## Helical Poly(phenylacetylene)s Containing Schiff-Base and Amino Groups: Synthesis, Secondary Structures, and Responsiveness to Benzoic Acid

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ABSTRACT: Novel acetylenic monomers containing Schiff-base and amino groups, (*S*)-*N*-(4-ethynylbenzylidene)-1-phenylethanamine (**1a**), (*R*)-*N*-(4-ethynylbenzylidene)-1-phenylethanamine (**1b**), *N*-(4-ethynylbenzylidene)-1-phenylethanamine (**1c**), (*R*)-*N*-(4-ethynylbenzyl)-1-phenylethanamine (**1d**), and (*R*)-*N*-(4-ethynylbenzyl)-1-phenylethanamine (**1e**) were synthesized and polymerized with [(nbd)RhCl]<sub>2</sub>/Et<sub>3</sub>N catalyst to afford the corresponding polymers **2a-e** with moderate molecular weights ( $M_n = 9000-60,000$ ) in high yields (85–97%). All the polymers were soluble in common organic solvents including toluene, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, and DMF. Large optical rotations and strong CD signals demonstrated that **2a**, **2b**, **2d**, and **2e** take helical structures with a predominantly one-handed screw

**INTRODUCTION** The design and synthesis of artificial helical polymers have attracted considerable attention.<sup>1</sup> Such studies aim at not only the imitation of elegant and sophisticated structures of biomacromolecules such as DNA and protein in nature but also the development of novel functional materials with unique properties. Several synthetic helical polymers including polyisocyanides, polymethacrylates, polyisocyanates, polysilanes, and polyacetylenes have been successfully synthesized so far. As a category of typical conjugated polymers, polyacetylene and its derivatives have been extensively studied because of their interesting physical and chemical properties.<sup>2-5</sup> Substituted polyacetylenes can form helical structures with a predominantly one-handed screw sense by the introduction of appropriate chiral substituents into the side chain or helix-sense-selective polymerization of achiral monomers.<sup>6-9</sup> Such polymers are of great interest for potential applications as functional materials in molecular recognition,<sup>10</sup> asymmetric catalysis,<sup>11</sup> and chemical sensors<sup>12</sup> based on their electronic and optical propersense. The effects of solvents and temperature revealed that these polymers took dynamic helical structure based on the steric effect of side groups. The CD patterns of **2d** and **2e** containing free amino moieties were completely inverted by the addition of benzoic acid. Upon further addition of NaOH, the CD pattern returned to the original one, indicating the reversible conformational change of these polymers according to pH. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 5248–5256

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ties, which are derived from their conjugated main chain and secondary structures. Since the pioneering work by Ciardelli on helical poly(1-alkyne)s,<sup>6</sup> a variety of helical polyacetylene derivatives based on optically active side groups have been successfully synthesized; for example, poly(alkyl propio-late)s,<sup>13</sup> poly(*N*-propargylalkylamide)s,<sup>7</sup> poly(*N*-propargylcar-bamate)s,<sup>14</sup> and poly(methylpropargyl ester)s.<sup>15</sup> As examples of dynamic helical polymers, some polyacetylenes undergo helix/random coil transition and/or helix inversion by external stimuli such as temperature, light, and change of medium conditions including polarity and pH.<sup>16–18</sup> These properties are attractive in a wide variety of fields including life science, pharmacy, and chemical engineering.

Meanwhile, Schiff-bases are an important class of ligands in scientific research because they can be easily synthesized by the condensation of a variety of amines and aldehydes and form complexes with various metal ions.<sup>19,20</sup> Besides the extensively studied low molecular weight Schiff-bases,

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SCHEME 1 Synthesis of Schiff-base- and amine-containing polyacetylene derivatives.

