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# Synthesis and Properties of Polyaniline Derivatives with Liquid Crystallinity

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ABSTRACT: Polyanilines with liquid crystalline (LC) substituents, which consist of a flexible methylene spacer and phenylcyclohexyl moiety as a mesogenic core, were synthesized. Polymerizations were performed using ammonium persulfate and perchloric acid as the catalytic system. The polymers were quite soluble in organic solvents such as THF and chloroform. The polymers were characterized by IR, UV−vis, $^1$H NMR, and $^{13}$C NMR spectroscopies. The oxidized form of the pristine polyaniline derivative with a liquid crystalline group and neutral form prepared by ammonia treatment were examined with respect to the liquid crystallinity. The polymers with the longer flexible methylene spacer ($n = 10$) of the oxidized form and neutral form exhibited thermotropic liquid crystallinity. Phase transitions and the corresponding enthalpy changes were evaluated using differential scanning calorimeter measurements. The smectic liquid crystallinity was characterized by fan-shaped texture through polarizing optical microscope observations. The LC domains of polyaniline derivative were growing like strings and aligned parallel to the magnetic field.

## Introduction

Polyaniline is one of the most promising electrically conducting polymers because of its chemical stability, relatively high conductivity, and unique optical property. The conducting form is generated from an oxidation through a protonation, giving rise to remarkable changes in electrical and optical properties.[1,2] The emeraldine base of protonated polyaniline film can be stretched up to 20 times to exhibit a higher conductivity. The proton doping of polyaniline using camphorsulfonic acid in *m*-cresol increases the conductivity by several orders of magnitude.[3] This is the concept of secondary doping, based on the change in the conformation of polyaniline from a compact coil to an expanded coil.[4] These results imply the importance of the morphological effect in electrical conductivity. Introduction of a liquid crystal to the conjugated polymer should give macroscopic alignment in the polymeric system, which would allow us to control the conductivity using an external force such as an electrical or magnetic force field.[5] Here we report the synthesis of a LC polyaniline derivative with a mesogenic group in side chain to enhance electrical and optical properties. The LC group consists of a phenylcyclohexyl moiety as the mesogen core and flexible methylene spacer. The main-chain polyaniline derivative has various forms based on the redox and acid−base reactions, as shown in Figure 1.

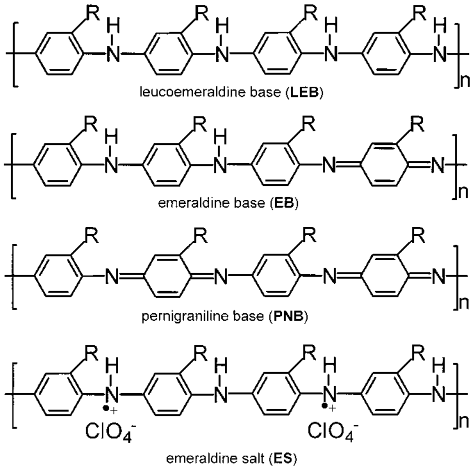

**Figure 1.** Schematic chemical structure diagrams of polyaniline in various oxidation states.

Since the polymer of the as-grown form (pristine polyaniline) had been acidified and doped by the catalyst, it was reduced with ammonia solution to give the neutral emeraldine. The liquid crystallinity of the pristine and neutral emeraldine forms of the polyaniline derivatives were examined. The polyaniline derivative with decamethylene spacer ($n = 10$) in the LC side chain indeed showed liquid crystallinity, although that with hexamethylene spacer ($n = 6$) showed no LC.

## Experimental Section

**General Aspects.** All experiments were performed under an argon atmosphere using Schlenk/vacuum line techniques. Tetrahydrofuran (THF), ethanol, acetone, and ether were distilled prior to use.

Proton ($^1$H) and carbon ($^{13}$C) nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ using a Bruker AM-500. Chemical shifts are represented in parts per million downfield from tetramethylsilane as an internal standard. Gel permeation chromatographic (GPC) analyses were carried out at room temperature. The GPC column was calibrated with a polystyrene standard. Optical absorption spectra were measured at room temperature using a HITACHI U-2000 spectrometer with a quartz cell. Infrared spectra were measured using a JASCO FT-IR 550 spectrometer.

**1-[*p*-(*trans*-4-*n*-Pentylcyclohexyl)phenoxy]-6-bromohexane (1).** Sodium (4.6 g, 0.2 mol) was added to 150 mL of ethanol in a three-necked round-bottom flask equipped with a magnetic stirrer and Ar line at room temperature. After sodium was completely dissolved in ethanol, *p*-(*trans*-4-pentylcyclohexyl)phenol (49.3 g, 0.2 mol) was added to the solution and stirred at room temperature for 12 h. Subsequently, the solution was transferred to a pressure equalized dropping funnel, and it was connected to a four-necked round-bottom flask with a mixture of 1,6-dibromohexane (195.2 g, 0.8 mol) and 100 mL of ethanol. The solution was very slowly added to the 1,6-dibromohexane in ethanol at 60 °C under an argon

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atmosphere. The addition was completed after 4 h, and the reaction mixture was stirred for another 8 h. After evaporating the solvent and excess dibromohexane under reduced pressure, the solution was thoroughly washed with 1 N HCl and water and then extracted with ether. The ether layer was dried over CaCl$_2$, and the organic solvent was removed under reduced pressure. The crude product was recrystallized from ethanol to give 47.5 g (0.12 mol) of white prisms (yield 58%). Anal. Calcd for $C_{23}H_{37}BrO$: C, 67.47; H, 9.11; Br, 19.51. Found C, 67.65; H, 9.27; Br, 19.50. IR (KBr, cm$^{-1}$): 3039, 2955, 2919, 2847, 1613, 1581, 1515, 1469, 1447, 1390, 1304, 1282, 1246, 1180, 1111, 1075, 966, 836, 812, 722, 624, 565, 541. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.89 (t, 3H, CH$_3$), 1.03 (q, 2H, CH$_2$), 1.19−1.43 (m, 15H, c-hex(CH$_2$)$_3$), c-hex = cyclohexyl, 1.76 (2H, t, CH$_2$), 1.86 (m, 8H, (CH$_2$)$_4$), 2.39 (t, 1H, bridgehead CH of c-hex), 3.42 (t, 2H, BrCH$_2$), 3.91 (t, 2H, *CH$_2$*OPh), 6.80 (d, 2H, Ph) 7.10 (d, 2H, Ph) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.09, 22.69, 25.31, 26.64, 27.91, 29.15, 32.20, 32.69, 33.65, 33.73, 34.57, 37.31, 37.38, 43.71, 67.64, 114.22, 127.57, 140.01, 157.11 ppm (TMS).

