃ C ₆ H ₄	Et	5a	CH ₃	6d	87	88
5	4e	4-CH ₃ C ₆ H ₄	Et	5a	CH ₃	6e	85	88
6	4f	2-FC ₆ H ₄	Et	5a	CH ₃	6f	84	80
7	4g	2,4-Cl ₂ C ₆ H ₃	Et	5a	CH ₃	6g	81	66
8	4h	2-Naphthyl	Et	5a	CH ₃	6h	79	86
9	4i	2-Furyl	Et	5a	CH ₃	6i	78	82
10	4j	2-Thienyl	Et	5a	CH ₃	6j	82	87
11	4k	C ₆ H ₅	Me	5a	CH ₃	6k	84	82
12	4l	C ₆ H ₅	<i>i</i> Pr	5a	CH ₃	6l	80	90
13	4m	C ₆ H ₅	Bn	5a	CH ₃	6m	81	85
14	4a	C ₆ H ₅	Et	5b	H	6n	72	40

^a Unless otherwise specified, all reactions were carried out with **4** (0.2 mmol), **5** (0.6 mmol), poly-**3a**₆₀ (10 mol%) in CHCl₃ (2 mL) at –10 °C for 24 h; the absolute configurations of **6** were assigned by comparison with optical rotation in literature^[28]; ^b Yield of isolated products; ^c Determined by chiral HPLC analysis using a chiral stationary phase

used in the reaction. The results are summarized in Table 3. It was found that the bulky ester group, such as isopropyl group, was beneficial for the higher enantioselectivity and the desired **6l** was generated in 80% yield with 90% *ee* (Table 3, entries 11–13). It is well known that acrolein is a persistently challenging substrate in the asymmetric cross Rauhut-Currier reaction, however the aldehyde group of the cross Rauhut-Currier adducts would be valuable for further versatile transformation. Thus, acrolein was used as the substrate in the reaction, but unfortunately, the result was not satisfied. The *ee* value of the product was only 40% (Table 3, entry 14).

Lastly, the recyclability of the helical polyisocyanides-based organocatalyst was investigated. Because of large difference in the molecular weights between the polymer catalysts and the reaction products, it is much easy to separate the catalysts from reaction solutions. Herein, we take the reaction of **4b** with **5a** as an example. At the end of the reaction, most of the starting materials were converted into the products, as indicated by thin layer chromatography. A large amount of *n*-hexane was then added into the reaction solution and the clear reaction solution became turbid, as a result of the precipitation of the polymer catalyst. The polymer catalyst and the reaction solution containing the product were easily separated by centrifugation (Fig. 3a). Poly-**3a**₆₀ was recovered in almost quantitative yield. CD and UV-Vis spectra of the recovered poly-**3a**₆₀ were almost the same as those of the fresh one. The Δε₃₇₄ value of the recovered poly-**3a**₆₀ is –10.50 L/(mol·cm) (Table S1, in ESI), indicating that the optical activity and the helical structure were maintained after the cross Rauhut-Currier reaction. Thus, the recovered poly-**3a**₆₀ was reused in the same cross Rauhut-Currier reaction using **4b** with **5a** as the substrates. It was found that the recovered poly-**3a**₆₀ showed excellent

catalytic activity in the reaction, similar to the reaction using the fresh poly-**3a**₆₀. For example, the *ee* value of the product using the fifthly cycled poly-**3a**₆₀ is 87% with a yield of 85% (Fig. 3b). In this context, it can be concluded that the helical polyisocyanide organocatalyst can be reused in the cross Rauhut-Currier reaction without significantly losing its enantioselectivity and catalytic activity.

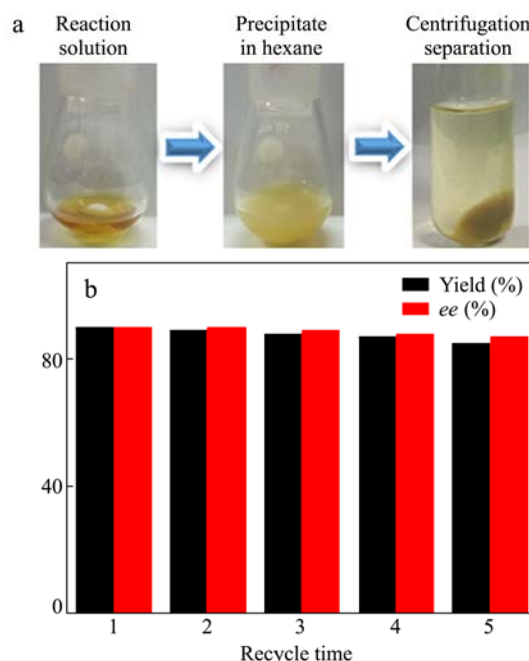


Fig. 3 (a) The separation of polymer catalyst poly-**3a**₆₀ from the reaction solution (CHCl₃); (b) Yield and *ee* of the cross Rauhut-Currier reaction of **4b** and **5a** catalyzed by recovered poly-**3a**₆₀

CONCLUSIONS

In summary, we have synthesized three new enantiopure phenyl isocyanide monomers containing BH_3 -protected phosphine substituents with different steric hindrances. Polymerizations of these monomers using alkyne-Pd(II) catalyst lead to the formation of three expected helical poly(phenyl isocyanide)s. All these polymers show high optical activities due to the helical conformations of the main chains, as revealed by CD and UV-Vis spectroscopies, and polarimetry. Interestingly, their helical conformations are maintained after the removal of the protecting BH_3 groups. Moreover, the helical structures are quite stable in various solvents with different polarities and in a wide temperature range. Thanks to the phosphine pendants, these polymers show excellent catalytic activities in cross Rauhut-Currier reaction with good enantioselectivities. After optimizing the reaction conditions, the *ee* values of the products can be up to 90%. The polymer organocatalysts can be easily recovered and reused at least five cycles without significant loss of their enantioselectivities and catalytic activities. In addition to Rauhut-Currier reaction, the utilizations of these polymer organocatalyst in other asymmetric reactions such as [3 + 2] cycloadditions of allenones with olefin, and Morita-Baylis-Hillman reactions are now in progress in this laboratory. We believe that the present study provides not only a series of novel chiral materials for asymmetric reactions but also a clue for designing novel helical polymer catalysts.

Electronic Supplementary Information

The experimental section is included in the electronic supplementary information (ESI), which is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2044-8>.

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