Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 5696–5701
polymer
www.elsevier.com/locate/polymer

Helical conformation of the copolymers of L-proline derivatives based propargylether and chiral *N*-propargylamide

Jian Dai [a,b], Chengyong Ha [a,*], Dongliang Chang [a], Minmin Shen [a]

[a] *Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China*

Received 6 April 2007; received in revised form 17 June 2007; accepted 6 July 2007

Abstract

The novel acetylene monomers, L-proline derivatives based propargylethers **PR** (**PA**, **PC**, and **PL**) were synthesized by alkylation of Boc-hydroxyproline with propargyl bromide and acylation of achiral amine. The homopolymers of the novel acetylene monomer exist in no regulated higher order structure in solvents because of the lack of hydrogen bond and the unique ring structure in the pendant. Consequently, the copolymerization of L-proline-derived chiral propargylether **PR** with the L-alanine-derived *N*-propargylamide (**LA**) was formed and the chiroptical properties of the formed copolymers were examined. We conclude that (1) N–H of the amide group at 2-position in proline play an important role in the formation of helical conformation of poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PR}_{12}$); (2) improving the amount of **PC** of poly(**LA**-*co*-**PC**) changes the conformation of the copolymer in $CHCl_3$ and perturbs the leadership of **LA**; (3) the conformation of poly($\mathbf{LA}_{75}$-*co*-$\mathbf{PC}_{25}$) remarkably changes with changing temperature and **PC** obtains the leadership in the competition on the conformation of poly($\mathbf{LA}_{75}$-*co*-$\mathbf{PC}_{25}$) in $CHCl_3$ with the improvement of temperature.

Keywords: Propargylether; Copolymerization; Helical conformation

1. Introduction

The research on conformation and function of chiral copolymers attracts the particular interest of synthetic polymer scientists [1], which has some unique features, such as self-assembly, nanoreactors, the sergeants and soldiers principle, and molecular scaffold function for controlled special alignment of muti-functional groups and so on, compared with the correlative homopolymers. For example, Green and coworkers [2] have reported that incorporation of chiral monomer units into achiral polyisocyanates induces remarkable optical activity in the copolymers and the chiral unit is referred to as a sergeant because it forces the achiral unit, a soldier to adopt the helical conformation with the same sense as itself. Since Ciardelli firstly reported the helical conformation of polyacetylene derivative bearing chiral pendants in 1974 [3], this research has attracted many polymer scientists (Grubbs, Okamoto, Yashima, Masuda, Tang, etc.) [4]. For example, Masuda and coworkers have performed the copolymerization of chiral and achiral *N*-propargylamide with functional side groups and studied the relation between conformation and function of the copolymers [5].

On the other hand, proline and its 4-substituted derivatives play a unique and important role in the conformation of peptides and proteins [6], and proline itself can be an effective organocatalyst of several powerful asymmetric transformations [7]. But so far polyacetylene with proline pendant has not been reported. We synthesized a novel acetylene monomer, L-proline derivatives based propargylether, and studied the properties of monomers and polymers, and found that

---

* Corresponding author.
E-mail address: cyha@gic.ac.cn (C. Ha).

0032-3861/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2007.07.002

poly(propargylether) didn't exist in helical conformation in solvents. For analyzing reasons and reconstructing chiral polymers, we performed the copolymerization of chiral propargylethers (**PA**, **PC**, and **PL**) and L-alanine-derived-*N*-propargylamide (**LA**). Because the copolymerization of different acetylene monomers was formed firstly, we wish that the copolymers exhibit different conformation properties from that of the same monomer type and then we can find some special function materials such as catalysts, chiral recognition, and sensors.

2. Experimental section

2.1. Materials

The solvents were distilled by usual methods prior to use. Propargylamine (Acros Oganics), propargyl bromide (Sigma-Aldrich Co.), *trans-N-*(*tert*-butoxycarbonyl)-4-hydroxy-L-proline (Boc-Hyp-OH; Sigma-Aldrich Co.), 1-hydroxybenzotriazole monohydrate (HOBt; Acros Oganics), 1-(3,3-dimethylamino-propyl)-3-ethylcarbodiimide hydrochloride (DCC; Acros Oganics) (bicyclo[2,2,1]hepta-2,5-diene)chlororhodium(I) dimer {$[Rh(nbd)Cl]_2$, nbd = 2,5-norbornadiene; Sigma-Aldrich Co.}, were used as purchased without purification. As described in the literature [8] $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ was prepared by the reaction of $[(nbd)RhCl]_2$ with $NaB(C_6H_5)_4$. **LA** was synthesized according to the reported method [9].