**1-[*p*-(*trans*-4-Pentylcyclohexyl)phenoxy]-10-bromodecane (2).** The synthetic procedure and purification of this compound are the same method as for the preparation of **1**, utilizing 1,10-dibromodecane instead of 1,6-dibromodecane. Yield 62% (white powder). Anal. Calcd for $C_{27}H_{45}BrO$: C, 69.66; H, 9.74; Br, 17.16. Found: C, 69.60; H, 9.21; Br, 17.12. IR (KBr, cm$^{-1}$): 2924, 2913, 2847, 1610, 1580, 1512, 1466, 1445, 1394, 1279, 1244, 1178, 1114, 1040, 1018, 970, 894, 836, 809, 765, 723, 645, 624, 541. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.88 (t, 3H, CH$_3$), 1.01 (q, 2H, CH$_2$), 1.19−1.43 (m, 21H, c-hex-(CH$_2$)$_3$, (CH$_2$)$_3$), 1.76 (t, 2H, CH$_2$),1.84 (m, 10H, (CH$_2$)$_5$), 2.38 (t, 1H, bridgehead CH of c-hex), 3.46 (t, 2H, BrCH$_2$), 3.90 (t, 2H, *CH$_2$*OPh, 6.70 (d, 2H, Ph), 7.09 (d, 2H, Ph) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.11, 22.72, 25.62, 26.07, 26.68, 28.17, 28.75, 29.37, 29.45, 32.24, 32.84, 33.57, 33.70, 33.94, 34.62, 37.36, 37.43, 43.76, 67.96, 114.27, 127.57, 139.91, 157.25 ppm (TMS).

**2-[6-(*p*-(*trans*-4-Pentylcyclohexyl)phenoxy)hexyloxy]-acetanilide (3).** Sodium (0.28 g, 12 mmol) was added to 50 mL of ethanol in a three-necked round-bottom flask equipped with a magnetic stirrer. 2-Hydoxyacetanilide (1.85 g, 12 mmol) was then added to the solution. The color of the solution turned from pale yellow to green. After 24 h, 1-[*p*-(*trans*-4-pentylcyclohexyl)phenoxy]-6-bromohexane **(1)** (5 g, 12 mmol) and KI (2 g, 12 mmol) were added to the solution. After refluxing 24 h at 60 °C, the reaction mixture was thoroughly washed with 1 N HCl and water and then extracted with ether. The ether layer was dried over CaCl$_2$, and the organic solvent was removed under reduced pressure. The crude product was passed through a column chromatograph (ethyl acetate/hexane = 2/1) and recrystallized from ethanol to give 3.8 g (8 mmol) as a white powder (yield 67%). Anal. Calcd for $C_{31}H_{45}NO_3$: C, 77.62; H, 9.46; N, 2.47. Found: C, 77.32; H, 9.75; N, 2.47. IR (KBr, cm$^{-1}$): 3744, 3368, 3305, 2854, 1666, 1603, 1539, 1517, 1449, 1375, 1325, 1242, 1179, 1110, 1039, 999, 889, 833, 748, 700, 613. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.88 (t, 3H, CH$_3$), 1.03 (q, 2H, CH$_2$), 1.19−1.54 (m, 15H, c-hex(CH$_2$)$_3$, c-hex = cyclohexyl), 1.82 (m, 8H, (CH$_2$)$_4$), 2.15 (s, 3H, C=O(CH$_3$)), 2.37 (t, 1H, bridgehead CH of c-hex), 3.73 (t, 2H, *CH$_2$*OPh-c-hey), 3.93 (t, 2H, *CH$_2$*OPh), 6.81 (d, 2H, Ph), 6.85 (d, 1H, Ph), 6.92 (m, 1H, Ph), 6.99 (t, 1H, Ph), 7.09 (d, 2H, Ph), 7.74 (s, 1H, NH), 8.34 (d, 1H, Ph) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.12, 16.76, 22.66, 24.90, 25.63, 25.96, 26.66, 29.14, 30.90, 32.24, 33.68, 34.62, 37.34, 43.76, 67.66, 68.56, 110.93, 114.24, 119.62, 121.00, 123.58, 127.58, 140.12, 145.16, 147.07, 157.13, 168.05 ppm (TMS).

