Optically Active Helical Polymers with Pendent Thiourea Groups: Chiral Organocatalyst for Asymmetric Michael Addition Reaction

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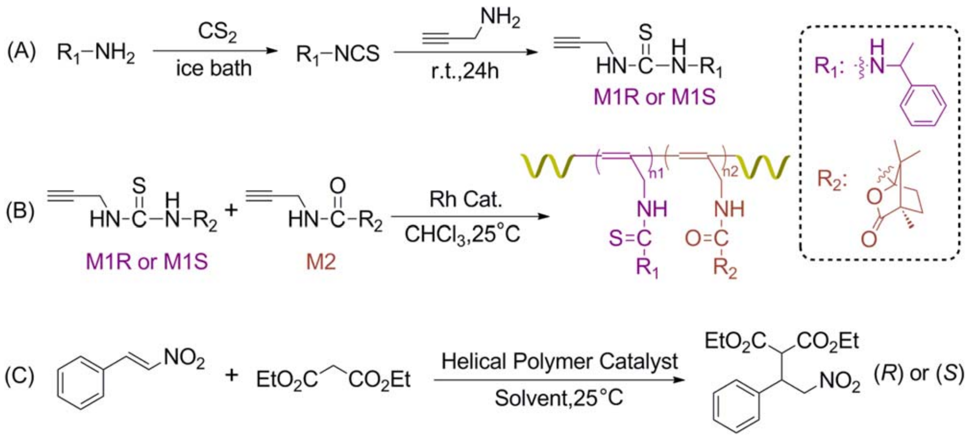
ABSTRACT: This article reports a novel category of helical substituted polyacetylenes bearing pendant thiourea groups and showing remarkable asymmetric catalysis ability. Thiourea-based monomer and another chiral monomer underwent copolymerization, affording copolymers with considerable optical activity. The copolymers were used as chiral organocatalyst to homogeneously catalyze the asymmetric Michael addition of diethyl malonate to trans-β-nitrostyrene. During catalysis, a synergetic effect occurred between the pendant thiourea moieties and the helical structures in the polymer backbones. The enantioselectivity of the reaction was governed by the thiourea moieties. Meanwhile, the concaves along the helices provided specific domains where the substrates and catalytic groups were packed together, leading to a remarkable enhancement of product yield and enantioselectivity. Product with high yield (85%) and satisfactory ee (up to 72%) can be obtained. The present helical polymers open up new opportunities for developing macromolecules as mimetic enzymes catalyzing asymmetric reactions. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 1816–1823

KEYWORDS: asymmetric catalysis; catalysts; chiral; copolymerization; helical polymer

INTRODUCTION Asymmetric catalysis has gathered ever-increasing interest and become one of the most active research areas in chemistry, since it provides an inexpensive and readily accessible approach to obtain enantiomerically pure compounds.[1–4] Over the last decade, chiral organocatalysts have been established as an essential branch of asymmetric catalysis,[5,6] among which thiourea and the derivatives play important roles for their high selectivity and efficiency. Since the pioneering work by Vachal and Jacobsen[7] and Takemoto et al,[8] a number of thiourea-based organocatalysts have been designed and applied for a wide range of reactions.[9–11] However, some inherent shortcomings also exist in these small molecule catalysts, such as large usage amount, difficulty in recovery, and possible contamination. Meanwhile, artificial macromolecules as mimetic enzymes are emerging for their outstanding catalytic efficiency and particularly the much ease in recycling. The investigations by Reggelin et al.,[12,13] Suginome and coworkers,[14,15] and Roelfes and coworkers[16,17] demonstrated outstanding catalytic performance of helical macromolecular scaffolds in asymmetric catalysis. Nevertheless, taking into account their complicated structures, designing and preparing such macromolecular catalysts is still a challenging topic. The helical polymers reported in this article provide a new strategy for combining macromolecules with functional organic molecules to generate a novel category of green catalyst.

Chiral macromolecules extensively exist in nature, such as DNA, enzymes, and peptides. Owing to their unique helical structures, these biomacromolecules play extremely significant roles in living organisms. Stimulated by natural helical macromolecules, so far various artificial polymers with chiral helical structures have been successfully designed and prepared.[18–27] These helical polymers demonstrated fascinating features and found applications in enantioselective crystallization,[28] chiral recognition,[29,30] and so forth. Particularly, helical polymers with catalytic moieties can be elegantly utilized as mimetic enzymes to catalyze asymmetric reactions efficiently. To date some groups[12–17,31–34] have made remarkable contribution to this significant research field. Regrettably, as a typical class of helical polymers, substituted polyacetylene has been rarely involved in the literature concerning macromolecular catalysts yet, except the studies from Yashima and coworkers,[31,32] Masuda and coworkers,[33,34] and from us.[35,36] Therefore, the investigations along this direction are of great significance in both fundamental research and practical applications.

