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Synthesis and Properties of Liquid-Crystalline Polyacetylenes with a Phenylcyclohexyl Mesogenic Moiety in the Side Group

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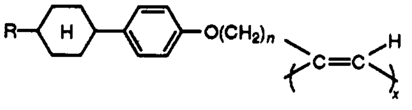
ABSTRACT: We present a series of side-chain liquid-crystalline conjugative polymers, poly(monosubstituted acetylenes), where the side group is composed of a phenylcyclohexyl moiety as a mesogenic core, a methylene chain as a spacer, and an alkyl chain as a terminal group. Monosubstituted acetylene monomers are synthesized and then polymerized by using Ziegler–Natta and metathesis catalysts. Through measurements of DSC (differential scanning calorimetry) and polarizing microscopy, the polymers prepared are found to show a smectic A liquid-crystalline phase with a fan-shaped texture. Characterizations of these polymers are also made in view of molecular weight, thermal isomerization of the *cis* to *trans* form, and enthalpy changes associated with phase transitions.

Introduction

In recent years, side-chain liquid-crystalline polymers with a flexible main chain have been widely investigated.[1–3] However, the synthesis and characterization of liquid-crystalline polymers with a rigid main chain have been less studied so far.[4] Among them, the conjugated polymer with a liquid-crystalline moiety in the side group is very interesting, since an alignment of the side-chain liquid-crystalline moiety would cause an improvement of orientation and effective conjugation in the main chain.

In the previous work, we have reported the synthesis, structures, and thermal stability of new type monosubstituted polyacetylenes with a liquid-crystalline moiety in the side chain as shown below. These polymers are prepared by polymerizing corresponding monomers using Ziegler–Natta (Fe(acac)$_3$–AlEt$_3$, etc.) and metathesis (MoCl$_5$–Ph$_4$Sn, etc.) catalysts.[5]



PPCH001A: R = H, *n* = 1
PPCH003A: R = H, *n* = 3
PPCH004A: R = H, *n* = 4
PPCH303A: R = *n*-propyl, *n* = 3
PPCH503A: R = *n*-pentyl, *n* = 3

Among the above polymers, for example, poly[5-(*p*-(*trans*-4′-*n*-propylcyclohexyl)phenoxy)-1-pentyne] is abbreviated as PPCH303A, where P, PCH, 3, 03, and A represent polymer, phenylcyclohexyl mesogenic moiety, number of carbons in the alkyl group attached to the cyclohexyl group, ether linkage + number of methylenic units in the spacer between the phenoxy and acetylenic groups, and terminal acetylene, respectively.

We now report the thermotropic liquid-crystalline properties of polymers PPCH303A, PPCH503A, and PPCH803A through polarizing microscopy and DSC measurements.

Experimental Section

Catalysts and Solvent. Tris(acetylacetonato)iron, (Fe(acac)$_3$), molybdenum pentachloride, (MoCl$_5$), triethylaluminum (AlEt$_3$), and tetraphenyltin (Ph$_4$Sn) were used as received. Commercial-grade toluene was distilled over sodium under argon gas prior to use.

Table I. Polymerization[a] of PCHR01As with Fe(acac)$_3$–AlEt$_3$ and MoCl$_5$–Ph$_4$Sn as Catalysts

	Fe(acac)$_3$–AlEt$_3$[b]			MoCl$_5$–Ph$_4$Sn[c]		
polymer	yield (%)	M_n	M_w	yield (%)	M_n	M_w
PPCH303A	60	6.1×10^5	2.5×10^6	61	1.5×10^4	3.4×10^4
PPCH503A	65	5.1×10^5	2.2×10^6	67	1.4×10^4	3.3×10^4
PPCH803A	60	5.6×10^6	2.4×10^6	73	1.2×10^4	2.7×10^4

[a] Polymerized in toluene for 21 h at room temperature. [b] Polymers are soluble in organic solvents such as CHCl$_3$, THF, and benzene at 50–60 °C. GPC spectra were measured by using the polymers which were first dissolved in THF with the aid of heating and then allowed to cool to room temperature. [c] Polymers are soluble in the same solvents at room temperature.