**2-[10-(*p*-(*trans*-4-Pentylcyclohexylphenoxy)decyloxy)]-acetanilide (4).** The synthetic procedure and purification of this compound are the same method as for the preparation of **3**, utilizing **2** instead of **1**. Yield 70% (white powder). Anal. Calcd for $C_{35}H_{53}NO_3$: C, 78.46; H, 9.97; N, 2.61. Found: C, 78.96; H, 10.71; N, 1.80. IR (KBr, cm$^{-1}$): 3422, 3368, 2923, 2852, 1687, 1604, 1519, 1448, 1384, 1242, 1117, 1112, 103.8, 830, 758, 630, 588, 545. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.76 (t, 3H, CH$_3$), 1.04 (q, 2H, CH$_2$CH$_3$), 1.16−1.42 (m, 21H, c-hex-(CH$_2$)$_3$, (CH$_2$)$_3$), 1.60 (m, 2H, CH$_2$), 1.69 (m, 10H, (CH$_2$)$_5$), 2.01 (s, 3H, C=OCH$_3$), 2.24 (t, 1H, bridgehead CH of c-hex), 3.49 (t, 2H, *CH$_2$*OPh-c-hex), 3.86 (t, 2H, *CH$_2$*OPh), 6.66 (d, 2H, Ph), 6.71 (d, 1H, Ph), 6.76 (t, 1H, Ph), 6.85 (t, 1H, Ph), 6.94 (d, 2H, Ph), 7.86 (s, 1H, NH), 8.10 (d, 1H, Ph) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 13.68, 14.69, 17.64, 22.57, 24.31, 25.38, 25.93, 26.00, 26.55, 29.00, 29.22, 29.34, 32.16, 33.55, 34.48, 37.22, 37.30, 43.63, 67.78, 68.58, 111.02, 114.14, 120.23, 120.63, 123.91, 127.38, 139.74, 139.78, 147.50, 157.06, 168.70 ppm (TMS).

**2-[6-(*p*-(*trans*-4-Pentylcyclohexyl)phenoxy)hexyloxy]-aniline Hydrochloric Salt (5).** To a solution of 9.5 N HCl (10 mL) in ethanol (100 mL) which was maintained at 60 °C, 2-[6-(*p*-(*trans*-4-pentylcyclohexyl)phenoxy)]acetanilide **(3)** (2.8 g, 5.9 mmol) was added with vigorous stirring in a three-necked round-bottom flask equipped with a magnetic stirrer and linked with the Ar line. The resulting slurry was stirred for 48 h. The voluminous precipitate was filtered off and recrystallized from ethanol to give a white solid 2.0 g (4.2 mmol, yield 71%). Anal. Calcd for $C_{29}H_{43}NO_2Cl$: C, 73.68; H, 9.18; N, 2.96, Cl; 7.40. Found: C, 73.64; H, 9.56; N, 2.71; Cl, 7.38. IR (KBr, cm$^{-1}$): 2921, 2852, 2564, 1968, 1619, 1503, 1455, 1254, 1173, 1121, 1002, 823, 752, 556. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.81 (t, 3H, CH$_3$), 0.96 (q, 2H, CH$_2$), 1.12−1.56 (m, 15H, c-hex(CH$_2$)$_3$), 1.78 (m, 8H, (CH$_2$)$_4$), 2.33 (t, 1H, bridgehead CH of c-hex), 3.68 (t, 2H, CH$_2$OPh-c-hex), 3.94 (t, 2H, PhOCH$_2$), 6.72 (d, 2H, Ph), 6.82 (m, 2H, Ph), 6.85 (m, 2H, Ph), 7.17 (m, 1H, Ph), 7.65 (d, 1H, Ph), 10.43 (s, 1H, NH) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.11, 22.65, 25.62, 25.76, 26.86, 28.97, 29.31, 32.24, 33.69, 34.63, 37.36, 37.43, 43.74, 67.98, 68.68, 112.21, 114.22, 119.65, 120.61, 124.42, 127.54, 129.68, 139.85, 152.20, 157.22 ppm (TMS).

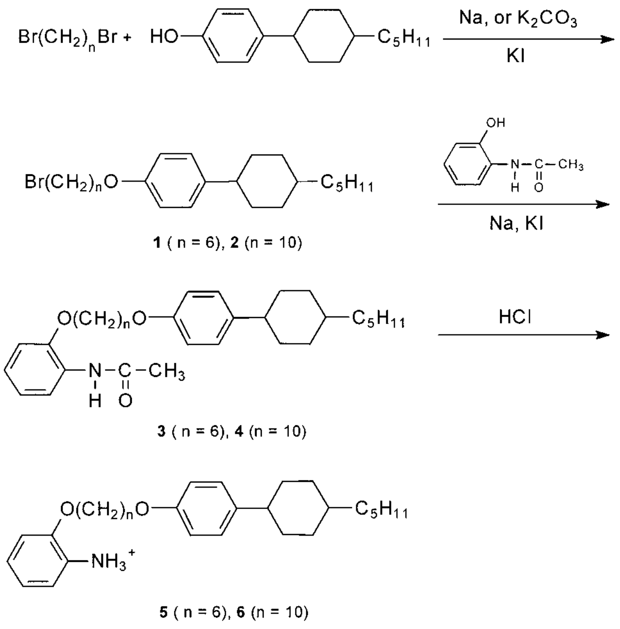
**2-[10-(*p*-(*trans*-4-Pentylcyclohexyl)phenoxy)decyloxy]-aniline Hydrochloric Salt (6).** The synthetic procedure and purification of this compound are the same method as for the preparation of **5**, utilizing **4** instead of **3**. Yield 84% (white solid). Anal. Calcd for $C_{33}H_{51}NO_2Cl$: C, 74.89; H, 9.71; N, 2.65; Cl, 6.70. Found: C, 74.41; H, 9.59; N, 2.63; Cl, 6.24. $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.13, 15.26, 22.73, 25.63, 25.08, 26.12, 26.22, 26.66, 28.93, 29.30, 29.40, 32.25, 33.70, 34.62, 37.36, 37.43, 43.76, 67.96, 69.11, 112.20, 114.26, 119.67, 120.53, 124.50, 127.59, 129.64, 139.93, 152.27, 157.26 ppm (TMS).