various polymers containing Schiff-base moieties have been synthesized, and they exhibit interesting and important properties such as metal ion recognition, antibacterial and antifungal activities, high thermal stability, catalytic activity, and photoluminescence.<sup>21-25</sup> For instance, vertically standing nanowalls of polyazomethines on graphite are synthesized by polycondensation of diamine and dialdehyde/diketone, and the morphology and luminescent properties can be wellcontrolled.<sup>26</sup> Recent examples of polymers containing Schiffbase type groups include polystyrene,<sup>27</sup> polyacrylate,<sup>28</sup> and polynorbornene.<sup>29,30</sup> However, only a few polyacetylenes containing achiral Schiff-base groups have been reported by Balcar's and our groups so far,<sup>31,32</sup> and the studies are restricted to the polymerizability of the corresponding monomers. Recently, the research interest is focused on the chiral Schiff-bases because their metal complexes are efficient in asymmetric catalysis for a variety of enantioselective reactions such as Diels-Alder cyclization, aziridination, and hydrogenation.<sup>19,33</sup> The combination of functional Schiff-base group as a chiral auxiliary and conjugated main chain of polvacetylene will afford functional helical polymer materials, which may find potential application in asymmetric catalysis. On the other hand, the Schiff-base group can be easily changed into amino group by reduction. By using this reaction, incorporation of free amino groups into the polymer is possible, which may lead to acid-responsive helical polymers.

The present study deals with the synthesis and polymerization of novel phenylacetylenes having chiral Schiff-base moieties (**1a-c**) as well as their hydrogenated analogues with secondary amino groups (**1d** and **1e**) (Scheme 1). The secondary structure of the resultant polymers was investigated in detail. Moreover, chiroptical responsiveness of the polymer possessing secondary amino groups to benzoic acid was examined.

#### **EXPERIMENTAL**

#### Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Unity-400 spectrometer. IR spectra were measured on a BRUKER Vertex-70 spectrophotometer. The number- and weightaverage molecular weights ( $M_n$  and  $M_w$ ) of polymers were determined with a gel permeation chromatograph equipped with a Waters 515 HPLC pump and a Waters 2414 differential refractometer using THF as eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standard. Elemental analysis of monomers was carried out at the Analytical Center of Dalian University of Technology. Specific rotations ([ $\alpha$ ]<sub>D</sub>) were measured on a JASCO DIP-1000 digital polarimeter. CD and UV-vis spectra were recorded on a JASCO J-810 spectropolarimeter. Thermogravimetric analyses (TGA) were conducted under nitrogen at a heating rate of 10  $^{\circ}$ C/min with a Perkin-Elmer TGA7 thermal analyzer.

#### Materials

THF used for polymerization was distilled over  $CaH_2$  prior to use. Triethylamine was distilled and dried over potassium hydroxide. 4-Bromobenzaldehyde (Aladdin Co.), (*R*)-(+)-1phenylethylamine (Aldrich), (*S*)-(+)-1-phenylethylamine (Aldrich), trimethylsilylacetylene (Acros), bis(triphenylphosphine)palladium(II) dichloride (Aldrich), and [(nbd)RhCl]<sub>2</sub> (Aldrich) were used as received. Other solvents such as methanol, toluene, and CHCl<sub>3</sub> were of high purity and used without further purification. 4-Ethylnylbenzaldehyde was synthesized referring to the literature.<sup>34</sup>

#### **Monomer Synthesis**

#### (R)-N-(4-Ethynylbenzylidene)-1-Phenylethanamine (1a)

A 100 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, (*R*)-1-phenylethanamine (1.21 g, 10 mmol) and 4-ethylnylbenzaldehyde (1.3 g, 10 mmol) were dissolved in toluene (70 mL). The reaction mixture was heated at reflux temperature for 10 h. The generated water was separated with a Dean-Stark apparatus. After that, toluene in the reaction mixture was evaporated off, and the crude product was purified by recrystallization in ethanol to give light yellow crystals; yield 54%.  $[\alpha]_{\rm D} = -154^{\circ}$  (c = 0.1 g/dL, CHCl<sub>3</sub>, room temperature).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (s, 1H, CH=N), 7.72–7.23 (m, 9H, Ar*H*), 4.53 (s, 1H, N-C*H*), 3.15 (s, 1H, *H*C≡C), 1.58 (m, 3H, C*H*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.7 (*C*H=N), 145.1, 136.8, 132.4, 128.6, 128.3, 127.1, 126.8, 124.3, 83.5, 79.0, 70.0, 25.0. IR (cm<sup>-1</sup>, KBr): 3377, 3298, 3080, 3027, 2967, 2849, 1646 (C=N), 1638, 1599, 1491, 1449, 1377, 837, 763, 700. ANAL. CALCD. for C<sub>17</sub>H<sub>15</sub>N: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.32; H, 6.40; N, 5.87.

