

Article

Helical Polycarbenes Bearing *D*-Prolinol Ester Pendants: An Efficient Catalyst for Asymmetric Michael Addition Reaction

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Abstract: A novel diazoacetate monomer (**1**) carrying *tert*-butyloxycarbonyl (Boc) protected *D*-prolinol ester was designed and synthesized successfully. Molecular weight-controlled polymerization of **1** using the complex of π -allylPdCl coordinated Wei-phos (L^R) ligand gives a series of helical polycarbenes (poly-**1**_ms) with well-defined molecular weights (M_n s) and low polydispersity (M_w/M_n s). Removing the protecting Boc groups on the *D*-prolinol ester pendants leads to the formation of helical poly-**1**_m-As, which showed high optical activity. Furthermore, the poly-**1**_m-As showed high catalytic ability on asymmetric Michael addition reaction (up to 76% *ee* and 94/6 *dr*). Both the enantioselectivity and diastereoselectivity of the Michael addition reaction were increased comparing to *D*-prolinol as catalyst. Moreover, the helical polycarbene catalyst can be easily recovered and reused at least four times without significant loss of its enantioselectivity and diastereoselectivity.

Keywords: helical polymer; polycarbene; *D*-prolinol ester; michael addition reaction



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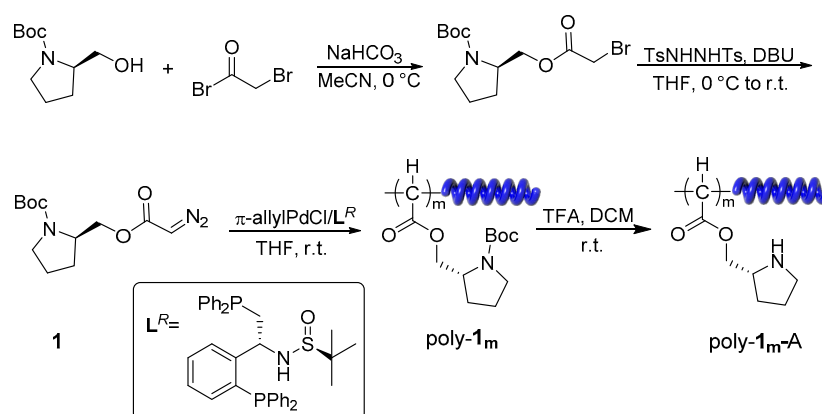
1. Introduction

Asymmetric organocatalysis, which commonly feature mild reaction conditions and wide functional groups tolerance, attracted considerable attention in recent years [1–3]. Despite these advantages, higher catalyst loading is necessary in many organocatalyzed reactions [4–6]. To solve these challenges, polymer-supported catalysts were developed [7–9]. Attaching organic catalysts to polymers can solve the problem of the reusing of the catalyst [10,11]. Meanwhile, there is a risk of reducing the catalytic activity and selectivity of the catalysts. To overcome these limitations, the design and synthesis of polymer which is not only just serve as a scaffold but also can regulate the asymmetric induction effect during the reaction process is highly desirable [12,13].

The helix is the most prominent feature for biological macromolecules like DNA and proteins [14,15]. In recent years, great attention was paid to artificial helical polymers to imitating the structure and function of natural helical polymers, and to develop new functional polymers [16–19]. Optically active helical polymers were widely applied in many fields, including chiral recognition [20,21], enantiomer separation [22,23], asymmetric catalysis [24,25], liquid crystal, and so forth [26,27]. Among of this series of applications, helical polymer-supported catalyst is of great significance. On the one hand, the high molecular weight contributed to the recovery and recycle use of polymer catalyst. On the other hand, the helical sense of polymer backbone can provide additional asymmetric environment, which amplify the stereoselectivity of asymmetric reactions by exhibit synergistic effect [28,29]. The groups of Suginome, Yashima, Deng, and Wan have done excellent works in the field of asymmetric catalysis catalyzed by helical polymer catalysts [30–33]. Despite these elegant achievements, the research of helical polymer catalyst is still at the initial stage.