2.2. Measurements

^1H and ^{13}C NMR spectra were recorded in chloroform-*d* ($CDCl_3$) on a Bruker DRX-400 spectrometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a Jasco Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using THF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. CD and UV–vis spectra were recorded in a quartz cell (thickness: 1 cm) at room temperature using a Jasco J810 spectropolarimeter. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Specific rotations ($[\alpha]_D$) were measured on a Jasco DIP-1000 digital polarimeter with a sodium lamp as a light source (wavelength 598 nm, temperature 20 °C).

2.3. Monomer synthesis and polymerization

Full details about synthesis of chiral propargylethers (**PA**, **PC**, and **PL**) and poly(**LA**-*co*-**PR**) [10] in Chart 1 and spectroscopic analysis will be given in our subsequent full articles. In this work, for explaining complete polymerization of **PR**, IR and ^1H NMR spectra of poly(**PC**) and **PC** were analyzed.

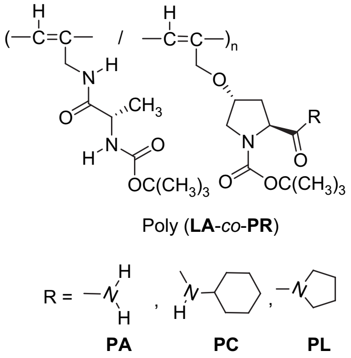

Chart 1. Copolymers of two different acetylene monomers (**LA** and **PR**).

3. Results and discussion

3.1. Synthesis and polymerization of *PR*

L-Proline derivatives based propargylethers (**PA**, **PC**, and **PL**) in Chart 1 were synthesized by alkylation of Boc-hydroxy-proline with propargyl bromide and acylation of achiral amine. We use two catalytic systems to polymerize the novel acetylene monomer, L-proline derivatives based propargylether: (1) by $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ in CH_2Cl_2 at 30 °C for 12 h; (2) by $[(nbd)RhCl]_2/Et_3N$ in THF at room temperature for 24 h. It has been reported that the Rh^+ catalyst efficiently catalyzes the polymerization of monosubstituted acetylenes by the insertion mechanism to give *cis*-transoidal polyacetylenes [11]. The novel propargylether was polymerized using Rh catalyst, which had not been reported until now. The orange polymers were obtained with medium M_n.

An example of the IR spectrum of poly(**PC**) by $[(nbd)RhCl]_2/Et_3N$ in THF is shown in Fig. 1, the spectrum of whose monomer **PC** is also given in the same figure for comparison. The monomer shows absorption bands at 2111 cm^{-1} associated with C≡C stretching. No C≡C stretching bands are observed in the spectrum of poly(**PC**). On the other hand, a new band associated with C=C stretching of the polyene backbone can't be recognized (Fig. 1B). But Fig. 2 shows the ^1H NMR spectra of polymer poly(**PC**) and

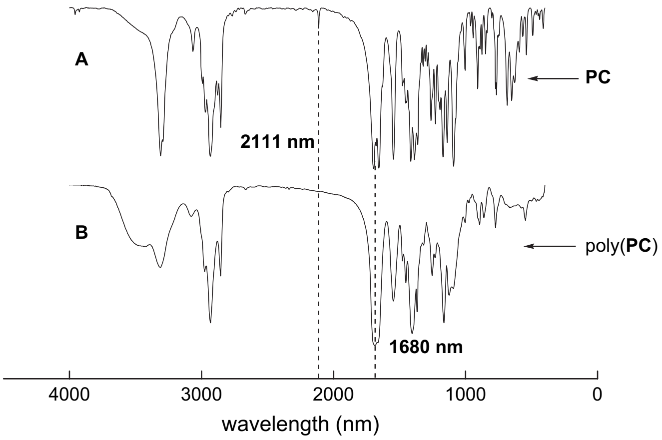

Fig. 1. IR spectra of (A) monomer **PC** and (B) its polymer poly(**PC**).