***Poly*[2-(6-(*p*-(*trans*-4-pentylcyclohexyl)phenoxy)hexyloxy)aniline] (Pristine, Oxidized Form) (7).** 2-[6-(*p*-(*trans*-4-Pentylcyclohexyl)phenoxy)hexyloxy]aniline hydrochloric salt (1.5 g, 3.2 mmol) **(5)**, 1 mL of 70% HClO$_4$ in 20 mL of distilled water, and 10 mL of CHCl$_3$ were stirred in an Erlenmeyer flask at 0 °C. 1 g of $(NH_4)_2S_2O_8$ in 20 mL of water was then added dropwise to the solution. The color of the solution was changed from gray-blue to purple as the reaction progressed. After 24 h, the solution was filtered and washed with a large amount of distilled water. Subsequently, the polymer was washed with a large amount of methanol until the liquid was clear. The polymer was dried under reduced pressure to yield 1.2 g of the oxidized form of the polyaniline derivative. $^1$H NMR: (CDCl$_3$, 500 MHz): $\delta$ 0.89 (t, 3H, CH$_3$), 0.95 (q, 2H, CH$_2$), 1.03−1.56 (m, 15H, c-hex(CH$_2$)$_3$), 1.89 (m, 8H, (CH$_2$)$_4$), 2.38 (s, 3H, bridgehead CH of c-hex), 3.79 (s, 4H, *CH$_2$*OPh × 2), 6.78 (d, 2H, Ph), 7.08 (d, 2H, Ph) ppm (TMS).$^{13}$C NMR: (CDCl$_3$, 500 MHz): $\delta$ 14.12, 22.72, 25.61, 25.93, 26.66, 29.17, 29.33, 32.24, 33.67, 34.60, 37.34, 37.42, 43.73, 67.75, 68.69, 114.24, 127.59, 139.99, 157.15 ppm (TMS).

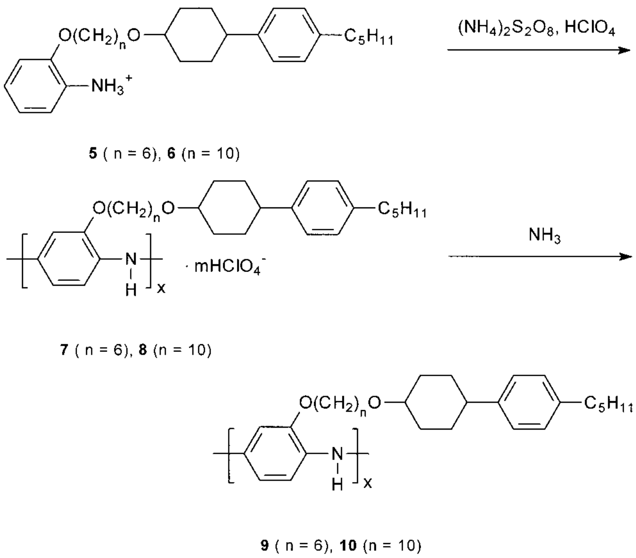
***Poly*[2-(10-(*p*-(*trans*-4-pentylcyclohexyl)phenoxy)decyloxy)aniline] (Pristine, Oxidized Form) (8).** The synthetic procedure and purification of this polymer are the same method as for the preparation of polymer **7**. $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.11, 22.65, 22.72, 25.61, 26.07, 26.67, 29.38, 29.49, 29.54, 30.90, 31.66, 32.23, 33.67, 34.81, 37.35, 37.42, 43.74, 67.97, 68.60, 114.26, 127.57, 139.91, 157.25 ppm (TMS).

***Poly*[2-(6-(*p*-(*trans*-4-pentylcyclohexyl)phenoxy)hexyloxy)aniline] (Neutral Form) (9).** *Poly*[2-(6-(*p*-(*trans*-4-pentylcyclohexyl)phenoxy)hexyloxy)aniline]-pristine **(7)** (1 g) and 50 mL of 1 N ammonia solution were prepared in a three-necked round-bottom flask equipped with a magnetic stirrer. The solution was stirred for 24 h at room temperature. The

**Scheme 1**



**Scheme 2**



solution was then washed with distilled water. The polymer was dried under reduced pressure to yield 0.8 g of the neutral form. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.81 (t, 3H, CH$_3$), 0.93 (q, 2H, CH$_2$), 1.13−1.45 (m, 15H, c-hex(CH$_2$)$_3$), 1.77 (m, 8H, (CH$_2$)$_4$), 2.29 (s, 1H, bridgehead CH of c-hex), 3.66 (s, 4H, *CH*$_2$-OPh × 2), 6.71 (d, 2H, Ph), 7.12 (d, 2H, Ph) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.11, 22.72, 25.51, 25.78, 26.87, 28.93, 29.19, 32.23, 33.66, 34.61, 37.34, 37.42, 43.73, 67.96, 68.69, 112.25, 114.23, 119.52, 120.63, 124.48, 127.54, 129.94, 139.84, 152.16, 157.19 ppm (TMS).

***Poly*****[2-(10-(*****p*****-(*****trans*****-4-pentylcyclohexyl)phenoxy)decyloxy)aniline] (Neutral Form) (10).** The synthetic procedure and purification of this polymer are the same method as for the preparation of polymer **9**. $^1$H-NMR (CDCl$_3$, 500 MHz): $\delta$ 0.89 (t, 3H, CH$_3$), 0.93 (q, 2H, CH$_2$), 1.12−1.46 (m, 15H, c-hex(CH$_2$)$_3$), 1.77 (m, 8H, (CH$_2$)$_4$), 2.31 (s, 1H, bridgehead CH of c-hex), 3.65 (s, 4H, *CH*$_2$OPh × 2), 6.52 (d, 2H, Ph), 7.28 (d, 2H, pH) ppm (TMS). $^{13}$C NMR (CDCl$_3$, 500 MHz): $\delta$ 14.12, 22.73, 25.63, 26.06, 26.86, 29.08, 29.39, 29.50, 29.54, 30.90, 31.60, 32.25, 33.69, 34.62, 37.35, 37.43, 43.75, 67.97, 68.57, 112.27, 114.28, 120.12, 121.32, 124.57, 131.96, 129.12, 131.91, 152.18, 157.28 ppm (TMS).

## Results and Discussion

**Monomer Synthesis.** Two kinds of monomers consisting of a liquid crystalline group with a hexamethylene spacer or decamethylene spacer ($n$ = 6, 10) were synthesized in three steps, as shown in Scheme 1.

