Synthesis and Physical Properties of Side-Chain Type Liquid Crystalline Poly(arylenevinylene)s

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In recent years, much attention has focused on the applications of multifunctional conjugated polymers in electrical and optical devices. In particular for the liquid crystalline conjugated polymers, the polymer backbone would be easily oriented in the mesophase. As a result, they should exhibit an anisotropic conductivity, and give rise to improving the physical properties.[1−4] The successful control of conductivity was achieved by the cis−trans isomerization of azobenzene-containing polythiophene derivatives.[5]

In this report, poly(arylenevinylene) [PAV] was selected as the main chain for its high electronic and optical performance. In order to control the orientation, we synthesized and characterized PAVwith a pendant mesogenic group (Figure 1).

A typical reaction scheme for synthesis is shown in Figure 1. The products in each reaction step were detected based on ^{1}H-NMR (JEOL JNP-PMX60 spectrometer) and IR measurements (JEOL JIR100 Series FT-IR spectrometer). 3-Thiophenemethanol was the starting material for the dibromothiophene monomers. 2,5-Dibromo-3-thiophenemethanol (**1**) was synthesized by bromination of 3-thiophenemethanol using *N*-bromosuccinimide (NBS) at room temperature (84.0% yield).[6] Compound **1** was etherified with an excess of 1,12-dibromododecane to yield 2,5-dibromo-3-(12-bromododecanoxy)methylthiophene (**2**) (86.0% yield).[7] In order to obtain the mesogen-containing dibromothiophene monomers [**3-a** and **3-b**], 4-cyano-4′-hydroxybiphenyl or 4-cyano-4′-hydroxyazobenzene was introduced into compound **2** (70−80% yield).[8]

The cyanobiphenyl-containing dibromothiophene monomer (**3-a**) demonstrated a homeotropic orientation on the cooling scan confirmed by the conoscopic measurement. On the other hand, the liquid crystalline phase was not observed for the azobenzene-containing dibromothiophene monomer (**3-b**).

There are many polymerization methods for PAVs.[9−11] We chose the Heck reaction, which is a relatively mild reaction.[12−14] The reaction was carried out between the dibromothiophene derivatives and divinylbenzene (about *p*-isomer 55% and *m*-isomer 45%).[15] Palladium acetate was used as a catalyst with tris(*o*-methylphenyl)phosphine as its ligand.[16]

The color of these polymers are orange, and they are soluble in common organic solvents, such as chloroform, toluene, THF, and DMF. Table 1 shows the phase transition temperatures and number average molecular weight of the PAV derivatives. Molecular weight determinations for the polymers were conducted using GPC (Tosoh HLC-8020) with a Tosoh 254 nm lamp and a refractive index detector vs polystyrene standards in chloroform. Strictly speaking, the polymers with DPs in the range of 5−8 could not be considered polymers. However, the physical properties in these materials differ completely from that in the monomers. It is very difficult to obtain high molecular weight polymers using this polymerization method.

Table 1. Phase Transition Temperatures of Poly(arylenevinylene) Derivatives

Polymers	Transition temperatures (°C)	Molecular weight [$\overline{Mn}$]
4-a	g $\underset{?}{\overset{?}{\rightleftharpoons}}$ N $\underset{75.9}{\overset{77.1}{\rightleftharpoons}}$ I	3,300
4-b	g $\underset{?}{\overset{?}{\rightleftharpoons}}$ N $\underset{88.2}{\overset{88.3}{\rightleftharpoons}}$ I	4,700

g:glassy, N:nematic, I:isotropic

Their thermal properties were examined by differential scanning calorimetry (Mettler TA-3000 systems) and optical microscopy (Nikon polarizing microscope equipped with a Mettler FP-82 hot stage and Mettler FP-80 temperature controller). Both PAV derivatives exhibited an enanthiotropic liquid crystalline phase. The optical texture of polymer **4-a** is shown in Figure 2. A schlieren texture characteristic of a nematic phase was observed using optical microscopy. The optical texture was maintained below room temperature. The assignment of the nematic phase was also confirmed by a small enthalpy change (about 2.0 J/g) at the liquid crystalline−isotropic phase transition temperature. Only one peak arising from the clearing temperature was detected by DSC thermal analysis. However, a glass transition peak was not clearly confirmed. X-ray diffraction patterns were recorded on a Rigaku X-ray diffractometer RAD-2B system using Ni-filtered Cu Kα radiation. No diffraction pattern in the small-angle range and a broad diffraction pattern over the wide angle range were observed for the polymers. Consequently, these mesophases were identified as a nematic phase, not consisting of the layer structure for the smectic phase.