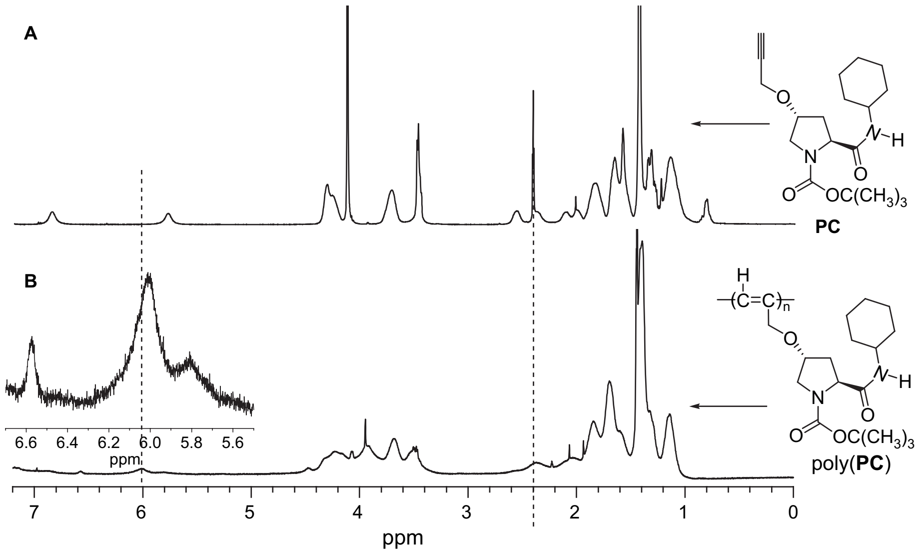

Fig. 2. ^{1}H NMR spectra of chloroform solutions of (A) **PC** and (B) its polymer poly(**PC**).

its monomer **PC** in chloroform. We can obtain the resonance of the olefinic double bond. The proton of the acetylene triple bond of **PC** resonates at δ 2.42 (Fig. 2A), which disappears in the spectrum of poly(**PC**) (Fig. 2B). And the resonance of the olefinic double bond occurs at δ 6.0 (Fig. 2B). No unexpected signals are observed in the spectrum of the polymer in Fig. 2B. The ^{1}H NMR analyses thus confirm that the triple bonds have been consumed by the acetylene polymerization and that the molecular structure of the polymer is indeed poly(**PC**).

3.2. *Conformation of poly(**PR**)*

The conformation of the poly(**PR**) was examined by CD, and UV–vis spectroscopic methods. But the result disappoints us and the CD signal of poly(**PA**) and poly(**PL**) doesn't come out. The results lead to the conclusion that poly(**PA**) and poly(**PL**) exist in no regulated higher order structure. And an example of the CD signal of poly(**PC**) (**PC**, L-proline based propargylether having cyclohexylamide group) was small negative from Fig. 3. It is illustrated from Fig. 3A that by the first catalytic system, the CD spectrum (a) of poly(**PC**)$_1$ has two small signals (positive signal at 260 nm and negative signal at 335 nm), on the other hand, by the second catalytic system, that of poly(**PC**)$_2$ has also two small negative signals at ~260 nm and 350 nm. The CD signal of poly(**PC**)$_2$, however, disappears in $CHCl_3$ and $CHCl_3$/THF (1:1). We conclude that although poly(**PC**) can be polymerized by the two different catalytic systems of Rh, the mechanism of polymerization between the two systems is different and leads to the different conformation in solvents. Poly(**PC**) exists in no regulated higher order structure by the catalytic systems of Rh. In concluding the analyses of molecular structure of L-proline derivatives based propargylether and its polymer, we obtain three possible reasons: (1) the effect of five-membered pyrrolidine ring; (2) the proline pendant is too near the main chain and holds back the formation of helical structure; (3) the absence of hydrogen bond near the main chain.