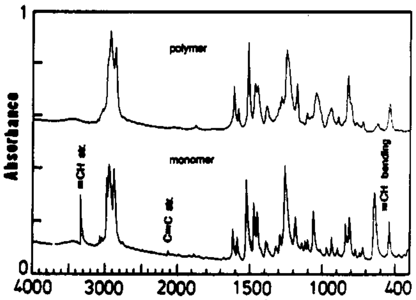


Figure 1. IR spectra of monomer (PCH503A) and polymer (PPCH503A) prepared by the Fe(acac)$_3$–AlEt$_3$ catalyst.

Monomers. The synthesis of the monomers, 1-[*p*-(*trans*-4′-alkylcyclohexyl)phenoxy]alkyne (PCHR03A) where R = *n*-propyl, *n*-pentyl, and *n*-octyl, was carried out according to procedures previously reported.[5]

Polymerization Procedure. A typical procedure for the polymerization is as follows: A catalyst solution was prepared by dissolving Fe(acac)$_3$ (0.011 g, 0.03 mmol) [or MoCl$_5$ (0.008 g, 0.03 mmol)] with 2.2 mL of toluene in a Schlenk flask with stirring under argon gas. To the solution was added AlEt$_3$ (0.025 mL, 0.18 mmol) [or in the case of MoCl$_5$, Ph$_4$Sn (0.006 g, 0.015 mmol)] at room temperature. After aging the solution at room temperature for 30 min, 3 mmol of monomer dissolved with 0.4 mL of toluene was added. Polymerization was carried out at 25 °C for 21 h, and it was terminated by pouring a large amount of methanol into the reaction mixture. The polymer produced was filtered off, washed with methanol, and then dried under vacuum.

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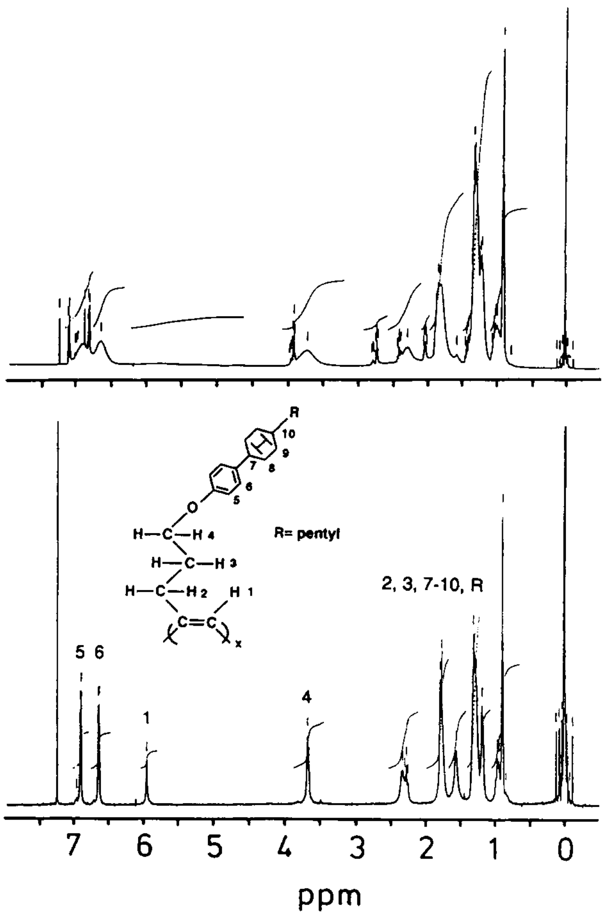

Figure 2. ^{1}H-NMR spectra of PPCH503A prepared by the Fe(acac)$_3$–AlEt$_3$ (bottom) and MoCl$_5$–Ph$_4$Sn (top) catalysts.

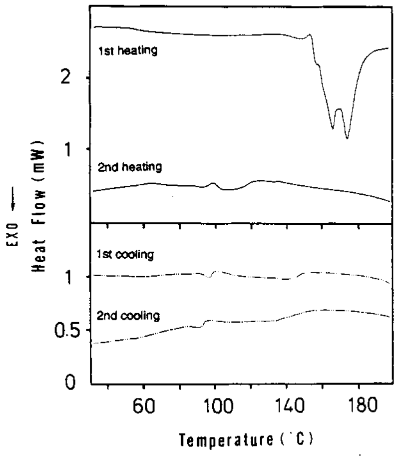

Figure 3. DSC thermogram of PPCH503A prepared by the Fe(acac)$_3$–AlEt$_3$ catalyst at a rate of 5 °C/min.