Polycarbene, which has good environmental stability, is one of the most important helical polymers, which has C–C main-chain bearing substituents on each main-chain

carbon [34–37]. Accordingly, the introduction of organic molecular to helical polycarbene might be a promising method for the design of new chiral catalyst. In this contribution, we report our effort on the design and synthesis of a new diazoacetate monomer **1** bearing Boc-*D*-prolinol ester (Scheme 1). Polymerization of monomer **1** using a chiral π -allylPdCl/ L^R catalyst gives a series of helical polycarbenes (poly-**1**_{*m*}) with well-defined molecular weights (M_n s) and low polydispersity (M_w/M_n s). Poly-**1**_{*m*}-A which bearing secondary amine pendants was acquired from poly-**1**_{*m*} by removing Boc group. Under the optimized reaction conditions, poly-**1**₁₅₀-A displays best performance in the asymmetric Michael addition of nitrostyrene and cyclohexanone. Furthermore, poly-**1**_{*m*}-A can be facily recovered and used for at least 4 cycles with maintained selectivity and activity.



Scheme 1. Synthesis of poly-**1**_{*m*} and poly-**1**_{*m*}-A.

2. Results

As shown in Scheme 1, monomer **1** was prepared according to the literature reported previously with slight modifications [38]. After the structures were characterized by ^1H NMR and FT-IR (Figures S1 and S2, Supporting Information (SI)), monomer **1** were polymerized by the complex of π -allylPdCl and Wei-phos (L^R), which was an excellent initiator for polymerization of diazoacetate reported by our group (Scheme 1) [38,39]. Variation on the initial feed ratio of monomer to catalyst produced a range of poly-**1**_{*m*}s with different M_n and narrow M_w/M_n in satisfied yields. The results for the polymerization of monomer **1** were summarized in Table 1.

Table 1. Characterization data for poly-**1**_{*m*}s and poly-**1**_{*m*}-As ^a.

| Run | Polymer ^b | M_n ^c [kDa] | M_w/M_n ^c | Yield ^d [%] | g_{218} ^e ($\times 10^{-4}$) |
|-----|----------------------------------|--------------------------|------------------------|------------------------|---|
| 1 | poly- 1 ₅₀ | 15.8 | 1.24 | 83 | 4.24 |
| 2 | poly- 1 ₅₀ -A | 5.7 | 1.34 | 86 | 3.64 |
| 3 | poly- 1 ₇₅ | 16.4 | 1.27 | 80 | 5.46 |
| 4 | poly- 1 ₇₅ -A | 6.8 | 1.33 | 88 | 4.24 |
| 5 | poly- 1 ₁₀₀ | 17.2 | 1.20 | 84 | 6.06 |
| 6 | poly- 1 ₁₀₀ -A | 7.8 | 1.31 | 89 | 4.85 |
| 7 | poly- 1 ₁₂₅ | 18.0 | 1.23 | 82 | 7.58 |
| 8 | poly- 1 ₁₂₅ -A | 8.7 | 1.33 | 85 | 5.15 |
| 9 | poly- 1 ₁₅₀ | 19.1 | 1.26 | 84 | 7.88 |
| 10 | poly- 1 ₁₅₀ -A | 9.8 | 1.31 | 86 | 5.15 |

^a These polymers were prepared according to Scheme 1. ^b Footnote indicated value of $[1]_0/[Pd(II)]_0$. ^c M_n and M_w/M_n values were determined by SEC. ^d Isolated yields. ^e Asymmetric factor at 218 nm of poly-**1**_{*m*}s and poly-**1**_{*m*}-As measured in THF at 25°C ($c = 0.1$ mg/mL).

