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Synthesis and Characterization of Novel Side-Chain Liquid Crystalline Polymers with a Poly(1,6-heptadiyne) Main Chain

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ABSTRACT: A new class of thermotropic side-chain liquid crystalline polymers containing a poly(1,6-heptadiyne) main chain was prepared by metathesis polymerization with transition-metal catalysts. It was found that the $MoCl_5$-based catalyst systems were very effective for the cyclopolymerization of presently investigated monomers. Resulting polymers exhibited good solubility in common organic solvents such as tetrahydrofuran (THF), chloroform, etc., and could be easily cast on glass plates to give black shiny thin films. The structure of the products was confirmed by IR, MS, UV–visible, and ^1H and ^{13}C NMR. The number-average molecular weight (M_n) values of the polymers were in the range of 4.9×10^3–1.1×10^5 relative to polystyrene standards by GPC. Thermal behavior, morphology, and electrical conductivity were investigated by using differential scanning calorimetry (DSC), cross-polarized optical microscopy, X-ray diffraction analysis, and an LCR meter. Both monomer and polymer displayed enantiotropic liquid crystallinity showing the reversible phase transitions. Room-temperature conductivities of the undoped and I_2-doped polymers were found to be about 10^{-11} and 10^{-2}–10^{-3} S/cm, respectively.

Introduction

Liquid crystalline polymers (LCPs) have been an important subject for fundamental and technological studies because of their unusual anisotropic optical, electrical, and mechanical properties.[1–6] They fall into two major categories: (1) species with rigid mesogenic groups incorporated into the backbone structure (main-chain LCPs); (2) polymers with mesogenic units in the side-group structure (side-chain LCPs). The present work deals with polymers of the second type. In this category most of the side-chain LCPs known up to date have contained polyacrylates and methacrylates,[6,7] polysiloxanes,[8,9] and polyphosphazenes.[10–12] More recent studies on the effect of the backbone flexibility include the use of flexible poly(ethylene oxide),[13] or more rigid poly(α-chloro acrylate)[14] chains.

Finkelmann and Ringsdorf proposed the spacer concept in 1978 as a systematic method for obtaining side-chain LCPs, with the idea that a spacer must be introduced to partially decouple the mobility of the main chain from that of the mesogenic groups.[6,15–17] If this is so, in this premise it was thought possible to obtain side-chain LC behavior even with a very rigid polymer backbone.

There are numerous examples of side-chain LCPs prepared by the various methods such as radical, cationic, and group-transfer polymerizations. However, a metathesis reaction technique to synthesize LCPs has not been used until recently. Furthermore, no systematic studies to prepare the side-chain LCPs with electrical conductivity have been reported yet. In our previous paper,[18] we reported the synthesis and characterization of monosubstituted poly(1,6-heptadiyne) containing a 4-methoxy-4′-hydroxybiphenyl mesogenic group with six methylene units as the flexible spacer in order to obtain the thermotropic LC mesomorphism from such a rigid polymer backbone.

In this paper we describe the results on the synthesis and characterization of a novel class of several thermotropic side-chain LC monomers and their polymers.

Experimental Section

Materials. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemical Co., resublimed 99.9%) were used without further purification. Palladium(II) chloride and ethylaluminum dichloride (Aldrich Chemical Co.) were used without further purification, and tetrabutyltin was distilled under reduced pressure. All solvents were used after purification according to conventional methods. The compound 4-cyano-4′-hydroxybiphenyl was obtained from Tokyo Kasei and was used as received.

Instruments. ^1H and ^{13}C NMR spectra were recorded with the use of a Bruker AM-300 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as internal standard. Infrared spectra were measured as neat oil or as KBr pellets on a Bomen MB-100 spectrometer, and frequencies were given in reciprocal centimeters. Mass spectra were obtained on a Hewlett-Packard 5985A GC/MS system using the electron impact (EI) method. A Shimadzu UV-3100S spectrometer was used for UV spectral data. The number-average molecular weight ($\bar{M}_n$) and polydispersity were determined in THF solvent by a Waters GPC-150C calibrated with polystyrene standards. A Perkin-Elmer DSC-4 thermal analyzer was used to obtain the DSC thermograms with heating rates of 10 and 40 °C/min in a nitrogen atmosphere. A Leitz Ortholux-II optical microscope equipped with a Mettler FP-80 hot stage was used in cross-polarized mode for visual observation of the thermotropic behavior and optical texture of the monomers and polymers. X-ray equipment with unoriented samples was carried out with Cu Kα radiation by the use of a flat-plate camera at mesophase temperature. The electrical conductivity was determined by an Ando AG-4303 LCR meter at a fixed frequency of 100 Hz with the applied voltage of 1 V.

