Synthesis and Chiral Recognition of Helical Poly(phenylacetylene)s Bearing L-Phenylglycinol and its Phenylcarbamates as Pendants

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ABSTRACT: A series of novel stereoregular one-handed helical poly(phenylacetylene) derivatives (**PPA-1 and PPA-1a~g**) bearing L-phenylglycinol and its phenylcarbamate residues as pendants was synthesized for use as chiral stationary phases (CSPs) for HPLC, and their chiral recognition abilities were evaluated using 13 racemates. The phenylcarbamate residues include an unsubstituted phenyl, three chloro-substituted phenyls (3-Cl, 4-Cl, 3,5-Cl_2), and three methyl-substituted phenyls (3-CH_3, 4-CH_3, 3,5-$(CH_3)_2$). The acidity of the phenylcarbamate N-H proton and the hydrogen bonds formed between the N-H groups of the phenylcarbamate residues were dependent on the type, position, and the number of substituents on the phenylcarbamate residues. The chiral recognition abilities of these polymers significantly depended on the dynamic helical conformation of the main chain with more or less regularly arranged pendants. The chiral recognition abilities seem to be improved by the introduction of substituents on the phenylcarbamate residues, and **PPA-1d** bearing the more acidic N-H groups due to the 3,5-dichloro substituents, exhibited a higher chiral recognition than the others. **PPA-1d** showed an efficient chiral recognition for some racemates, and baseline separation was possible for racemates **5**, **11**, **12**, and **15**. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 809–821

KEYWORDS: chiral; chiral recognition; helical conformation; high performance liquid chromatography (HPLC); L-phenylglycinol; molecular recognition; phenylcarbamate; polyacetylenes; poly(phenylacetylene)

INTRODUCTION Chiral compounds often exhibit different physiological and metabolic activities in organisms between enantiomers, though most of their chemical and physics properties are identical. Therefore, the chirality of compounds is an important issue, in particular, for chiral drugs and food additives, and it is valuable to prepare pure enantiomers of various chiral compounds.[1,2] Chiral separation, especially direct enantioseparation by high-performance liquid chromatography (HPLC) has been recognized as one of the most efficient techniques to obtain pure enantiomers on analytical and preparative scales.[3–5] One of the key points of this separation technique is to design and prepare the efficient chiral stationary phases (CSPs) with high chiral recognition abilities. Although polysaccharide derivatives, especially the phenylcarbamates and benzoates of cellulose and amylose with high chiral recognition abilities have been developed as the popular CSPs for a wide range of chiral compounds,[4,6,7] various optically active synthetic polymers with a controllable helical sense have also been applied as the CSPs for the HPLC separation of enantiomers in the last two decades.[7–16] Among the synthetic polymers, the helical poly(phenylacetylene) derivatives bearing chiral pendants have been proved to be good candidates as novel CSPs for the HPLC separation of enantiomers due to their helical structures induced by chiral pendants.[16–21] Up to now, there have been only a few reports on the poly(phenylacetylene) derivatives as CSPs for HPLC, their chiral recognition mechanism as CSPs and the influencial factors for chiral recognition are still not so totally clarified.

The poly(phenylacetylene)s possessing dynamic helical conformations can be internally tuned and externally manipulated, resulting in the change of the helical pitch and inversion of the helicity. The former is usually achieved by changing their

molecular structures, especially their functional pendants, while the latter is accomplished by applying external stimuli, such as temperature and solvent. Previously, we reported a series of the poly(phenylacetylene)s bearing different L-amino acid ethyl ester pendants with different linkages, and discussed the influences of the main chain helicity, linkage group between the main chain and chiral pendants, coating solvents on silica gel, polymerization conditions, and structures of the amino acids on their chiral recognition abilities.[20–22] To the best of our knowledge, the helical poly(phenylacetylene)s bearing phenylcarbamate derivatives of L-amino alcohols as pendants have never been reported. In this study, based on our previous studies, a series of novel stereoregular one-handed helical poly(-phenylacetylene) derivatives bearing L-phenylglycinol and its phenylcarbamate residues as pendants was designed and synthesized, and their chiral recognition abilities as CSPs for HPLC were evaluated. The main focus was on the influence of unsubstituted and substituted phenylcarbamate residues on the helical structures of the stereoregular main chain and the chiral recognition abilities of these poly(phenylacetylene) derivatives. The influence of the position and the number of chloro-substituents and methy L-substituents on the phenyl group of the phenylcarbamate residues was investigated in detail.

EXPERIMENTAL

Materials

L-Phenylglycinol (purity 99%) was purchased from Shanghai Jingchun Reagent Co., Ltd. (Shanghai, China). 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium chloride (DMT-MM) (purity 98%) was purchased from Sahn Chemical Technology Co., Ltd. (Shanghai, China). Triphenylphosphine (purity 99%) was purchased from J&K Chemical Co., Ltd. (Beijing, China). 4-Ethynylbenzoic acid was synthesized according to a previously reported method.[23] 3-Chlorophenylisocyanate (purity 98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Shanghai, China). Phenyl isocyanate, 4-chlorophenyl isocyanate, 3,5-dichlorophenyl isocyanate, 3-methylphenyl isocyanate, 4-methylphenyl isocyanate, and 3,5-dimethylphenyl isocyanate (purity 98%) were purchased from Puyang Hongda Shengdao Mew Materials Co., Ltd. (Henan, China). Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)$B(C_6H_5)_3$] (Rh(nbd)BPh_4) was prepared based on a previous report.[24] All the solvents used in the reactions were of analytical grade, carefully dried, and distilled before use. The solvents (methanol (MeOH), tetrahydrofuran (THF), *N*,*N*-dimethylformide (DMF), dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylacetamide (DMAc)) for the solubility test of the polymers were commercially available and used without further purification. Silica gel with a mean particle size of 37 to 56 μm for column chromatography was purchased from Qingdao Haiyang Chemical Co., Ltd. (Qingdao, China). The porous spherical silica gel with a mean particle size of 7 μm and a mean pore diameter of 100 nm (Daiso gel SP-1000−7) for HPLC was kindly supplied by Daiso Chemicals (Osaka, Japan), then silanized with (3-aminopropyl)triethoxysilane in toluene at 80 °C before use. All solvents used in the preparation of the chiral stationary phases were of analytical grade. Hexane and 2-propanol used in the chromatographic experiments were of HPLC grade. The racemates were commercially available or were prepared by the usual methods.

Instrumentation

The NMR spectra were recorded using a Bruker AVANCE III-500 instrument. The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity (M_w/M_n) of the polymers were determined by size exclusion chromatography (SEC) calibrated with standard polystyrenes at 40 °C using a JASCO SEC system (PU-980 Intelligent pump, CO-965 column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 5 μm; exclusion limit, 4×10^4) and a Shodex Asahipak GF-7 M HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 9 μm; exclusion limit, 4×10^7) in DMF containing lithium chloride (0.01 M) at the flow rate of 0.4 mL min^{-1}. The optical rotation was measured in $CHCl_3$ at room temperature using a Perkin-Elmer Model 341 polarimeter. 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. All the enantioseparation experiments were performed using a JASCO PU-2089 high performance liquid chromatograph (HPLC) system equipped with UV-Vis (JASCO-UV-2070) and circular dichroism (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.

Monomer Synthesis

Synthesis of N-(4-Ethynylbenzoyl)-L-Phenylglycinol (PA-1)

PA-1 was synthesized by the amidation reaction between 4-ethynylbenzoic acid and L-phenylglycinol. A typical procedure is described as follows. To a solution of 4-ethynylbenzoic acid (5.00 g, 34.21 mmol) and DMT-MM (10.41 g, 37.64 mmol) in MeOH (175 mL) was added L-phenylglycinol (4.69 g, 34.21 mmol). After stirring at room temperature for 18 h, the reaction mixture was purified by column chromatography on silica gel with hexane/acetone (5/4, v/v) to give **PA-1** as white crystals.

Yield: 6.93 g (76.3%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.78–7.76 (d, Ar-***H***, 2H), 7.57–7.55 (d, Ar-***H***, 2H), 7.42–7.35 (m, Ar-***H***, 4H), 7.35–7.30 (m, Ar-***H***, 1H), 6.84–6.82 (d, Ar-N***H***-, 1H), 5.29-5.25 (q, Ar-C***H***-, 1H), 4.06-3.98 (m, -O-C$\boldsymbol{H}_2$-, 2H), 3.20 (s, C≡C***H***, 1H), 2.40 (s, -O***H***, 1H). ^{13}C NMR (125 MHz. DMSO-d_6, 20 °C, ppm): δ = 165.3 (−***C***O− (amino)), 141.2 (aromatic), 134.7 (aromatic), 131.5 (aromatic), 128.1 (aromatic), 127.7 (aromatic), 126.9 (aromatic), 126.8 (aromatic), 124.3 (aromatic), 82.9 (−***C***≡CH), 82.7 (−C≡***C***H), 64.4 (−$\boldsymbol{C}H_2$−O), 56.0 (−***C***H−NH-). Anal. Calcd. for $C_{17}H_{15}NO_2$ (265.31): C, 76.96; H, 5.70; N, 5.28. Found: C, 76.93; H, 5.72; N, 5.25.