3.3. *Conformation of poly(**LA$_{88}$**-co-**PR$_{12}$**)*

Since poly(**PR**) has the limitation of forming regulated higher order structure, we anticipate that the copolymerization of the novel acetylene monomer, chiral propargylether, with

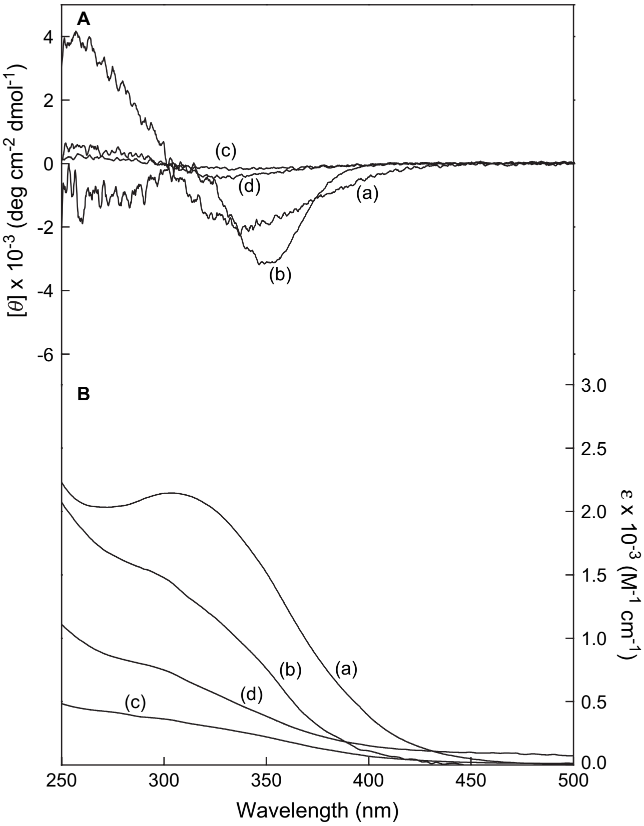

Fig. 3. [A] CD and UV–vis spectra of poly(**PC**) measure in (a) $CHCl_3$, using (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] and CH_2Cl_2; (b) THF, (c) $CHCl_3$ and (d) $CHCl_3$/THF = 1:1, using $[Rh(nbd)Cl]_2/Et_3N$ and THF, at room temperature, $c = 3 \times 10^{-4}$ mol/L.

Chiral propargylamide (**LA**), whose polymer can form helical conformation in $CHCl_3$ [9], can mend the lack of poly(**PR**) to form regulated higher order structure.

We synthesized three novel acetylene monomers, propargylether having L-proline derivatives groups, and studied the copolymerization of relatively small amounts of the chiral propargylether monomers with *N*-(*tert*-butoxycarbonyl)-L-alanine-*N*-propargylamide and analyzed the chiroptical properties of the copolymers.

The CD spectrum of poly(**LA**) exhibited very large molar ellipticity [θ] at 401 nm in $CHCl_3$ (Fig. 4A), corresponding to the main chain UV–vis absorption (Fig. 4B). And that the CD signals of poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PC}_{12}$) and poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PL}_{12}$) were much larger at 401 nm than that of poly(**LA**). The results lead to the conclusion that the copolymers effectively take helical conformations in the presence of relatively small amounts of the chiral monomer (**PC**) unit, and especially in the comonomer (**PL**), while poly ($\mathbf{LA}_{88}$-*co*-$\mathbf{PA}_{12}$) exists in no regulated higher order structure. The drastic difference may be attributable to N–H of the amide group at 2-position in proline, which plays an important role in the formation of helical conformation. The UV–vis spectra of poly ($\mathbf{LA}_{88}$-*co*-$\mathbf{PC}_{12}$) and poly ($\mathbf{LA}_{88}$-*co*-$\mathbf{PL}_{12}$) showed an absorption maximum at 400 nm, which agrees with the wavelength of the CD signals. On the other hand, the main absorption was seen not at 400 nm but at 320 nm in poly ($\mathbf{LA}_{88}$-*co*-$\mathbf{PA}_{12}$). This indicates that it is less conjugated than poly(**LA**) is. Hence, the random structure seems to reduce the π-conjugation compared with the helical structure.