Synthesis of 4-Methoxy-4′-hydroxybiphenyl. To a 500-mL three-neck flask equipped with an addition funnel and a mechanical stirrer was added 8.8 g (0.22 mol) of NaOH and 100 mL of H_2O. After dissolving 20 g (0.11 mol) of biphenyl in the NaOH solution, 15 g (0.11 mol) of dimethyl sulfate was added dropwise over 20 min. The reaction was slightly exothermic. The reaction mixture was stirred for 2 h and then filtered. The light-green filter cake was placed in 80 mL of a 10% NaOH aqueous solution and was heated and then allowed to cool. After it was filtered, the filter cake was added to 600 mL of water. The

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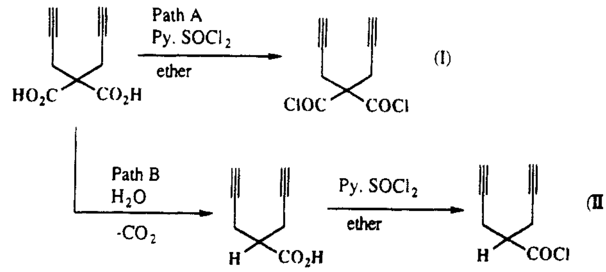
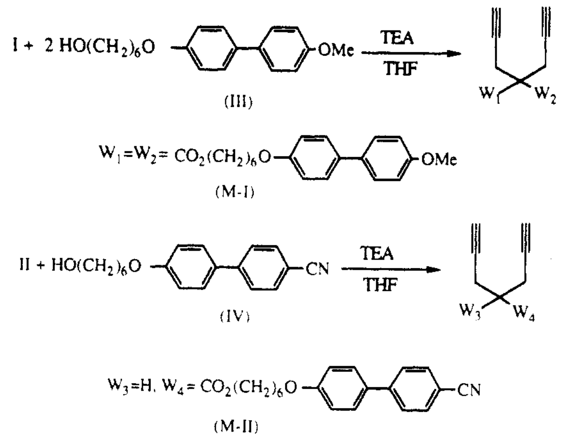
Scheme I



Scheme II



Scheme III

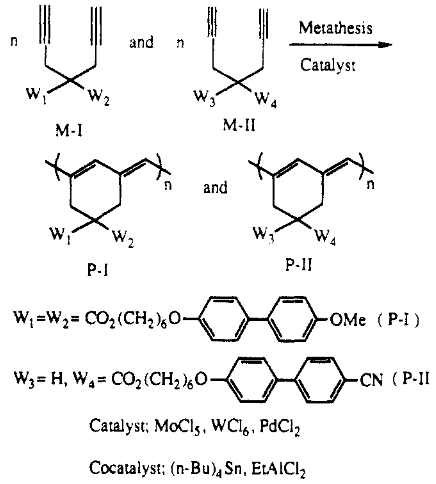


Table I
Polymerization of M-I with Various Transition-Metal Catalysts[a]

exp. no	catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	polym yield (%)[e]	$\bar{M}_n$/ 10^3 [f]	$\bar{M}_w$/ $\bar{M}_n$[f]
1	$MoCl_5$	50	0.125	95	42	1.8
2	$MoCl_5$	50	0.25	100	110	3.5
3	$MoCl_5$-$(n\text{-}Bu)_4Sn$ (1:1)	50	0.25	90	78	3.1
4	$MoCl_5$-$(n\text{-}Bu)_4Sn$ (1:4)	50	0.25	88	70.1	2.7
5	$MoCl_5$-$EtAlCl_2$ (1:1)	50	0.25	80	64.9	2.4
6	WCl_6	50	0.25	trace		
7	WCl_6-$(n\text{-}Bu)_4Sn$ (1:1)	50	0.25	trace		
8	WCl_6-$EtAlCl_2$ (1:1)	50	0.25	trace		

[a] Polymerization was carried out at 60 °C for 24 h in dioxane. [b] Mixture of catalyst and cocatalyst in chlorobenzene was aged out for 15 min before use as catalyst. [c] Monomer to catalyst mole ratio. [d] Initial monomer concentration. [e] Methanol-insoluble polymer. [f] Values were obtained by GPC analysis with polystyrene standard calibration.

Table II
Polymerization of M-II with Various Transition Metal Catalysts[a]

exp. no.	catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	polym yield (%)[e]	$\bar{M}_n$/ 10^3 [f]	$\bar{M}_w$/ $\bar{M}_n$[f]
1	$MoCl_5$	12.5	0.25	83	76	3.4
2	$MoCl_5$	25	0.25	60	75	3.1
3	$MoCl_5$	50	0.125	80	25	2.2
4	$MoCl_5$	50	0.25	84	60	2.9
5	$MoCl_5$-$(n\text{-}Bu)_4Sn$ (1:1)	50	0.25	42	38	2.1
6	$MoCl_5$-$EtAlCl_2$ (1:1)	50	0.25	46	47	
7	WCl_6	50	0.25	trace		
8	WCl_6-$(n\text{-}Bu)_4Sn$ (1:1)	50	0.25	trace		
9	WCl_6-$EtAlCl_2$ (1:1)	50	0.25	trace		
10	$PdCl_2$[g]	50	0.25	50	4.9	

