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Side Chain Liquid Crystalline Polyacetylene Derivatives
- Synthesis and Properties -

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Liquid crystalline (LC) polyacetylene derivative with a hexamethylene chain as a spacer in LC side chain was synthesized. The acetylene monomer substituted with LC group showed both nematic and smectic phases in the cooling process. The polymerizations of the monomers were carried out using Ziegler-Natta and metathesis catalysts. The polymers thus prepared showed smectic phases in heating and cooling processes, indicating an enantiotropic nature. We found that the mesophase of the present polymer is more stabilized with a longer methylene spacer.

Keywords: conjugated polymer, liquid crystallinity, electrical conductivity

1. Introduction

Recently we developed novel conducting polymers by introducing LC groups in the side chains of polyacetylenes [1-12]. The LC group is composed of a phenylcyclohexyl (PCH) or biphenyl (BP) moiety as a mesogenic core, a trimethylene chain linked with an ether-type oxygen atom [-(CH$_2$)$_3$O-] as a spacer, and an alkyl chain as a terminal group. The polymers are abbreviated as PPCHn03A (n = 2, 3, 5 ~ 8) or PBP503A. Examinations of a series of PPCHn03A polymers showed that temperature ranges of LC phases tend to increase with an increase of the terminal alkyl chain length [7,12]. At the present stage, however, it remains unsettled how the methylene chain length in the LC group affects the stability of the mesophase [10].

Here we synthesized an acetylene derivative with a hexamethylene spacer through newly designed synthetic routes, and then polymerized it using Ziegler-Natta [Fe(acac)$_3$-AlEt$_3$] and metathesis [MoCl$_5$-Ph$_4$Sn] catalysts. The monomer and polymers are abbreviated as PCH506A and PPCH506As, respectively. They are compared with the corresponding monomer (PCH503A) and polymers (PPCH503As) with the trimethylene spacer in terms of thermal stability and LC phase.

2. Experimental

2.1. Synthesis of monomer

(i) 6-*p*-(*trans*-4'-pentylcyclohexyl) phenoxy-1 bromohexane, PCH506Br

p-(*trans*-4-Pentylcyclohexyl)phenol, [PCH500] (24.5 g, 100 mmol) was dissolved in 150 ml of ethanol, and then added to a solution of sodium (2.3 g, 100 mmol) dissolved in 50 ml of ethanol. After the solution was allowed to stir overnight, it was added drop wise to a 1,6 dibromohexane (46.1 ml, 300 mmol). The solution was heated during the reaction and stirred overnight, to give a white solid (NaBr). After evaporation, ether was added and organic layer was extracted and washed with water several times. After the compound insoluble to hexane was removed, the product was recrystallized with ethanol. White needle solid (PCH506Br) was obtained in yield of 39 %.

(ii) 8-*p*-(*trans*-4'-pentylcyclohexyl) phenoxy 1-octyne, PCH506A

To a solution of PCH506Br (14.3 g, 35 mmol) in 30 ml of DMF and 20 ml of THF was added an excess amount of sodium acetylide. The reaction was carried out at 60 °C for 20 h. The color was changed from muddy brown to muddy violet. The reaction was terminated by adding a small amount of water into the solution. After evaporation, ether was added and organic layer was washed with water several times. Then CaCl$_2$ was added. After removal of CaCl$_2$, ether was evaporated and the residue was recrystallized with ethanol. The white solid obtained was purified with column chromatography, where an equimolar mixture of