We can conclude that N–H of the amide group at 2-position in proline is the key to helical conformation of poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PR}_{12}$). Since poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PA}_{12}$) has two N–H bonds, its conformation in $CHCl_3$ is unstable and the two CD signals exist at 320 nm and 401 nm, while the main absorption is seen not at 401 nm but at 320 nm. The conformation of poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PA}_{12}$) is inclined to the transition from 401 nm to 320 nm. And due to the presence of the two N–H bonds, chiral pendant of **LA** cannot lead **PA** to form the conformation of poly(**LA**). On the other hand, the copolymers of **PC** with one N–H bond and **PL** with no N–H bond with **LA**, poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PC}_{12}$) and poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PL}_{12}$), obtain larger CD signal than poly(**LA**) at 401 nm. We can conclude that **LA** obtains leadership and forces **PC** and **PL** to form the helical conformation and little amounts of **PC** and **PL** strengthen the helical conformation of poly(**LA**).

3.4. Conformation of poly(**LA**-*co*-**PC**)

In order to investigate conformation transformation of the copolymer, we synthesized the copolymer of **PC** with **LA** by different unit ratios and analyzed the chiroptical properties of the copolymers in Fig. 5. CD and UV–vis spectra of poly($\mathbf{LA}_{75}$-*co*-$\mathbf{PC}_{25}$) are different from that of poly($\mathbf{LA}_{88}$-*co*-

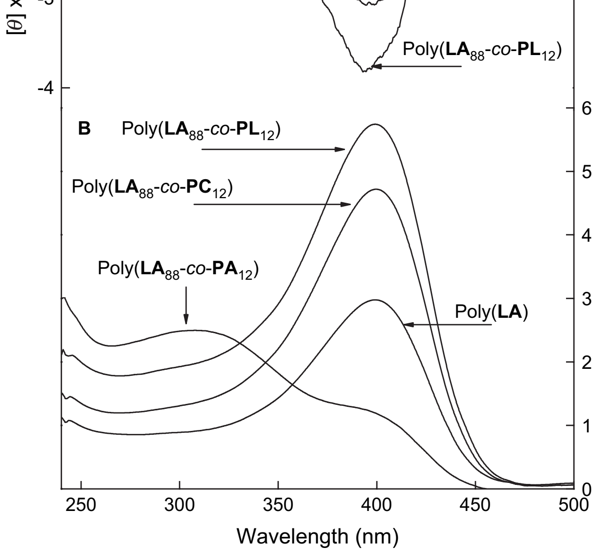

Fig. 4. [A] CD and UV–vis spectra of poly($\mathbf{LA}_{88}$-*co*-$\mathbf{PR}_{12}$) and poly(**LA**) measure in $CHCl_3$ at room temperature, $c = 3 \times 10^{-4}$ mol/L.

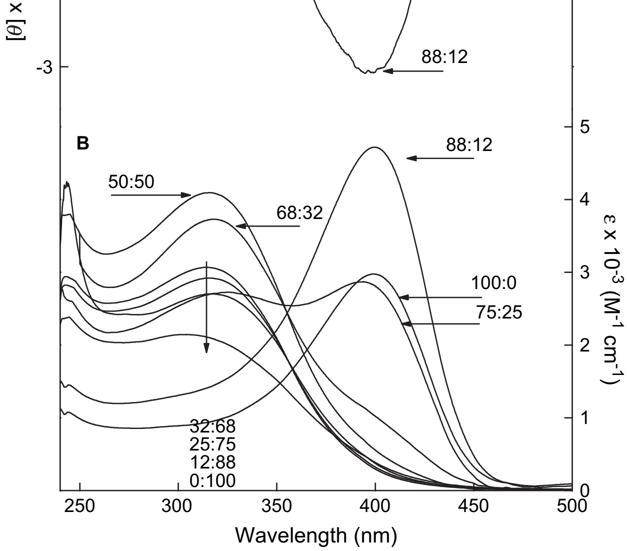

Fig. 5. [A] CD and [B] UV–vis spectra of poly(**LA**-*co*-**PC**) measure in $CHCl_3$, at room temperature, $c = 3$–4×10^{-4} mol/L.