Spectroscopic Measurements. FT-IR spectra were measured by a Jasco FT-IR 8000 spectrometer using the KBr method. NMR spectra were recorded on a JEOL FT-NMR spectrometer using CDCl$_3$ as a solvent and TMS as an internal standard for both ^{1}H and ^{13}C NMR measurements. The molecular weight distribution was observed by gel permeation chromatography (GPC) evaluated by using a Shodex A-80M column and a Jasco HPLC 870-UV detector. Number- and weight-average molecular weights were calculated using a calibration curve obtained with polystyrene standards. Thermal transition characteristics were determined by using a Perkin-Elmer differential scanning calorimeter (DSC 7) at a rate of 5 °C/min under an argon atmosphere. Liquid-crystalline textures were examined under crossed polarizers by using a Nikon polarizing microscope equipped with a Linkam THMS 600 hot stage.

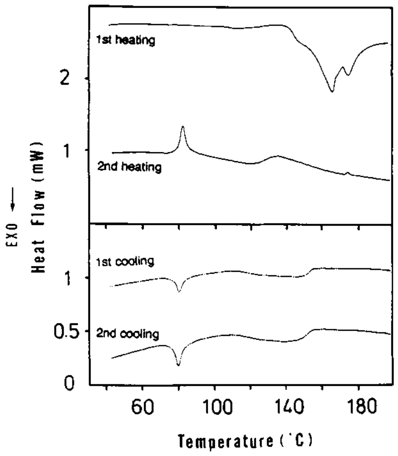

Figure 4. DSC thermogram of PPCH803A prepared by the Fe(acac)$_3$–AlEt$_3$ catalyst at a rate of 5 °C/min.

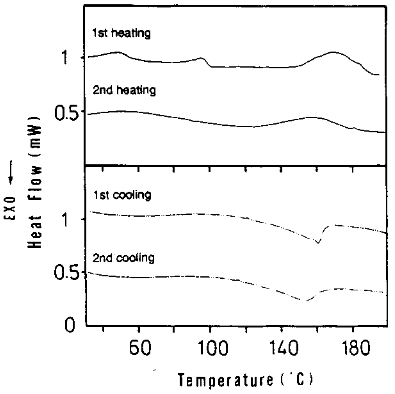

Figure 5. DSC thermogram of PPCH503A prepared by the MoCl$_5$–Ph$_4$Sn catalyst at a rate of 5 °C/min.

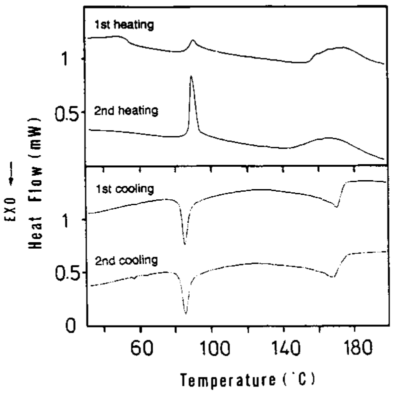

Figure 6. DSC thermogram of PPCH803A prepared by the MoCl$_5$–Ph$_4$Sn catalyst at a rate of 5 °C/min.

Table II. DSC Results of PPCHR03As Prepared by the Fe(acac)$_3$–AlEt$_3$ and MoCl$_5$–Ph$_4$Sn Catalysts[a]

		phase transitions (°C) and corresponding enthalpy changes (J/g)			
		first cooling		second heating	
catalyst	polymer	$k \rightarrow s_A$	$s_A \rightarrow i$	$k \rightarrow s_A$	$s_A \rightarrow i$
Fe	PPCH303A	60 (0.7)	107 (4.5)	70 (0.7)	102 (3.3)
	PPCH503A	98 (1.1)	146 (6.3)	100 (1.3)	128 (6.2)
	PPCH803A	81 (3.2)	151 (8.2)	83 (3.3)	142 (5.8)
Mo	PPCH303A[b]		133 (4.2)		134 (3.7)
	PPCH503A[b]		160 (6.2)		160 (4.5)
	PPCH803A	86 (3.4)	171 (6.7)	91 (3.7)	166 (6.4)

[a] k = crystalline, s_A = smectic A, and i = isotropic. [b] No distinct DSC peak associated with the phase transition between the crystalline phase and smectic A phase was observed (see Figure 5).