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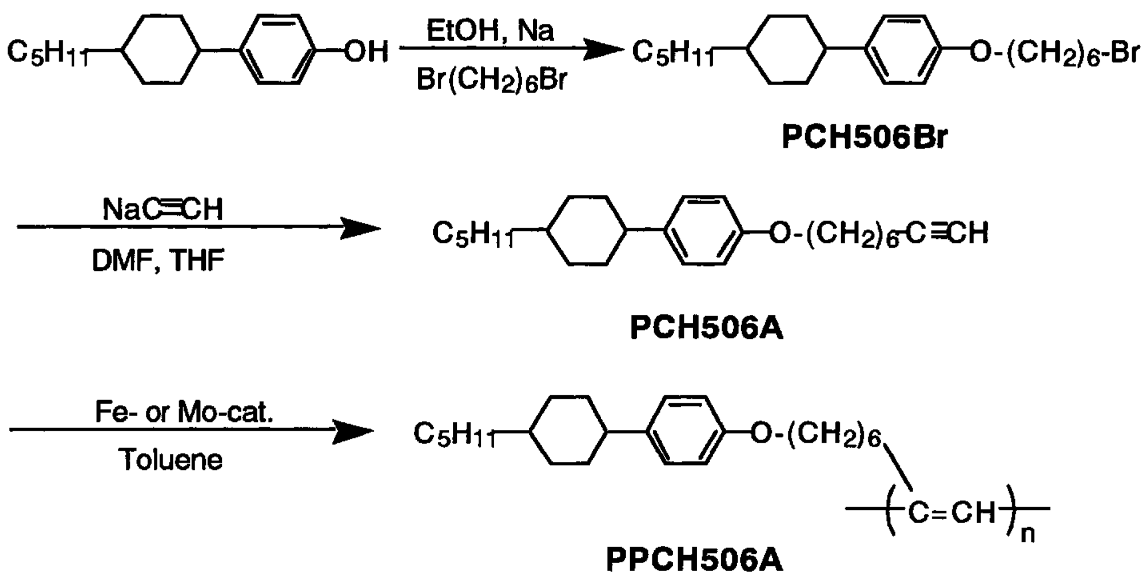

CH_2Cl_2 and hexane was used as an eluant. White solid (1.2 g, 3.5 mmol) [PCH506A] was obtained in yield of 10%.

Anal. Calcd. for $C_{25}H_{38}O$, C : 84.7, H : 10.8 ; Found, C : 84.6 H : 10.9.

2.2. Polymerization

A typical procedure for the polymerization is as follows. A catalyst solution was prepared by dissolving $Fe(acac)_3$ (2.8 mg, 0.008 mmol) in toluene solution of Et_3Al (0.8 ml, 0.03 mol/l). After aging the solution at room temperature for 1h, the monomer [PCH506A] (0.8 mmol) was added to the solution. Polymerization was carried out at room temperature for 20 h, and it was terminated by pouring a large amount of methanol into the reaction mixture. The polymer prepared was washed with methanol through decantation three times, and filtered off, and then dried under vacuum.

Table I. Polymerization of PCH506A with $Fe(acac)_3$-Et_3Al and $MoCl_5$-Ph_4Sn catalysts

Cat.	Yield (%)	Mn	Mw	Mw / Mn
Fe	32	3.3×10^5	8.1×10^5	2.5
Mo	48	5.9×10^4	8.4×10^4	1.4