As depicted on Figure 1a and Table 1, symmetrical and unimodal elution peaks of all the isolated poly-**1**_{*m*}s with desired M_n and narrow M_w/M_n could be discerned. The SEC curves shifted to higher- M_n region according with the increased ratio of **1** to Pd(II) catalyst. Besides SEC analyses, the structures of obtained polymers were additionally verified by

^1H NMR investigations and FT-IR spectra (Figures S3 and S4, Supplementary Materials). The new obvious resonance signals of CH in the main chain of the poly- $\mathbf{1}_{150}$ could be distinguished at 4.28–3.94 ppm from the ^1H NMR spectrum of poly- $\mathbf{1}_{150}$ (Figure S3, Supplementary Materials). From the FT-IR spectrum of poly- $\mathbf{1}_{150}$, characteristic vibration of the $-\text{N}_2$ group at 2107 cm^{-1} disappeared thoroughly, indicating that all of the monomer was polymerized. Meanwhile, the vibration of methylbenzyl ester located at 1738 cm^{-1} could be clearly observed (Figure S4, Supplementary Materials). Furthermore, circular dichroism (CD) and UV-vis spectra were used to confirm the optical activity of poly- $\mathbf{1}_m$ s shown in Figure 1b. The isolated poly- $\mathbf{1}_m$ s showed distinctive positive CD at 218 nm, the absorption region of the polycarbene backbone, suggesting the formation of a preferred right-handed helix [40]. The CD values at 218 nm increased gradually with the increase of M_n s of poly- $\mathbf{1}_m$ s and remained as a constant until the M_n up to 18.0 kDa, indicating a stable helix formed. There were no obvious changes on the CD and UV-vis spectra of poly- $\mathbf{1}_{150}$ from: -10 to $30\text{ }^\circ\text{C}$, suggested that the helicity of poly- $\mathbf{1}_{150}$ didn't change with temperature (Figures S5 and S6, Supplementary Materials).

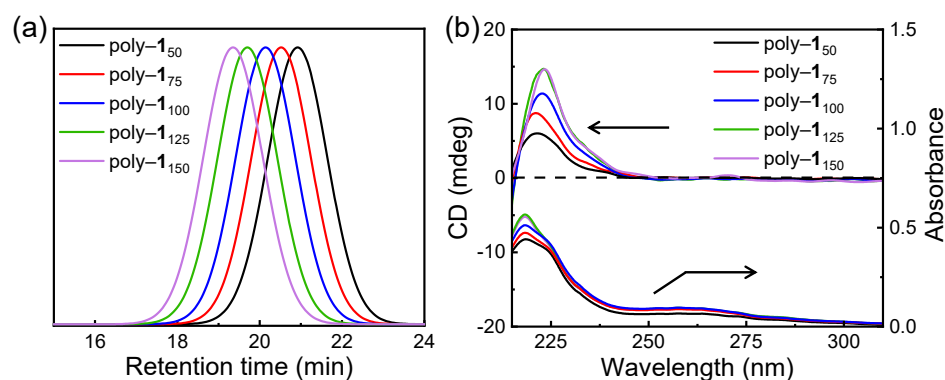


Figure 1. (a) Size exclusion chromatograms of poly- $\mathbf{1}_m$ s prepared from polymerization of $\mathbf{1}$ with π -allylPdCl/ L^R in THF at room temperature in different initial feed ratios of $[\mathbf{1}]_0/[\text{Pd}(\text{II})]_0$. (b) CD and UV-vis spectra of poly- $\mathbf{1}_m$ s with different M_n measured in THF at $25\text{ }^\circ\text{C}$ ($c = 0.1\text{ mg/mL}$).