[a] Polymerization was carried out at 60 °C for 24 h in dioxane. [b] Mixture of catalyst and cocatalyst in chlorobenzene was aged out for 15 min before use as catalyst. [c] Monomer to catalyst mole ratio. [d] Initial monomer concentration. [e] Methanol-insoluble polymer. [f] Values were obtained by GPC analysis with polystyrene standard calibration. [g] Polymerization was carried out at 90 °C for 24 h in dioxane.

resulting dispersion was heated to boiling. The slurry was filtered, and the filtrate was acidified by a 20% HCl aqueous solution at 70 °C. After cooling, the precipitate formed was filtered and crystallized from ethanol to yield 12.5 g (57%) of a white powder.[19]

Preparation of Dipropargylmalonyl Dichloride (I) and Dipropargylacetyl Chloride (II). Scheme I outlines the synthesis of the main-chain backbone. Dipropargylmalonic acid, the starting compound, was prepared as described in the literature.[20,21] To a flask charged with an ether solution (100 mL) of dipropargylmalonic acid (18 g, 0.1 mol) under a nitrogen atmosphere was added pyridine (15.8 g, 0.2 mol) dropwise at room temperature. Thionyl chloride (35.7 g, 0.3 mol) was added dropwise to the reaction mixture, which was kept at −30 °C for 2 h. The reaction was completed just by stirring, and then the mixture was filtered and evaporated. The crude product was distilled twice under reduced pressure to give dipropargylmalonyl dichloride (I). Yield: 60%, 13.2 g. Bp: 54–55 °C (1 mmHg). ^1H NMR ($CDCl_3$): δ 2.1 (t, 2 H), 2.9 (d, 4 H).

Dipropargylmalonic acid in an aqueous solution was heated in a three-neck flask in an oil bath at 125–130 °C, until no more carbon dioxide was evolved. The reaction mixture was then cooled, the crude product was extracted with 50 mL of ether, and the extract was dried over anhydrous magnesium sulfate. The ether is removed by evaporation, and the residue was distilled under reduced pressure to give dipropargylacetic acid. Yield: 90%. Bp: 100 °C (1 mmHg).

Dipropargylacetyl chloride (II) was prepared by the same procedure as described for the preparation of compound I. Yield: 55%. Bp: 35 °C (1 mmHg). ^1H NMR ($CDCl_3$): δ 2.1 (t, 2 H), 2.7 (d, 4 H), 3.2 (m, 1 H).

Synthesis of III and IV. The side-chain alcohol, 4-methoxy-4′-[(ω-hydroxyhexyl)oxy]biphenyl, and 4-cyano-4′-[(ω-hydroxyhexyl)oxy]biphenyl were synthesized according to literature procedures.[22,23]

Synthesis of Bis[[(4-methoxybiphenyl-4′-yl)oxy]hexyl] Dipropargylmalonate (M-I). The reaction scheme for the synthesis of the M-I is shown in Scheme II. Under a nitrogen atmosphere, a flask was charged with a THF solution (100 mL) of compound III (5.4 g, 0.018 mol) and triethylamine (2.0 g, 0.02 mol) was added to it at room temperature. Upon completion of the addition, a mixture of dipropargylmalonyl dichloride (I) (2.2 g, 0.01 mol) and THF (60 mL) was added dropwise at 0 °C for 2 h. The reaction mixture was allowed to warm up to room temperature overnight. Finally, it was poured into water, and the precipitated product was filtered and dried under vacuum. The crude product was purified by passing through a column of silica gel using ethyl acetate and hexane (1:3) as an eluent, which was further purified by recrystallization from methanol to yield 5.9 g (80%) of a white powder.

MS: *m/e* 744 (parent), 200 (base). ^1H NMR ($CDCl_3$): δ 1.4–1.8 (m, $-(CH_2)_4-$), 2.0 (t, CH), 2.7 (d, CH_2C), 3.68 (s, CH_3O-), 3.9 (t, CH_2O-), 4.2 (t, CO_2CH_2), 6.9–7.5 (m, phenyl rings).