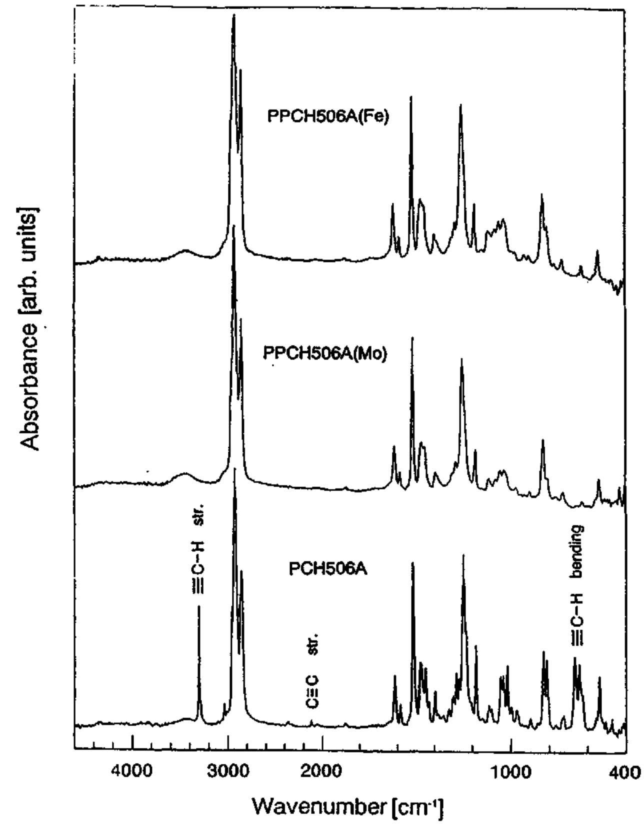

Fig. 1. IR spectra of monomer, PCH506A and polymers, PPCH506As.

3. Results and Discussion

Table I summarizes polymerization results of PCH506A with two kinds of catalysts, Fe(acac)$_3$-Et$_3$Al and MoCl$_5$-Ph$_4$Sn. Hereafter, the polymers synthesized with the former and the latter catalysts are abbreviated as PPCH506A(Fe) and PPCH506A(Mo), respectively. High molecular weight of 8 × 10^5 in Mw was obtained by the Fe(acac)$_3$-Et$_3$Al catalyst. The molecular weight of Fe-based polymer was higher than that of Mo-based one. The tendency was also observed in the polymers of PPCHn03As with the trimethylene spacer [1,6,7].

The IR spectra of the polymers showed no absorption peak characteristic of the monomer, e.g., $\nu_{\equiv C\text{-}H}$ stretching at 3298 cm^{-1}, $\nu_{C\equiv C}$ stretching at 2118 cm-1, and $\nu_{\equiv C\text{-}H}$ out-of-plane vibration at 663 and 638 cm^{-1}. This indicates an occurrence of polymerization at acetylene moiety (Fig. 1).

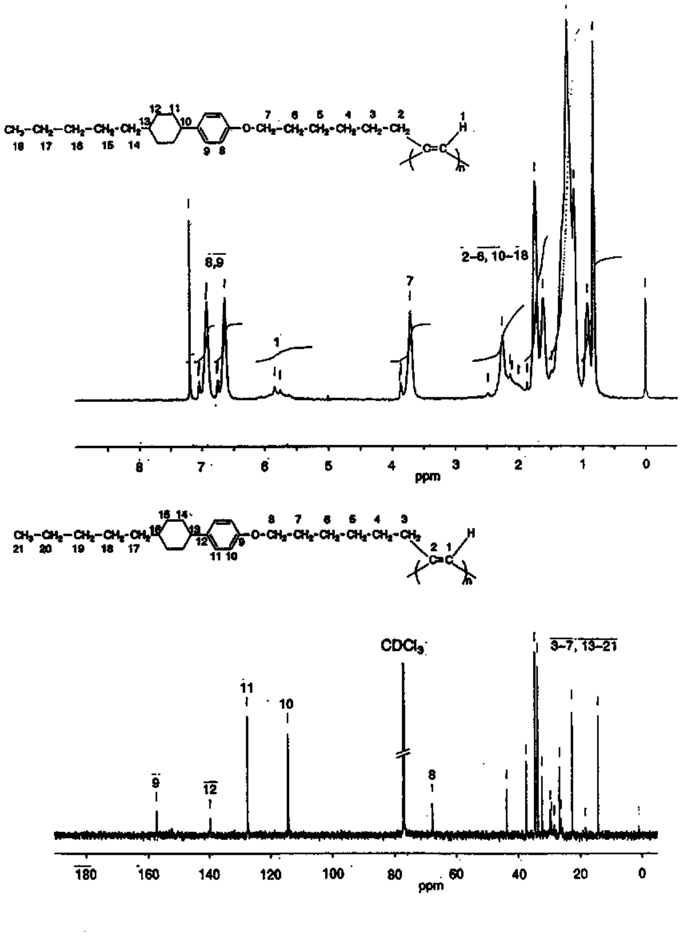

Fig. 2. ^{1}H- (upper) and ^{13}C-(lower) NMR spectra of PPCH506A(Fe).