*p*-(*trans*-4-Pentylcyclohexyl)phenol was reacted with 4-fold excess of a dibromoalkane in ethanol by the Williamson's etherification to obtain **1** or **2**. Evaporation was carried out to remove any excess dibromoalkane, followed by recrystallization from ethanol in ca. 60% yield. In the next step, the LC group (**1** or **2)** was introduced to the ortho position of an acetanilide by the same etherification method in ethanol to yield **3** or **4**. Compound **3** or **4** was purified by column chromatography (ethyl acetate/hexane = 2/1), followed by recrystallization from ethanol, to yield 67−70%. Subsequently, this compound was treated with HCl at 60 °C to remove the acetyl fragment. The analytically pure compound of the hydrochloric aniline salt as a monomer **5** or **6** was obtained through recrystallization from ethanol.

**Polymerization.** Interfacial polymerization was performed between organic layer (CHCl$_3$) and water using ammonium peroxodisulfate and 1 M HClO$_4$, where the bulky LC substituents on the aniline rendered the monomer insoluble in aqueous media. The product was washed with a large amount of methanol to give the purple color oxidized form of the polyaniline derivative (**7** or **8**). The pristine polyaniline was reduced in a 1 M ammonia aqueous solution and washed with methanol to yield the neutral form (**9** or **10**), as shown in Scheme 2.

**Characterization.** The monomers of **5** and **6** were produced in good yields. Molecular weights of the corresponding polymers (neutral forms, **9** and **10**) are summarized in Table 1. These values range from 9200 to 14 100 in $M_n$ according to polystyrene standard, which indicates that the compounds are real polymers. The results of the elemental analyses of the polymers are also listed in Table 1.

The small amount of chlorine in the neutral forms is due to residual ClO$_4^-$ ion which was not be able to be removed by ammonia treatment. Figure 2 shows IR absorption spectra of **6** (monomer), **8**, and **10** (polymers).

The IR spectrum of the monomer **6** showed a broad peak at 2560 cm$^{-1}$, which was assigned to overlapped −CH$_3$ stretching and −NH$_3^+$ stretching vibrations. The IR spectra of the polymers **8** or **10** showed no absorption peak due to the −NH$_3^+$ moiety. These results indicate that the oxidative polymerization gives a polyaniline structure. In the spectra of the polymers, the absorption at 2800−3000 cm$^{-1}$ is assigned to C−H stretching vibrations of the alkyl moiety in the liquid crystalline substituent. The ring stretching vibrations of the quinoid and benzenoid forms in the polymer were observed at 1590 and 1500 cm$^{-1}$, respectively. The C−N stretching vibration[6] was observed at 1380 cm$^{-1}$. The absorption at 1240 cm$^{-1}$ is due to the C−O−C stretching vibration. The stretching vibration of the counterion (ClO$_4^-$) appeared at 624 cm$^{-1}$ in the pristine polymers (**7** or **8**). The absorption intensity is decreased during the ammonia treatment. The absorption around 1030 cm$^{-1}$ is attributed to the CH in-plane vibration of the 1,4 position on the phenylene ring in the main chain, and 742 cm$^{-1}$ is due to the CH out-of-plane vibration at the 1,2 position of the phenylene ring in the main chain. A presence of the 827 cm$^{-1}$ is characteristic of the C−H out-of-plane bending vibrations of the para-substituted

**Table 1. Molecular Weights and Elemental Analyses for the Polymers of Neutral Forms**

| polymer | $M_w$ | $M_n$ | MWD | DP | C (%) | H (%) | N (%) | Cl (%) | composition (found) | composition (calcd) |
|---|---|---|---|---|---|---|---|---|---|---|
| **9** | 22 600 | 14 100 | 1.6 | 32 | 77.18 | 9.30 | 3.12 | 1.44 | $C_6H_{8.68}N_{0.20}Cl_{0.07}$ | $C_6H_{8.48}N_{0.21}$ |
| **10** | 16 560 | 9 200 | 1.8 | 19 | 78.40 | 9.88 | 2.77 | 1.55 | $C_6H_{9.08}N_{0.18}Cl_{0.04}$ | $C_6H_{8.91}N_{0.18}$ |

**Table 2. Assignments of the IR Spectra of the Polymers**

| polymer | $\nu_{NH}$ | $\nu_{CH_2}$ | N=Q[a]=N | N−B[b]−N | $\nu_{CN}$ | $\nu_{COC}$ | N=Q$^+$=N | Q=NH$^+$−B or B−NH$^+$−B | C−H in-plane on benzene ring | CH out-of-plane on benzene ring | aromatic ring deformation |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **7** | 3382 | 3033<br>2921 | 1604 | 1504 | 1361 | 1241 | 1168 | 1135 | 1047 | 823<br>734 | 636 |
| **8** | 3260 | 2921<br>2852 | 1590 | 1517 | 1390 | 1243 | 1187 | 1108 | 1054 | 825<br>757 | 628 |
| **9** | 3450 | 2917<br>2847 | 1576 | 1503 | 1381 | 1242 | 1157 | 1138 | 1024 | 827<br>736 | 640 |
| **10** | 3350 | 2921<br>2852 | 1590 | 1513 | 1396 | 1245 | 1187 | 1130 | 1039 | 827<br>750 | 630 |

[a] Q = quinoid unit. [b] B = benzenoid unit.