#### (S)-N-(4-Ethynylbenzylidene)-1-Phenylethanamine (1b)

This monomer was prepared by the same method as for monomer **1a** using (S)-1-phenylethanamine instead of (R)-1-phenylethanamine to give light yellow crystals. Yield 50%. [ $\alpha$ ]<sub>D</sub> = +131° (c = 0.1 g/dL, CHCl<sub>3</sub>, room temperature).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (s, 1H, CH=N), 7.73–7.24 (m, 9H, Ar*H*), 4.54 (s, 1H, N-C*H*), 3.16 (s, 1H, *H*C≡C), 1.58 (m, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.7 (*C*H=N), 145.1, 136.8, 132.4, 128.6, 128.3, 127.1, 126.8, 124.3, 83.5, 79.0, 70.0, 25.0. IR (cm<sup>-1</sup>, KBr): 3376, 3297, 3078, 3028, 2966, 2850, 1645 (C=N), 1638, 1600, 1491, 1450, 1378,



838, 763, 699. Anal. calcd. for  $C_{17}H_{15}N$ : C, 87.52; H, 6.48; N, 6.00. Found: C, 87.42; H, 6.21; N, 5.88.

#### N-(4-Ethynylbenzylidene)-1-Phenylethanamine (1c)

This monomer was prepared by the same method as for monomer **1a** using racemic 1-phenylethanamine instead of (R)-1-phenylethanamine to give light yellow crystals. Yield 50%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (s, 1H, *CH*=N), 7.73–7.24 (m, 9H, Ar*H*), 4.54 (s, 1H, N-C*H*), 3.16 (s, 1H, *H*C≡C), 1.58 (s, 3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.7 (*C*H=N), 145.1, 136.8, 132.4, 128.6, 128.3, 127.1, 126.8, 124.3, 83.5, 79.0, 70.0, 25.0. IR (cm<sup>-1</sup>, KBr): 3375, 3300, 3080, 3029, 2969, 2847, 1646 (C=N), 1638, 1598, 1490, 1450, 1378, 837, 763, 700. ANAL. CALCD. for C<sub>17</sub>H<sub>15</sub>N: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.59; H, 6.55; N, 5.73.

#### (R)-N-(4-Ethynylbenzyl)-1-Phenylethanamine (1d)

A 100 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, **1a** (1.0 g, 4.3 mmol) was dissolved in dry methanol, and sodium borohydride (NaBH<sub>4</sub>, 0.49 g, 12.9 mmol) was added. The reaction mixture was stirred under nitrogen at room temperature for 72 h. After the solvent was removed by rotary evaporation, the residue was dissolved in diethyl ether, washed with aqueous NaOH solution (1.0 mol/L; 50 mL) and water (50 mL × 3), and dried over MgSO<sub>4</sub>. The crude product was purified by silica gel chromatography with hexane/diethyl ether (1/1, v/v) as eluent to give the desired product as a colorless liquid. Yield 85%.  $[\alpha]_D = -26^{\circ}$  (c = 0.1 g/dL, CHCl<sub>3</sub>, room temperature).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.22–7.44 (m, 9H, ArH), 3.83 (m, 3H), 3.09 (1H,  $HC\equiv$ C), 1.69 (1H, NH), 1.41 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 145.5, 141.7, 132.3, 128.7, 128.2, 127.2, 126.8, 120.6, 83.8, 77.5, 57.6, 51.4, 24.6. IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3423, 3286, 2933, 2780, 2485, 2417, 2105, 1658, 1577, 1498, 1453, 1384, 1084, 1026, 920,824, 766, 701, 559. ANAL. CALCD. for C<sub>17</sub>H<sub>17</sub>N: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.41; H, 7.59; N, 5.73.