Synthesis of PA-1a-g

Seven carbamate derivatives **PA-1a-g** were synthesized via the reaction between PA-1 and unsubstituted phenyl

isocyanate or a series of substituted phenyl isocyanates. A typical procedure is described as follows. To a solution of the **PA-1** (1.00 g, 3.77 mmol) in THF (38 mL) was added phenyl isocyanate (0.53 g, 4.52 mmol) under a nitrogen atmosphere. After stirring at 35 °C for 10 h, the reaction mixture was purified by column chromatography on silica gel with hexane/ethyl acetate (5/2, v/v) to give (*S*)-2-(4-ethynylbenzamino)−2-phenylethyl phenylcarbamate (**PA-1a**) as white crystals.

Yield: 1.05 g (72.7%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.78–7.76 (d, Ar-***H***, 2H), 7.52-7.50 (d, Ar-***H***, 2H), 7.37–7.41 (m, Ar-***H***, 4H), 7.28–7.37 (m, Ar-***H***, 5H; -CO-N***H***-, 1H), 7.67–7.12 (m, Ar-***H***, 1H), 6.74 (s, Ar-N***H***-, 1H), 5.50–5.43 (m, Ar-C***H***-, 1H), 4.74–4.68 (q, -O-C$\boldsymbol{H}_2$-, 1H), 4.40–4.36 (q, -O-C$\boldsymbol{H}_2$-, 1H), 3.18 (s, C≡C***H***, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): δ = 165.3 (−***C***O− (ester)), 153.4 (−***C***O− (amino)), 139.7 (aromatic), 139 (aromatic), 134.3 (aromatic), 131.7 (aromatic), 128.7 (aromatic), 128.5 (aromatic), 127.7 (aromatic), 127.5 (aromatic), 127 (aromatic), 124.6 (aromatic), 122.5 (aromatic), 118.3 (aromatic), 118.2 (aromatic), 83.0 (−***C***≡CH), 82.9 (−C≡***C***H), 66.2 (−***C***H_2−O), 52.7 (−***C***H−NH-). Anal. Calcd. for $C_{24}H_{20}N_2O_3$ (384.43): C, 74.98; H, 5.24; N, 7.29. Found: C, 74.96; H, 5.26; N, 7.28.

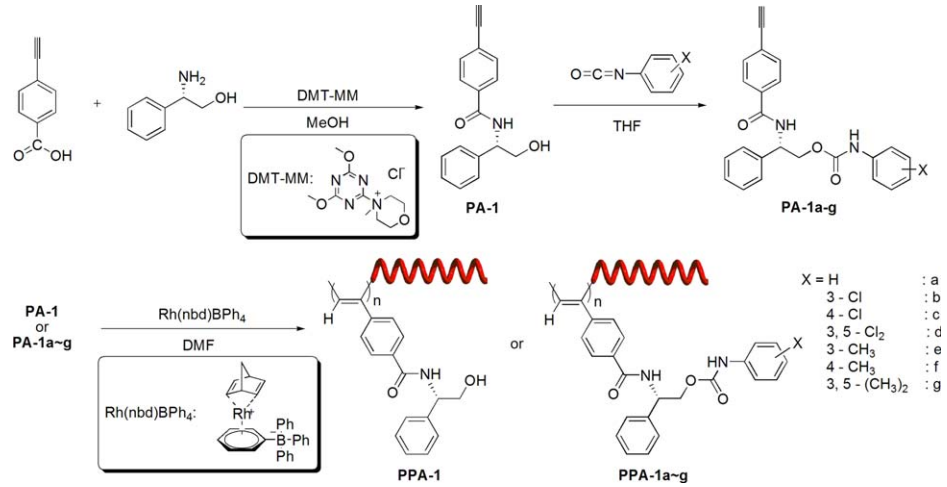
Based on the above procedure, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3-chlorophenylcarbamate (**PA-1b**) was successfully synthesized and purified by column chromatography on silica gel with chloroform/ethyl acetate (9/1, v/v) to give white crystals. Yield: 1.18 g (74.7%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.77–7.75 (d, Ar-***H***, 2H), 7.53–7.51 (d, Ar-***H***, 2H), 7.47 (s, Ar-***H***, 1H), 7.42–7.35 (m, Ar-***H***, 4H), 7.35–7.28 (m, Ar-***H***, 1H), 7.24–7.19 (m, Ar-***H***, 1H), 7.19-7.11 (m, Ar-***H***, 2H), 7.08–7.03 (d, -CO-N***H*** -, 1H), 6.74 (s, Ar-N***H***-, 1H), 5.55–5.47 (m, Ar-C***H***-, 1H), 4.74-4.69 (q, -O-C$\boldsymbol{H}_2$-, 1H), 4.42–4.38 (q, -O-C$\boldsymbol{H}_2$-, 1H), 3.19 (s, C≡C***H***, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): δ = 165.8 (−***C***O− (ester)), 153.7 (−***C***O− (amino)), 141.1 (aromatic), 140.1 (aromatic), 134.7 (aromatic), 133.6 (aromatic), 132.1 (aromatic), 130.9 (aromatic), 128.9 (aromatic), 128.1 (aromatic), 128.0 (aromatic), 127.4 (aromatic), 125.1 (aromatic), 122.6 (aromatic), 118.0 (aromatic), 117.1 (aromatic), 83.4 (−***C***≡CH), 83.3 (−C≡***C***H), 66.8 (−***C***H_2−O-), 53.1 (−***C***H−NH-). Anal. Calcd. for $C_{24}H_{19}ClN_2O_3$ (418.87): C, 68.82; H, 4.57; Cl, 8.46; N, 6.69. Found: C, 68.88; H, 4.55; Cl, 8.51; N, 6.64.

Based on the above procedure, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 4-chlorophenyl- carbamate (**PA-1c**) was successfully synthesized and purified by column chromatography on silica gel with chloroform/ethyl acetate (10/1, v/v) to give white crystals. Yield: 1.23 g (77.8%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.77–7.75 (d, Ar-***H***, 2H), 7.53–7.51 (d, Ar-***H***, 2H), 7.47 (s, Ar-***H***, 1H), 7.40-7.36 (m, Ar-***H***, 4H), 7.35–7.30 (m, Ar-***H***, 1H), 7.30–7.26 (m, Ar-***H***, 4H), 7.22–7.20 (d, -CO-N***H***-, 1H), 6.77 (s, Ar-N***H***-, 1H), 5.50-5.45 (m, Ar-C***H***-, 1H), 4.74-4.68 (q, -O-C$\boldsymbol{H}_2$-, 1H), 4.42–4.36 (q, -O-C$\boldsymbol{H}_2$-, 1H), 3.20 (s, C≡C***H***, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): δ = 165.8 (−***C***O− (ester)), 153.8 (−***C***O− (amino)), 140.1 (aromatic), 138.4 (aromatic), 134.8 (aromatic), 132.1 (aromatic), 129.1 (aromatic), 129.0 (aromatic), 128.1 (aromatic), 128.0 (aromatic), 127.4 (aromatic), 126.6 (aromatic), 125.1 (aromatic), 120.3 (aromatic), 120.2 (aromatic), 83.3 (−***C***≡CH), 83.2 (−C≡***C***H), 66.7 (−***C***H_2−O-), 53.1 (−***C***H−NH-). Anal. calcd. for $C_{24}H_{19}ClN_2O_3$ (418.87): C, 68.82; H, 4.57; Cl, 8.46; N, 6.69. Found: C, 68.90; H, 4.58; Cl, 8.49; N, 6.61.

Based on the above procedure, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3,5-dichlorophenylcarbamate (**PA-1d**) was successfully synthesized and purified by column chromatography on silica gel with hexane/ethyl acetate (5/2, v/v) to give white crystals. Yield: 1.21 g (70.9%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.76–7.74 (d, Ar-***H***, 2H), 7.53-7.51 (d, Ar-***H***, 2H), 7.41–7.35 (m, Ar-***H***, 4H), 7.35–7.28 (m, Ar-***H***, 3H), 7.19 (s, Ar-N***H***-, 1H), 7.13-7.08 (d, -CO-N***H***-, 1H), 7.05 (s, Ar-***H***, 1H), 5.5,6–5.49 (m, Ar-C***H***, 1H), 4.76–4.70 (q, -O-C$\boldsymbol{H}_2$-, 1H), 4.41–4.35 (q, -O-C$\boldsymbol{H}_2$-, 1H), 3.19 (s, C≡C***H***, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): δ = 165.3 (−***C***O− (ester)), 153.1 (−***C***O− (amino)), 141.6 (aromatic), 139.5 (aromatic), 134.2 (aromatic), 131.7 (aromatic), 128.5 (aromatic), 127.7 (aromatic), 127.6 (aromatic), 127.0 (aromatic), 124.7 (aromatic), 121.7 (aromatic), 116.3 (aromatic), 83.0 (−***C***≡CH), 82.9 (−C≡***C***H), 66.6 (−***C***H_2−O-), 52.6 (−***C***H−NH-). Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_3$ (453.32): C, 63.59; H, 4.00; Cl, 15.64; N, 6.18. Found: C, 63.68; H, 3.96; Cl, 15.59; N, 6.22.