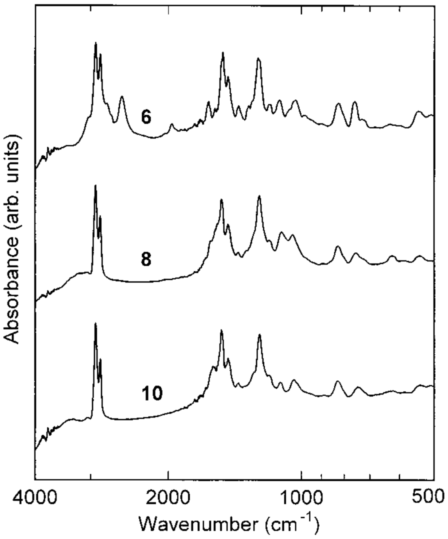


**Figure 2.** IR absorption spectra of the monomer and the polymers.

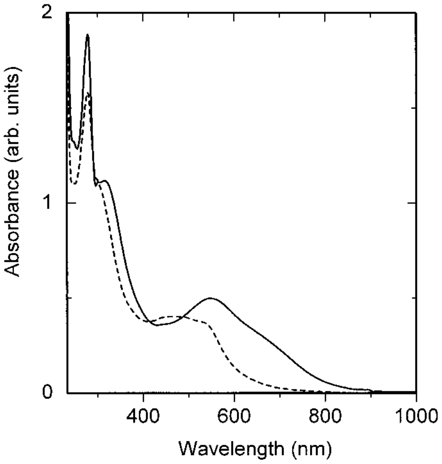


**Figure 3.** UV−vis absorption spectra of the polymers in THF solution: **8** (solid line); **10** (dashed line).

phenylene ring of the polymers. The results are summarized in Table 2.

The UV−vis absorption spectra of the polymers in THF are shown in Figure 3. The absorption band of **8** (pristine, oxidized form) or **10** (neutral form) at 277 nm is assignable to the phenylene unit in LC group. A purple pristine polymer of **8** showed three absorption peaks at 277, 316, and 552 nm and shoulder at 692 nm.

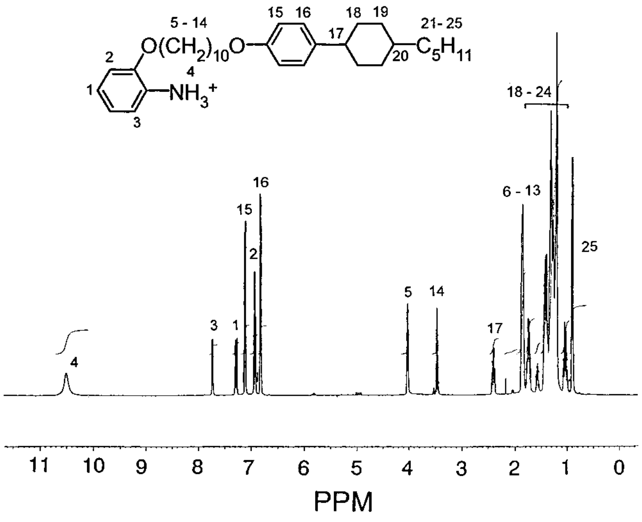


**Figure 4.** $^1$H NMR spectrum of **6**.

By the reduction with ammonia, the color of the polymer changed from purple to dark red, and the peak at 552 nm shifted to the shorter wavelength of 468 nm. This result implies that the absorption of 552 nm of the pristine polyaniline may be due to the doping band of the $ClO_4^-$ ions.

**$^1$H and $^{13}$C NMR Spectra.** Additional information about the monomer and polymer structures were obtained from NMR spectra. The 500 MHz $^1$H NMR spectrum of **6** as a monomer is shown in Figure 4. Protons of the ammonium ion ($-NH_3^+$) give a broad peak at 10.50 ppm. Aromatic protons of aniline unit appear as sharp peaks at 7.71, 7.27, and 7.10 ppm. The aromatic protons on the liquid crystalline substituent of the phenylene moiety appear at 6.92 and 6.81 ppm. The protons of the other methylene groups appear at 1.04−4.01 ppm, and the terminal methyl group appears at 0.89 ppm. The $^1$H NMR spectrum of the polymer **8** is shown in Figure 5.

The peaks related to the protons on the aniline units are difficult to be assigned. This is due to the delocalized electron or charged species. A signal at 10.50 ppm originating from the $-NH_3^+$ of the monomer is disappeared in the $^1$H NMR after the polymerization.

**Liquid Crystallinity.** The liquid crystalline properties of **8** and **10** were examined with a differential scanning calorimeter (DSC) and polarizing optical microscopy. The phase transition temperatures and their

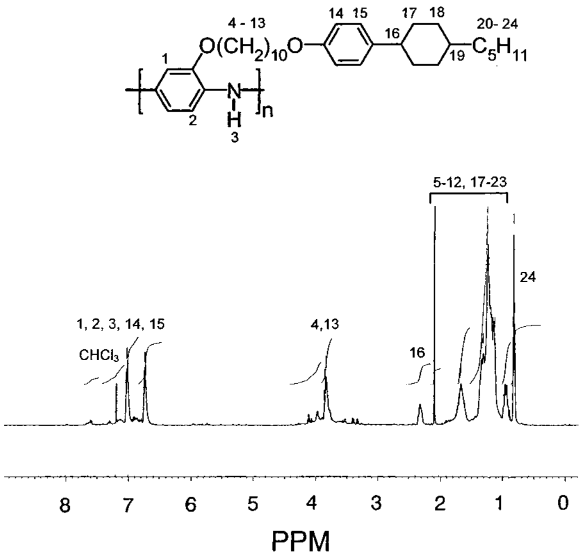


**Figure 5.** $^1$H NMR spectrum of **8**.

**Table 3. Phase Transition Temperatures[a] (°C) and Corresponding Enthalpy Changes (J/g)[b]**

| | first cooling | | second heating | |
|---|---|---|---|---|
| polymer | g−s | s−i | g−s | s−i |
| **8** | *c* | 97 (−2.1) | 75 (1.2) | 102 (7.8) |
| **10** | *c* | 64 (−1.2) | 54 (0.2) | 65 (1.1) |

[a] Determined by DSC. [b] g = glassy state, s = smectic, i = isotropic. Scanning rate: 10 °C/min. [c] No distinct DSC peak.

corresponding enthalpy changes are summarized in Table 3.