With the poly- $\mathbf{1}_m$ s in hand, the protecting Boc groups on the poly- $\mathbf{1}_m$ s pendants could be readily removed by treating it with the mixture of trifluoroacetic acid (TFA) and dichloromethane ($v/v = 1/10$) at room temperature, after the finish of the reaction, the reaction mixture was neutralized to $\text{pH} = 8$ by triethylamine (TEA) (Scheme 1). The afforded poly- $\mathbf{1}_m$ -As had symmetric and single model elution peaks on SEC curves. Compared to that of their precursor poly- $\mathbf{1}_m$ s, they shifted to low M_n -region (Table 1 and Figure 2a). Removing the Boc groups on the pendants led to the decrease of the M_n reasonably. Furthermore, the disappearance of the resonance signals of *t*-butyl at 1.38 ppm on the ^1H NMR spectrum of poly- $\mathbf{1}_{150}$ -A was another confirmation for the success of deprotection for Boc groups on the pendants. (Figure S7, Supplementary Materials). Meanwhile, a new broad vibration band located at 3427 cm^{-1} appeared apparently on the FT-IR spectra of poly- $\mathbf{1}_{150}$ -A, indicated that new N-H bonds constructed (Figure S8, Supplementary Materials). At the absorption region of the polycarbene backbone, poly- $\mathbf{1}_{150}$ -As also showed obviously positive CD, indicating the preferred right-handed helix of the main chain formed. The CD intensity of poly- $\mathbf{1}_m$ -As was decreased attributing to the removing of the bulky Boc group. From the Figure 2c,d, we could conclude that the poly- $\mathbf{1}_m$ -As could maintain a stable helical conformation in most of tested common solvents. What's more, its helical structure could be maintained even when the temperature changes from $-10\text{ }^\circ\text{C}$ to $30\text{ }^\circ\text{C}$ in THF.

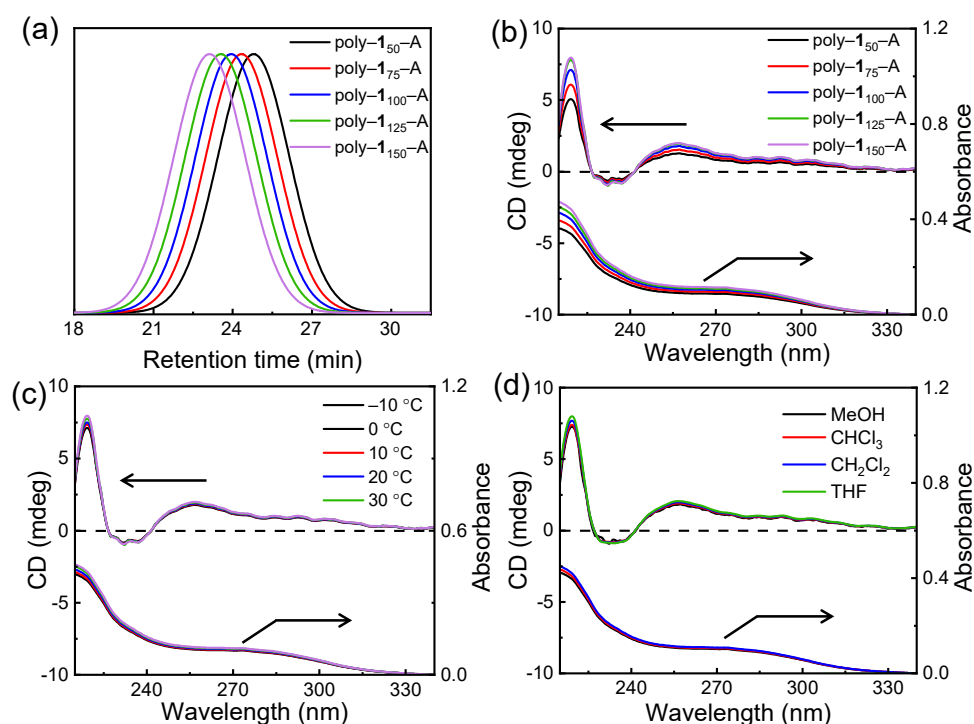


Figure 2. (a) SEC curves for poly- 1_m -As with different M_n s. (b) CD and UV-vis spectra of poly- 1_m -As with different M_n measured in THF at 25 °C ($c = 0.1$ mg/mL). (c) CD and UV-vis spectra of poly- 1_{150} -A measured in THF at different temperature ($c = 0.1$ mg/mL). (d) CD and UV-vis spectra of poly- 1_{150} -A measured at various organic solvents at 25 °C ($c = 0.1$ mg/mL).