Based on the above procedure, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3-methylphenylcarbamate (**PA-1e**) was successfully synthesized and purified by column chromatography on silica gel with chloroform/ethyl acetate (15/1, v/v) to give white crystals. Yield: 1.23 g (81.6%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.78–7.76 (d, Ar-***H***, 2H), 7.52–7.50 (d, Ar-***H***, 2H), 7.42–7.33(m, Ar-***H***, 4H; -CO-N***H***-, 1H), 7.33–7.28 (m, Ar-***H***, 1H), 7.20-7.14 (m, Ar-***H***, 3H), 6.92–6.90 (d, Ar-***H***, 1H), 6.69 (s, Ar-N***H***-, 1H), 5.48–5.44 (m, Ar-C***H***, 1H), 4.74–4.69 (q, -O-C$\boldsymbol{H}_2$-, 1H), 4.39–4.35 (q, -O-C$\boldsymbol{H}_2$-, 1H), 3.19 (s, C≡C***H***, 1H), 2.33(s, -C$\boldsymbol{H}_3$, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): δ = 165.8 (−***C***O− (ester)), 153.8 (−***C***O− (amino)), 140.2 (aromatic), 139.4 (aromatic), 138.3 (aromatic), 134.8 (aromatic), 132.1 (aromatic), 129.0 (aromatic), 128.9 (aromatic), 128.2 (aromatic), 128.0 (aromatic), 127.4 (aromatic), 125.1 (aromatic), 123.7 (aromatic), 119.3 (aromatic), 83.4 (−***C***≡CH), 83.3 (−C≡***C***H), 66.6 (−***C***H_2−O-), 53.2 (−***C***H−NH-), 21.7 (-***C***H_3). Anal. Calcd. for $C_{25}H_{22}N_2O_3$ (398.45): C, 75.36; H, 5.57; N, 7.03. Found: C, 75.43; H, 5.65; N, 6.91.

Based on the above procedure, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 4-methylphenylcarbamate (**PA-1f**) was successfully synthesized and purified by column chromatography on silica gel with chloroform/ethyl acetate (13/1, v/v) to give white crystals. Yield: 1.33 g (88.7%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): δ = 7.78–7.76 (d, Ar-***H***, 2H), 7.52–7.50 (d, Ar-***H***, 2H), 7.44–7.34 (m, Ar-***H***, 4H; -CO-N***H***-, 1H), 7.28–7.33 (m, Ar-***H***, 1H), 7.21 (Ar-***H***, 2H), 7.11–7.09 (d, Ar-***H***, 2H), 6.72 (s, Ar-N***H***-, 1H), 5.47–5.42 (m, Ar-C***H***, 1H), 4.72-4.68 (q, -O-C$\boldsymbol{H}_2$-, 1H), 4.36–4.33 (q, -O-C$\boldsymbol{H}_2$-, 1H), 3.19



SCHEME 1 Synthesis of poly(phenyacetylene)s bearing L-phenylglycinol derivatives as pendants **PPA-1** and **PPA-1a~h**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(s, C≡C***H***, 1H), 2.31(s, -C***H***$_3$, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): $\delta = 165.8$ (−***C***O− (ester)), 153.8 (−***C***O− (amino)), 140.2 (aromatic), 136.9 (aromatic), 134.8 (aromatic), 132.1 (aromatic), 131.7 (aromatic), 129.6 (aromatic), 129.5 (aromatic), 128.9 (aromatic), 128.1 (aromatic), 128.0 (aromatic), 127.4 (aromatic), 125.1 (aromatic), 118.7 (aromatic), 83.4 (−***C***≡CH), 83.3 (−C≡***C***H), 66.5 (−***C***H$_2$−O-), 53.2 (−***C***H−NH-), 20.8 (-***C***H$_3$). Anal. Calcd. for $C_{25}H_{22}N_2O_3$ (398.45): C, 75.36; H, 5.57; N, 7.03. Found: C, 75.40; H, 5.55; N, 6.96.

Based on the above procedure, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3,5-dimethylphenyl- carbamate (**PA-1g**) was successfully synthesized and purified by column chromatography on silica gel with chloroform/ethyl acetate (10/1, v/v) to give white crystals. Yield: 1.14 g (73.6%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 20 °C, ppm): $\delta = 7.79$–7.77 (d, Ar-***H***, 2H), 7.53–7.51 (d, Ar-***H***, 2H), 7.35–7.42 (m, Ar-***H***, 4H), 7.28–7.34 (m, Ar-***H***, 1H; -CO-N***H***-, 1H), 6.94 (s, Ar-***H***, 2H), 6.74 (s, Ar-***H***, 1H), 6.55 (s, Ar-N***H***-, 1H), 5.48-5.44 (m, Ar-C***H***, 1H), 4.73-4.68 (q, -O-C***H***$_2$, 1H), 4.38-4.35 (q, -O-C***H***$_2$, 1H), 3.18 (s, C≡C***H***, 1H), 2.28(s, -C***H***$_3$, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C, ppm): $\delta = 165.7$ (−***C***O− (ester)), 153.8 (−***C***O− (amino)), 140.2 (aromatic), 139.3 (aromatic), 138.2 (aromatic), 138.1 (aromatic), 134.8 (aromatic), 132.1 (aromatic), 128.9 (aromatic), 128.1 (aromatic), 128.0 (aromatic), 127.4 (aromatic), 125.1 (aromatic), 124.5 (aromatic), 116.5 (aromatic), 83.4 (−***C***≡CH), 83.3 (−C≡***C***H), 66.6 (−***C***H$_2$−O-), 53.2 (−***C***H−NH-), 21.6 (-***C***H$_3$). Anal. Calcd. for $C_{26}H_{24}N_2O_3$ (412.48): C, 75.71; H, 5.86; N, 6.79. Found: C, 75.74; H, 5.92; N, 6.76.

Polymerization

The polymerizations of the phenylacetylenes bearing the L-phenylglycinol pendants (**PA-1**, **PA-1a-g**) were carried out in dry DMF using Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] ($Rh(nbd)BPh_4$) as the catalyst under a nitrogen atmosphere for 24 h at 28 °C with $[monomer]_0 = 0.03$ M, and $[monomer]_0/[Rh(nbd)BPh4]_0 = 50$. A typical procedure is described as follows. **PA-1** (0.50 g, 1.88 mmol) was weighed into a flask and dissolved in dry DMF (50.3 mL) before a solution of Rh(nbd)BPh4 (19.4 mg, 37.7 μmol) in dry DMF (12.5 mL) was added. After stirring at room temperature for 24 h, triphenylphosphine (19.8 mg, 75.4 μmol) was added to the reaction mixture. The solution was concentrated and then poured into a large amount of MeOH (1000 mL). The precipitates were purified by reprecipitation using MeOH and then dried under reduced pressure to give **PPA-1** as a yellow solid.

Yield: 0.49 g (98%). $M_n = 4.15 \times 10^5$; $M_w/M_n = 3.88$. Based on the above procedure, the other monomers (**PA-1a-g**) were polymerized to give the corresponding polymers (**PPA-1a-g**).

