Influence of Stereoregularity and Linkage Groups on Chiral Recognition of Poly(phenylacetylene) Derivatives Bearing L-Leucine Ethyl Ester Pendants as Chiral Stationary Phases for HPLC

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ABSTRACT: Stereoregular poly(phenylacetylene) derivatives bearing L-leucine ethyl ester pendants, poly-1 and poly-2a, were, respectively, synthesized by the polymerization of N-(4ethynylphenylcarbamoyl)-L-leucine ethyl ester (1) and N-(4ethynylphenyl-carbonyl)-L-leucine ethyl ester (2) using Rh(nbd)BPh₄ as a catalyst, while stereoirregular poly-2b was synthesized by solid-state thermal polymerization of 2. Their chiral recognition abilities for nine racemates were evaluated as chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) after coating them on silica gel. Both poly-1 and poly-2a with a helical conformation showed their characteristic recognition depending on coating solvents and the linkage groups between poly(phenylacetylene) and L-leucine ethyl ester pendants. Poly-2a with a shorter amide linkage showed higher chiral recognition than poly-1 with a longer urea linkage. Coating solvents played an important role in the chiral recognition of both **poly-1** and **poly-2a** due to the different conformation of the polymer main chains induced by the solvents. A few racemates were effectively resolved on the **poly-2a** coated with a MeOH/CHCl₃ (3/7, v/v) mixture. The separation factors for these racemates were comparable to those obtained on the very popular CSPs derived from polysaccharide phenylcarbamates. Stereoirregular **poly-2b** exhibited much lower chiral recognition than the corresponding stereoregular, helical **poly-2a**, suggesting that the regular structure of poly-(phenylacetylene) main chains is essential to attain high chiral recognition. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2271–2278

KEYWORDS: chiral stationary phase; helical conformation; highperformance liquid chromatography (HPLC); L-leucine ethyl ester; poly(phenylacetylene)

INTRODUCTION Chirality, in particular, that of chiral drugs has attracted considerable attention in the recent few decades because of the different pharmacologies of enantiomers. For example, one enantiomer of a chiral drug exhibits the desirable therapeutic effect, while the other may have no effect, and even shows a side or toxic effect.^{1,2} Therefore, it is very important to develop practical techniques for the preparation of enantiomers with a high enantiomeric excess (ee), and chiral separation, which can easily provide both enantiomers with a high ee, has attracted great interest. Especially, chiral separation by high-performance liquid chromatography (HPLC), which is recognized as a reliable tool not only for

determining ee, but also for obtaining pure enantiomers on analytical and industrial scales, has been significantly advanced in recent years. $^{3-6}$

The key to the chromatographic chiral separation is the development of effective chiral stationary phases (CSPs) with high chiral recognition abilities. CSPs for HPLC can be prepared using both chiral molecules and polymers with chiral recognition abilities.^{7,8} A wide range of chiral molecules, such as amino acids and cyclodextrins, can be used as molecular-type CSPs, which are usually immobilized on silica gel or organic polymer gel as achiral supports.^{9,10} The polymer-type CSPs consist of natural and synthetic chiral

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polymers. Polysaccharide derivatives, especially cellulose and amylose derivatives, are the most popular natural polymertype CSPs, which show unique advantages in chiral recognition and attain effective chiral separation of many racemates.^{4,8,11-14} Currently, a large number of polysaccharide derivatives have been developed and commercialized as CSPs for HPLC. However, research on the synthetic polymerbased CSPs has been mainly focused on polymethacrylates,¹⁵⁻¹⁷ poly(meth)acrylamides,^{18,19} poly(phenyl isocyanide)s,²⁰⁻²² poly(phenylacetylene)s,²³⁻²⁵ and polyamides.²⁶ However, up to now, only a few synthetic polymer-based CSPs are commercially available.