PC$_{12}$) and resemble that of poly(**LA**$_{88}$-*co*-**PA**$_{12}$). We can find that improving amount of **PC** of poly(**LA**-*co*-**PC**) changes the conformation of poly(**LA**) in $CHCl_3$ and perturbs the leadership of **LA**. We analyze that the ring structure of proline in **PC** hinders the conjugation along the main chain and it becomes short from UV–vis spectrum. In other words, the relationship of **PC** and **LA** is going to change. The main absorption of poly(**LA**$_{68}$-*co*-**PC**$_{32}$) is seen at 320 nm as that of poly(**PC**) in Fig. 1. But the CD signal is the same as that of poly(**LA**). We can find that poly(**LA**$_{68}$-*co*-**PC**$_{32}$) forms helical conformation in $CHCl_3$ at 320 nm, which isn't different from helical conformation of poly(**LA**). In other words, **PC** leads **LA** to form the new conformation and **LA** makes up the lack of **PC** on hydrogen bond. The CD and UV–vis spectra of poly(**LA**$_{50}$-*co*-**PC**$_{50}$) are the same as that of poly(**LA**$_{68}$-*co*-**PC**$_{32}$). With improvement of the content of **PC** in poly(**LA**-*co*-**PC**), the lack of the copolymer on hydrogen bond becomes obvious and lead to the disappearance of helical conformation as shown in Fig. 5.

*3.5. Conformation of poly(**LA**$_{75}$-co-**PC**$_{25}$) with temperature change*

The conformation of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) is unstable and exists in the transition state between the conformation at 396 nm and that at 320 nm. To examine the thermal effect on the conformation transformation, we measured CD and UV–vis spectra of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) in $CHCl_3$ at various temperatures. The CD spectrum of the copolymer showed remarkably decreased molar ellipticity by heating up at 396 nm except below 0 °C. However, the shape did not change at 320 nm (Fig. 6). More specifically, the intensity of CD signal at 0 °C was slightly higher than that at −10 °C and it means that lower temperature (below 0 °C) isn't helpful to form helical conformation of poly(**LA**$_{75}$-*co*-**PC**$_{25}$). At 30 °C the CD spectrum of the copolymer has two CD signals of the same intensity at 320 nm and 396 nm. And at 50 °C–60 °C the CD signal at 396 nm disappears and only one CD signal exists at 320 nm. We can conclude that the conformation of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) remarkably changed with changing temperature and **PC** obtains the leadership in the competition on the conformation of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) in $CHCl_3$ with the improvement of temperature. From UV–vis spectra we can also clearly see that the change of the role between **PC** and **LA**. On the other hand, poly(**LA**$_{75}$-*co*-**PC**$_{25}$) is less conjugated in $CHCl_3$ by the improvement of temperature than poly(**LA**).

4. Conclusion

In this article, the chiroptical properties of copolymers of chiral propargylether **PR** and L-alanine-derived-*N*-propargylamide **LA** were examined. In poly(**LA**$_{88}$-*co*-**PR**$_{12}$), **LA** can lead **PC** and **PL** to form more effective helical conformation, while **LA** cannot lead **PA** having two N–H bonds of the amide group at 2-position in proline. And improving amount of **PC** of poly(**LA**-*co*-**PC**) changes the conformation of poly(**LA**) in $CHCl_3$ from 400 nm to 320 nm, due to less conjugate main chain. The conformation of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) was unstabilized with two simultaneous waves (396 nm and 320 nm) and the conformation of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) gets sensitive with the change of temperature. We are going to explore whether poly(**LA**-*co*-**PR**) can be used as helical chiral catalyst materials and stimuli response materials of temperature sense.