With several chiral helical poly- 1_m -As in hands, we concentrated our investigation on their application. Asymmetric Michael addition reaction of *trans*-nitrostyrene and cyclohexanone is an efficient method for the access of γ -nitrocarbonyl compounds which were valuable in the synthesis of natural products and medicines [41,42]. Firstly, cyclohexanone and *trans*-nitrostyrene were selected as model substrates. For comparison, the *D*-prolinol and helical poly- 1_m -As were employed under the same reaction condition. In the presence of *D*-prolinol, the diastereomeric ratio (*dr*) and enantiomeric excess (*ee*) of the product was determined to be 68/32 and 18%, respectively. On the other hand, the *dr* and *ee* values of the product using poly- 1_{75} -A as catalyst were reached to 71/29 and 54%, which were much higher than the results of *D*-prolinol as catalyst at the same conditions (run 2, Table 2). This result suggested that the incorporation of catalytic prolinol onto the helical polycarbene could significantly improve the enantioselectivity and diastereoselectivity of Michael addition reaction. Next, the detailed studies of the Michael addition reaction catalyzed by the helical catalysts were investigated. As anticipated, the *dr* and *ee* values of the products were increased according to the increasing of the M_n of the polymer catalyst. For example, the *dr* and *ee* of the obtained main product was 71/29 and 54% using poly- 1_{75} -A, which increased to 72/28 and 65% when poly- 1_{100} -A were used as a catalyst, respectively (runs 2,3, Table 1). As the M_n of the polymer catalyst continued to increase, the enhance of the enantioselectivity and diastereoselectivity also increased (run 2–4, Table 2). The *dr* and *ee* values of the main product of the model reaction catalyzed by poly- 1_{150} -A were almost the same to those of the poly- 1_{125} -A (run 4,5, Table 2). These results were consisted to the relationship between the M_n -dependent helicity and poly- 1_m -A backbone (Figure 1b). Furthermore, the *D*-prolinol-derived poly(acrylate) (PAA), which lacked the same level of tertiary structure as polycarbene, was used as the catalyst for Michael addition reaction under the same conditions. The *ee* and *dr* values of the product were up to 57% and 72/28, which were much lower than the results catalyzed by poly- 1_{150} -A (run 12 and 14, Table 2). It could be further supported that the enhanced enantioselectivity came from the helicity of

the polycarbene. Next, poly-1₁₅₀-A was chosen as the catalyst for the asymmetric Michael addition reaction for investigating the other optimized conditions.

Table 2. Optimizing reaction condition for Michael addition reaction ^a.

| Run | Catalyst | Solvent | X (%) | Temp (°C) | Syn/Anti ^b | ee (%) ^b | Yield (%) ^c |
|-----------------|--------------------------|---------------------------------|-------|-----------|-----------------------|---------------------|------------------------|
| 1 ^d | D-prolinol | CH ₂ Cl ₂ | 20 | r.t. | 68/32 | 18 | 71 |
| 2 | poly-1 ₇₅ -A | CH ₂ Cl ₂ | 20 | r.t. | 71/29 | 54 | 67 |
| 3 | poly-1 ₁₀₀ -A | CH ₂ Cl ₂ | 20 | r.t. | 72/28 | 65 | 70 |
| 4 | poly-1 ₁₂₅ -A | CH ₂ Cl ₂ | 20 | r.t. | 87/13 | 71 | 79 |
| 5 | poly-1 ₁₅₀ -A | CH ₂ Cl ₂ | 20 | r.t. | 87/13 | 72 | 80 |
| 6 | poly-1 ₁₅₀ -A | THF | 20 | r.t. | 73/27 | 60 | 76 |
| 7 | poly-1 ₁₅₀ -A | CHCl ₃ | 20 | r.t. | 77/23 | 68 | 78 |
| 8 | poly-1 ₁₅₀ -A | MeOH | 20 | r.t. | 72/28 | 60 | 74 |
| 9 | poly-1 ₁₅₀ -A | Toluene | 20 | r.t. | — | — | n.d. ^e |
| 10 | poly-1 ₁₅₀ -A | CH ₂ Cl ₂ | 30 | r.t. | 86/14 | 73 | 85 |
| 11 | poly-1 ₁₅₀ -A | CH ₂ Cl ₂ | 10 | r.t. | 84/16 | 65 | 68 |
| 12 ^f | poly-1 ₁₅₀ -A | CH ₂ Cl ₂ | 20 | 0 | 94/6 | 76 | 77 |
| 13 | poly-1 ₁₅₀ -A | CH ₂ Cl ₂ | 20 | −10 | 93/7 | 78 | 45 |
| 14 | D-prolinol-derived PAA | CH ₂ Cl ₂ | 20 | 0 | 72/28 | 57 | 71 |