To the best of our knowledge, there are a few reports so far on poly(phenylacetylene) derivatives as CSPs for HPLC. Stereoregular poly(phenylacetylene) having chiral carbamoyl groups with one-handed helical conformation showed chiral recognition abilities as CSPs for HPLC and resolved some racemates, such as Tröger's base derivatives, spiropyran derivatives, and alcohols.^{23,24} Recently, Yashima et al. prepared a series of helical poly(phenylacetylene)s bearing cinchona alkaloid pendant groups as CSPs for HPLC, whose chiral recognition abilities were significantly influenced by the macromolecular helicity induced by the alkaloid pendants.²⁵ However, our previous work on the well-defined helical poly(phenylacetylene)s with chiral side chains revealed that the poly(phenylacetylene)s functioned as powerful anion selectors,27-31 suggesting that the polymers may also be good candidates as the novel CSPs for HPLC because of their helical structure induced by chiral pendants. This study is mainly focused on the development of effective CSPs based on the poly(phenylacetylene) derivatives with high chiral recognition ability. Herein, three polymers (poly-1, poly-2a, and poly-2b) were prepared as CSPs for HPLC according to the previous method^{27,28} and their chiral recognition abilities were evaluated by HPLC. **Poly-1** and **poly-2a** are stereoregular poly(phenylacetylene) derivatives bearing an L-leucine ethyl ester via a urea linkage and an amide linkage, respectively, while poly-2b is a stereoirregular poly(phenylacetylene) derivative bearing an L-leucine ethyl ester via amide linkage. Therefore, in this study, the influence of the linkage between the poly(phenylacetylene) and the chiral side group and the stereoregularity of the main chain on chiral recognition will be mainly discussed.

EXPERIMENTAL

Materials

N-(4-Ethynylphenylcarbamoyl)-L-leucine ethyl ester (**1**) and *N*-(4-Ethynylphenyl-carbonyl)-L-leucine ethyl ester (**2**) were synthesized according to our previous studies.^{27,28} Rh⁺(2,5-norbornadiene)[(η 6-C₆H₅)B-(C₆H₅)₃] (Rh(nbd)BPh₄) was prepared in accordance with a previous report.³² All solvents used in the reactions were of analytical grade, carefully dried and distilled before use. The porous spherical silica gel with a mean particle size of 7 μ m and a mean pore diameter of 100 nm (Daiso gel SP-1000) was kindly supplied by Daiso Chemicals (Osaka, Japan) and was silanized with (3-aminopropyl)triethoxysilane in toluene at 80 °C before use. All solvents used in the preparation of CSPs were of analytical

grade. Hexane and 2-propanol used in chromatographic experiments were of HPLC grade. The racemates were commercially available or were prepared by the usual methods.

Measurements

The ¹H NMR spectra (500 MHz) were recorded using a Bruker AVANCE III-500 instrument at room temperature. The circular dichroism (CD) and ultraviolet visible (UV-vis) spectra were measured in a 1-mm path length cell using a JASCO J-815 spectropolarimeter. The gel permeation chromatography (GPC) was performed at 35 °C in tetrahydrofuran (THF) using a Waters 2659 GPC system equipped with Styragel columns (HT0.5, HT4, and HT5). The number-average molecular weight $(M_{\rm n})$, weight-average molecular weight $(M_{\rm w})$, and polydispersity (M_w/M_n) of the polymers were obtained on the basis of a polystyrene calibration. All chromatographic experiments were performed using a JASCO PU-2089 chromatograph equipped with UV-vis (JASCO-UV-2070) and CD (JASCO-CD-2095) detectors. A solution of a racemate (3 mg/mL) was injected into the chromatographic system through an intelligent sampler (JASCO AS-2055). The thermogravimetric analyses (TGA) were performed using a TGA Q 50 (TA) instrument.