^{1}H-NMR spectrum of PPCH506A(Fe) showed a peak assignable to the olefinic proton of *cis* form at 5.8 ppm (Fig. 2). However, PPCH506A(Mo) had no signal of the olefinic proton of the *cis* form, indicating a formation of *trans* form (Fig. 3) [5,10].

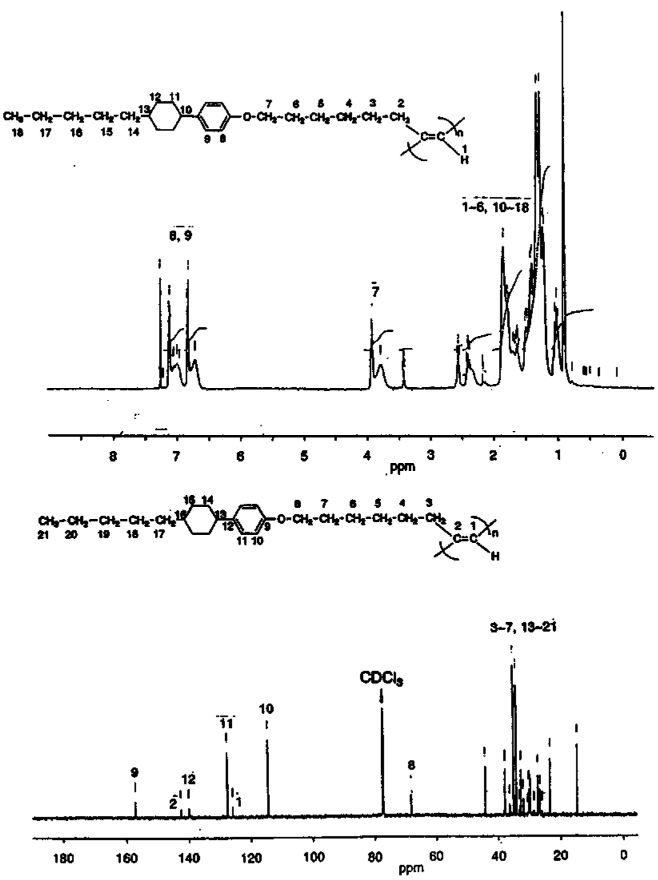

Fig. 3. ^{1}H- (upper) and ^{13}C-(lower) NMR spectra of PPCH506A(Mo).

Mesophase textures of the monomer [PCH506A] and the polymers [PPCH506As] were observed in polarizing optical micrographs. In the cooling process from the isotropic phase, the monomer showed Schlieren texture characteristic of nematic phase at 29.7 °C (Fig. 4a), and subsequently it showed a mosaic texture assignable to smectic phase at 18.4 °C (Fig. 4b). This result is quite different from those of other kinds of monomers, e.g., PCH503A and PCH803A, which showed only a nematic phase (Fig. 5).