^a Unless otherwise denoted, all reactions were carried out with *trans*-nitrostyrene (0.20 mmol), cyclohexanone (0.80 mmol) in a specific solvent (1.0 mL) were stirred for 48 h. ^b *dr* and *ee* values were determined by HPLC analysis using a chiral stationary phase. ^c Yield of isolated products. ^d Reaction time was 6 h. ^e Not detected. ^f Reaction time was 72 h.

Then, a series of solvents including CH₂Cl₂, THF, CHCl₃, MeOH and toluene were chosen as the solvent for asymmetric Michael addition reaction to optimize the best reaction medium. Unfortunately, no product was detected in toluene, and the reason may be due to the poor solubility of polymer catalysts in toluene (run 9, Table 1). The results revealed that the highest *dr* and *ee* values of the main product could be obtained when dichloromethane using as solvent (run 5–9, Table 2). Furthermore, the loading of the polymer catalyst also had effects on the enantioselectivity and diastereoselectivity of the products. Increased the poly-1₁₅₀-A loading from 20 to 30%, there was a bit increase on the yield but no significant increase on the *ee* value of the main product (run 10, Table 2). Meanwhile, decreasing the loading of the catalyst from 20 to 10% caused the enantioselectivity reduced from 72 to 65% (run 11, Table 2). The enantioselectivity was increased to 76% by lowering the reaction temperature to 0 °C. A significant increase in *dr* value was discerned, which was up to 94/6 from 87/13 (run 12, Table 2). Much lower reaction temperature was not beneficial for this Michael addition reaction (run 13, Table 2). Finally, the best reaction conditions for this *trans*-formation were confirmed to using 20 mol% poly-1₁₅₀-A in dichloromethane at 0 °C and the desired γ -nitrocarbonyl compound was obtained in 77% yield with 94/6 *dr* and 76% *ee* (run 12, Table 2).

Compared with that of traditional organocatalyst, the polymer-based organocatalyst could be recovered and reused due to its high *M_n*. Therefore, we further performed the recovery and recycle experiments of poly-1₁₅₀-A. As expected, poly-1₁₅₀-A could be facilely isolated from the reaction system in almost quantitative yield via simple centrifugation and filtration. CD and UV-vis spectra demonstrated that the main chain of poly-1₁₅₀-A was maintained after the asymmetric Michael addition reaction. Gratifiedly, both the reactivity and enantioselectivity of recovered poly-1₁₅₀-A catalyst were not decreased and the desired product was produced in 76% yield with 94/6 *dr*, and 76% *ee*. Further studies demonstrated that the poly-1₁₅₀-A can be recycled at least 4 times without obvious loss in its activity and stereoselectivity (Figure 3).

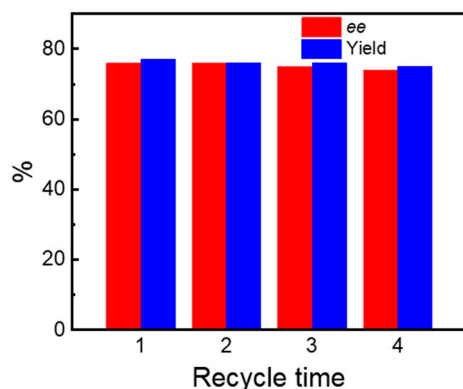


Figure 3. Recycle use of poly-1150-A (with 20% loading) in Michael addition reaction of *trans*-nitrostyrene (0.20 mmol) and cyclohexanone (0.80 mmol) in dichloromethane at 0 °C for 48 h.