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 (A) Synthesis of monomer (M1R, M1S), (B) copolymerization of M1R or M1S with M2, and (C) asymmetric Michael addition reaction catalyzed by chiral helical copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In this article, we successfully manufactured a novel optically active helical copolymer, which possessed catalytic ability and further efficiently catalyzed asymmetric Michael reaction. Thiourea-based monomer and another chiral monomer (defined as M1 and M2, respectively) were copolymerized, providing copolymers with stable helical conformations and pendant thiourea groups, as shown in Scheme 1. Significantly, a synergetic effect was observed between helical polymer backbones and the side thiourea moieties in catalyzing the asymmetric reaction. Additionally, the helical structures existed in the polymer backbones can provide plenty of concaves, which, together with the pendant chiral thiourea units, served as specific domains for catalyzing asymmetric reactions. The present copolymers are of high importance for further developing novel mimics of bioenzymes as efficient green catalysts.

EXPERIMENTAL

Materials

$(nbd)Rh^+B^-(C_6H_5)_4$ (nbd = 2,5-norbornadiene) was prepared according to the procedure reported in literature.[37] Monomer M1R and M1S were synthesized according to the method described in our previous work.[38] Both the two monomers were obtained in a high yield (ca. 80%), and were structurally identified by FT-IR and ^1H NMR spectra (Figs. S1 and S2, Supporting Information). Monomer M2 was prepared by the method reported earlier.[39] Propargylamine, trans-β-nitrostyrene, diethyl malonate, (*R*)-(+)−1-phenylethylamine, and (*S*)-(−)−1-phenylethylamine were bought from Aldrich and used without further purification. All solvents were purified by distillation before use.

Measurements

Circular dichroism (CD) and UV–vis absorption spectra were conducted on a Jasco-810 spectropolarimeter. Specific rotations were measured on a JASCO P-1020 digital polarimeter with a sodium lamp as the light source at room temperature. The molecular weight (M_n) and molecular weight polydispersity (M_w/M_n) were determined by GPC (Waters 515–2410 system) calibrated by using polystyrenes as standards and THF as eluent. FT-IR spectra were recorded with a Nicolet NEXUS 670 spectrophotometer (in KBr tablet). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer. Organic elemental analyses were carried out on varioEL-cube elemental analyzer. HPLC analyses were performed on FL2200-2 (FL2200-2 pump and Absorbance Detector). Chiralpak AD-H column was purchased from Daicel Chemical Industries Ltd.

Polymerization

The typical procedure for polymerization is stated as below. Taking homopolymerization as example, the polymerizations were carried out in $CHCl_3$ at 30 °C for 24 h, with $(nbd)Rh^+B^-$ $(C_6H_5)_4$ (1 mol % of monomer) as catalyst. Subsequently, the mixture was added into hexane to precipitate the formed polymer. After filtered and dried, the homopolymer was obtained. The copolymerizations were conducted in a similar way, with varied feed ratio of monomers. FT-IR and ^1H NMR spectra of the copolymers are shown in Supporting Information Figures S3 and S4.

Michael Reaction

Diethyl malonate (0.16 g, 1 mmol), triethylamine (0.0101 g, 0.1 mmol), helical copolymer (2 mol % of nitrostyrene, based on thiourea unit), and 5 mL CH_2Cl_2 were added in a reactor. The mixture was stirred for 20 min and then trans-β-nitrostyrene (0.0745 g, 0.5 mmol) was added. 72 h later, the reaction was completed based on TLC analysis. The crude product was concentrated under reduced pressure and purified by flash column chromatography (hexane/EtOAc = 4/1, v/v) to remove the copolymer and unreacted substrates. The product (ethyl 2-carboethoxy-4-nitro-3-phenylbutyrate) was subjected to FT-IR, ^1H and ^{13}C NMR spectroscopy measurements, as shown in Supporting Information Figures S6–S8. Enantiomeric excess (ee%) was determined