The DSC exothermic peak showed one thermal transition during the first cooling of **8**; no distinct peak was observed on the phase transition from the mesophase to the glassy state. In the heating scan, two peaks due to the phase transition from the glassy state to the mesophase and from the mesophase to the isotropic phase were observed. Moreover, polarizing optical microscopy confirmed the two phase transitions. Beyond 75 °C, the polymer becomes fluid and remains birefringent. Above 102 °C, the polymer changed into an isotropic phase. In the mesophase between 75 and 102 °C, the polymer exhibited a purple birefringence under polarizing light. The polymer of **10** exhibited thermal behavior similar to polymer **8**, although the phase transition temperatures were shifted to the lower temperature region. This may be due to the decrease in rigidity of the polymer main chain accompanied by a decrease of effective conjugation length.

Note that the polymers of **7** and **9** showed no liquid crystallinity. This may be due to the shorter methylene spacer of the LC substituent; the length of hexamethylene spacer is not enough to enable a spontaneous orientation.[7] The polarizing optical micrograph of **8** without external force is shown in Figure 6a. Randomly oriented optical texture of LC is observed. Although ordinary LCs have no color, the present polymer exhibits a red-purple color due to the existence of conjugated absorption band in the visible region. We examined macroscopic alignment of the polymer of **8** under a magnetic force field. The polymer was first melted by heating on the quartz substrate, and it was gradually cooled to LC temperature by applying an external magnetic field of 10 T. Figure 6c indicates the macroscopic alignment of the LC polyaniline derivative.

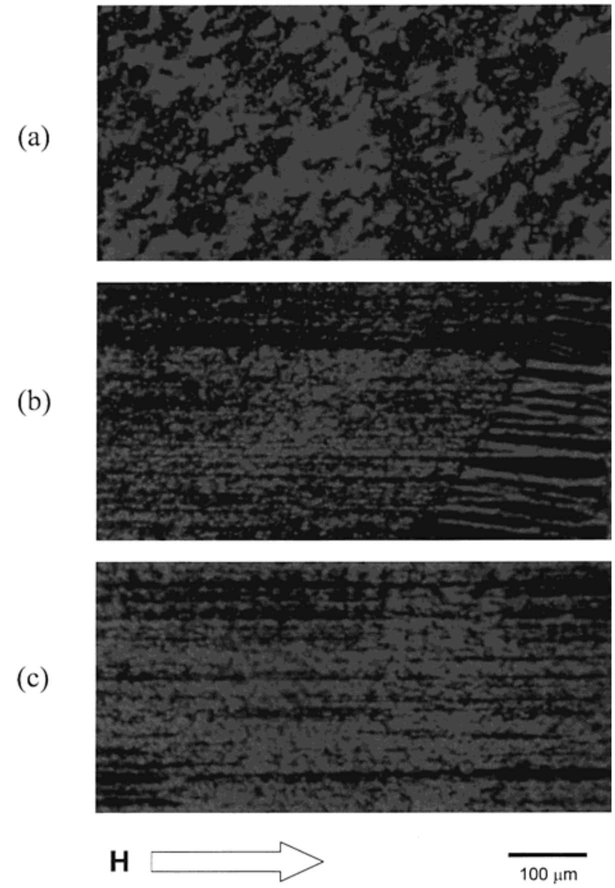


**Figure 6.** Polarizing optical micrographs of **8**: (a) without external force; (b) intermediate state in growing of aligned LC domains under the magnetic field; (c) macroscopic alignment of the polyaniline derivative.

The direction of magnetic field is parallel to a horizontal line of the photograph. It is seen that the LC domains are growing like strings and aligned parallel to the magnetic field. We also performed polarized UV−vis measurement for the aligned polymer to comprehend the orientational behavior of the polymer (Figure 7).

In the linear dichroism measurements, the absorption was recorded with a polarizer placed parallel and perpendicular to the applied magnetic field direction on the sample. The absorption intensity in the perpendicular direction ($A_\perp$) to the magnetic field was larger than that in the parallel one ($A_\|$). Note that $A_\|$ stands for absorbance perpendicular to the polyaniline main chain and $A_\perp$ parallel to the main chain. This result indicates that the transition dipole moment of the conjugated segment was perpendicular to the direction of the macroscopic alignment. Namely, the polymer main chain was oriented perpendicular to the magnetic field.[5] The dichloic ratio ($R$) and order parameter ($S$) of **8** were estimated to be 5.3 and 0.68, respectively.

$$R = A_\perp / A_\|$$

$$S = (R - 1)/(R + 1)$$

where $A_\|$ and $A_\perp$ were defined as absorbances at 580 nm assignable to the $\pi \rightarrow \pi^*$ transition of conjugated polyaniline main chain that are parallel and perpendicular to the magnetic field, respectively. It is clear that the aligned polymer exhibits a linear dichroism in absorption.

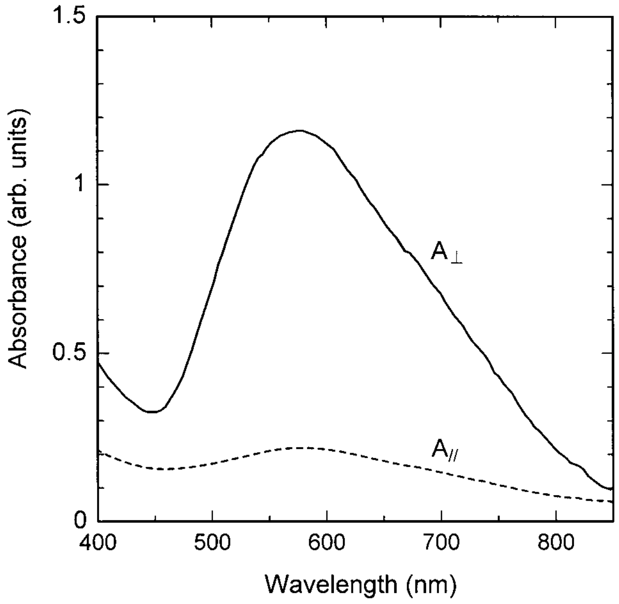


**Figure 7.** Polarized absorption spectra of **8**. $A_{\parallel}$ and $A_{\perp}$ stand for the absorbances that are parallel and perpendicular to the magnetic field, respectively.