Synthesis of Helical Poly(phenylacetylene) Derivatives

The polymerization of functionalized phenylacetylene monomers **1** and **2** were carried out using Rh(nbd)BPh₄ as a catalyst in a dry flask under a nitrogen atmosphere to give **poly-1** and **poly-2a** according to previously reported methods.^{27,28} **Poly-1**: Yield, 98.5%, $M_n = 6.9 \times 10^3$, $M_w/M_n = 4.1$; **Poly-2a**: Yield, 99.3%, $M_n = 6.5 \times 10^4$, $M_w/M_n = 6.5$.

Synthesis of Nonhelical Poly(phenylacetylene) Derivative

Solid-state thermal polymerization of **2** (300 mg) was carried out under a nitrogen atmosphere at 140 °C for 3 days to give a dark reddish-colored transparent solid.³³ It was dissolved in chloroform (5 mL) and reprecipitated in hexane (100 mL), then dried under reduced pressure to give **poly-2b** as a yellowish powder. Yield, 99.2%, $M_{\rm n} = 2.8 \times 10^3$, $M_{\rm w}/M_{\rm n} = 1.7$.

Preparation of CSPs

The poly(phenylacetylene) derivatives poly-1, poly-2a, and poly-2b (0.2 g each) dissolved in a coating solvent (5 mL) were coated on aminopropyl silanized silica gel (0.8 g) according to the previous method.³⁴ The coating solvents were THF, *N,N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), chloroform (CHCl₃), methanol (MeOH), or a mixture of MeOH and CHCl₃. The weight ratio of the derivatives to silica gel was 1:4. The polymer-coated silica gels were then packed in a stainless-steel tube ($25 \times 0.20 \text{ cm}^2$ ID) by a slurry method. The plate numbers of the packed columns were 1200-4500 for benzene using a hexane/2-propanol (95/5, v/v) mixture as eluent at the flow rate of 0.1 mL/min at 25 °C. The dead time (t_0) of the columns was estimated with 1,3,5-tri-tert-butylbenzene as the nonretained compound.³⁵

RESULTS AND DISCUSSION

Synthesis of Poly(phenylacetylene) Derivatives Bearing L-Leucine Ethyl Ester Pendants

To provide the poly(phenylacetylene) derivatives as the novel CSPs for HPLC, L-leucine ethyl ester functionalized



poly-2b (non-helical)

SCHEME 1 Synthesis of poly(phenylacetylene) derivatives bearing L-leucine ethyl ester pendants.

phenylacetylene monomers **1** and **2** were synthesized and polymerized using Rh(nbd)BPh₄ as a catalyst to obtain helical polymers **poly-1** and **poly-2a**. As shown in Scheme 1, the difference between the two monomers is only the linkage group between the phenylacetylene group and the L-leucine ethyl ester. The linkage of **poly-1** is a urea group, and the linkage of **poly-2a** is an amide group. The M_n and polydispersity (M_w/M_n) of **poly-1** were 6.9×10^3 and 4.1, respectively, while the M_n and M_w/M_n of **poly-2a** were 6.5×10^4 and 6.5, respectively. The ¹H NMR spectra of **poly-1** and **poly2a** showed a peak at 5.88 ppm and 5.98 ppm, respectively (Fig. 1), indicating that both of **poly-1** and **poly2a** are stereoregular with a *cis*-configuration.^{27,28}

In addition, solid-state thermal polymerization of **2** was carried out under a nitrogen atmosphere at 140 °C for 3 days to obtain a stereoirregular polymer **poly-2b**. The M_n and

 $M_{\rm w}/M_{\rm n}$ of **poly-2b** were 2.8 × 10³ and 1.7, respectively. The ¹H NMR spectrum of **poly-2b** showed no signal due to *cis*-poly(phenylacetylene) or *trans*-poly(phenylacetylene), suggesting that **poly-2b** possesses a different configuration from that of **poly-2a** and must be a nonhelical polymer.