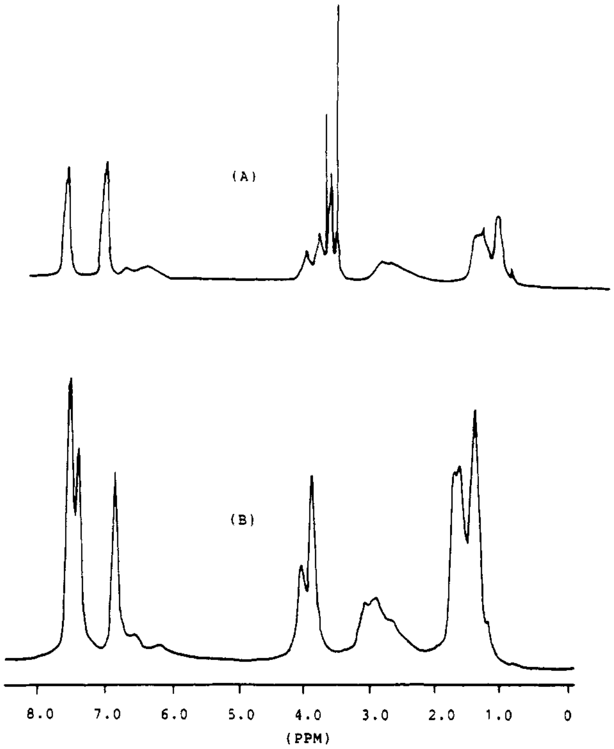


Figure 1. ^{1}H NMR spectra of P-I (A) and P-II (B) in $CDCl_3$ (sample: exp. no. 1 in Table I and exp. no. 3 in Table II).

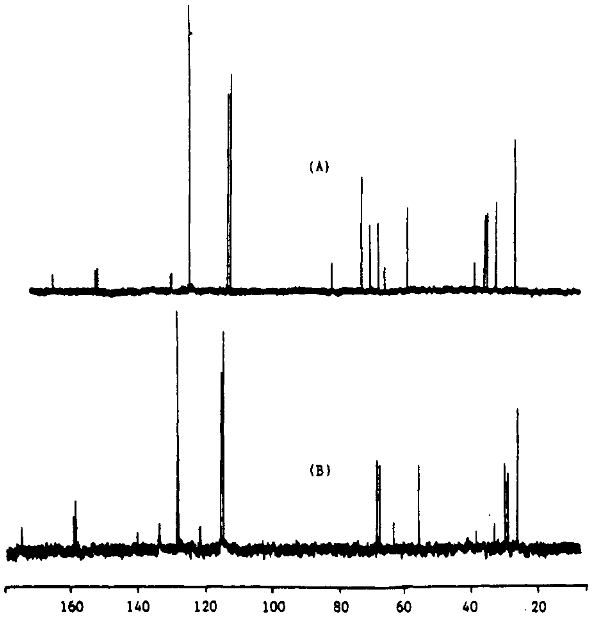


Figure 2. ^{13}C NMR spectra of M-I (A) and P-I (B) in $CDCl_3$ (sample: exp. no. 1 in Table I).

Synthesis of [(4-Cyanobiphenyl-4′-yl)oxy]hexyl Dipropargylacetate (M-II). The synthetic routes for M-II were illustrated in Scheme II. M-II was prepared by the same procedure as described for the preparation of M-I. Yield: 89%. M/S: *m/e* 413 (parent), 200 (base). ^{1}H NMR ($CDCl_3$): δ 1.4–1.8 (m, $-(CH_2)_4-$), 2.0 (t, CH), 2.6 (t, CH_2C), 2.8 (m, HC–), 4.0 (t, CH_2O), 4.2 (t, CO_2CH_2), 7.0–7.9 (m, phenyl rings).

Polymerization. Catalyst preparation and polymerization were carried out in a dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent to make 0.2 M solutions prior to use. A typical polymerization procedure was as follows: solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20-mL ampule equipped with a rubber septum in the order given. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, the monomer dissolved in each solvent was injected into the polymerization ampule. After the reaction mixture was allowed to react at 60 °C for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in 1,4-dioxane and precipitated with a large excess of methanol. The polymer

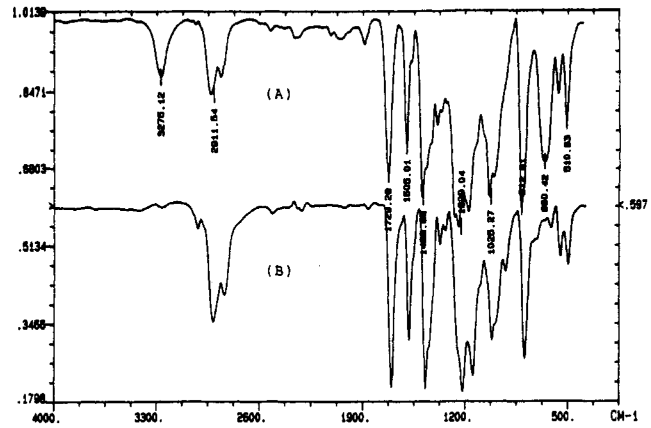


Figure 3. IR spectra of M-I (A) and P-I (B) in KBr pellet [sample: exp. no. 1 in Table I].