#### (S)-N-(4-Ethynylbenzyl)-1-Phenylethanamine (1e)

This monomer was prepared by the same method as for monomer **1d** using **1b** instead of **1a** to give a colorless liquid. Yield 87%.  $[\alpha]_D = +24^\circ$  (c = 0.1 g/dL, CHCl<sub>3</sub>, room temperature).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.22–7.44 (m, 9H, ArH), 3.83 (m, 3H), 3.09 (1H,  $HC\equiv$ C), 1.69 (1H, NH), 1.41 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ145.5, 141.7, 132.3, 128.7, 128.2, 127.2, 126.8, 120.6, 83.8, 77.5, 57.6, 51.4, 24.6. IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3423, 3286, 2933, 2780, 2485, 2417, 2105, 1658, 1577, 1498, 1453, 1384, 1084, 1026, 920,824, 766, 701, 559. ANAL. CALCD. for C<sub>17</sub>H<sub>17</sub>N: C, 86.77; H, 7.28; N, 5.95. Found: C, 87.12; H, 6.90; N, 5.68.

#### Polymerization

Polymerizations were carried out in a glass tube equipped with a three-way stopcock under dry nitrogen. [(nbd)RhCl]<sub>2</sub>

and Et<sub>3</sub>N were added to a monomer solution under nitrogen, and the resulting solution ( $[M]_0 = 0.25 \text{ mol/L}$ , [Rh]/ $[M]_0 = 50$ ,  $[Et_3N]/[Rh] = 10$ ) was kept at 30 °C for 4 h. The formed polymers were isolated by precipitation into a large amount of methanol or hexane, and dried to constant weight under reduced pressure; the polymer yields were determined by gravimetry.

#### **Spectroscopic Data of the Polymers**

**2a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (br, 1H, CH=N), 7.52– 6.60 (br, 9H, Ar), 5.81 (br, 1H, HC=C), 4.32 (br, 1H, NCH), 1.56 (br, 3H, HCC $H_3$ ). IR (cm<sup>-1</sup>, KBr): 3080, 3027, 2967, 2849, 1646 (HC=N), 1638, 1599, 1491, 1449, 1377, 837, 763, 700. **2b**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.82 (br, 1H, CH=N), 7.49-6.58 (br, 9H, Ar), 5.82 (br, 1H, HC=C), 4.31 (br, 1H, NCH), 1.54 (br, 3H, HCCH<sub>3</sub>). IR (cm<sup>-1</sup>, KBr): 3297, 3078, 3028, 2966, 2850, 1645 (C=N), 1638, 1600, 1491, 1450, 1378, 838, 763, 699. **2c**: <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (br, 1H, CH=N), 6.58-7.51 (br, 9H, Ar), 5.83 (br, 1H, HC=C), 4.30 (br, 1H, NCH), 1.53 (br, 3H, HCCH<sub>3</sub>). IR (cm<sup>-1</sup>, KBr): 3080, 3029, 2969, 2847, 1646 (C=N), 1638, 1598, 1490, 1450, 1378, 837, 763, 700. 2d: δ 7.81-6.20 (br, 9H, Ar), 5.82 (br, 1H, HC=C), 3.80 (br, 2H, H<sub>2</sub>CNH), 2.82 (br, 1H, HCNH), 1.56 (br, 3H, HCCH<sub>3</sub>). **2e**:  $\delta$  7.80–6.18 (br, 9H, Ar), 5.83 (br, 1H, HC=C), 3.80 (br, 2H, H<sub>2</sub>CNH), 2.82 (br, 1H, HCNH), 1.56 (br, 3H, HCCH<sub>3</sub>).

#### **RESULTS AND DISCUSSION**

#### Monomer Synthesis and Polymerization

Acetylenic monomers **1a-c** containing Schiff-base groups were synthesized by condensation of 4-ethynylbenzaldehyde with the corresponding amine according to Scheme 2. The hydrogenation of **1a** and **1b** with sodium borohydride in dry methanol gave secondary amine-containing monomers **1d** and **1e**. The structures of monomers were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectroscopies as well as elemental analysis.