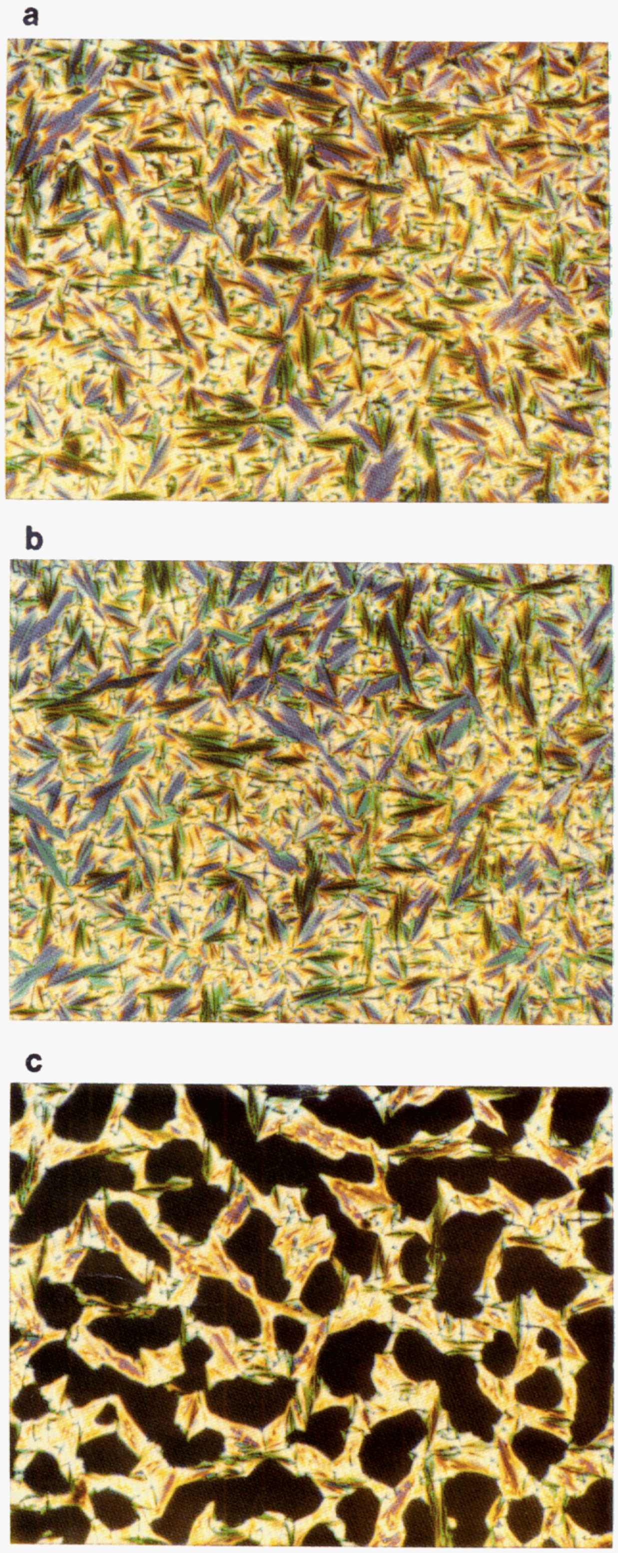

Figure 7. Polarizing optical micrographs of PPCH503A prepared by the Fe(acac)$_3$–AlEt$_3$ catalyst. Magnification ×200. Photographs have been reduced by 80% for publication. (a) Fan-shaped texture of smectic A phase obtained after cooling to 130 °C. (b) After cooling to 75 °C. (c) Mixture of smectic A phase and isotropic phase obtained after reheating to 150 °C.