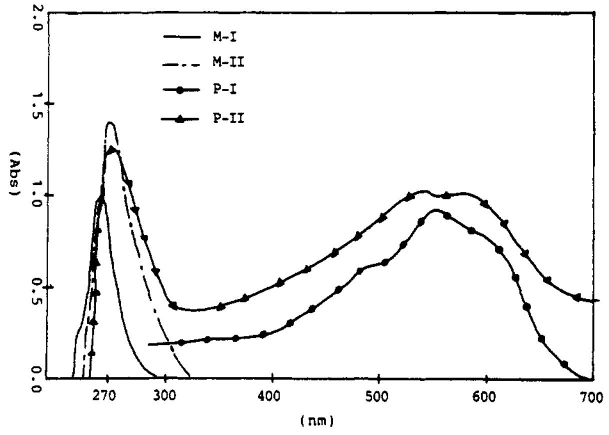


Figure 4. UV–visible spectra of P-I and P-II (sample: exp. no. 1 in Table I and exp. no. 3 in Table II; 1 × 10^{-4} M in $CHCl_3$).

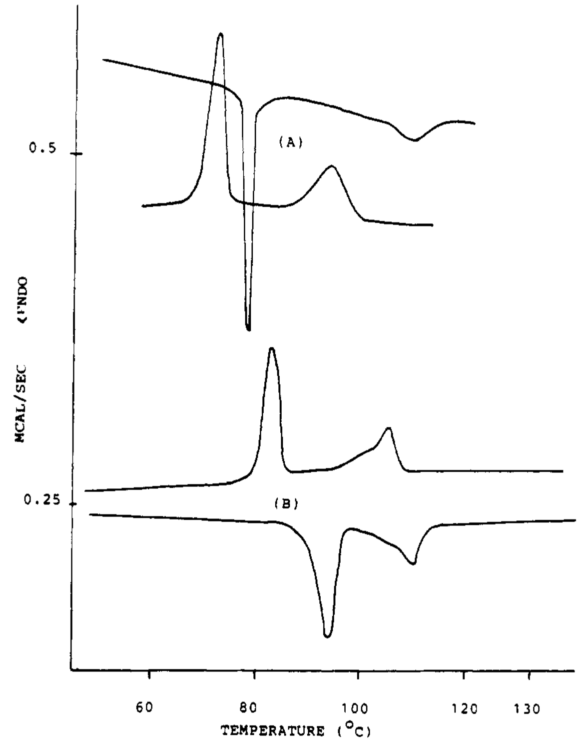


Figure 5. DSC thermograms of M-I (A) and P-I (B) (scanning rate = 10 °C) (sample: exp. no. 1 in Table I).

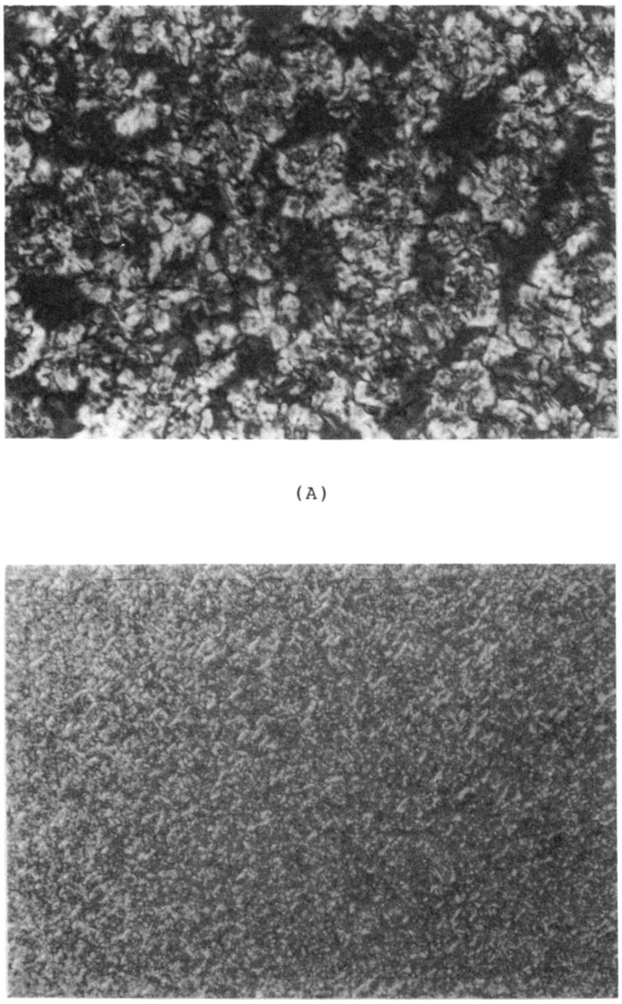


Figure 6. Microphotographs of M-I (A) taken at 90 °C and P-I (B) taken at 100 °C, annealing time, t_a = 2 days (sample: exp. no. 1 in Table I).

was filtered from the solution and dried under vacuum at 40 °C for 24 h. The polymer yield was determined by gravimetry.