TABLE 1 Data of Homopolymers and Copolymers From M1R, M1S, and M2

Polymer[a]	M_n[b]	M_w/M_n[b]	Yield (%)[c]	$[\alpha]_D$ (°)[d]
Poly-1R	3,100	1.31	73	+588
Poly-1S	2,900	1.21	70	−572
Poly-2	8,600	2.24	96	−823
Poly(M1R$_{0.1}$-*co*-M2$_{0.9}$)	5,400	2.40	82	−603
Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$)	4,800	2.55	78	−684
Poly(M1R$_{0.2}$-*co*-M2$_{0.8}$)	3,900	2.12	75	−476
Poly(M1S$_{0.2}$-*co*-M2$_{0.8}$)	3,500	1.97	72	−595

[a] With (nbd)Rh$^+$B$^-$(C$_6$H$_5$)$_4$ as catalyst; $[M]_0 = 0.5$ M; $[M]_0/[Rh] = 100$ (mol/mol); $T = 30$ °C; in CHCl$_3$ for 24 h.

[b] Determined by GPC (polystyrene as standards; THF as eluent).

[c] Determined gravimetrically, hexane-insoluble part.

[d] Measured by polarimeter at room temperature, $c = 0.1$ g dL^{-1}, CHCl$_3$.

by HPLC analysis, Chiralpak AD-H, hexane/EtOH = 80/20, v/v, 1.0 mL min^{-1}, 254 nm.

RESULTS AND DISCUSSION

Based on our earlier studies dealing with optically active helical polymers[35,40–42] and the strategy for preparing chiral *N*-propargylthiourea,[38] we in the present study designed and prepared a novel substituted polyacetylene bearing thiourea pendant groups. The major processes for monomer synthesis and copolymerization are schematically presented in Scheme 1(A and B). Thiourea-based monomers (M1R and M1S) were used because thiourea organocatalysts showed high reactivity and selectivity in catalyzing asymmetric reactions like Michael addition.[8] We first polymerized M1R and M1S to obtain the corresponding homopolymers. Unfortunately, the homopolymers' molecular weights were not satisfactory (Table 1). To increase the polymerization degree of poly(*N*-propargylthiourea)s, another monomer without the function of catalysis, M2,[35] was employed to carry out copolymerizations separately with M1R and M1S. Only one enantiomer of M2 was used in the copolymerization, because the raw material for preparing the other enantiomer is commercially unavailable. As reported previously,[39] the M2 units could afford the copolymers with helical conformations and in turn remarkable optical activity. In addition, it should be highlighted herein that the stable helical structures in the formed copolymers can severe as catalytic domains to provide multiple reactive sites for catalyzing asymmetric reactions.

We prepared copolymers with two varied monomer feed ratios (M1/M2 = 1/9 and 2/8, mol/mol, M1 = M1R and M1S), yielding copolymers designated as poly(M1R$_{0.1}$-*co*-M2$_{0.9}$), poly(M1S$_{0.1}$-*co*-M2$_{0.9}$), poly(M1R$_{0.2}$-*co*-M2$_{0.8}$), and poly(M1S$_{0.2}$-*co*-M2$_{0.8}$), respectively. The relevant data are presented in Table 1. It can be inferred that when the feed ratio of M1/M2 was 1/9, the copolymers were obtained with moderate molecular weights, higher than that of the corresponding homopolymers (poly-1R and poly-1S, Table 1). As the feed ratio increased to 2/8 (M1/M2), the copolymers' molecular weights decreased. We further conducted copolymerization with the feed ratio of 3/7 (M1/M2), but the molecular weights were rather low (<2000). The low polymerization activity of M1 should be due to the high tendency of the polar thiourea groups to form intermolecular hydrogen bonding, which was ever observed before.[38] Therefore, the molecular weights of the resulting copolymers had a downward trend as the proportion of M1 increased. To ensure the helical structures in copolymers, we selected the copolymers with the feed ratio of M1/M2 being 1/9 and 2/8 as macromolecular catalysts in the subsequent Michael reactions.

To verify the copolymerization of M1 and M2, the two monomers and their copolymers (defined as poly(M1$_{0.1}$-*co*-M2$_{0.9}$) and poly(M1$_{0.2}$-*co*-M2$_{0.8}$)) were structurally identified by FT-IR (Supporting Information Fig. S3). Both the copolymers showed the characteristic absorption peak of benzene group at 706 cm^{-1}, which only existed in monomer M1. Moreover, the relative intensity of this peak in the latter copolymer was stronger than in the former. This offers clear evidence for the presence of M1 units in the copolymers. To further determine their composition, copolymers with different monomer feed ratios were subjected to ^{1}H NMR spectroscopy. We suppose that the content of M1 unit is x, and M2 unit is $(1 - x)$. The ratio of the peak areas of phenyl hydrogen and methyl hydrogen can be expressed as $5x/[3x + 9(1 - x)]$. By integration, we can easily determine the real ratio of the two peak areas, and the value of x can be consequently calculated. Taking poly(M1$_{0.1}$-*co*-M2$_{0.9}$; see Fig. 1) as example, the ratio of peak areas of (a + b + c) to (d + e + f) is 16.3, and x is 0.103 accordingly. The composition of the copolymer was found to be equal to the