Preparation of Chiral Stationary Phases (CSPs)

The poly(phenylacetylene) derivatives (**PPA-1** and **PPA-1a~g**) (0.20 g each) were first dissolved in a coating solvent (5 mL) and then coated on aminopropyl silanized silica gel (0.80 g) according to a previous method.[25] The polymer-coated silica gels were then packed in a stainless-steel tube (25 cm × 0.20 cm i.d.) by the slurry method. The plate numbers of the packed columns were 1600 to 3000 for benzene using a hexane/2-propanol (95/5, v/v) mixture as the eluent at the flow rate of 0.1 mL/min at 25 °C. The dead time (t_0) of the columns was estimated using 1,3,5-tri-tert-butylbenzene as the nonretained compound.[26]

RESULTS AND DISCUSSION

Synthesis of Polymers, PPA-1 and PPA-1a∼g

The monomers and polymers were synthesized via the reaction route illustrated in Scheme 1. The amidation reaction of 4-ethynylbenzoic acid with the L-phenylglycinol proceeded using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium chloride (DMT-MM) as a catalyst in good yields to produce a novel monomer bearing the L-phenylglycinol pendant

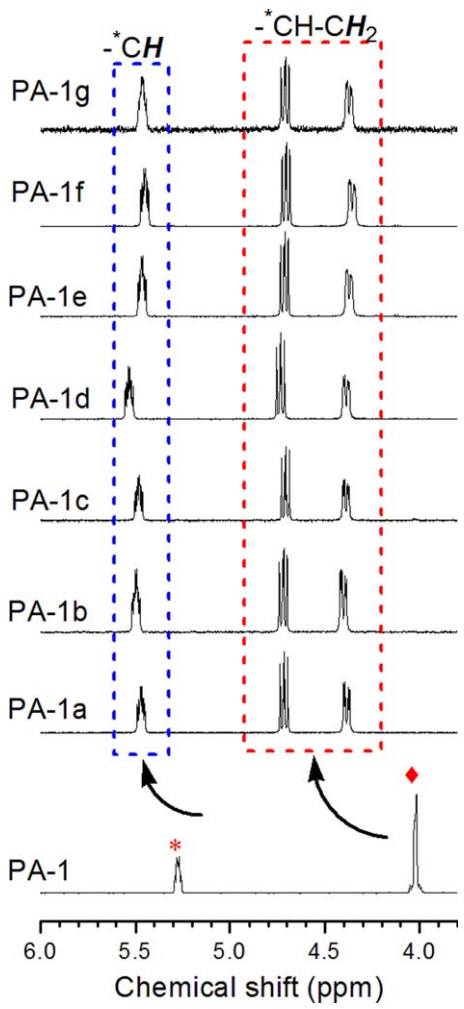


FIGURE 1 ^{1}H NMR spectra of chiral carbon atom (-C***H***-) and the methyne (-CH_2-) adjacent to the chiral carbon atom region of phenylacetylene derivatives (**PA-1** and **PA-1a~g**) at 20 °C in $CDCl_3$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with an active hydroxyl group, *N*-(4-ethynylbenzoyl)-L-phenylglycinol (**PA-1**). Various phenyl isocyanates (phenyl isocyanate, 3-chlorophenyl isocyanate, 4-chlorophenyl isocyanate, 3,5-dichlorophenyl isocyanate, 3-methylphenyl isocyanate, 4-methylphenyl isocyanate, and 3,5-dimethylphenyl isocyanate) were then used to react with the active hydroxyl of **PA-1** in good yields respectively, to produce a series of novel monomers with various phenylcarbamate groups, (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl phenylcarbamate **(PA-1a),** (*S*)-2-(4-ethynylbenzamino)- 2-phenylethyl 3-chlorophenylcarbamate **(PA-1b),** (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 4-chlorophenylcarbamate **(PA-1c),** (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3,5-dichlorophenylcarbamate **(PA-1d),** (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3-methylphenylcarbamate **(PA-1e),** (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 4-methylphenylcarbamate **(PA-1f),** and (*S*)-2-(4-ethynylbenzamino)-2-phenylethyl 3,5-dimethylphenylcarbamate **(PA-1g)**. The ^{1}H NMR spectra were used to characterize the monomer structure (see Experimental Section for details). The acetylenyl protons of these monomers appeared at about 3.18-3.20 ppm. Compared with the ^{1}H NMR spectrum of **PA-1**, the proton resonance signals on the chiral carbon atom of **PA-1a~g** shifted downfield and the proton signals of the methyne adjacent to the chiral carbon atom split after the introduction of the phenylcarbamate groups to **PA-1** (Fig. 1). The optical rotations of the phenylacetylene derivitives also varied with the change in the monomer structures (Table 1); **PA-1** showed a high levorotatory optical rotation ($[\alpha]_D^{20} = -87.0°$) in DMF, while the optical rotation values of **PA-1a~g** were quite low ($[\alpha]_D^{20} = -9$ to $-16°$ in DMF, though the sense of the optical rotations was the same.

To obtain the stereoregular poly(phenylacetylene)s and to investigate the influence of the various phenylcarbamate pendants on the helical conformation and chiral recognition abilities, the monomers were polymerized using $Rh(nbd)BPh_4$ as the catalyst and the polymerization results are shown in Table 2. **PPA-Phg-1** and **PPA-Phg-1a~g** were synthesized in DMF using the corresponding monomers with 0.03 M as the monomer concentration. The SEC profiles of all the polymers were monomodal with high molecular weights. Figure 2 depicts the ^{1}H NMR spectra of **PPA-1** and **PPA-1a** in DMSO-d_6 at 80 °C. The ^{1}H NMR spectra showed the characteristic signals due to the main chain proton at 5.78 ppm for **PPA-1** and at 5.66 ppm for **PPA-1a**, respectively. These signals suggest the formation of the highly *cis-transoidal* stereoregular structure of the poly(phenylacetylene) main chain.[27–30] For **PPA-1a**, there are two resonances assigned to the N-H protons; the signal in the lower field at 9.20 ppm was due to the N-H of the phenylcarbamate residues, while the signal at 8.41 ppm was attributed to the N-H of the amide groups, which shifted downfield after the introduction of a phenylcarbamate group. Figures 3 and 4 show the ^{1}H NMR spectra of the polymers bearing phenylcarbamate pendants (**PPA-1a~g**) in DMSO-d_6 at 80 °C. The ^{1}H NMR spectra of these polymers showed the characteristic signals due to the main chain proton at 5.55 to 5.70 ppm, indicating the stereoregular *cis-transoid* configuration in the main chains of these poly(phenylacetylene)s. As shown in Figure 3, the N-H proton signals of the amide groups in **PPA-1a~d** showed no obvious shift, while the N-H proton signals assigned to the phenylcarbamate residues in **PPA-1b~d** shifted downfield compared with **PPA-1a**. In Figure 4, the

TABLE 1 Specific Rotations of **PA-1** and **PA-1a~g** in DMF

	PPA-1	PPA-1a	PPA-1b	PPA-1c	PPA-1d	PPA-1e	PPA-1f	PPA-1g
$[\alpha]_D^{20}$	−87.0	−15.6	−15.3	−10.4	−9.7	−13.7	−12.0	−14.3

TABLE 2 Polymerization Results of **PA-1** and **PA-1a~g**

Polymer [a]	Yield/%	M_n [b] ($\times 10^{-5}$)	PDI [b]
PPA-1	97.0	4.15	3.88
PPA-1a	97.3	3.29	5.03
PPA-1b	90.0	4.05	3.95
PPA-1c	97.0	3.32	4.29
PPA-1d	99.3	3.95	4.76
PPA-1e	92.5	4.40	3.24
PPA-1f	93.3	3.85	2.98
PPA-1g	93.2	4.64	3.10

[a] Polymerization condition: catalyst, $Rh(nbd)BPh_4$; solvent, DMF; [Monomer]/[$Rh(nbd)BPh_4$] = 50/1; [Monomer] = 0.03 M; temperature, 28 °C; time, 24 h.
[b] Determined by SEC in DMF containing lithium chloride (0.01 M) at the flow rate of 0.4 mL min^{-1}, and using polystyrene standards.

phenylcarbamate N-H proton signals in **PPA-1e~g** shifted to a high field compared with **PPA-1a**, though the amide N-H proton signals showed almost no shift. This means that the phenylcarbamate N-H protons shifted downfield when the aromatic rings of the phenylcarbamates have an electron-withdrawing substituent (chloro group) (**PPA-1b~d**), and shifted to a high field when the aromatic rings of the phenylcarbamates have an electron-donating substituent (methyl group) (**PPA-1e~g**). The chemical shifts of the phenylcarbamate N-H resonances significantly depended on the acidity of the N-H protons and shifted downfield with an increase in the acidity of the N-H groups of the phenylcarbamate residues.[25,31] Therefore, the acidity of the phenylcarbamate N-H protons of these polymers may be as follows: **PPA-1d** > **PPA-**

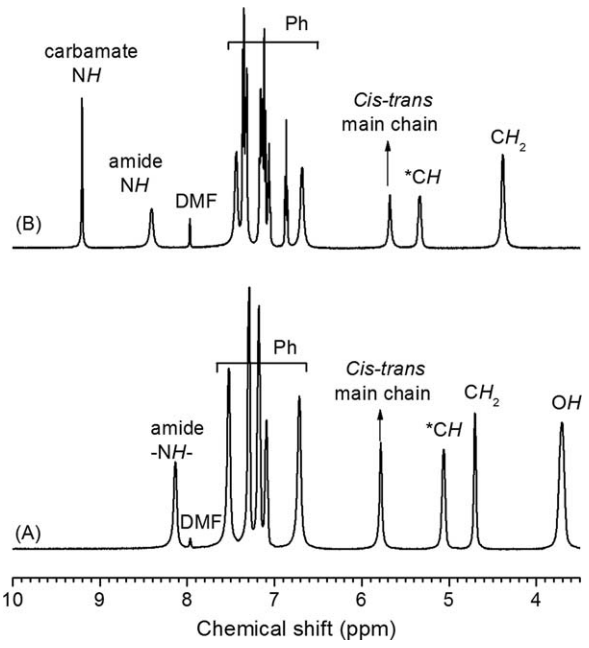


FIGURE 2 ^{1}H NMR spectra of (A) **PPA-1** and (B) **PPA-1a** in DMSO-d_6 at 80 °C.