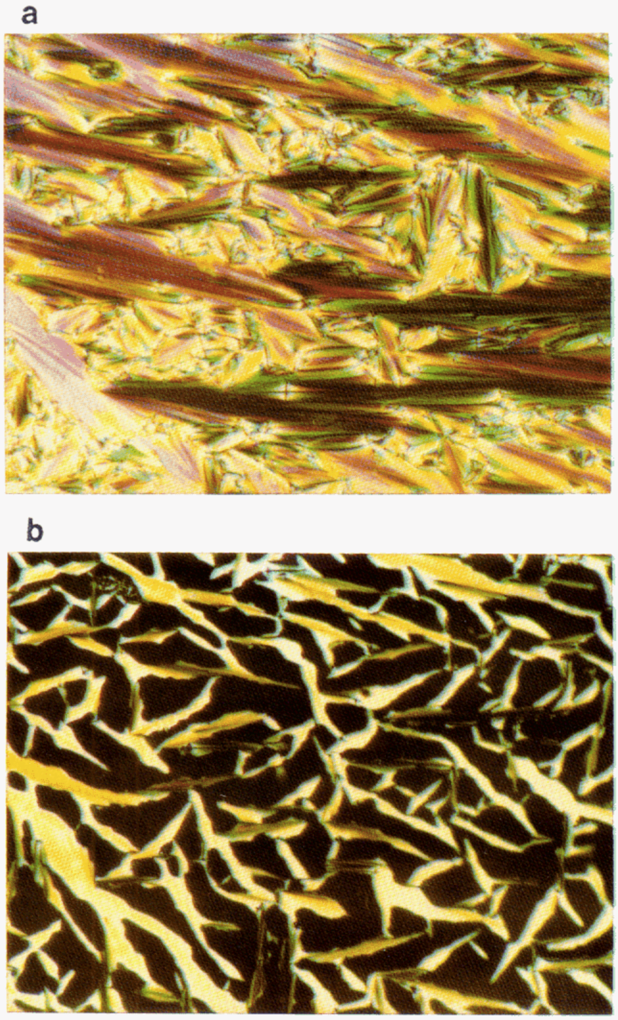

Figure 8. Polarizing optical micrographs of PPCH503A prepared by the MoCl$_5$–Ph$_4$Sn catalyst. Magnification ×200. Photographs have been reduced by 80% for publications. (a) Fan-shaped texture of smectic A phase obtained after cooling to 150 °C. (b) Mixture of smectic A phase and isotropic phase obtained after reheating to 160 °C.

Results and Discussion

Table I summarizes the results of polymerization of PPCHR03As with Fe(acac)$_3$–AlEt$_3$ and MoCl$_5$–Ph$_4$Sn as catalysts.

A satisfactory yield was obtained in the range of 60–73% for the present polymerization. No methanol-soluble product was checked in this study. Thus, the yield is based on the methanol-insoluble products. The polymers prepared using the metathesis catalyst were soluble in organic solvents such as CHCl$_3$, THF, and benzene at room temperature. However, the polymers prepared using the Ziegler–Natta type catalyst are insoluble at room temperature but become soluble with the aid of heating at 50–60 °C. Once the polymers are dissolved, their solutions gave no precipitate even after cooling down to room temperature. Thus, we measured GPC spectra of these polymers at room temperature, as in the case of the polymers prepared by the metathesis catalysts. High molecular weight polymers of M_w = ca. 3×10^6 were obtained by the Fe(acac)$_3$–AlEt$_3$ catalyst. A more detailed result of the polymerization was presented in the previous paper.[5] IR absorption spectra of monomer (PCH503A) and polymer (PPCH503A) prepared by the Fe(acac)$_3$–AlEt$_3$ catalyst are shown in Figure 1.

The IR absorption spectrum of the polymer shows no absorption peak characteristic to the monomer, e.g., $\equiv$CH stretching at 3310 cm^{-1}, C$\equiv$C stretching at 2121 cm^{-1}, and $\equiv$CH out-of-plane vibration at 630 cm^{-1}. ^{1}H-NMR spectra of PPCH503As prepared by the Fe(acac)$_3$–AlEt$_3$ and MoCl$_5$–Ph$_4$Sn catalysts are shown in Figure 2.

The polymer prepared by the Fe(acac)$_3$–AlEt$_3$ catalyst has a sharp peak characteristic of the olefin proton of the *cis* form at 5.97 ppm.[5] However, in the case of the polymer prepared by the $MoCl_5$0Ph_4Sn catalyst, the olefin proton of the *cis* form disappeared due to the *trans*-rich double bonds in the polymer.

Mesomorphic properties of PPCHR03As were examined by DSC and polarizing microscopy. Thermal transition characteristics were determined by DSC measurements, and mesophases were identified according to their birefringent textures. DSC thermograms of PPCH503A and PPCH803A prepared by the $Fe(acac)_3$–$AlEt_3$ catalyst are shown in Figures 3 and 4, respectively.