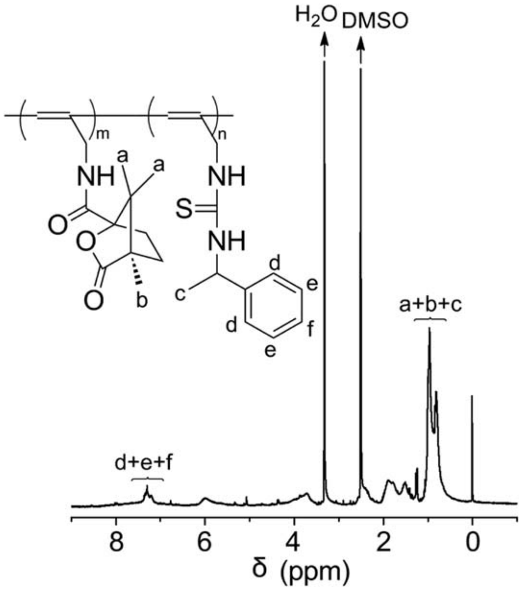


FIGURE 1 ^{1}H NMR spectrum of poly(M1$_{0.1}$-*co*-M2$_{0.9}$), measured in DMSO-d_6 at r.t.

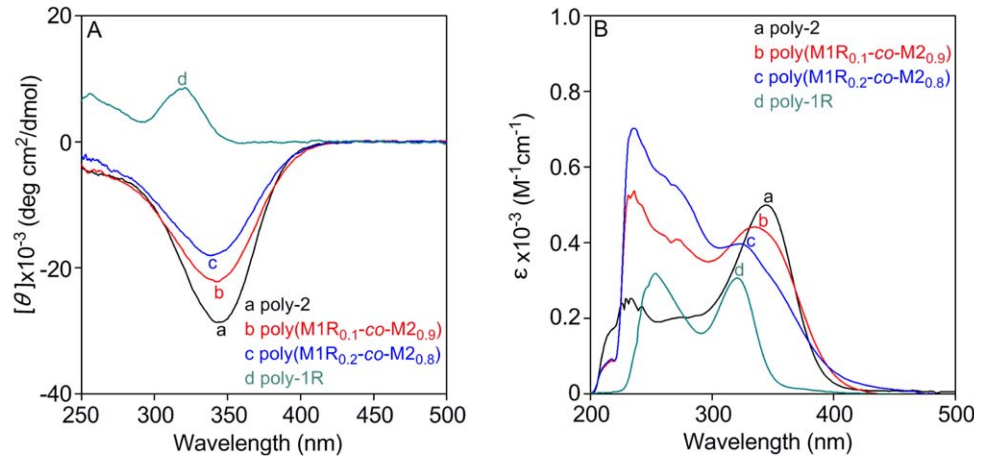


FIGURE 2 (A) CD and (B) UV–vis spectra of (a) poly-2 (homopolymer of M2); (b) poly($M1R_{0.1}$-*co*-$M2_{0.9}$); (c) poly($M1R_{0.2}$-*co*-$M2_{0.8}$); (d) poly-1R (homopolymer of M1R). Measured in $CHCl_3$ ($c = 0.1$ mM) at 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponding monomer feed ratio. For poly($M1_{0.2}$-*co*-$M2_{0.8}$; Supporting Information Fig. S4), the value of x is 0.218. The copolymers' compositions were also confirmed by elemental analysis [M1 content: 9.75% in poly($M1_{0.1}$-*co*-$M2_{0.9}$); 19.56% in poly($M1_{0.2}$-*co*-$M2_{0.8}$)]. Both poly($M1_{0.1}$-*co*-$M2_{0.9}$) and poly($M1_{0.2}$-*co*-$M2_{0.8}$) displayed high specific rotations (Table 1), reflecting that the copolymers were optically active, just as expected. The intense optical activity derived from the helical conformations of the copolymer backbones, as will be discussed in detail later on.