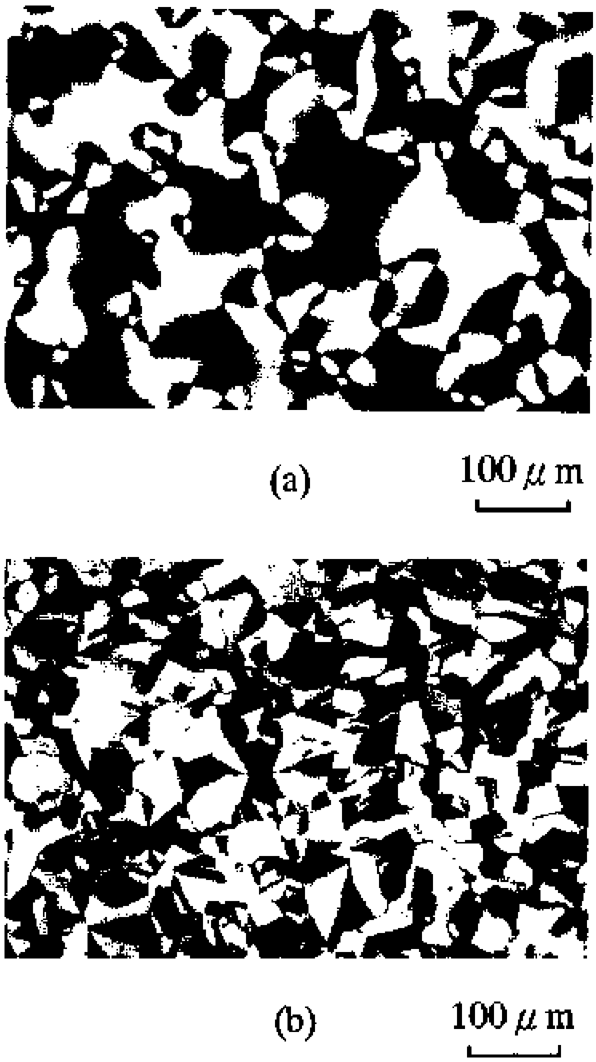

Fig. 4. Polarizing optical micrographs of PCH506A; (a) nematic phase, (b) smectic phase.

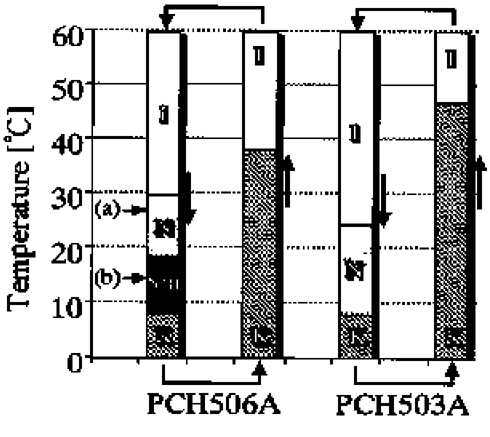

Fig. 5. Phase transition temperatures of acetylene monomers with different methylene spacers.

On the other hand, both polymers, PPCH506A(Fe) and PPCH506A(Mo), showed batonet textures characteristic of smectic phase around 140 °C in the cooling process (Fig. 6). The texture observed is different from those (fan-shaped texture) of the previously synthesized polymers with shorter spacer lengths such as PPCH503A and PPCH803A [2-4].