The DSC curves in the first heating show large exothermic peaks (corresponding to enthalpy changes of 3.5–3.6 kcal/mol) due to *cis* to *trans* thermal isomerization at 167 and 175 °C. Through the observation of a polarizing microscope, clearing points of these polymers were found around 175–195 °C. In the second heating, two endothermic peaks corresponding to crystal–mesophase transition and clearing point were observed, and the exothermic isomerization peak detected in the first heating disappeared. Upon the first cooling from the isotropic phase of the PPCH503A, two exothermic peaks were observed at 146 °C due to isotropic phase–mesophase transition and at 98 °C due to mesophase–crystal transition (in the case of PPCH803A at 151 and 81 °C, respectively). DSC thermograms of PPCH503A and PPCH803A prepared by the $MoCl_5$–Ph_4Sn catalyst are shown in Figures 5 and 6, respectively.

In the first heating of PPCH503A, a broad endothermic peak was observed between 149 and 190 °C (in the case of PPCH803A between 155 and 195 °C). In the polarizing optical micrograph, crystal to mesophase and mesophase to isotropic phase transitions were observed in this temperature range. It should be noted that no exothermic peak corresponding to *cis* to *trans* thermal isomerization was observed in the Mo-based polymers. Thus, it may be argued that the $MoCl_5$–Ph_4Sn catalyst gives *trans*-rich polymers, which is also supported from the result of ^{1}H-NMR measurements.[5] Upon cooling from the isotropic state of the PPCH503A a mesophase transition was found at 160 °C (in the case of PPCH803A at 171 °C). The DSC curve of PPCH803A shows a peak corresponding to mesophase–crystal transition at 86 °C, but no peak was observed in the case of PPCH503A. DSC thermograms of PPCH303As prepared by Fe and Mo catalysts were similar to those of PPCH503As. Table II summarizes the phase transition temperatures and corresponding enthalpy changes for the PPCHR03As evaluated from the DSC measurements.

The enthalpies and temperatures corresponding to isotropic phase–mesophase transitions increased with increasing the length of the alkyl group (R). Mo-based polymers show higher transition temperatures compared to Fe-based polymers. We have reported in the previous paper that thermal degradation of these polymers is accompanied with *cis* to *trans* thermal isomerization.[5] Mo-based polymers with *trans*-rich configurations are more stable than Fe-based polymers in the first heating process. Hence, the temperatures of isotropic–mesophase transitions of Mo-based polymers should be higher than those of Fe-based polymers. Here it is worth noting the influence of thermal degradation on molecular weight and transition temperature in DSC measurements. After the first heating up to 200 °C, the number-average molecular weights of the Mo- and Fe-based polymers decreased to ca. half and one-fiftieth the initial values, respectively. However, no drastic decrease in molecular weight was observed after the subsequent cooling and heating treatments. After repeating the heating and cooling cycles 10 times, the transition temperatures of the crystal–mesophase and mesophase–isotropic phases only shifted by 10–20 °C to a lower temperature region. In fact, the smectic A liquid-crystalline texture was still observed in the polarizing microscope.

The polarizing optical micrographs of the PPCH503As prepared by Fe and Mo catalysts are shown in Figures 7 and 8, respectively.

In the case of the Fe-based polymer, upon cooling from the clearing point of 181–188 °C, a smectic A phase with a fan-shaped texture was observed at 130–145 °C and no dramatic change of the texture was visible until the room temperature. On reheating of the polymer, a mixed phase of mesophase and isotropic phases was observed at 140–174 °C. In the first heating process of the Mo-based polymer, a smectic A phase appeared at 150–159 °C and changed to an isotropic phase at 163–185 °C. Upon cooling from the clearing point, a smectic A phase with a fan-shaped texture was observed at 165–169 °C. Its domain size is larger than that of the Fe-based polymer. This is probably due to less decrease in molecular weight after the first heating process compared to the case of the Fe-based polymer. The polarizing optical micrographs of the PPCH303As and PPCH803As show the fan-shaped texture similar to those of the PPCH503As.

Now, we are investigating X-ray diffraction and electrical conductivity of the present polymers. The study of other monosubstituted polyacetylenes with a biphenyl mesogenic moiety is also in progress.

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