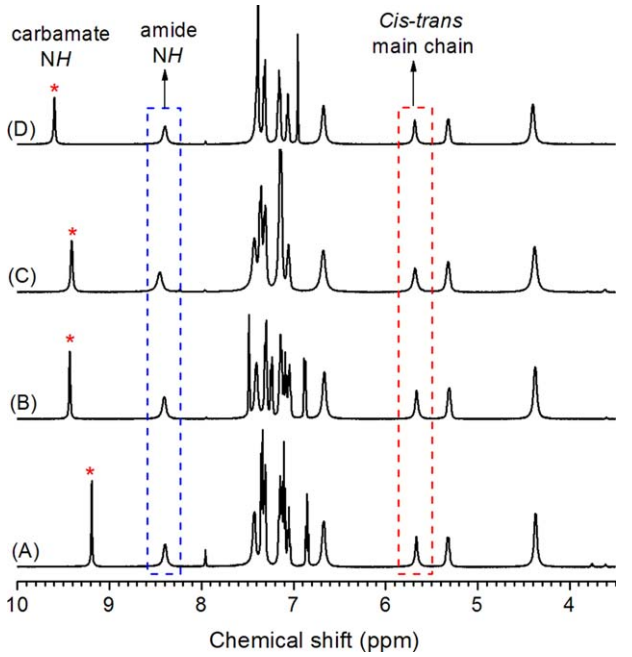


FIGURE 3 ^{1}H NMR spectra of poly(phenylacetylene) derivatives bearing chloro-substituted phenylcarbamate pendants in DMSO-d_6 at 80 °C ((A) **PPA-1a**, (B) **PPA-1b**, (C)**PPA-1c**, (D) **PPA-1d**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

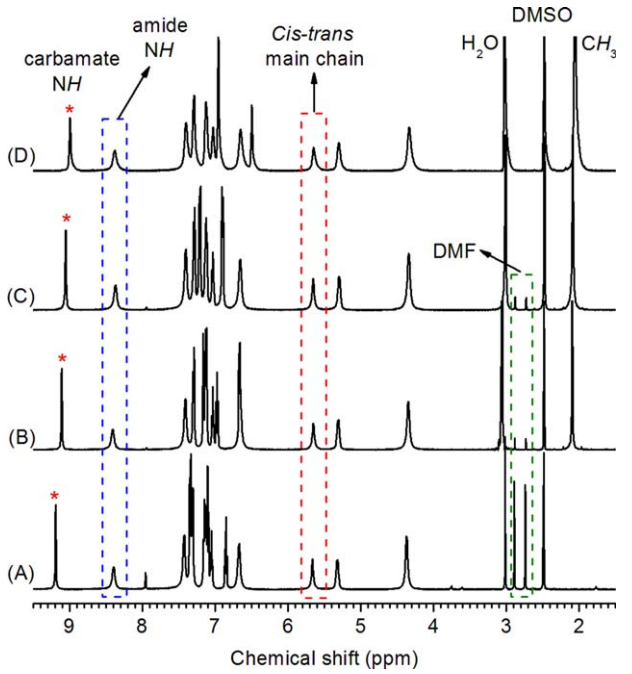


FIGURE 4 ^{1}H NMR spectra of poly(phenylacetylene) derivatives bearing methyl-substituted phenylcarbamate pendants in DMSO-d_6 at 80 °C ((A) **PPA-1a**, (B) **PPA-1e**, (C) **PPA-1f**, (D) **PPA-1g**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 3 Solubility of **PPA-1** and **PPA-1a~g**

Polymer	MeOH	$CHCl_3$	acetone	THF	DMF	DMAc	DMSO	Hexane	2-Propanol
PPA-1	−	−	−	+	+ +	+ +	+ +	−	−
PPA-1a	−	+	−	+	+ +	+ +	+ +	−	−
PPA-1b	−	+ +	+	++	+ +	+ +	+ +	−	−
PPA-1c	−	+	−	++	+ +	+ +	+ +	−	−
PPA-1d	−	+	−	+	+	+ +	+ +	−	−
PPA-1e	−	+ +	−	+	+ +	+ +	+ +	−	−
PPA-1f	−	+	−	+ +	+ +	+ +	+ +	−	−
PPA-1g	−	+ +	−	+ +	+ +	+ +	+ +	−	−

+ +, soluble, +, partly soluble, −, insoluble.

1c ≈ PPA-1b > PPA-1a > PPA-1e > PPA-1f > PPA-1g. Furthermore, the more acidic N-H protons of the phenylcarbamate groups probably have a much stronger interaction with the adjacent L-phenylglycinol or phenylcarbamate residues via hydrogen bonds, which induce and maintain a stable arrangement of the polymer main chain and the pendants. In addition, the specific association of the N-H group with DMSO, a typical hydrogen bonding solvent, should also not be ignored in this case.[32,33]

The solubilities of all the obtained polymers in several organic solvents are shown in Table 3. All the polymers were essentially soluble in polar solvents, such as DMAc, DMSO, and DMF, and insoluble in MeOH, hexane, and 2-propanol. Moreover, the solubility of these polymers in $CHCl_3$, acetone, and THF is somewhat different probably due to the different polarity of the carbamate groups depending on the substituent groups on the phenylcarbamate pendants.

Chiroptical Properties of the Polymers

The specific optical rotations ($[\alpha]_D^{20}$) of the obtained polymers (**PPA-1** and **PPA-1a~g**) in different solvents were determined in order to investigate the chiroptical properties of these polymers, and the results are shown in Table 4. As expected, the polymers exhibited high optical rotations in good solvents, especially in DMF. The optical rotations of all the polymers were positive in the tested solvents, though the corresponding monomers showed low negative optical rotations in DMF. As examples, **PPA-1** and **PPA-1b** showed $[\alpha]_D^{20}$ values of $+443^\circ$ and $+360^\circ$, respectively, in DMF, while the optical rotations of the corresponding monomers **PA-1** and **PPA-1b** were -87.0° and -15.3°, respectively, in the same solvent. The opposite and high optical rotations of the polymers suggest that a new structure, most likely a secondary helical structure, must be formed in the polymer chains.[34–37] The optical activities of the polymers were influenced by the helicity of the polymer backbones. Furthermore, the $[\alpha]_D^{20}$ values of the polymers obviously varied with the solvents. This may be attributed to the polarity and hydrogen-bonding ability of the solvents. The optical activities of the polymers were dependent on the solvents, suggesting that the polymers possess a dynamic helical structure highly dependent on the solvents. Moreover, the $[\alpha]_D^{20}$ values of the different polymers in the same solvent also varied with the unsubstituted or substituted phenylcarbamate residues as pendants, indicating that the chiral structures of these poly(phenylacetylene)s changed by altering the functional pendants.

The chiroptical properties of **PPA-1** and **PPA-1a~g** were also investigated using circular dichroism (CD) to confirm their helical structures. Figure 5 shows the CD and UV-Vis absorption spectra of the polymers in various solvents at room temperature. All the polymers exhibited intense Cotton effects biased by the covalently bonded L-phenylglycinol or its phenylcarbamate derivatives as pendants in the UV-Vis wavelength range from 300 nm to 550 nm, in which the π-conjugation of the polymer backbone typically appears. These distinctive Cotton effects clearly indicated that these polymers definitely possess a predominantly one-handed helical conformation induced by the chiral pendants of L-phenylglycinol or its phenylcarbamate derivatives.[21,38,39] These results suggest that the side groups of the polymers must be regularly arrayed in the helical structures.

Similar to the $[\alpha]_D^{20}$ values, the chain helicity of the polymers were also sensitive to solvents and exhibited obvious changes in their CD spectral patterns and intensities.

TABLE 4 Specific Rotations of **PPA-1** and **PPA-1a~g** in Different Solvents

Polymer	In DMF	In DMAc	In $CHCl_3$	In THF	Monomer[a]
PPA-1	+443	+163	—	—	−87.0
PPA-1a	+268	+123	—	—	−15.6
PPA-1b	+360	+58	+169	+102	−15.3
PPA-1c	+268	+41	—	+28	−10.4
PPA-1d	—	+59	—	—	−9.70
PPA-1e	+283	+75	+273	—	−13.7
PPA-1f	+206	+130	—	+4.7	−12.0
PPA-1g	+312	+105	+115	+98	−14.3

[a] Solvent: DMF. "−" means solubility of the polymer in the solvent is not sufficient for the measurement.