Chiral Recognition of Poly-1

The chiral recognition of **poly-1** was investigated as a CSP for HPLC. Because the stereoregular **poly-1** was soluble in THF, DMF, and DMAc, these were selected as the solvents for coating **poly-1** on silica gel, and CSP-**poly-1-1**, CSP-**poly-1-2**, and CSP-**poly-1-3** were obtained using these coating solvents, respectively. The chiral recognition abilities of these CSPs were evaluated with the nine racemates in Figure 2 by HPLC, and the results are summarized in Table 1. The three CSPs showed different chiral recognition abilities with low enantio-selectivities under the same chromatographic conditions with





FIGURE 1 ¹H NMR spectra of **poly-1**, **poly-2**a, and **poly-2b** in DMF- d_7 .

the eluent hexane/2-propanol (95/5) mixture. The retention factor k_1' [= $(t_1 - t_0)/t_0$], which is the factor indicating the strength of interaction between a CSP and a solute, was also different depending on the coating solvents of the CSPs. Separation factor α , which is the factor related to chiral recognition ability of a CSP, was nearly one, indicating a very low chiral recognition ability of the CSP-**poly-1**-1 coated with THF. However, a clear difference in enantioselectivity was observed on the three CSPs in the resolution of **11** as shown in Figure 3, where clear separation was attained on CSP-**poly-1**-2 and CSP-**poly-1**-3. These results suggested that the coating solvents had an obvious effect on the chiral recognition of **poly-1**.

The absorption and chiroptical properties of **poly-1** were investigated to obtain fundamental insight into the helical fashion in the three coating solvents. Figure 4 shows the UV-vis and CD spectra of **poly-1** in DMF, THF, and DMAc at room temperature. Distinctive Cotton effects in DMF and



FIGURE 2 Structures of racemates 3-11.

DMAc were observed in the UV-vis wavelength ranging from 300 to 550 nm, where the π -conjugation of the polymer backbone typically appears. The distinctive Cotton effects in the polymer backbone absorption clearly indicate that poly-1 takes a distinct one-handed helical conformation in DMF and DMAc. The embedded urea group between the L-leucine ethyl ester and the polymer backbone must be regularly arrayed in the helical structure when the polymer was dissolved in DMF and DMAc. In clear contrast, poly-1 exhibited a very weak UV-vis absorption and no Cotton effect in THF in the range from 300 to 550 nm. The very weak UV-vis absorption indicates the absence of the regular π -conjugation on the **poly-1** backbone. The polymer must be conformationally irregular and nonhelical in THF. Therefore, Poly-1 is a dynamic helical polymer, and its helical conformation varies when it is dissolved in different solvents. Combining the resolution results with the analyses of the CD spectra, the

TABLE 1 Resolution of Racemates on CSP-poly-1 Prepared with Various Coating Solvents^a

Coating Solvents Racemates	CSP-poly-1-1 THF		CSP-poly-1-2 DMF		CSP-poly-1-3 DMAc	
	3	0.31(+)	~1	2.60(-)	~1	4.68(-)
4	0.27(–)	~1	0.34	1.00	0.36	1.00
5	1.55	1.00	0.99	1.00	1.66	1.00
6	0.50	1.00	0.70	1.00	0.66	1.00
7	5.17	1.00	2.71	1.00	4.58	1.00
8	2.17(+)	~1	1.14	1.00	1.41	1.00
9	0.68	1.00	0.55	1.00	0.86	1.00
10	1.64(+)	~1	0.25	1.00	1.07	1.00
11	5.29	1.00	2.32(-)	1.08	5.82(-)	1.05

^a Column: 25 cm \times 0.20 cm ID. Flow rate: 0.1 mL/min. Eluent: hexane/2-propanol (95/5). The signs in parentheses represent the optical rotation of the first-eluted enantiomer.