Rhodium catalysts are known to be tolerant of polar and functional groups, and polymerize monosubstituted acetylenes to afford the corresponding polyacetylenes.35-37 The polymerizations of monomers **1a-e** were carried out in THF with [(nbd)RhCl]<sub>2</sub>/Et<sub>3</sub>N catalyst, whose results are listed in Table 1. Monomers 1a-c containing Schiff-base groups gave polymers **2a-c** as methanol-insoluble products with fairly high molecular weights  $(M_n = 4.7 \times 10^4 \text{ to } 6.0 \times 10^4)$  in high yields (91-97%). The polymerization of 1d and 1e having secondary amine moieties also proceeded smoothly, affording the corresponding polymers 2d and 2e in good yields (ca. 85%). Because 2d and 2e were partly soluble in methanol, which might be attributable to the affinity of polar amino groups to methanol, these polymers were isolated as hexane-insoluble products. The apparent molecular weights of 2d and 2e ( $M_{\rm n} \sim 1.0 \times 10^4$ ) were somewhat lower than those of 2a-c bearing Schiff-base moieties. This might be due to the presence of amino groups in the polymer structure, which commonly extends the retention time of GPC.



SCHEME 2 Synthesis of acetylenic monomers 1a-e.

Polymers **2a-e** showed good solubility in common organic solvents such as toluene,  $CH_2Cl_2$ ,  $CHCl_3$ , THF, and DMF.

The polymer structures were examined by IR and <sup>1</sup>H NMR spectroscopies. The monomers exhibited absorption bands at 3377 and 2100 cm<sup>-1</sup> assignable to the  $\equiv$ C-H and -C $\equiv$ Cstretching vibrations, respectively, which disappeared in the IR spectra of the polymers. The <sup>1</sup>H NMR spectra of the polymers were compatible with the IR data (see, e.g., Fig. 1). Namely, the ethynyl proton peak of the monomers was absent in the polymers, and meanwhile the azomethine proton signal at 7.8 ppm remained intact in the polymers. Thus, these results clearly indicate both conversion of the triple bond into the double bond during polymerization and no contamination with the monomer in the polymeric product. In general, Rh catalysts efficiently polymerize monosubstituted acetylenes by the insertion mechanism to give *cis*-stereoregular polyacetylenes.<sup>38,39</sup> The geometric structure of the polymers in the present study is also the case; that is, 2a-e possessed cis-rich structures (82-97%) in the main chain, which were determined by the integration ratio of *cis* vinyl proton and the other proton signals.

#### Chiroptical Properties of the Polymers Containing Schiff-Base Groups

The chiroptical properties of the polymers were examined by polarimetry, CD, and UV–Vis spectroscopy. As shown in Table

1, the polymers showed much larger  $[\alpha]_D$  values than those of the corresponding monomers, suggesting that the polymers formed helices with predominantly one-handed screw sense. The signs of  $[\alpha]_D$  of **2a** and **2b** as well as **2d** and **2e**, enantiomerically isomeric polymers, were opposite to each other and the absolute values were almost the same, as expected. Figure 2 depicts the CD and UV-Vis spectra of 2ac measured in DMF. 2a and 2b showed split-type intense Cotton effects at a UV-Vis region of 260-450 nm, where absorptions due to  $\pi$ -conjugated structure of the polymers typically appear. In contrast, the corresponding monomers showed rather weak CD signals and a strong UV absorption only in the range of 250-280 nm. These results indicate that the polymers take helical structures with predominantly one-handed screw sense based on higher-order structures of polyacetylene backbone. Polymers 2a and 2b having pendant groups with opposite absolute configurations exhibited mirror-image CD spectra at 260-450 nm and their optical rotations possessed practically the same absolute values with opposite signs (see Table 1; 2a:  $-412^{\circ}$  and 2b:  $+402^{\circ}$ ). Thus, it is concluded that these polymers have helical structures with opposite screw senses and that the helix sense is determined by the chirality of the Schiff-base groups.

Figure 3 illustrates the CD and UV-Vis spectra of **2a** measured in various solvents. **2a** showed CD profiles similar to

	$[\alpha]_{D}^{b}$ (deg)	Yield (%)	$M_{\rm n}  imes 10^{-4{\rm e}}$	$M_{\rm w}/M_{\rm n}^{\rm e}$	<i>cis</i> Content <sup>f</sup> (%)	[α] <sub>D</sub> <sup>g</sup> (deg)
1a	-154	96 <sup>c</sup>	4.7	3.2	96	-412
1b	+131	91 <sup>°</sup>	4.8	4.9	96	+402
1c	0	97 <sup>c</sup>	6.0	4.7	97	0
1d	-26	85 <sup>d</sup>	0.9	4.5	82	-108
1e	+24	87 <sup>d</sup>	1.0	4.8	83	+115

е

calibration.