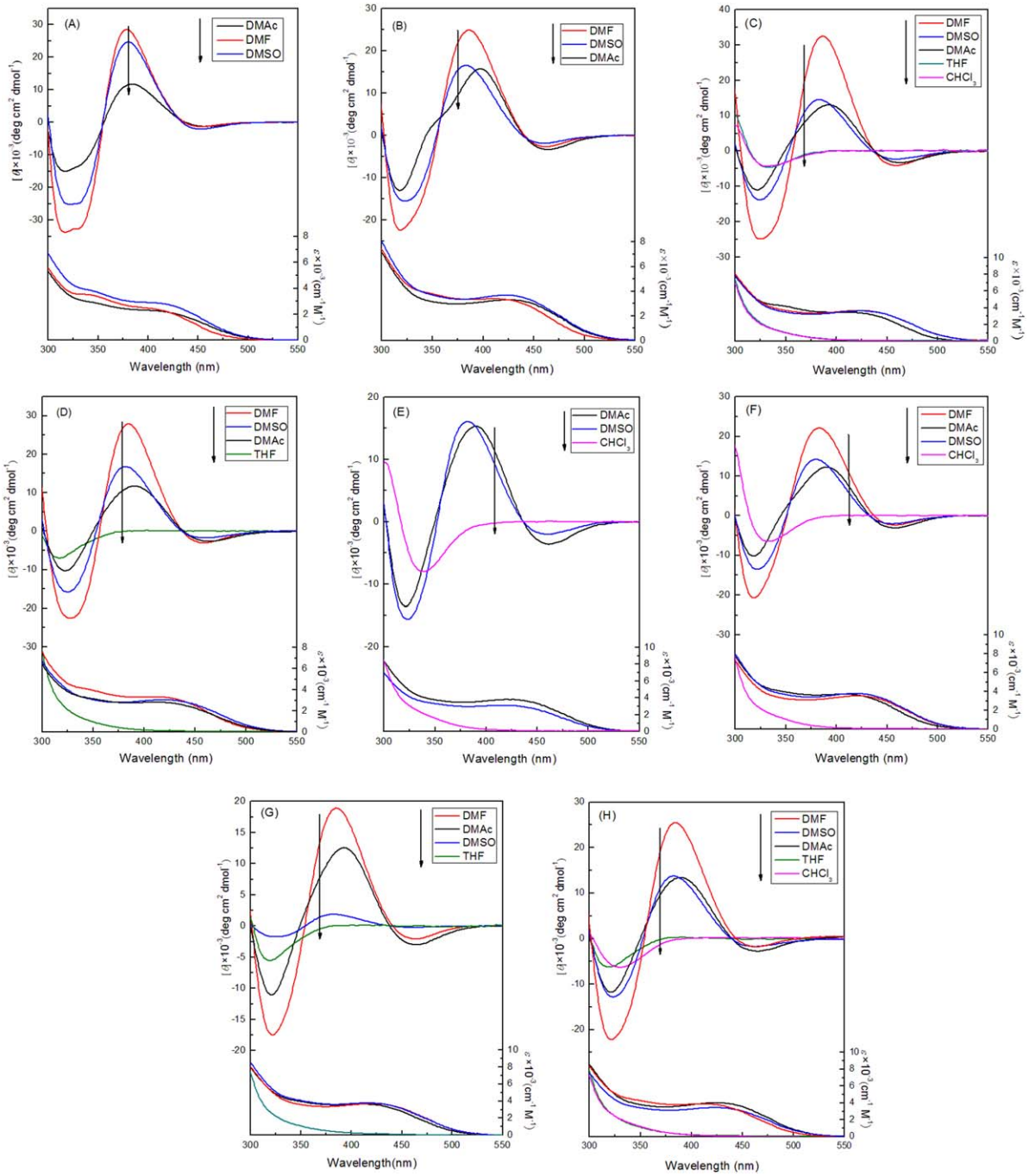


FIGURE 5 CD (upper) and UV-Vis (lower) spectra of **PPA-1** and **PPA-1a**~g in various solvents at 25 °C ($c = 1$ mg/mL) ((A) **PPA-1**, (B) **PPA-1a**, (C) **PPA-1b**, (D) **PPA-1c**, (E) **PPA-1d**, (F) **PPA-1e**, (G) **PPA-1f**, (H) **PPA-1g**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Although most polymers induced similar split-type Cotton effects in DMF, DMSO, and DMAc (i.e., the first negative Cotton effect at 465 to 450 nm, the second positive Cotton effect at 395–375 nm and the third negative Cotton effect at 335–315 nm), they showed quite different split-type Cotton effects in tetrahydrofuran (THF) and chloroform ($CHCl_3$) (i.e., the first negative Cotton effect at 338~330 nm, the second positive Cotton effect at 300 nm or lower than 300 nm) with a large blue-shift in the UV-Vis absorption spectra. These results mean that **PPA-1** and **PPA-1a~g** actually have dynamic helical conformations in the different solvents. The variation in the Cotton effects may originate from the polarity and hydrogen-bonding ability of the solvents. The solvents may have an important influence on the hydrogen-bond formation of L-phenylglycinol or its phenylcarbamate derivatives arrayed with a predominant screw-sense along

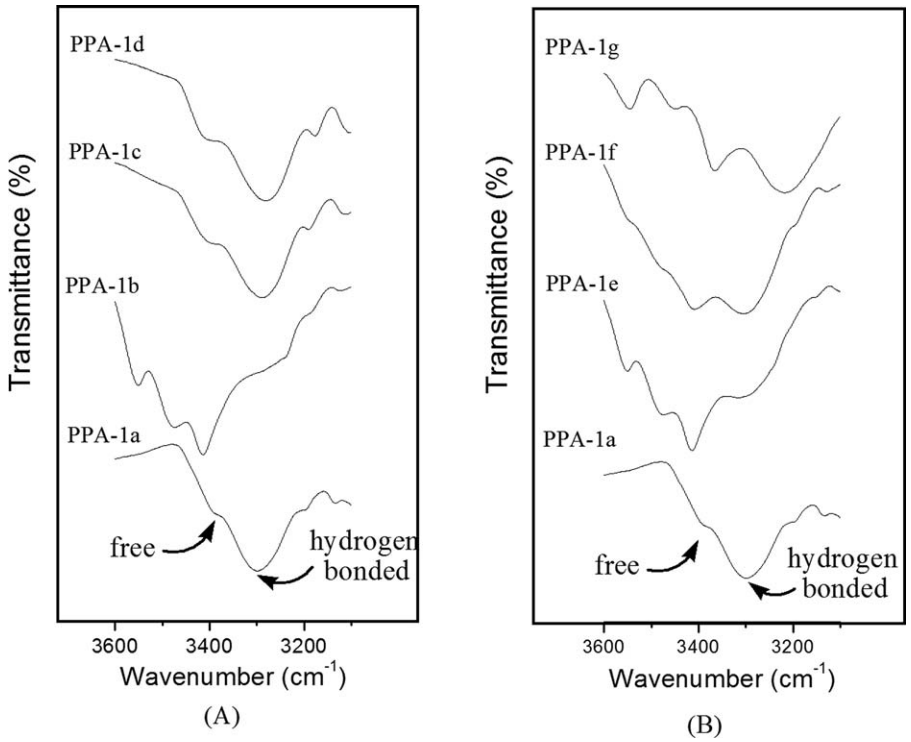


FIGURE 6 IR spectra of N–H region of PPAs bearing phenylcarbamate residues (A) **PPA-1a~d**, (B) **PPA-1a,** and **PPA-1e~g**.

the polymer backbones. The blue-shifts in the UV-Vis absorption spectra can be ascribed to a change in the twist angle of the conjugated double bonds, and the polymers may have a tightly twisted helical conformation in THF and $CHCl_3$.[40,41]

Intramolecular Hydrogen Bonding in the Polymers PPA-1a~g

The IR spectra of the phenylcarbamate N-H of the polymers **PPA-1a~g** are depicted in Figure 6. Two N-H peaks were observed in the IR spectra of these polymers. One peak in the higher wavenumber region was assigned to a free N-H bond and the other peak in the lower wavenumber region was due to an N-H group involved in the intramolecular hydrogen bond between the adjacent phenylcarbamate residues or amide groups arrayed along the polymer backbones.[27,28] Figure 6(A) shows that **PPA-1a**, **PPA-1c**, and **PPA-1d** possess a significant amount of hydrogen bonding N-Hs and a lower amount of free N-Hs, while **PPA-1b** possesses a low amount of hydrogen bonding N-Hs. The hydrogen bond may make the phenylcarbamate residues arrayed with a predominant screw-sense along the polymer helical main chains, leading to the formation of a regular arrangement of phenylcarbamate residues. The low content of the hydrogen bonding N-H in **PPA-1b** is probably due to the significant steric hindrance of the chloro-substituents at the meta-position, which prevents the intramolecular hydrogen bonding between the adjacent phenylcarbamate residues, resulting in the less regular arrangement of the phenylcarbamate residues along the polymer helical main chain. The hydrogen bonding N-H of **PPA-1b** may be assigned to the intramolecular hydrogen bonding between the adjacent amide groups, which induce and stabilize the dynamic helical conformation of the polymer main chain. The results in Figure 6(B) indicate that the methyl-substituents showed more steric hindrance by the phenylcarbamate residues than the corresponding chloro-substituents (except for the meta-position). The significantly lower amount of hydrogen bonding N-Hs of **PPA-1e** also suggests the greater steric hindrance of the substituents at the meta-position.