Before investigating the helical structures of the copolymers, the corresponding homopolymers were first subjected to CD and UV–vis spectroscopy measurements, which have been widely used for exploring the secondary structures of macromolecules.[35,38,40] In the CD and UV–vis spectra in Figure 2, poly-2 (homopolymer of M2, the homopolymers below follow the same denotation) showed negative CD signal and strong UV–vis absorption at ~350 nm, while poly-1R demonstrated positive CD signal and UV–vis absorption around 320 nm. According to our earlier studies concerning optically active helical substituted polyacetylenes,[35,40] we can conclude that the two homopolymers formed helices of preferential helicity. However, their helical senses were just opposite, which is in accordance with our earlier reports.[38] When M1R underwent copolymerization with M2 with the feed ratio of 1/9 and 2/8 (mol/mol), the resulting copolymers exhibited considerable CD signal and UV absorption at about 350 nm, indicating that the copolymer backbones adopted helical conformations of predominantly one-handed screw sense. Particularly, both the two copolymers showed negative CD effects, similar to that of poly-2. Furthermore, a slight blue shift was found to occur in the CD and UV–vis spectra of the copolymers compared with poly-2. As the ratio of M1R/M2 rose, the degree of blue shift increased. This is because the screw pitch of the helical conformations formed by poly-1R was shorter than that formed by poly-2. As a result, the addition of poly-1R units reduced the average helical pitch along the copolymer backbones, rendering the copolymers with lower absorption wavelength.

Since M1S and M1R are a pair of enantiomers, poly-1S exhibited negative CD signal at 320 nm, opposite to poly-1R (Fig. 3). Consequently, the copolymers composed of M1S and M2 have the same CD signal direction with poly-2. In addition, the increasing proportion of M1S also caused a slight blue shift, the reason for which is discussed previously. From the CD and UV–vis spectra presented in Figures 2 and 3, we can also see that with the content of poly-1 unit (poly-1R or poly-1S) increased, the intensity of absorption peaks over 300 nm decreased gradually. On the contrary, the UV–vis absorption below 300 nm was enhanced. Due to the insertion of poly-1 units, the regularity of helical conformations occurring in poly-2 backbones was somewhat affected, weakening the chiral amplification effect.[43,44] Therefore, the optical activity of the copolymers was reduced. The specific rotations displayed in Table 1 also support the previous consideration. Nevertheless, the copolymers still demonstrated considerable optical activity, stronger than that of the thiourea-based homopolymers.

Next, we explored the helical structures of the copolymers in varied solvents. Taking $M1R_{0.1}$-*co*-$M2_{0.9}$ as example, the relevant CD and UV–vis spectra are illustrated in Figure 4. It is obvious that the copolymer showed stronger CD signal and UV–vis absorption in CH_2Cl_2 and $CHCl_3$ than in other solvents. The reason may lie in the different helical content of the copolymer in varied solvents. It has been proved that helical structures became more stable in $CHCl_3$ and CH_2Cl_2 than in DMF and MeOH because polar solvent can destroy the intramolecular hydrogen bonding in the copolymer, which is essential for the formation of helical conformations.[45] Another observation is that the CD signal and UV–vis absorption of the copolymer became stronger when the temperature decreased from 25 to 0 °C. According to our previous work,[46] lower temperature is more desirable for