<sup>f</sup> Determined by <sup>1</sup>H NMR.

TABLE 1 Polymerizations of Monomers 1a-e<sup>a</sup>

 $^{\rm a}$  Polymerization conditions: in THF, 30 °C, 4 h,  $[M]_0=0.25$  mol/L,  $[M]_0/$  [Rh] = 50.

 $^{\rm b}$  Measured by polarimetry at 20 °C,  $c\,{=}\,0.10$  g/dL in CHCl<sub>3</sub>.

<sup>c</sup> Methanol-insoluble part.

<sup>d</sup> Hexane-insoluble part.



Determined by GPC using THF as eluent with a polystyrene

<sup>g</sup> Measured by polarimetry at 20 °C, c = 0.10 g/dL in DMF.



FIGURE 1 <sup>1</sup>H NMR spectra of 1a and 2a measured in CDCl<sub>3</sub>.



**FIGURE 2** CD and UV-Vis spectra of 1a and 2a-c measured in DMF at 20 °C (c = 0.05 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 3** CD and UV-Vis spectra of 2a measured in various solvents at 20 °C (c = 0.05 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

one another in these solvents. The intensity of the CD signals increased in the order of  $\text{CHCl}_3 < \text{THF} < \text{CH}_2\text{Cl}_2 < \text{DMF} < \text{toluene, while the molar absorptivity ($\varepsilon$) of UV-Vis spectra slightly increased in the same order. This order of solvents is not related with the polarity and basicity of solvents. These findings suggest that the present helical structure originates from steric effects and not from hydrogen bonding. Further, the variation of Cotton effects with solvents indicates that the helix is a dynamic one.$ 

We further examined the thermal stability of the helical conformation of the polymers. Figure 4 shows the temperature dependence of the CD and UV-vis spectra of 2a measured in DMF. The CD intensity decreased as the temperature was raised from 0 to 80 °C, and the molar ellipticity value [ $\theta$ ] became 50% of the value of 0 °C at 80 °C. In general, the helicity of polymer chain tends to decrease with increasing temperature, because the thermal perturbation activates the randomization of chain conformations, and the present temperature dependence of helix agrees with this tendency. The slight decrease in UV-Vis absorption with increasing temperature is also explicable in terms of thermal perturbation of polymer conformation. The magnitude of the CD signal reversibly recovered the original one by lowering the temperature. Similar results were observed with 2b and other helical polyacetylene derivatives including poly(1-methylpropargyl-N-alkylcarbamate)s,<sup>40</sup> poly(ethynylcarbazole),<sup>41</sup> and



**FIGURE 4** CD and UV-Vis spectra of 2**a** in DMF measured at various temperatures (c = 0.05 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

poly(phenylacetylene)s.<sup>42</sup> This is a characteristic of the dynamic helical conformation in polyacetylene derivatives.<sup>1</sup>

# Chiroptical Properties of the Polymers Containing Secondary Amino Groups

As aforementioned, polymers containing free secondary amino groups, 2d and 2e, were successfully synthesized by the polymerization of the corresponding monomers. Polymer 2d exhibited intense Cotton effects in THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and DMF (Fig. 5), and moderate solvent effects were observed. The molar absorptivity of UV-Vis spectra increased in the order of  $THF < CH_2Cl_2 < CHCl_3 < DMF\!\!,$  and the intensity of CD signal increased in the same order. Polymers 2d and 2e exhibited mirror-image CD spectra at 250-430 nm to each other (Fig. 6), which is consistent with their  $[\alpha]_D$  values. It is hence concluded that these polymers bearing amino groups also adopt helical conformations with an excess of predominantly one-handed screw sense in the solvents. Like the case of 2a and 2b, the CD intensity of 2d decreased by raising the temperature from 0 to 80 °C (Fig. 7), which indicates that the degree of predominance of one-handedness of screw sense decreased. A similar result was observed also with 2e. When the CD intensities of polymers are compared, the degrees of predominance of one-handedness of screw sense are somewhat lower in 2d and 2e than those in 2a and 2b.