Chiral Recognition of PPA-1 and PPA-1a~g

PPA-1 and PPA-1a~g are expected to exhibit chiral recognition abilities, because these polymers not only have a chirality at the pendants, but also possess a predominantly one-handed helical conformation at the main chains. Their chiral recognition abilities were evaluated as the CSPs by HPLC using the thirteen tested racemates shown in Figure 7.

The resolution results of the thirteen racemates (**3–15**) on **PPA-1** and **PPA-1a** are summarized in Table 5. The pendant of **PPA-1a** is an unsubstituted phenylcarbamate derivative of **PPA-1**. These two polymers showed different chiral recognition abilities under the same chromatographic conditions. The retention factor, k_1' $[=(t_1 - t_0)/t_0]$, for the first eluted enantiomer in Table 5 is the factor indicating the interaction strength between a CSP and the corresponding enantiomer, and can be obtained from its elution time t_1 and the dead time t_0. **PPA-1a** showed different k_1' values compared with those of **PPA-1** due to the introduction of the unsubstituted phenylcarbamate residue. The separation factor α, which is directly correlated to the chiral recognition ability of a CSP,

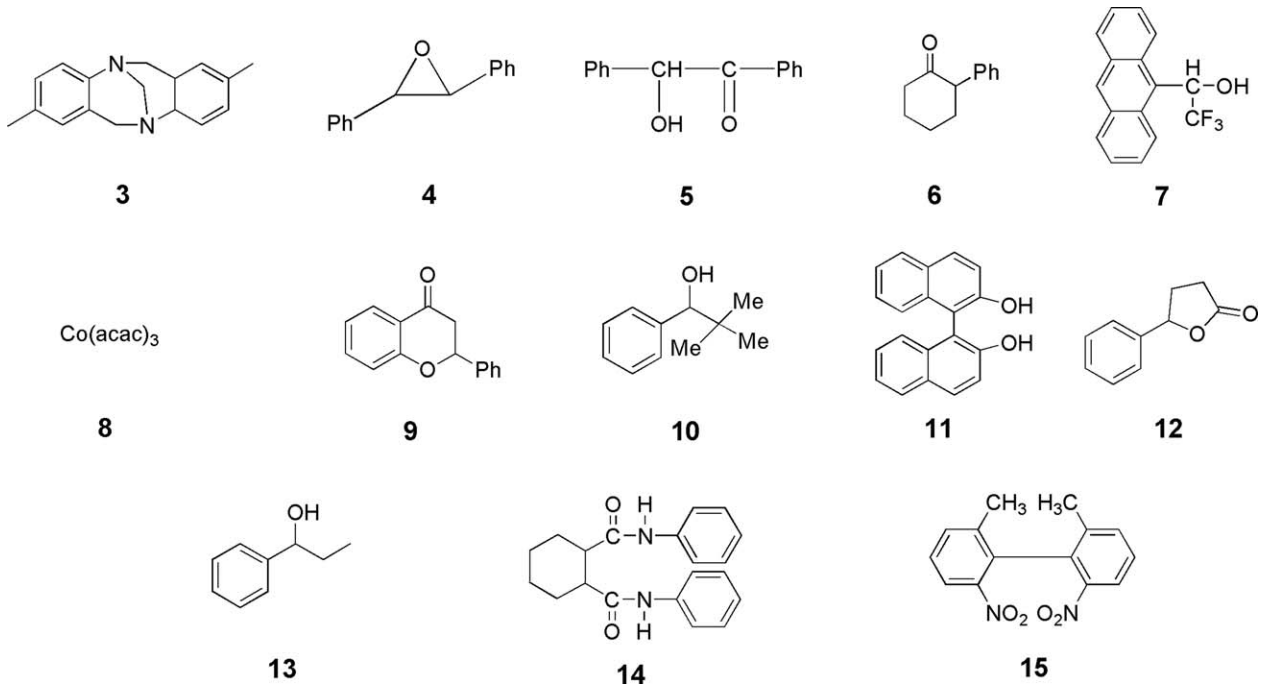


FIGURE 7 Structures of racemates.

is an important factor for evaluating a CSP. If α is equal to 1.00, this means no chiral recognition, and the higher the α value, the better chiral recognition ability of a CSP. As shown in Table 5, **PPA-1** bearing L-phenylglycinol as pendents exhibited an efficient chiral recognition for racemates **4**, **5**, **7**, **11**, **12**, and **15**, while **PPA-1a** with the phenylcarbamate residue seems to show much lower recognition abilities. Although the reason for the low chiral recognition ability of **PPA-1a** is not clear at present, it may be ascribed to the change in the chiral recognition sites as described below. The helical structure of the poly(phenylacetylene)s consists of the main chain helicity and the regular arrangement of the side chains along the main chain, and the side chain groups probably form hydrogen bonds between each other. The hydrogen bonds and steric hindrance of the side chain groups can alter the conformation of the helical structure, accompanying the change in the chiral recognition abilities. The helical grooves exist along the main chain of **PPA-1** and **PPA-1a**. For **PPA-1**, the phenyl amide groups should be arrayed inside of the helical grooves, and the L-phenylglycinol residues should be arrayed outside of the helical grooves.[42,43] The chiral recognition sites of **PPA-1** are mainly on the amide and L-phenylglycinol residue. The side chain of **PPA-1a** is longer than that of **PPA-1**. For **PPA-1a**, the phenylcarbamate residues should be arrayed outside of the helical grooves,[42,43] and the enantiomers may predominantly interact with the phenylcarbamate residues outside the grooves through the formation of intermolecular hydrogen bonds. The difference in the chiral recognition sites of **PPA-1** and **PPA-1a** must lead to the different chiral recognition abilities.

In order to clarify the influence of the electron-withdrawing substituents and the electron-donating substituents of the phenylcarbamate residues on chiral recognition abilities, the poly(phenylacetylene)s, **PPA-1b~d**, with chlorosubstituted phenylcarbamate residues as pendants and **PPA-1e~g** with methyl-substituted phenylcarbamate residues as pendants were synthesized. Their chiral recognition abilities were evaluated using the thirteen tested racemates. The resolution results of the racemates on **PPA-1a~d** are summarized in Table 6. As already discussed, the introduction of the

TABLE 5 Resolution of Racemates on **PPA-1** and **PPA-1a**[a]

	PPA-1		PPA-1a	
Racemates	k'_1	α	k'_1	α
3	0.50 (-)	~1	0.88	1
4	0.33 (-)	1.42	0.60	1
5	5.02 (-)	1.08	4.20 (-)	~1
6	1.39 (+)	~1	7.93 (-)	~1
7	7.99 (-)	1.33	3.91	1
8	2.42	1	5.31	1
9	1.64	1	3.01 (-)	~1
10	0.46 (+)	~1	0.53	1
11	14.82 (-)	1.14	2.44 (-)	~1
12	8.04 (-)	1.04	8.81 (-)	1.04
13	1.15	1	0.72	1
14	3.12	1	1.29	1
15	6.60 (-)	1.07	6.22 (-)	1.11

[a] Column: 25 cm × 0.20 cm id. Coating solvent: DMF. Eluent: hexane/2-propanol (95/5, v/v). Flow rate: 0.1 mL/min. The signs in parentheses represent the optical rotation of the first-eluted enantiomer.

TABLE 6 Resolution of Racemates on Helical Poly(phenylacetylene)s Bearing Phenylcarbamate and Chloro Substituted Phenylcarbamate Residues (**PPA-1a~d**)[a]

	PPA-1d (3,5-Cl_2)[b]		**PPA-1c** (4-Cl)[c]		**PPA-1b** (3-Cl)[c]		**PPA-1a** (H)[c]	
Racemates	k'_1	α	k'_1	α	k'_1	α	k'_1	α
3	1.28(+)	1.13	0.93(−)	∼1	0.90(−)	∼1	0.88	1
4	0.30	1	0.47	1	0.41	1	0.60	1
5	3.11(−)	1.79	4.74(−)	∼1	3.78	1	4.20(−)	∼1
6	1.61	1	2.05	1	1.47	1	7.93(−)	∼1
7	1.48	1	4.60(+)	∼1	3.17	1	3.91	1
8	8.08(+)	1.11	9.14(+)	1.50	3.35(+)	∼1	5.31	1
9	1.34	1	2.28(−)	∼1	1.94	1	3.01(−)	∼1
10	0.19	1	0.35	1	0.31	1	0.53	1
11	8.93(−)	1.52	16.84(−)	1.07	14.46(−)	∼1	2.44(−)	∼1
12	2.99(−)	1.28	7.59(−)	1.03	7.92	1	8.81(−)	1.04
13	0.47	1	0.72(−)	∼1	0.76(−)	∼1	0.72	1
14	0.68	1	0.77	1	0.83	1	1.29	1
15	4.49(−)	1.71	6.17(−)	∼1	5.54	1	6.22(−)	1.11

[a] Column: 25 cm × 0.20 cm i.d. Eluent: hexane/2-propanol (95/5, v/v). Flow rate: 0.1 mL/min. The signs in parentheses represent the optical rotation of the first-eluted enantiomer.