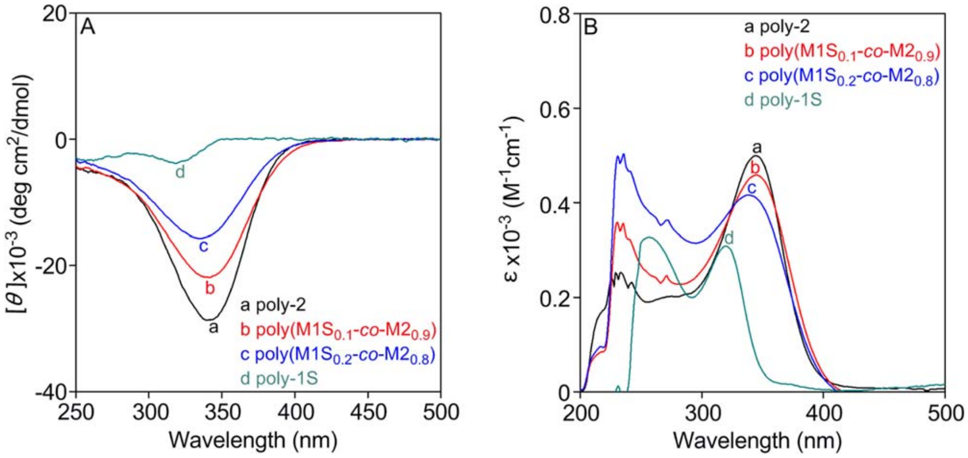


FIGURE 3 (A) CD and (B) UV–vis spectra of (a) poly-2; (b) poly($M1S_{0.1}$-*co*-$M2_{0.9}$); (c) poly($M1S_{0.2}$-*co*-$M2_{0.8}$); (d) poly-1S (homopolymer of M1S). Measured in $CHCl_3$ ($c = 0.1$ mM) at 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers to form stable helical structures. CD and UV–vis spectra of $M1S_{0.1}$-*co*-$M2_{0.9}$ in different solvents and at varied temperatures showed similar results (Supporting Information Fig. S5).

With the helical copolymers in hand, we further conducted asymmetric reactions using the copolymers as chiral catalyst. We took the direct Michael addition of diethyl malonate to trans-β-nitrostyrene as a model, as shown in Scheme 1(C). To promote the catalytic rate, we added triethylamine as a promotor, which had no catalytic effect when individually used. The product was characterized by FT-IR and NMR spectroscopy, as illustrated in Supporting Information Figures S6–S8.

Detailed data of the asymmetric catalysis are listed in Table 2. We present typical HPLC spectra for the products of the Michael reaction in Supporting Information (Figs. S9 and S10). The HPLC results were analyzed by referring to Refs. [7,47. Before discussing the factors affecting the reaction, it should be specially noted that the absolute configuration of the reaction products was related to the composition units of the copolymers. It seemed that the M1R-derived (co)polymers tended to yield *R*-configuration product. Meanwhile, when catalyzed by the polymers from M1S (homopolymer or copolymer), the absolute configuration of the product was determined to be *S*. Taking the products from Entries 8 and 16 (Table 2) as representative, the specific rotations were, respectively, +5.75° and −4.30°. The CD and UV–vis spectra in Supporting Information Figure S11 also indicate the two types of products were enantiomers. These facts clearly suggest that the thiourea moieties totally control the enantioselectivity during catalysis. Furthermore, the ee value of the two types of products varied significantly (the M1R-derived organocatalyst gave a higher ee). This phenomenon was also found in literature when a pair of enantiomeric catalysts were used for asymmetric catalysis.[48,49] The inversion of configuration and the differentiation in ee is attributed to

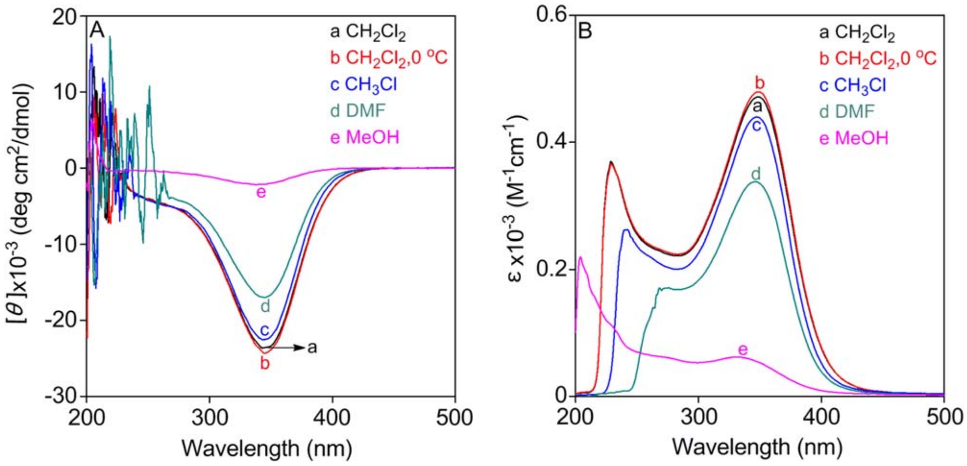


FIGURE 4 (A) CD and (B) UV–vis spectra of poly($M1R_{0.1}$-*co*-$M2_{0.9}$) in CH_2Cl_2 (0 °C and 25 °C), $CHCl_3$, DMF and MeOH (25 °C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Asymmetric Michael Addition Reactions Catalyzed by Homopolymers and Copolymers[a]