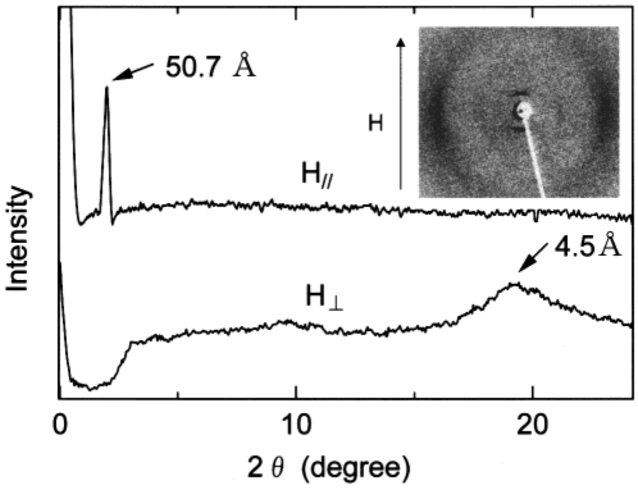


**Figure 8.** XRD result of **10** oriented by external magnetic force field of 10 T: $H_{\parallel}$ and $H_{\perp}$ stand for parallel and perpendicular directions to the magnetic field, respectively.

The X-ray diffraction (XRD) pattern and profile of the aligned polymer of **10** are shown in Figure 8. Two diffraction peaks were observed at small angle in the meridian direction of 1.9° (50.7 Å) and at large angle of 19.2° (4.5 Å) in the equator direction. These correspond to the interlayer and inter-side-chain distances, respectively. The result suggests that polymer **10** has bilayer smectic A phase where the side chains are located on the both sides of main chain (see Figure 9). This is also supported by molecular mechanics (MM) calculations.

The electrical conductivity of the polymer was measured with the four-probe method. The results are summarized in Table 4.

The conductivity of dedoped (neutral) polymer of **10** was $2.3 \times 10^{-11}$ S/cm. On the other hand, the doped (oxidized) polymer of **8** was $3.5 \times 10^{-9}$ S/cm. Through the magnetically forced alignment, the conductivity in parallel direction to the polymer main chain ($\sigma_{\perp}$) (where the polymer main chain was oriented perpendicular to the magnetic field) and that in perpendicular direction to the polymer main chain ($\sigma_{\parallel}$) were $8.4 \times 10^{-6}$ S/cm and $2.3 \times 10^{-8}$ S/cm, respectively. The anisotropy between the conductivity ($\sigma_{\perp}/\sigma_{\parallel}$) was $\sim 3 \times 10^{2}$. The increase of parallel conductivity ($\sigma_{\perp}$) after magnetically forced alignment is due to an increase of effective conjugation length and partly due to an enhancement of coplanarity of the polyaniline main chain accompanied by the alignment. This suggests that, in analyzing the change of conductivity upon the molecular orientation, an in-plane alignment of the polyaniline chain must be considered at the same time as well as the parallel alignment of the polymer main chain.

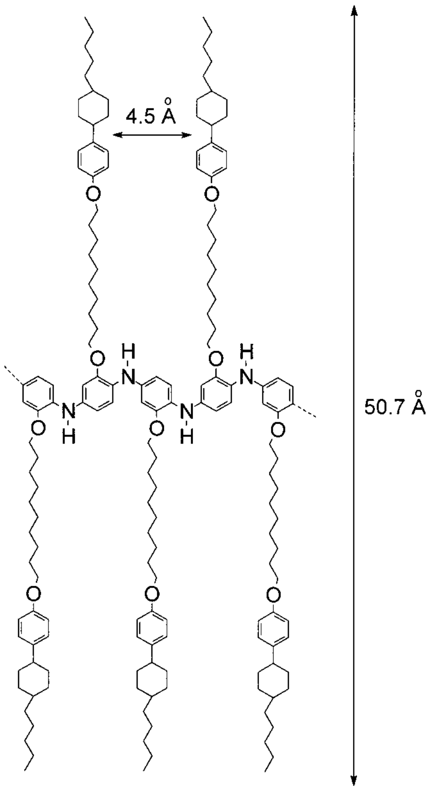


**Figure 9.** Stacking structure of bilayer smectic A phase of polymer **10**.

**Table 4. Electrical Conductivities of Polymer 8**

| polymer | $\sigma^{a}$ | $\sigma_{(\mathrm{random})}{}^{b}$ | $\sigma_{\perp}{}^{b,c}$ | $\sigma_{\parallel}{}^{b,d}$ |
|---|---|---|---|---|
| **8** | $3.5 \times 10^{-9}$ | $6.2 \times 10^{-8}$ | $8.4 \times 10^{-6}$ | $2.3 \times 10^{-8}$ |

[a] Cast film. [b] In LC order. [c] Parallel to polymer main chain. [d] Perpendicular to polymer main chain. $\sigma$ = unit of S/cm.

## Conclusion

We synthesized polyaniline derivatives with LC side chains through the interfacial polymerization. The soluble and fusible polyaniline derivatives were characterized by the IR, UV–vis, NMR, and GPC. The polyaniline derivatives with the longer decamethylene spacer in the LC side chain ($n = 10$) exhibit a thermotropic LC. This was confirmed by DSC and polarizing optical microscope measurements. The ammonia treatment for the oxidized form of the polymer caused a lowering of the phase transition temperatures. The alignment of the polymer main chain accompanied by the side-chain orientation using the external magnetic force of 10 T enhanced the electrical conductivity, giving rise to a notable electrical anisotropy.

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