3. Materials and Methods

3.1. Synthesis of Monomer 1

The procedure was followed the literature reported with slight modification [38]. Under a N₂ atmosphere, bromoacetyl bromide (1.1 mL, 12.92 mmol, 1.3 eq.) was added dropwise to a stirred suspension of Boc-*D*-Prolinol (2.0 g, 9.93 mmol, 1.0 eq.) and NaHCO₃ (2.5 g, 29.81 mmol, 3.0 eq.) in acetonitrile (60 mL) at 0 °C. The resulting mixture was stirred for 30 min at this temperature. After the addition of H₂O, the mixture was extracted with CH₂Cl₂, and the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was then evaporated under reduced pressure, and the obtained residue was directly used in next step without further purification. The obtained residue and TsNHNHTs (3.7 g, 10.93 mmol, 1.1 eq.) was dissolved in THF (70 mL). After cooling to 0 °C, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (4.5 mL, 29.79 mmol, 3.0 eq.) was added dropwise to the mixture, and kept stirring for 30 min at this temperature. Then, the reaction solution was quenched by the addition of saturated aqueous NaHCO₃, and extracted with diethyl ether. The combined organic phase was then washed with brine, dried over anhydrous Na₂SO₄, and evaporated to dryness to give a crude product. The obtained residue was further purified by column chromatography using petrol ether and ethyl acetate as eluent (*v/v* = 8:1), afforded monomer 1 as a yellowish oil (2.19 g, 82% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 4.74 (s, 1H, N₂CH), δ 4.23–4.10 (m, 2H, CH₂), 3.95 (m, 1H, CH), 3.39–3.31 (m, 2H, CH₂), 1.97–1.78 (m, 4H, (CH₂)₂), 1.46 (s, 9H, CH₃). FT-IR (KBr, 25 °C): 3103 (ν_{C-H}), 2974 (ν_{C-H}), 2876 (ν_{C-H}), 2109 (ν_{N≡N}), 1684 (ν_{C=O}) cm⁻¹.

3.2. Typical Polymerization Procedure for Poly-1_{ms}

Taking poly-1₁₅₀ as an example following the literature reported with slight modification [38]. A solution of the as-prepared π-allylPdCl/L^R catalyst in THF (0.37 mL, 0.01 mol/L, 0.0037 mmol) was added to a solution of monomer 1 (150 mg, 0.557 mmol) in THF (1.05 mL) at 25 °C. The concentrations of the monomer and the catalyst were 0.39 mol/L and 0.0026 mol/L, respectively. The initial feed ratio of monomer to catalyst was 150/1 ([1]₀/[Pd]₀ = 150). The reaction mixture was stirred at 25 °C, and lots of bubbles were released upon the addition of the π-allylPdCl/L^R catalyst. After the polymerization solution was stirred for 2.5 h at 25 °C, it was precipitated into a large amount of *n*-hexane. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight, affording poly-1₁₅₀ as a yellowish solid (127 mg, 84% yield). SEC: *M*_n = 19.1 kDa, *M*_w/*M*_n = 1.26. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 4.29 (br, 1H, CH of main chain), δ 3.94 (br, 2H, CH₂), 3.25 (br, 3H, CHCH₂), 1.92 (br, 4H, (CH₂)₂), 1.39 (br, 9H, (CH₃)₃). FT-IR (KBr, 25 °C): 2975 (ν_{C-H}), 2855 (ν_{C-H}), 1687 (ν_{C=O}) cm⁻¹.