Absorption spectra were obtained using a Hitachi U-3410 spectrophotometer. Figure 3 shows the UV-vis spectra of polymer **4-a**. The absorption peak at about 300 nm was attributed to a cyanobiphenyl group. The top of the $\pi-\pi^*$ absorption peak was observed at 407 nm in the $CHCl_3$ solution. In the film, the top of the peak was shifted to the longer wavelength of 448 nm. The bathochromic shift is attributed to enhancement of the direct interaction between the main chains in the film. It is well-known that the absorption peak is shifted to the longer wavelength in the film.[17] The top of the absorption peak of the polymers was observed at a longer wavelength compared with that of the polythiophene derivatives.[2] So, the π-conjugation system is sufficiently extended regardless of the low molecular weight. Moreover, the top of the absorption peak was similar to that of the alkyl-substituted PAV derivatives. This demonstrated that the planarity of the polymer backbone was not impaired even with the introduction of a bulky pendant mesogenic group. In the case of the azobenzene-containing PAV derivative, the $\pi-\pi^*$ absorption peak was not clearly observed because of overlap with the absorption peak arising from the azobenzene moiety.

PAV derivatives exhibited a fluorescence. A strong yellow-green fluorescence was observed by UV irradiation of polymer **4-a** in $CHCl_3$ solution. However, a weak fluorescence was observed for polymer **4-b**. This phenomenon implies occurrence of a self-absorption by the azobenzene moiety.

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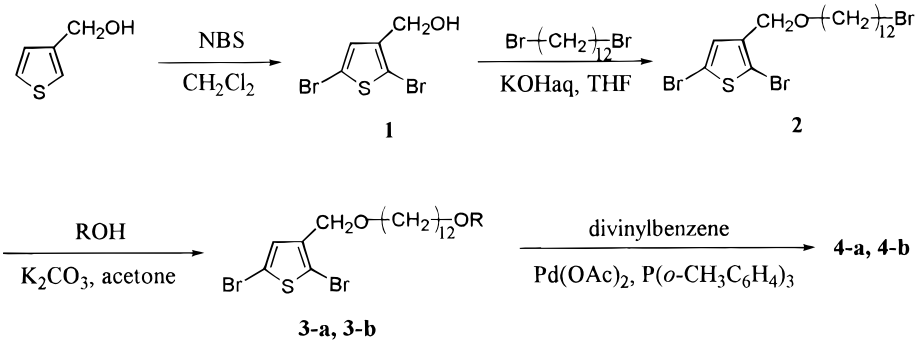

Figure 1. Structure of polymers.

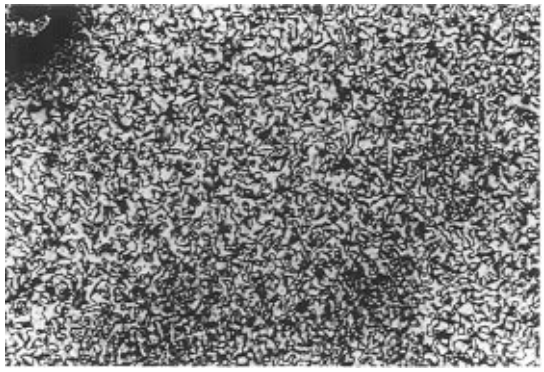

Figure 2. Optical texture of polymer **4-a** at 65.6 °C.

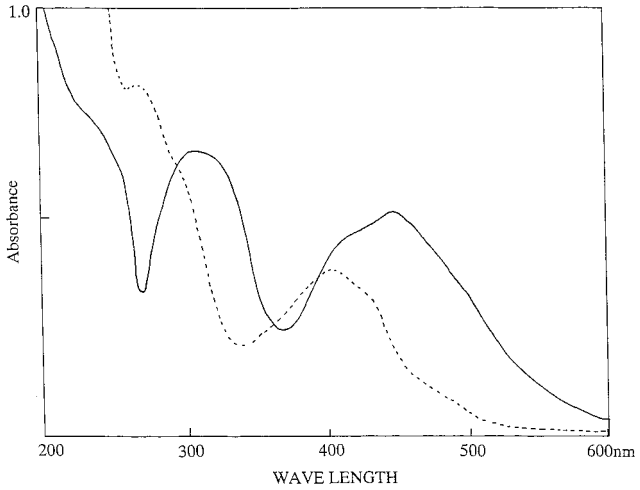

Figure 3. UV−vis spectra of polymer **4-a:** (a) film (—); (b) $CHCl_3$ solution (- - -).

The electrochemical properties of polymer **4-a** were examined using cyclic voltammetric measurements (Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko HA-111 function generator equipped with a Riken Denshi F-45 XY recorder). The polymer film on the ITO glass was prepared by casting from the $CHCl_3$ solution. The electrode was positioned in the cell containing a 0.1 M $LiClO_4$ solution in CH_3CN. A platinum electrode was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode. The color of the polymer film changed from orange to blue with oxidation. There are two oxidation peaks. The first oxidation potential was detected at +0.86 V, and the second one was at +1.04 V. These two peaks would be attributed to a distribution of molecular weight in the low molecular weight polymer. Because of a high molecular weight, poly(phenylenevinylene) showed only one oxidation peak. However, the reduction peak was not clearly detected. This suggested that the oxidative state was comparatively stable, and once the polymer was doped with an anion, undoping was very difficult. As a result, the oxidation peak significantly decreased on the second cycle.