Results and Discussion

Scheme III outlines the cyclopolymerization of the monomers with transition-metal catalyst systems.

The polymerization of M-I was carried out with $MoCl_5$- and WCl_6-based catalysts, and results are summarized in Table I. The catalytic activity of $MoCl_5$ is greater than that of WCl_6. As shown in Table I, $(n\text{-Bu})_4Sn$ exhibited excellent cocatalyst activity compared with $EtAlCl_2$ for the polymerization of M-I. These results are similar to those reported for the polymerization of dipropargylmalonate.[24,25] The $\bar{M}_n$ and the polydispersity of P-I are also listed in Table I. The highest $\bar{M}_n$ of P-I obtained was ca. 1.1×10^5 (with $MoCl_5$ as catalyst). Table II lists the results of the polymerization of M-II by using $MoCl_5$- and WCl_6-based catalysts. $MoCl_5$ alone catalyzes more efficiently the polymerization of M-II than $MoCl_5$-cocatalyst systems. The $\bar{M}_n$ of P-II was in the range of 4.9×10^3–7.6×10^4 with polystyrene standards.

The ^1H NMR spectra of P-I (A) and P-II (B) are shown in Figure 1. As the polymerization proceeded, the acetylenic proton peak at about 1.8 ppm disappeared, and new vinylic proton peaks appeared at 6.2–7.7 ppm together with aromatic biphenyl rings. Figure 2 exhibits the ^{13}C NMR spectra of M-I (A) and P-I (B). The monomer gave the acetylenic carbon peaks at 70–80 ppm, while the polymer did not show any peaks. Instead, the olefinic carbon peaks of the polymer backbone appeared at about 123 and 140 ppm in P-I. The peak of the methylene carbon adjacent to the polymer backbone shifted from 24 to 38 ppm in P-I. Figure 3 shows the IR spectra for M-I (A) and P-I (B). The IR spectrum of P-I shows no absorption at 3275 or 2150 cm^{-1} which are expected to be present for the acetylenic carbon–hydrogen stretching and carbon–carbon triple bond stretching of M-I, respectively. The development of the band characteristic of conjugated $-C{=}C-$ sequences unfortunately cannot be clearly identified, due to interference in the region of 1605–1650 cm^{-1} of benzene ring absorption bands dominating the weight of the molecule. ^1H and ^{13}C NMR data of P-II were similar to those of P-I.

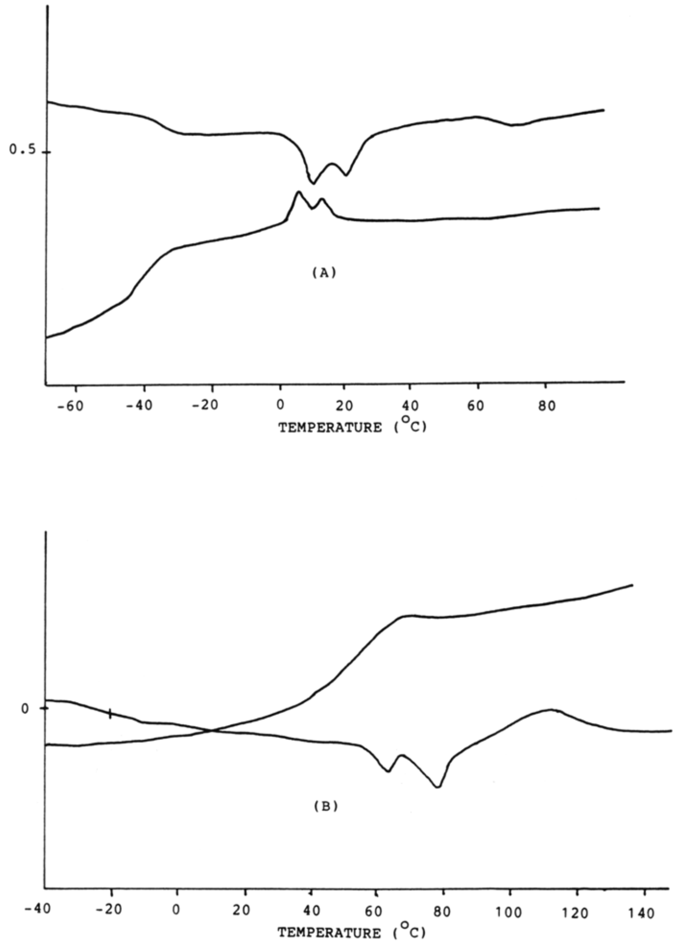
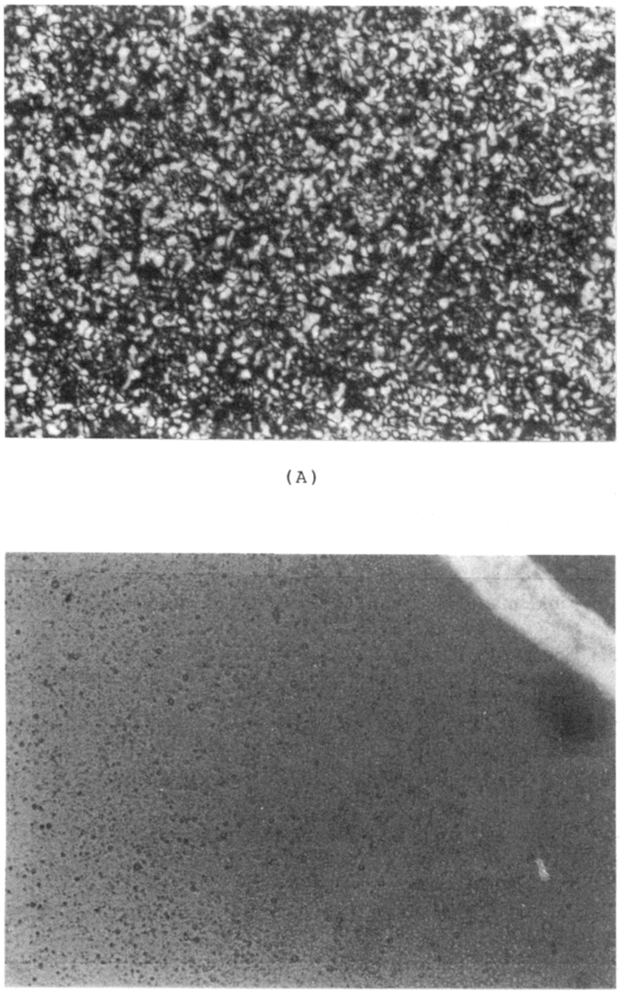