Entry	Catalyst	Solvent	Temp. (°C)	Yield (%)[b]	ee%[c] (config.)[d]
1	Poly-2	CH_2Cl_2	25	–[e]	–
2	M1R	CH_2Cl_2	25	43	15 (*R*)
3	Poly-1R	CH_2Cl_2	25	45	38 (*R*)
4	Poly(M1R$_{0.1}$-*co*-M2$_{0.9}$)	CH_2Cl_2	25	58	62 (*R*)
5	Poly(M1R$_{0.1}$-*co*-M2$_{0.9}$)	$CHCl_3$	25	55	60 (*R*)
6	Poly(M1R$_{0.1}$-*co*-M2$_{0.9}$)	DMF	25	Trace[f]	–
7	Poly(M1R$_{0.1}$-*co*-M2$_{0.9}$)	MeOH	25	–	–
8	Poly(M1R$_{0.1}$-*co*-M2$_{0.9}$)	CH_2Cl_2	0	85	72 (*R*)
9	Poly(M1R$_{0.2}$-*co*-M2$_{0.8}$)	CH_2Cl_2	25	70	68 (*R*)
10	M1S	CH_2Cl_2	25	25	6 (*S*)
11	Poly-1S	CH_2Cl_2	25	41	22 (*S*)
12	Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$)	CH_2Cl_2	25	62	42 (*S*)
13	Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$)	$CHCl_3$	25	60	38 (*S*)
14	Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$)	DMF	25	Trace	–
15	Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$)	MeOH	25	–	–
16	Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$)	CH_2Cl_2	0	78	51 (*S*)
17	Poly(M1S$_{0.2}$-*co*-M2$_{0.8}$)	CH_2Cl_2	25	65	45 (*S*)

[a] The reaction was conducted with trans-β-nitrostyrene (1 equiv) and diethyl malonate (2 equiv) in the presence of various additives (0.05 equiv).

[b] Isolated yield.

[c] Determined by HPLC.

[d] Determined by specific rotation.

[e] "–" indicates no reaction occurred.

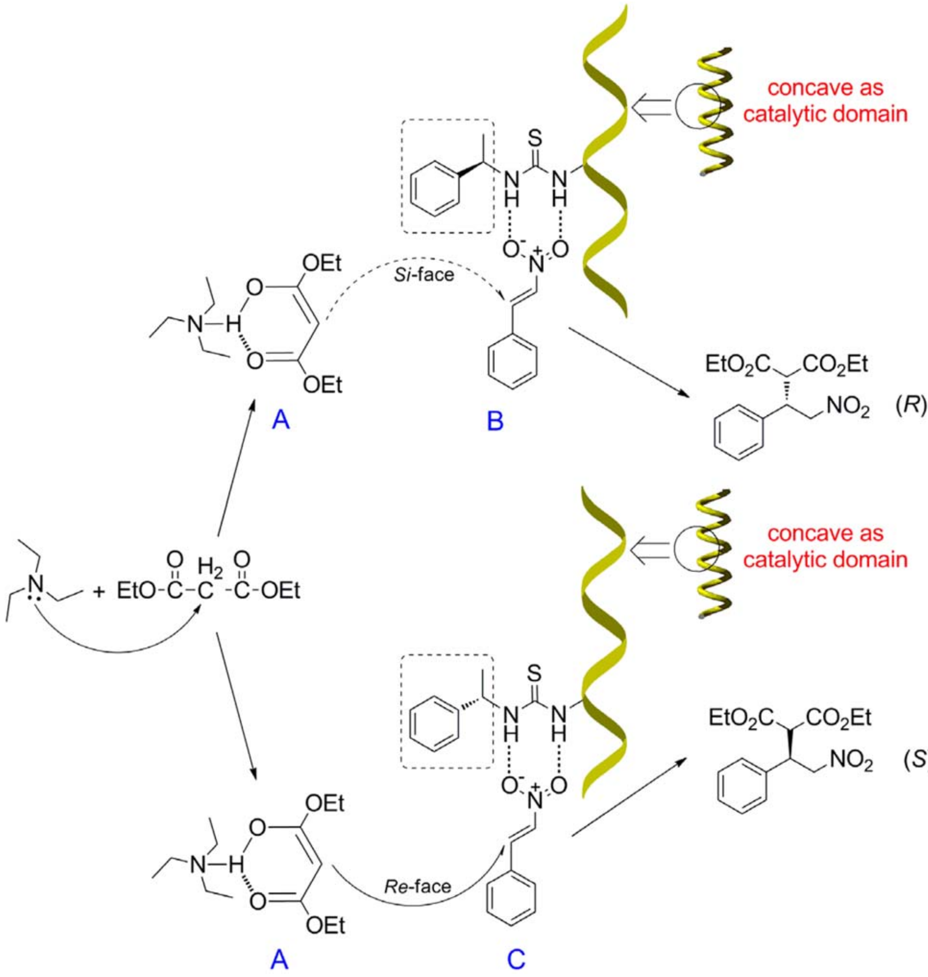
[f] According to TLC, the amount was too little to be determined.

the reaction mechanism, which will be specifically discussed later.