In summary, we successfully synthesized the side-chain type liquid crystalline poly(arylenevinylene)s. These mesophases were identified as nematic phases. The effective conjugated length for the polymers was similar to that of the alkyl-substituted PAV derivative. The polymers were found to be electrochemically active based on the cyclic voltammetric measurements. The detailed characterization, optical, and electrochemical properties of the polymers will be described in a forthcoming paper.

References and Notes

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(6) 3-Thiophenemethanol (15.0 g, 1.3×10^{-1} mol) was dissolved in 200 ml of dry dichloromethane. *N*-bromosuccinimide (50.0 g, 2.8×10^{-1} mol) was slowly added to the solution and stirred at the room temperature for 1.5 h. The solution was washed with 200 mL of 10% KOH (aq) and then with water until the solution was neutral. The organic layer was dehydrated with $MgSO_4$ and then evaporated. Upon recrystallization from hexane, 30.0 g (84.0% yield) of compound **1** was obtained as white needles. Mp: 45 °C. IR (Nujol, cm^{-1}): 3500−3200 (O−H), 850 (C−H, heterocyclic), 562 (C−Br). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.8−2.2 (1H, s), 4.6−4.8 (2H, s), 7.2−7.3 (1H, s).
(7) Compound **1** (5.0 g, 1.8×10^{-2} mol) was dissolved in 200 mL of THF, and 1,12-dibromododecane (13.7 g, 4.2×10^{-2} mol), KOH(aq) (2.0 g, 8.9×10^{-2} mol), tetra-*n*-butylammonium bromide (2.0 g 6.0×10^{-3} mol), and a small amount of KI were added to the solution. The solution was refluxed for 48 h, and then THF was evaporated. A 200 mL aliquot of chloroform was added to the residue which washed with water until the organic layer was neutral. The organic layer was dehydrated with $CaCl_2$ and then evaporated. Compound **2** was isolated by column chromatography (hexane, ethyl acetate). A 8.0 g (86.0%) yield of light yellow oil was obtained. IR (neat, cm^{-1}): 2930−2850 (C−H), 1105 (C−O), 850 (C−H, heterocyclic), 562 (C−Br). ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.7−2.2 (20H, m), 2.9−3.6 (4H, m), 4.3−4.4 (2H, s), 7.1−7.2 (1H, s).
(8) Compound **2** (8.0 g, 1.5×10^{-2} mol) was dissolved in 200 mL of acetone, and 4-cyano-4′-hydroxybiphenyl (3.0 g, 1.5×10^{-2} mol), K_2CO_3 (7.9 g, 5.7×10^{-2} mol), and a small amount of KI were added to the solution. The solution was refluxed for 10 h, and then the resulting salts were removed by filtration. The filtrate was evaporated, and the residue was purified by column chromatography (chloroform, hexane). A 6.8 g (75.0%) yield of compound **3-a** was obtained as a white powder. Mp: 57 °C. T_{i-1c}: 30 °C. IR (KBr, cm^{-1}): 2937−2846 (C−H), 2225 (CN), 1606, 1498 (C−C, Ar),

1245 (C−O, Ar), 1101 (C−O), 821 (C−H, Ar), 562 (C−Br). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.2−2.0 (20H, m), 3.3−3.7 (2H, t), 4.0−4.4 (2H, t), 4.5 (2H, s), 6.9−7.9 (9H, m). Compound **3-b.** IR (KBr, cm^{-1}): 2922−2864 (C−H), 2224 (CN), 1601, 1500 (C−C, Ar), 1581 (N=N), 1238 (C−O, Ar), 1107 (C−O), 821 (C−H, Ar), 562 (C−Br). ^{1}H-NMR ($CDCl_3$, δ ppm): 1.2−2.0 (20H, m), 3.3−3.7 (2H, t), 4.0−4.3 (2H, t), 4.5 (2H, s), 7.1−8.3 (9H, m). Mp: 82 °C.

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(15) The content of divinylbenzene isomers in the reagent is based on ^{13}C-NMR and ^{1}H-NMR.

(16) A dried three-necked flask was charged with compound **3-a** (1.0 g, 1.6×10^{-3} mol), palladium acetate (14 mg, 6.2×10^{-5} mol), and tris(*o*-methylphenyl)phosphine (96 mg, 3.2×10^{-4} mol). The flask was evacuated and filled with nitrogen. Then 10 mL of dry DMF, 1.5 mL of dry triethylamine and divinylbenzene (0.21 g, 1.6×10^{-3} mol) were added via syringe, and the reaction mixture was stirred at 100 °C for 20 h in a steam of nitrogen. After the reaction, the mixture was poured into 5% HCl−methanol to precipitate the polymer. The polymer was further purified by dissolution in THF and reprecipitated with methanol. IR (KBr, cm^{-1}): 2923−2852 (C−H), 2224 (CN), 1670 (C=C, trans), 1603, 1495 (C−C, Ar), 1252 (C−O, Ar), 1101 (C−O), 948 (C−H, alkene), 821 (C−H, Ar). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.0−1.9 (20H, m), 3.3−3.6 (2H, t), 3.8−4.0 (2H, t), 4.5 (2H, s), 6.5−6.7 (4H, m), 6.7−7.7 (13H, m).

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