Figure 7. DSC thermograms of M-II (A) and P-II (B) (scanning rate = 40 °C) (sample: exp. no. 3 in Table II).

UV–visible spectra of all monomers and polymers were obtained in $CHCl_3$ (Figure 4). The spectra of the polymer exhibit the characteristic broad peak of 340–650 nm (λ_{max} = 560 nm) that is due to the $\pi \rightarrow \pi^*$ transition of the conjugated polyene. P-I and P-II were completely soluble in various organic solvents such as chloroform, methylene chloride, THF, and 1,4-dioxane, and film could be easily cast on the glass plates to give black shiny thin films. It is, however, insoluble in n-hexane, acetone, diethyl ether, and ethyl acetate. One minor difference was found in that P-I was soluble in toluene and DMF but P-II was not.

From the above spectral and solubility data, it is proposed that the polymer structure is believed to be a cyclized form (P-I and P-II) as described in Scheme III.[18,24–26]



(A)

(B)

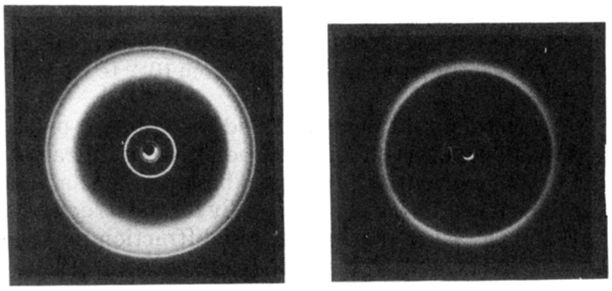
Figure 8. Microphotographs of M-II (A) taken at 11.2 °C and P-II (B) taken at 75 °C, annealing time, t_a = 2 days (sample: exp. no. 3 in Table II).

Table III
Electrical Conductivity of P-I and P-II[a]

polym	composition of doped polym[b]	conductivity,[c] S/cm
P-I	$(C_{47}H_{52}O_8)_1(I_2)_0$	5.2×10^{-11}
P-I	$(C_{47}H_{52}O_8)_1(I_2)_{0.27}$	6.1×10^{-2}
P-II	$(C_{27}H_{27}O_3N)_1(I_2)_0$	3.7×10^{-11}
P-II	$(C_{27}H_{27}O_3N)_1(I_2)_{0.13}$	1.5×10^{-3}

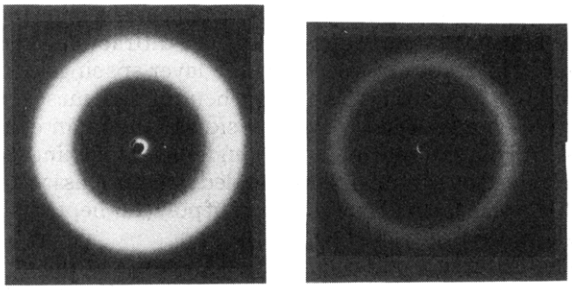
[a] These polymers were doped by exposure to iodine vapor under vacuum (1 mmHg) for 2 h. [b] Extent of doping was obtained by a weight uptake method. [c] Measured at a frequency of 100 Hz with an applied voltage of 1 V by an Ando AG-4304 LCR meter.