FIGURE 3 Chromatograms for the resolution of *rac*-11 on (a) CSP-poly-1-2 and (b) CSP-poly-1-3 with hexane/2-propanol (95/5) as eluent.

chiral recognition abilities of CSP-**poly-1-1**, CSP-**poly-1-2**, and CSP-**poly-1-3** were varied probably due to the different conformation of **poly-1** on the silica surface induced by changing the coating solvents. Low chiral recognition of the **poly-1** coated with THF for racemate **11** may be due to this low helicity.

Chiral Recognition of Poly-2a

To elucidate the role of linkage groups between polymer main chains and chiral pendants on chiral recognition of poly(phenylacetylene) derivatives, the polymerization of **2** with an amide linkage was carried out using $Rh(nbd)BPh_4$ as a catalyst to give **poly-2a**. The solubility of **poly-2a** is better



FIGURE 4 UV-vis (lower) and CD (upper) spectra of **poly-1** in variable solvents (c = 1 mg/mL) at 25 °C.

than that of **poly-1**, and it is quite soluble in THF, MeOH, DMF, DMAc, and a MeOH/CHCl₃ (3/7, v/v) mixture. Therefore, THF, DMF, MeOH, and a MeOH/CHCl₃ (3/7, v/v) mixture were selected for coating **poly-2a** on silica gel to obtain CSP-**poly-2a-1**, CSP-**poly-2a-2**, CSP-**poly-2a-3**, and CSP-**poly-2a-4**, respectively. The chiral recognition of these CSPs coated with different solvents was evaluated with eight racemates **3-10** by HPLC, and the resolution results are summarized in Table 2.

For most racemates, **poly-2a** showed higher chiral recognition compared to **poly-1**. All the tested racemates except for racemate **8** were resolved on CSP-**poly-2a-4**. Moreover, racemic *trans*-stilbene oxide (**4**) and *trans*-cyclopropanedicarboxylic acid dianilide (**10**) were resolved with baseline separation on CSP-**poly-2a-2**, CSP-**poly-2a-3**, and CSP-**poly-2a-4**. The structures of **poly-1** and **poly-2** are different only in the linkage groups between the poly(phenylacetylene) main chains and L-leucine ethyl ester. This means that linkage groups play an important role in the chiral recognition of poly(phenylacetylene) derivatives. The amide linkage of **poly-2a** is shorter than the urea linkage of **poly-1**. The shorter amide linkage seems to be better for chiral recognition of the poly(phenylacetylene) derivatives.

Figure 5 shows the chromatograms for racemates **4** and **10** on CSP-**poly-2a-4** coated with a mixture of MeOH/CHCl₃ (3/ 7, v/v). The enantiomers were completely separated resulting in the separation factors of 2.19 for **4** and 1.98 for **10**. These large values are rather similar to those obtained on the very popular CSPs derived from phenylcarbamate derivatives of cellulose and amylose,^{4,34,36} suggesting that the helical poly(phenylacetylene) derivatives with the regular arrangement of chiral side chains may show a high chiral recognition for some racemates.^{23–25} The chiral recognition ability of CSP-**poly-2a-4** was maintained for at least several months, indicating that the **poly-2a** is conformationally stable over this period.

As shown in Table 2, the elution orders of the enantiomers on the four CSPs of **poly-2a** were the same, but their chiral recognition abilities were somewhat different. CSP-**poly-2a-1**,

	CSP-poly-2a-1 THF		CSP-poly-2a-2 DMF		CSP-poly-2a-3 MeOH		CSP-poly-2a-4 MeOH/CHCl ₃ (3/7, v/v)	
Coating Solvents Racemates								
	k ₁ ′	α	k ₁ ′	α	k ₁ ′	α	k ₁ ′	α
3	0.16(+)	~ 1	0.44(+)	~ 1	0.33(+)	1.21	0.33(+)	1.26
4	0.22(+)	1.24	0.63(+)	1.39	0.35(+)	1.85	0.31(+)	2.19
5	1.55	1.00	2.27(+)	1.15	1.66(+)	1.12	0.70(+)	1.25
6	0.29(-)	~1	0.90(-)	\sim 1	0.70(-)	1.11	0.78(-)	1.13
7	3.84	1.00	5.95	1.00	4.34(-)	~ 1	5.55(-)	1.15
8	0.29(+)	~1	0.36	1.00	0.29(+)	~1	0.38	1.00
9	0.31	1.00	1.05	1.00	0.74(-)	1.11	0.85(-)	1.12
10	1.45	1.00	1.95(+)	1.55	1.61(+)	1.45	0.87(+)	1.98