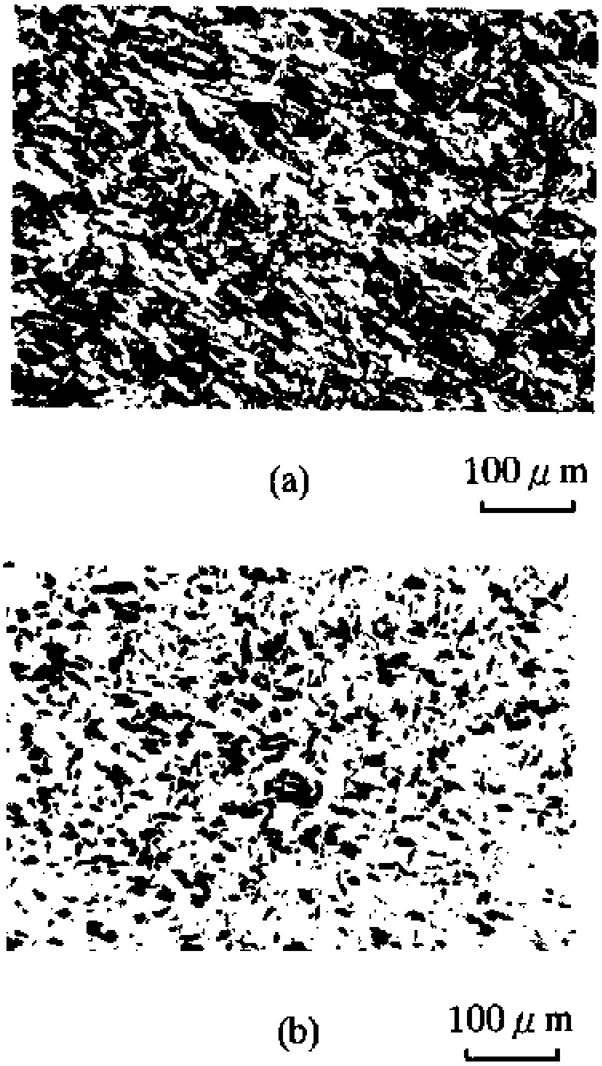

Fig. 6. Polarizing optical micrographs of PPCH506A; (a) Fe-based polymer, (b) Mo-based polymer.

DSC measurements for the polymers also showed the existence of mesophase. In the polymer prepared by the Fe(acac)$_3$ - Et$_3$Al catalyst, large and broad exothermic peak due to *cis* to *trans* thermal isomerization was observed around 140 ~ 180 °C in the first heating (Fig. 7).

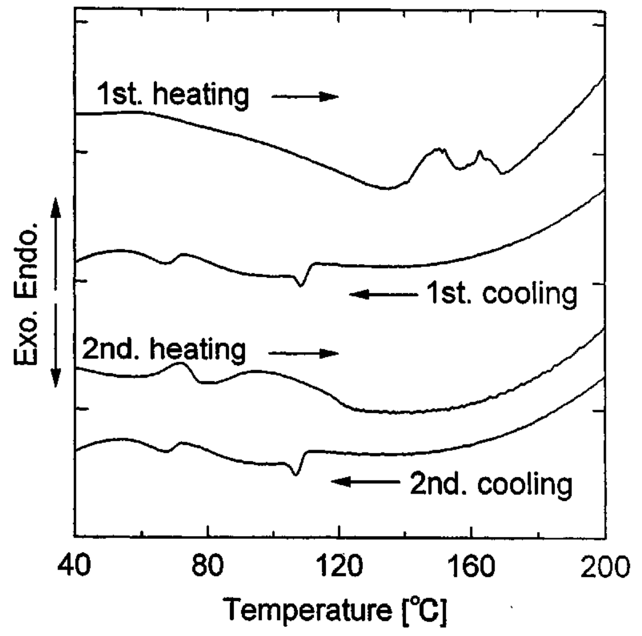

Fig. 7. DSC thermograms of PPCH506A (Fe).

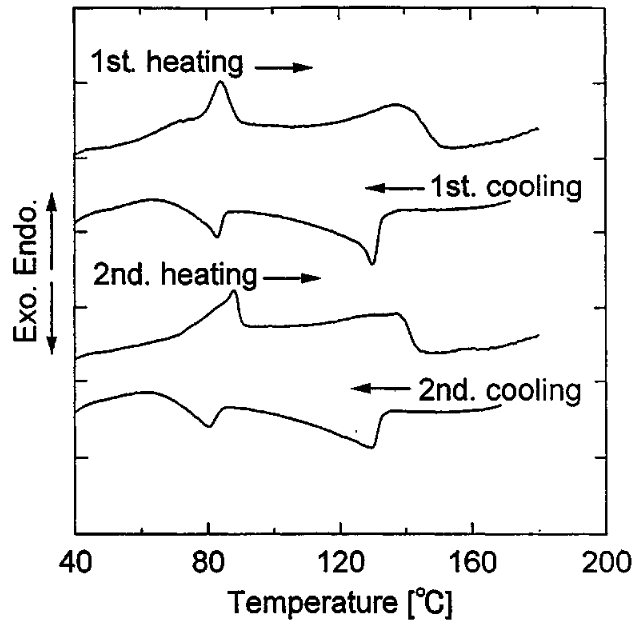

Fig. 8. DSC thermograms of PPCH506A (Mo).