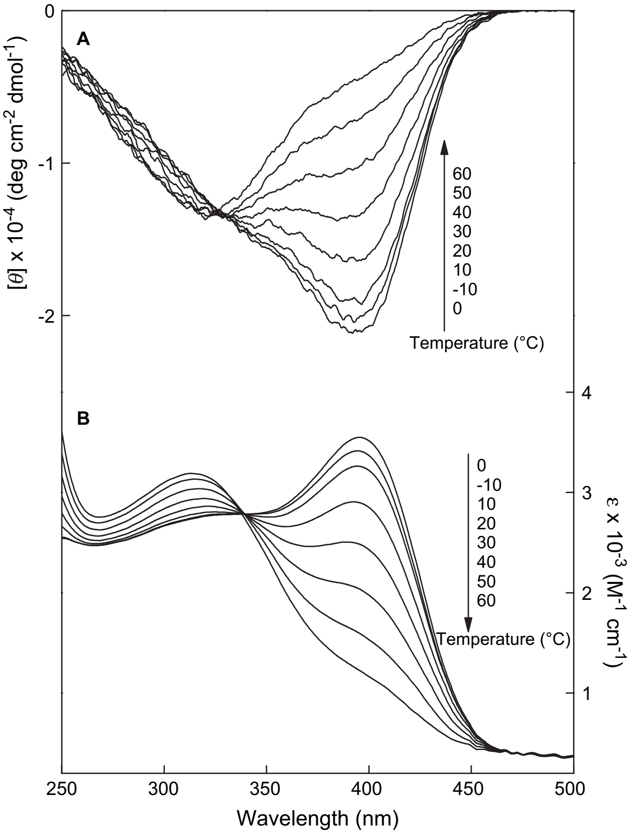

Fig. 6. Variable temperature CD and UV–vis spectra of poly(**LA**$_{75}$-*co*-**PC**$_{25}$) measured in $CHCl_3$, $c = 3 \times 10^{-4}$ mol/L.

Acknowledgment

The work described in this paper was partially supported by the Group Programs of Nature Science Foundation of Guangdong Province (Project E06200692). This project was also benefited from the financial support of the Postgraduate Science Innovation Scheme of Chinese Academy of Sciences (2005).

References

[1] (a) Lockman JW, Paul NM, Parquette JR. Prog Polym Sci 2005;30:423–52;
(b) Tabei J, Shiotsuki M, Sato T, Sanda F, Masuda T. Chem Eur J 2005;11:3591–8;
(c) Ho R, Chiang Y, Tsai C, Lin C, Ko B, Huang B. J Am Chem Soc 2004;126:2704–5;
(d) Yorozuya S, Osaka I, Nakamura A, Inoue Y, Akagi K. Synth Met 2003;93:135–6;
(e) Yue D, Shiotsuki M, Sanda F, Masuda T. Polymer 2007;48:68–73.

[2] (a) Green MM, Peterson NC, Sato T, Teramoto A, Lifson S. Science 1995;268:1860–6;

(b) Green MM, Park JW, Sato T, Teramoto A, Lifson S, Selinger RLB, et al. Angew Chem Int Ed 1999;38:3138–54.

[3] Ciardelli F, Lanzillo S, Pieroni O. Macromolecules 1974;7:174–9.

[4] (a) Moore JS, Gorman CB, Grubbs RH. J Am Chem Soc 1991; 113:1704–12;
(b) Nakano T, Okamoto Y. Chem Rev 2001;101:4013–8;
(c) Yashima E, Maeda K, Nishimura T. Chem Eur J 2004;10:42–51;
(d) Nomura R, Fukushima Y, Nakako H, Masuda T. J Am Chem Soc 2000;122:8830–6;
(e) Lam JWY, Tang BZ. Acc Chem Res 2005;38:745–54.

[5] (a) Gao G, Sanda F, Masuda T. Macromolecules 2003;36:3938–43;
(b) Zhao H, Sanda F, Masuda T. Macromolecules 2004;37:8893–6.

[6] Taylor CM, Hardré R, Edwards PJB. J Org Chem 2005;70:1306–15.

[7] (a) List B. Tetrahedron 2002;58:5573–90;
(b) Dalko PI, Moisan L. Angew Chem Int Ed 2004;43:5138–75.

[8] Schrock RR, Osborn JA. Inorg Chem 1970;9:2339–43.

[9] Gao G, Sanda F, Masuda T. Macromolecules 2003;36:3932–7.

[10] All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. A solution of **LA** (199 mg, 0.88 mmol) and **PC** (42 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) was added to $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ (10.6 mg, 0.02 mmol), and the resulting mixture was vigorously stirred. It was kept in a water bath at 30 °C for 12 h. The resulting mixture was poured into *n*-hexane (200 mL) to precipitate a copolymer. It was separated by filtration, and dried under reduced pressure.

[11] Kishimoto Y, Itou M, Miyatake T, Ikariya T, Noyori R. Macromolecules 1995;28:6662–6.