3.3. Typical Procedure for Poly-1_m-As

Poly-1₁₅₀ (0.20 g) was dissolved in CH₂Cl₂ (5.0 mL), and trifluoroacetic acid (TFA, 0.5 mL) was slowly added to the stirring solution at 0 °C [29]. After the resulting solution was stirred at room temperature overnight, the solution was adjusted to pH = 8.5 by triethylamine (TEA). After concentrated to dryness, the resulting residues were dissolved in CH₂Cl₂ (1.8 mL), then a large amount of *n*-hexane was added, and a yellowish solid was precipitated gradually. The solid was collected through centrifugation, and dried in vacuum at room temperature overnight (102 mg, 86% yield). SEC: $M_n = 9.8$ kDa, $M_w/M_n = 1.31$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 4.30 (br, 1H, CH of main chain), δ 4.09 (br, 2H, CH₂), 3.32 (br, 2H, CH₂), 3.15 (br, 1H, CH), 2.01 (br, 4H, (CH₂)₂), 1.25 (br, 1H, NH). FT-IR (KBr, 25 °C): 3397 (ν_{N-H}), 2975 (ν_{C-H}), 2776 (ν_{C-H}), 1665 (ν_{C=O}) cm⁻¹.

3.4. General Procedure for Michael Addition Reaction

Poly-1₁₅₀-A (6.73 mg, 0.04 mmol, with respective to repeating units, calculated by dividing mass of polymer by molecular mass of repeating unit (omitting the end groups of the polymer)) was added to the stirring solution of cyclohexanone (7.85 mg, 0.80 mmol) in CH₂Cl₂. Then *trans*-nitrostyrene (29.62 mg, 0.20 mmol) was added to this solution via a microsyringe. The resulting solution was stirred at 0 °C, followed by thin layer chromatography (TLC) until the reaction was accomplished. Then, *n*-hexane was added to the solution to precipitate the polymer catalyst. The precipitated polymer catalyst was redissolved in CH₂Cl₂. Then, a large amount of *n*-hexane was added to the solution to precipitate the polymer again, the process was repeated three times to remove the product and unreacted materials. At last, the recycled polymer catalyst was dried under vacuum for next recycle. The organic phase was collected and concentrated. Then, the crude product was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (*v/v* = 8:1) as an eluent to afford the product.

4. Conclusions

In summary, a set of structural novel helical polycarbene-based organocatalysts, which, bearing *D*-prolinol ester pendants, were developed. The right-handed helix of the main chain played an important role for the catalytic activity. Compared to that of typical small molecules with similar structure, the present polymers catalyst exhibited better stereoselectivity in the Michael addition reaction of *trans*-nitrostyrene and cyclohexanone. The stereoselectivity of the Michael addition reaction is closely related to the helical excess of the polymer catalyst. The higher g_{218} of the polymer catalyst, the higher stereoselectivity of the product was achieved. Satisfied *ee* and *dr* values (76% *ee* and 94/6 *dr*) of the product can be obtained under the optimized reaction conditions. Moreover, it is convenient to recover and reuse the polymer catalyst at least 4 times without obvious decrease in its activity and stereoselectivity. In addition to providing an important method for modifying helical polycarbenes, this study also provides a series of functional materials with potential applications in the field of asymmetric catalysis.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111369/s1>, Figures S1 and S2: ¹H NMR and FT-IR spectra of monomer **1**, Figures S3 and S4: ¹H NMR and FT-IR spectra of poly-1₁₅₀, Figure S5: CD and UV-vis spectra of poly-1₁₅₀ measured in different concentrations at 25 °C, Figure S6: CD and UV-vis spectra of poly-1₁₅₀ measured in THF at different temperatures. Figures S7 and S8: ¹H NMR and FT-IR spectra of poly-1₁₅₀-A, Figure S9: ¹H NMR spectrum of *D*-prolinol-derived PAA measured in CDCl₃ at 25 °C. Figure S10: ¹H NMR spectrum of (*R*)-2-((*S*)-2-nitro-1-phenylethyl) cyclohexanone measured in CDCl₃ at 25 °C. Figures S11–S13: HPLC curve of racemic (2-nitro-1-phenylethyl)cyclohexanone and (*R*)-2-((*S*)-2-nitro-1-phenylethyl).

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Data Availability Statement: All the data presented in this study are available in the Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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