In the first cooling from the isotropic phase, two exothermic peaks were observed at 110 °C due to isotropic - mesophase transition and at 68 °C due to mesophase - solid phase transition. In the second heating, two endothermic peaks corresponding to solid phase-mesophase transition and clearing point were observed. However there was no exothermic peak in the first heating, implying that the polymer has already become a thermally stable *trans* form after the first heating.

In the first heating of the polymer prepared by the $MoCl_5$-Ph_4Sn catalyst, two endothermic peaks corresponding to solid phase-mesophase transition and clearing point were observed (Fig. 8). It should be noted that no exothermic peak corresponding to *cis* to *trans* thermal isomerization was observed even in the first heating of the Mo-based polymer. Thus, it can be argued that the $MoCl_5$-Ph_4Sn catalyst gives a *trans*-rich polymer. This is supported from the result of ^{1}H-NMR measurement, where no peak around 6 ppm assignable to *cis*-olefin proton was observed (see, Fig. 3). The result is also coincident with that of PPCH503A(Mo) [4,10]. In the cooling process of PPCH506A(Mo), the exothermic peak due to the mesophase - solid phase transition was clearly observed at 80 ~ 88 °C. In contrast, no notable peak was observed in PPCH503A(Mo). The DSC curves of PPCH506A(Mo) is rather similar to that of PPCH803A, where the octyl moiety is adopted as the terminal alkyl group in LC side chain.

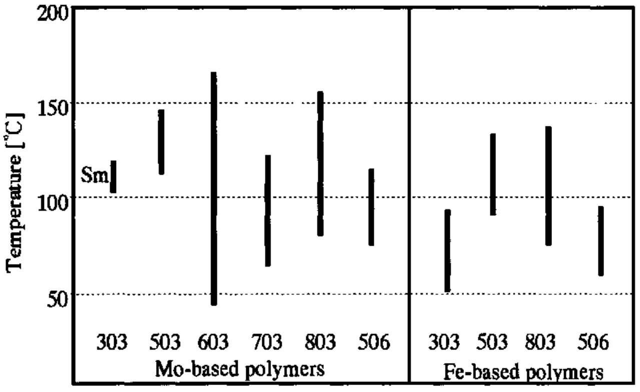

Fig. 9. Phase transition temperatures of PPCHn03A and PPCH506A in the first cooling process of DSC measurements.

It may be remarked from Fig. 9 that the longer LC side chain stabilizes the mesophase, especially by expanding the lower temperature region. In other words, the longer side chain decouples the molecular motion coupled between the main chain and LC side chain, resulting in the stabilization of the mesophase.

Lastly it is worthy noting that the Fe-based polymer, PPCH506A(Fe), showed a broad absorption band at 320 ~ 340 nm, assigned to the π → π* transition in the conjugated polyene chain (Fig. 10). The relatively shorter wavelength of the absorption band is characteristic of the mono-substituted polyacetylene, in which the steric hindrance between bulky substitutions such as LC groups causes a lowering of coplanarity of main chain, resulting in a short effective conjugation length. The broadening of the absorption band implies that the polymer is composed of finite polyenes with various conjugation lengths. Meanwhile, the Mo-based polymer, PPCH506A (Mo), gave a shoulder band with less intensity (see also Fig. 10). This is primarily due to the difference in the polymerization degree that can be evaluated from number-average molecular weight (Mn), as already shown in Table I.