[b] Coating solvent: DMAc.
[c] Coating solvent: DMF.

chloro-substituent (electron-withdrawing) may increase the acidity of the phenylcarbamate N-H groups, i.e., the acidity of these four polymers may be as follows: **PPA-1d** > **PPA-1c** ≈ **PPA-1b** > **PPA-1a**. In Table 6, the polymers from left to right are listed in the order of decreasing acidity of the N-H groups of the phenylcarbamate residues. As can be seen from Table 6, **PPA-1a~d** showed different chiral recognition abilities under the same chromatographic conditions. Their chiral recognition abilities varied with the position and the number of chloro-substituents. It seems that the chiral recognition abilities were improved with the increase in the acidity of N-H groups, probably because stronger interactions were formed between the polymers and some racemic compounds via hydrogen bonds. **PPA-1d** with the most acidic N-H groups due to the 3,5-dichlorophenylcarbamate residues among the four polymers, exhibited a higher chiral recognition than the others. **PPA-1d** showed an efficient chiral recognition for racemates **3**, **5**, **8**, **11**, **12**, and **15**. Moreover, the racemates **5**, **11**, **12**, and **15** were resolved with a baseline separation or nearly baseline separation. Figure 8 shows the chromatograms for racemates **5** and **15** on **PPA-1d**. The enantiomers were completely separated with the separation factors of 1.79 for **5** and 1.71 for **15**. Compared with **PPA-1d**, **PPA-1c** with the lower acidic N-H groups showed lower recognition abilities. Although the acidity of the phenylcarbamate N-H groups of **PPA-1b** is similar to that of **PPA-1c**, it exhibited a much lower chiral recognition than **PPA-1c**, and **PPA-1b** resolved only **8, 11**, and **12** with a very

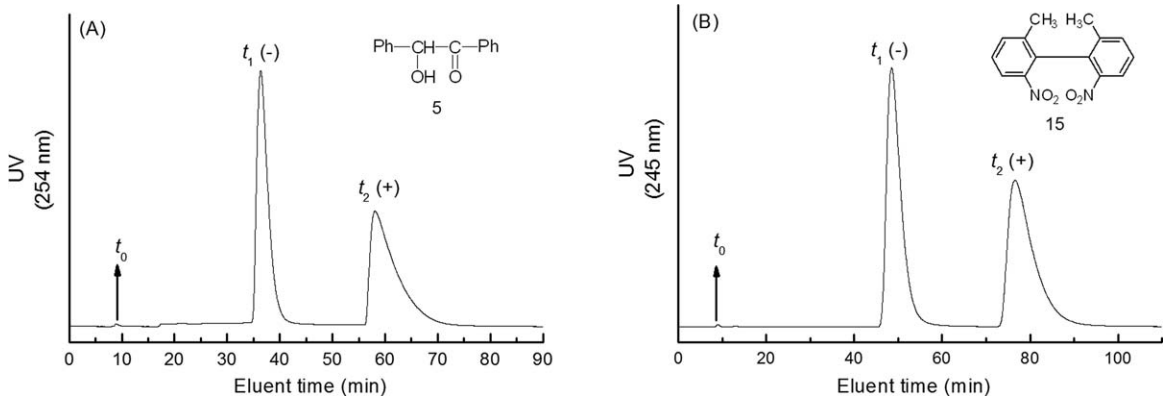


FIGURE 8 Chromatograms for the resolution of (A) benzoin (**5**) and (B) 2,2′-dimethyl-6,6′-dinitrobiphenyl (**15**) on **PPA-1d** with hexane/2-propanol (95/5) as eluent.

TABLE 7 Resolution of Racemates on Helical Poly(phenylacetylene)s Bearing Phenylcarbamate and Methyl Substituted Phenylcarbamate Residues (**PPA-1a** and **PPA-1e~g**)

	PPA-1a (H)		**PPA-1e** (3-CH3)		**PPA-1f** (4-CH3)		**PPA-1g** (3,5-(CH3)2)	
Racemates -	k'_1	α	k'_1	α	k'_1	α	k'_1	α
3	0.88	1	0.72(−)	~1	0.59(−)	~1	0.69(−)	~1
4	0.60	1	0.50(+)	~1	0.46(+)	~1	0.57(+)	~1
5	4.20(−)	~1	2.72(−)	~1	4.20(−)	~1	3.29	1
6	7.93(−)	~1	1.13(+)	1.32	1.80(+)	1.07	1.26(+)	1.06
7	3.91	1	4.62(+)	~1	5.06(+)	1.07	4.16	1
8	5.31	1	3.76(+)	1.27	4.27(+)	~1	3.88(−)	~1
9	3.01(−)	~1	2.17(−)	~1	2.21(−)	~1	1.57(−)	~1
10	0.53	1	0.34	1	0.49	1	0.27	1
11	2.44(−)	~1	26.92(−)	1.07	27.26(−)	~1	17.35(−)	1.25
12	8.81(−)	1.04	1.87	1	2.43	1	1.34	1
13	0.72	1	0.68(−)	~1	0.82	1	0.72	1
14	1.29	1	0.98	1	0.87	1	1.27	1
15	6.22(−)	1.11	6.56	1	7.01	1	5.06	1

Column: 25 cm × 0.20 cm i.d. Coating solvent: DMF. Eluent: hexane/2-propanol (95/5, v/v). Flow rate: 0.1 mL/min. The signs in parentheses represent the optical rotation of the first-eluted enantiomer.

low chiral recognition. The reason for this low ability is not clear at present, but it may be ascribed to the irregular structure of the phenylcarbamate residues along the helical main chain induced by the greater steric hindrance of the chlorosubstituents at the meta-position as discussed for the IR spectra analysis.

Table 7 shows the resolution results of the racemates on **PPA-1** and **PPA-1e~g** bearing the methyl-substituted phenylcarbamate residues. Similar to the chloro derivatives, these polymers exhibited different recognition abilities depending on the position and the number of methyl-substituents. The introduction of methyl-substituents (electron-denoting) seems to improve the chiral recognition abilities for some racemates, though the acidity of the N-H groups of the phenylcarbamate residues decreased. This is probably relevant to the substituted phenylcarbamate pendants arrayed along the helical main chains. The derivatives with the 3-methylphenylcarbamate residues can be explained as follows. As previously discussed regarding the IR spectra, the free N-H groups of the phenylcarbamate residues increased after the introduction of the 3-methyl groups, suggesting that the hydrogen bonds between the phenylcarbamate pendants were partly disturbed by the steric hindrance of the 3-methyl substituents and the main chains became less regular. However, new chiral recognition sites should be formed at the same time, resulting in the improvement of the chiral recognition abilities for some racemates. As shown in Table 7, **PAA-1e** with the 3-methylphenylcarbamate residues as pendants exhibited a higher chiral recognition than the others, and showed an efficient chiral recognition on racemates **6**, **8**, and **11**. In addition, comparing **PPA-1e** to **PPA-1b**, it is also indicated that a methyl group is probably more preferable than a chloro group as the meta-substituent of **PAA-1a**.

CONCLUSIONS

A series of novel poly(phenylacetylene) derivatives, **PPA-1** and **PPA-1a~g**, with an amide linkage bearing L-phenylglycinol and its phenylcarbamate derivatives as pendants, respectively, were synthesized to evaluate their chiral recognition as CSPs in HPLC using the thirteen racemates. The main chains of these polymers possessed helical conformations, and the pendants are arrayed along polymer main chains depending on the pendants including L-phenylglycinol and its unsubstituted or substituted phenylcarbamate residues. The chain helicities of the polymers were tunable by changing the pendants and solvents. The results of the IR and ^{1}H NMR spectra indicated that the N-H groups of the phenylcarbamate residues formed more or less hydrogen bonds, which varied with the type, position, and the number of substituents on the phenylcarbamate residues. The acidity of the phenylcarbamate N–H proton of the polymers was also influenced by the various substituents on the phenylcarbamate residues. The hydrogen bonds and the acidity of the phenylcarbamate N-H proton significantly influenced the arrangements of the phenylcarbamate pendants and the main chain helicity, and the chiral recognition abilities of the polymers depended on these stereochemical arrangements.

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