In order to check the role of helical macromolecular scaffold, we first examined catalytic ability of the thiourea-based monomers, as shown in Table 2 (Entries 2 and 10). It is obvious that whether *R*- or *S*-isomer was used, the results were very poor. Then (co)polymers were used in asymmetric catalysis. As mentioned previously, the prepared copolymers possessed higher content of helical conformations compared to the corresponding thiourea-based homopolymers. So we examined their catalytic efficiency under the same reaction conditions. Excitingly, the copolymers displayed more satisfactory results, and they were both better than the monomers (Table 2, Entries 2–4 and 10–12). On the basis of our earlier studies,[35,36] we conclude that stable helical structures are favorable for the asymmetric reaction. To verify our assumption, we conducted several groups of catalytic reactions in different solvents and at varied temperatures. Taking poly(M1R$_{0.1}$-*co*-M2$_{0.9}$) as representative, solvents with weak polarity were suitable for its catalysis (Table 2, Entries 4 and 5). However, in polar solvents like DMF and MeOH, the copolymer hardly performed catalytic function (Table 2, Entries 6 and 7). Poly(M1S$_{0.1}$-*co*-M2$_{0.9}$) gave similar results (Table 2, Entries 12–15). This variation tendency accorded with the effect of solvents on the helices formed in the copolymers (shown in Fig. 4 and Fig. S5). Furthermore, we investigated the effects of reaction temperature. Both the two copolymers generated products with higher yield and ee at 0 °C (Table 2, Entries 8 and 16), at which temperature the helical conformations of the copolymers are more stable. Taking the effect of solvents and temperature into consideration, the helical structures in the copolymer played an important role in the asymmetric reaction.

Additionally, we also explored the influence of copolymer composition on the Michael reaction. As the content of M1 increased from 10% to 20%, products with enhanced yield and ee were obtained, as shown in Table 2 (Entries 9 and 17). It means increasing proportion of catalytic thiourea groups will lead to more satisfactory reaction results, on condition that enough degree of helical structures was formed in the copolymer. Referring to our earlier study and according to the investigations previously, we can conclude that the presence of catalytic groups and stable helical conformations are two essential factors toward asymmetric catalysis. Taking into account the unique helical structures of the copolymer and meanwhile according to the reported mechanism of asymmetric Michael reaction catalyzed by thiourea,[50] we herein proposed a possible reaction mechanism, as depicted in Scheme 2.

In the process of reaction, the promotor triethylamine initially deprotonated an acidic proton of diethyl malonate, generating a cyclic complex A (Scheme 2). Meanwhile, trans-β-nitrostyrene was activated by the thiourea groups on the helical copolymers through hydrogen bonding, forming the complex B or C. The steric hindrance of helical macromolecular



SCHEME 2 Proposed catalytic mechanism of Michael reaction catalyzed by chiral helical copolymers with pendent thiourea groups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

scaffold and the benzene ring connected with thiourea group influenced the attack direction of complex A, consequently leading to adduct bearing *R* or *S* configuration with high enantioselectivity. Particularly, the concaves along the helices formed by the copolymer can serve as domains to provide a three-dimensional environment for the asymmetric reaction. Within the scope of the concaves, the concentration of reaction substrates and catalytic groups were relatively increased, resulting in a higher probability of molecular interaction. In conclusion, the thiourea pendants and the helical polymer backbones worked well together in a favorable synergy effect in the asymmetric reaction. To acquire deeper insights into the detailed catalyzing mechanism and to elucidate the advantages of the novel chiral macromolecules catalysts, much more investigations will be performed. Nonetheless, the present study provides a novel class of chiral macromolecular catalysts. We are continuing this important work in our group.

CONCLUSIONS

We successfully prepared a novel category of optically active helical copolymers, which combined the unique helical structures and highly functional thiourea groups into one entity. The copolymers with pendant thiourea groups demonstrated remarkable catalyzing ability toward asymmetric Michael addition reaction. In the process of reaction, the thiourea moieties totally control the enantioselectivity. Furthermore, the macromolecular helical structures and the thiourea moieties undertook synergic effects in the asymmetric catalysis. This is the first report on successfully using thiourea-based helical substituted polyacetylene as chiral catalyst. We are highly convinced that by optimization of the copolymer composition and reaction conditions, product with higher yield and ee value can be further obtained.

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