Figure 5 presents the second heating and the cooling DSC curves of M-I (A) and P-I (B), which indicated two well-separated transition regions of the samples, and the liquid crystal to isotropic transition was relatively broad. This is probably due to the high viscosity, polydispersity, and rigid backbone of the polymeric product.[11,18] Figure 6 shows the microphotographic property of the liquid crystalline state of M-I (A) and P-I (B), respectively. It was shown that the mesophases of M-I (A) and P-I (B) were in the range of 78–110 and 95–112 °C on heating cycles (71–94 and 85–108 °C on cooling cycles), respectively. M-I corresponds to a smectic texture at 90 °C. P-I was observed as a highly ordered smectic texture at 101 °C on cooling from the isotropic state as seen in Figure 6B and Figure 9, which will be shown later.



(A) (B)

Figure 9. Wide-angle X-ray diffraction diagram of P-I (A, overexposed; B, underexposed).



(A) (B)

Figure 10. Wide-angle X-ray diffraction diagram of P-II (A, overexposed; B, underexposed).

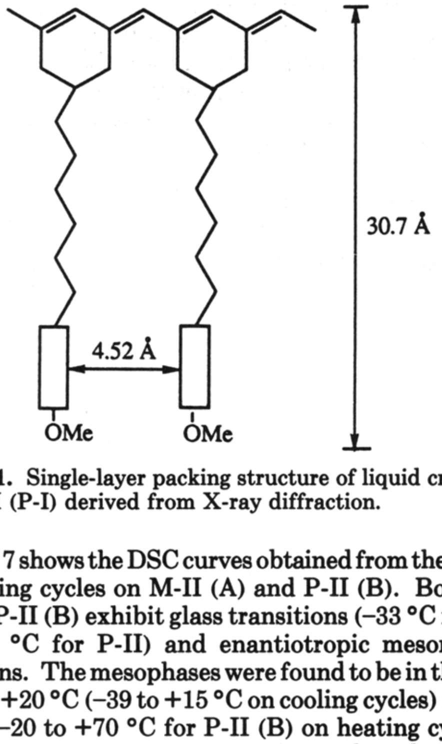


Figure 11. Single-layer packing structure of liquid crystalline polymer I (P-I) derived from X-ray diffraction.

Figure 7 shows the DSC curves obtained from the heating and cooling cycles on M-II (A) and P-II (B). Both M-II (A) and P-II (B) exhibit glass transitions (−33 °C for M-II and −20 °C for P-II) and enantiotropic mesomorphic transitions. The mesophases were found to be in the range of −33 to +20 °C (−39 to +15 °C on cooling cycles) for M-II (A) and −20 to +70 °C for P-II (B) on heating cycles. In the first cooling curve of P-II, only one broad exotherm is shown at 67 °C (ΔH = 1.44 J/g). The peak shown at higher temperature in the DSC thermogram of P-II could be a first-order melting process with a semirigid backbone.

Figure 8 shows the microphotographs of the liquid crystalline mesophases of M-II (A) and P-II (B), respectively. Figure 8A of M-II which was obtained after cooling from the isotropic phase to 11.2 °C might be a nematic texture. Figure 8B of P-II shows a nematic mesophase of which the structure will be clearly identified in the X-ray analysis as described later. Table III lists the electrical conductivities of the undoped and I_2-doped polymers. When the film type polymers were exposed to iodine vapor, the electrical conductivity increased from 10^{-11} to 10^{-3}–10^{-2} S/cm.

In order to obtain more detailed information on the mesophase structure of the polymers, X-ray diffraction studies were carried out. X-ray studies provided detailed morphological information, especially for the structure of LCPs and the layer spacing. X-ray diffraction patterns of P-I at 100 °C and P-II at 75 °C are shown in Figures 9 and 10, respectively. Figure 9 shows the presence of the discrete sharp inner ring, indicating that P-I has the smectic structure. On the other hand, Figure 10 does not show any sharp inner ring, indicating that P-II has the nematic structure. The small-angle diffraction (inner ring) corresponds to the Bragg maximum of d = 30.7 Å for P-I. The wide-angle diffraction (outer ring) corresponds to an inter molecular spacing (or the diffuse diffraction) in the layer. The results suggest that the layer spacings correspond to a single-layer packing, when the side mesogenic groups are arranged on a single side of the main chain. The calculated spacing of a single-layer packing was determined by assuming the extended structure, associated with the planar backbone geometry of poly(1,6-heptadiyne) as shown in Figure 11.

The difference between the calculated and observed layer spacings is about 28.6 ± 2.1 Å. In addition, the wide halo at wide angle corresponds to an intermolecular spacing (or diffuse diffraction) of 4.52 Å.

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