TABLE 2 Resolution of Racemates on CSP-poly-	2a Prepared with Various Coating Solvents ^a
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^a Column: 25 cm \times 0.20 cm ID. Flow rate: 0.1 mL/min. Eluent: hexane/2-propanol (95/5). The signs in parentheses represent the optical rotation of the first-eluted enantiomer.

which was coated with THF showed lower chiral recognition than the other three CSPs coated with DMF or MeOH or MeOH/CHCl₃. Only racemate **4** was effectively resolved on CSP-**poly-2a-1**, while more racemates were resolved and higher chiral recognition was attained on the other three CSPs of **poly-2a**, especially CSPs coated with MeOH or MeOH/CHCl₃. The effects of coating solvents on the chiral recognition of **poly-2a** may be due to the different conformation of **poly-2a** induced by the coating solvents.

Figure 6 shows the UV-vis and CD spectra of **poly-2a** in THF, DMF, MeOH, MeOH/CHCl₃ (3/7, v/v), and CHCl₃ at room temperature. It was found that **poly-2a** exhibited a very weak UV-vis absorption and no Cotton effect in THF in the range from 300 to 500 nm. The weak UV-vis absorption in THF demonstrates the absence of a helical conformation of **poly-2a** as discussed before. This may be the reason why CSP-**poly-2a**-1 coated with THF showed a lower chiral recognition. In clear contrast, distinctive Cotton effects in DMF, MeOH, MeOH/CHCl₃ (3/7, v/v), and CHCl₃ were observed in the UV-vis wavelength ranging from 300 to 500 nm, where the π -conjugation of the polymer backbone typically appears. This indicates that **poly-2a** has a prevailing one-handed heli-

cal conformation in DMF, MeOH, MeOH/CHCl₃ (3/7, v/v), and CHCl₃. These CD data are well correlated with the resolution results, and the helical conformation induced by changing the coating solvents really made a valuable contribution to the chiral recognition abilities of **poly-2a**. The helical poly(phenylacetylene) derivatives with the regular arrangement of chiral side chains can show high chiral recognition for some racemates.^{23–25,37}

To investigate the influence of the mixture of $MeOH/CHCl_3$ on the structure of **poly-2a**, the ¹H NMR spectra of **poly-2a** were measured in deuterated methanol/chloroform mixtures (Fig. 7). The spectrum in chloroform was broad, possibly due to the association of the polymer chains in the nonpolar solvent through intrachain and interchain hydrogen bonding. The poor resolution of the spectrum made it difficult to assign the signals. Addition of a protonic solvent (methanol, 20 vol %) to the chloroform solution improved the spectral resolution, and the amide resonance was identified at 8.09 ppm. Further addition of methanol progressively shifted the resonance peak of the amide proton to a lower field. When the volume proportion of methanol increased to 80%, the proton signal of the amide group shifted to 8.35 ppm.



FIGURE 5 Chromatograms for the resolution of (a) rac-4 and (b) rac-10 on CSP-poly-2a-4 with hexane/2-propanol (95/5) as eluent.

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Wavelength (nm)

FIGURE 6 UV-vis (lower) and CD (upper) spectra of poly-2a in variable solvents (c = 1 mg/mL) at 25 °C.

Clearly, hydrogen bond formation between the hydroxyl groups of methanol and the amide groups of the polymer pendants resulted in the change in helical conformation and chiral recognition abilities of **poly-2a**.