**FIGURE 5** CD and UV-Vis spectra of 2d measured in various solvents (c = 0.05 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 6** CD and UV-Vis spectra of 2d and 2e measured in DMF at 20 °C (c = 0.05 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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**FIGURE 7** CD and UV-Vis spectra of 2d in DMF measured at various temperatures (c = 0.05 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

#### Responsiveness of 2d and 2e to Benzoic Acid

Polyacetylenes bearing free carboxy or amino groups in side chains change the conformation according to pH.43-46 For instance, the helix content of poly(N-propargylamides) with free amino groups decreases upon addition of o-phthalic acid,<sup>45</sup> and poly[(1*R*,2*S*)-*N*-(4-ethynylbenzyl)norephedrine] exhibits a unique helix-helix transition upon complexation with chiral acids.<sup>46</sup> Thus, it is anticipated that the conformational structure of 2d and 2e with free amino groups is affected by the addition of acids. In fact, as seen in Figure 8, a drastic change occurred in the CD spectrum of 2d in the presence of benzoic acid in CHCl<sub>3</sub>. With increasing amount of benzoic acid, the CD signals at about 325 and 380 nm gradually decreased, and they almost disappeared upon addition of an equimolar amount of acid. Further addition of benzoic acid gave rise to an opposite-signed CD signals with the same shapes. These results suggest that helix inversion progressively proceeded by complexation of the side-chain amino groups with relatively small amounts of benzoic acid. Thus, an achiral benzoic acid can be used to control the helix sense of 2d. It is noted that the addition of two equivalents of benzoic acid brought about a practically mirror-imaged CD pattern to that of 2d alone and that five equivalents of benzoic acid resulted into even more intense CD signals. The  $[\theta]$  value of **2d** at 380 nm varied from -5000 to 15000 deg cm<sup>2</sup> dmol<sup>-1</sup>, when five equivalents of benzoic acid was added. The detailed mechanism of the helix inversion is not clear, but it is speculated that complexation of benzoic acid



**FIGURE 8** CD and UV-Vis spectra of 2d upon addition of benzoic acid measured in CHCl<sub>3</sub> at 20 °C (c = 0.05 mg/mL; the curve of 5.0 equiv NaOH denotes that 5.0 equivalents of NaOH was added to the polymer solution containing 5.0 equivalents of benzoic acid). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 9 TGA curves of the polymers (in nitrogen, heating rate 10  $^\circ$ C/min).

with the amino groups of the polymer changes the shape and bulkiness of the side groups, leading to helix inversion. When an equimolar amount of NaOH to the acid was added to the solution of **2d** containing five equivalents of benzoic acid, the CD spectroscopic pattern completely returned to the one before the acid addition. Similar results were also observed with **2e**. Thus, we could confirm the reversible conformational change of **2d** and **2e** according to pH.

#### **Thermal Stability of the Polymers**

The thermal stability of the polymers was examined by TGA in air (Fig. 9). The onset temperatures of weight loss of **2a** and **2d** were approximately 260 °C, which is about same as that of poly(phenylacetylene). The weight residue at 800 °C for **2a** was 68%, whereas those of **2d** and poly(phenylacetylene) were approximately 10%. This indicates that all these polymers begin to be oxidized at similar temperatures, while certain involatile materials remain at high temperatures up to 800 °C in **2a**.

#### CONCLUSIONS

In this study, we have demonstrated the polymerization of novel acetylenic monomers containing Schiff-base and secondary amino groups with a Rh catalyst. The polymerization satisfactorily proceeded to afford the corresponding polymers **2a-e** in good yields. These polymers were soluble in common organic solvents. Polymers **2a**, **2b**, **2d**, and **2e** exhibited large optical rotations and intense CD signals, indicating that they formed helical structure with predominantly one-handed screw sense. The effects of solvents and temperature revealed that these polymers took dynamic helical structure based on the steric effect of side groups. Polymers bearing free amino groups **2d** and **2e** exhibited a helix-helix transition upon complexation with an achiral benzoic acid, and their helical senses underwent reversible transformation of helicity upon further addition of NaOH.

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