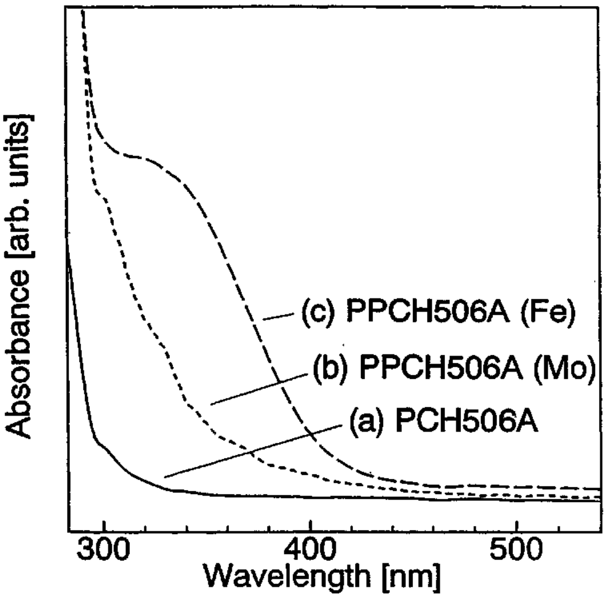

Fig. 10. UV-Vis spectra of monomer and polymers in chloroform.

4. Conclusion

We synthesized new LC polyacetylene derivatives (PPCH506As) with the hexamethylene spacer in the LC side chain, by polymerizing the corresponding monomer, PCH506A, using Ziegler-Natta and metathesis catalysts. The monomer showed two kinds of monotropic mesophases, nematic and smectic, in the cooling process. No smectic phase was observed in PCH503A with the shorter methylene spacer. ^{1}H-NMR and DSC measurements confirmed that PPCH506As prepared by the Ziegler-Natta and the metathesis catalysts are of *cis* and *trans* forms, respectively. Both polymers showed smectic phases in the heating and cooling processes, implying enantiotropic natures. PPCH506A(Mo) exhibited a notable DSC peak corresponding to the phase transition from the LC phase to solid state, although such a peak was not clearly observed in PPCH503A(Mo). This should come from the difference of the spacer length in the LC side chain.

References

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1. S.-Y. Oh, K. Akagi and H. Shirakawa, *J. Polym. Sci., Part A : Polym. Chem.*, **31**, (1993) 2977.
2. S.-Y. Oh, K. Akagi, H. Shirakawa, and K. Araya, *Macromolecules*, **26** (1993) 6203.
3. K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S-Y. Oh and K. Araya, *Synth. Met.*, **69** (1995) 13.
4. K. Akagi, H. Goto, K. Iino, H. Shirakawa, and J. Isoya, *Mol. Cryst. Liq. Cryst.*, **267** (1995) 277.
5. K. Akagi, H. Goto, H. Shirakawa, T. Nishizawa, and K. Masuda, *Synth. Met.*, **69** (1995) 33.
6. H. Goto, K. Akagi, H. Shirakawa, S.-Y. Oh and K. Araya, *Synth. Met.*, **71**, (1995) 1899.
7. K. Akagi and H. Shirakawa, *Macromol. Symp.*, **104** (1996) 137.
8. K. Akagi, H. Goto, and H. Shirakawa, *Synth. Met*, **84**, (1997) 313.
9. H. Goto, K. Akagi, and H. Shirakawa, *Synth. Met*, **84**, (1997) 373.
10. K. Iino, H. Goto, K. Akagi, H. Shirakawa, and A. Kawaguchi, *Synth. Met*, **84**, (1997) 967.
11. K. Akagi and H. Shirakawa, *The Polymeric Materials Encyclopedia. Synthesis, Properties and Applications,* CRC Press (1996), 5, pp. 366 - 3675.
12. K. Akagi and H. Shirakawa, *Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications*, Ed. by D.L. Wise, et al., Marcel Dekker (1998), Chap. 28, pp. 983 - 1010.