Moreover, the Cotton effects of poly-2a in a mixture of $MeOH/CHCl_3$ (3/7, v/v) are opposite to those in DMF or MeOH, while the elution orders of the enantiomers on the CSP-poly-2-4 coated with MeOH/CHCl₃ (3/7, v/v) are the



FIGURE 7 ¹H NMR spectra of poly-2a in $CD_3OD/CDCI_3 = 20/80$ - 80/20 (v/v).

FIGURE 8 UV-vis (lower) and CD (upper) spectra of poly-2b in MeOH and CHCl₃ (c = 1 mg/mL) at 25 °C.

same as those coated with DMF or MeOH. These results suggest that the chiral pendants play the main role in chiral recognition and that the helical conformation of the poly-2 chain can adjust its chiral recognition.

Chiral Recognition of Poly-2b

To investigate the influence of main chain regularity of poly-(phenylacetylene) derivatives on their chiral recognition abilities, solid-state thermal polymerization of 2 was carried out under a nitrogen atmosphere at 140 °C for 3 days to obtain a stereoirregular polymer **poly-2b**. As shown in Figure 1, the ¹H NMR spectrum of **poly-2a** demonstrates a peak at 5.98 ppm, indicating the propensity of the *cis*-configuration in the main chain,²⁹ whereas the ¹H NMR spectrum of **poly-2b** showed no signal due to cis-poly(phenylacetylene) or transpoly(phenylacetylene), suggesting that poly-2b must be a stereoirregular polymer. Although poly-2a and poly-2b were polymerized from the same monomer, the stereoregularities of poly-2a and poly-2b are different.

Figure 8 shows the CD and UV-vis spectra of poly-2b in CHCl₃ and MeOH at room temperature. As predicted, poly-2b exhibited a very weak UV-vis absorption and no Cotton effect in these solvents in the range from 300 to 500 nm, indicating that poly-2b does not possess a helical conformation.

CSP-poly-2b was prepared by coating poly-2b on silica gel using a MeOH/CHCl₃ (3/7, v/v) mixture as the coating solvent. The chiral recognition of CSP-poly-2b was evaluated with the eight racemates 3-10 by HPLC, and the resolution



TABLE 3 Resolution of Racemates on CSP-poly-2ba

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	3	4	5	7	8	9	10
k1 [′]	0.27(-)	0.33	0.27	0.18	1.63	1.32(+)	0.64
α	~ 1	1.00	1.00	1.00	1.00	~ 1	1.00

 a Column: 25 cm \times 0.20 cm ID. Coating solvent: MeOH. Flow rate: 0.1 mL/min. Eluent: hexane/2-propanol (99/1). The signs in parentheses represent the optical rotation of the first-eluted enantiomer.

results are summarized in Table 3. CSP-**poly-2b** exhibited much lower chiral recognition than CSP-**poly-2a**-4 and showed very low chiral recognition only for **3** and **9**. These results indicate that irregular arrangements of chiral side chains can show only low chiral recognition and that their regular arrangement is essential to attain high chiral recognition.

CONCLUSIONS

Helical and nonhelical poly(phenylacetylene) derivatives bearing L-leucine ethyl ester pendants (poly-1, poly-2a, and poly-2b) were synthesized and coated on silica gel using various solvents to evaluate their chiral recognition abilities as CSPs for HPLC. Both helical poly-1 and poly-2a exhibited chiral recognition ability. The linkage groups between the poly(phenylacetylene) main chains and L-leucine ethyl ester pendants played an important role in chiral recognition, and poly-2a with a shorter amide linkage showed higher chiral recognition than **poly-1** with a longer urea linkage. Coating solvents also played an important role in chiral recognition because different conformations of helical poly(phenylacetylene) derivatives were induced by changing the coating solvents. Non-helical poly-2b exhibited much lower chiral recognition than the corresponding helical poly-2a, suggesting that the regular structure the of poly(phenylacetylene) main chains is essential for high chiral recognition.

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