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SYNTHESIS AND CHARACTERIZATION OF NEW THERMOTROPIC SIDE-CHAIN LIQUID CRYSTAL POLYMERS CONTAINING 1,6-HEPTADIYNE BACKBONE

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ABSTRACT

Poly(1,6-heptadiyne) derivatives with side-group liquid crystalline mesogens are prepared by ring-forming metathesis polymerization with transition metal catalysts. $MoCl_5$-based catalyst systems are more effective for the polymerization of 1,6-heptadiyne monomers with various mesogenic groups than are WCl_6-based catalyst systems. The resulting polymers exhibit good solubility in common organic solvents such as chloroform and THF, and they can be easily spin-coated on ITO glass. The weight-average molecular weights of the polymers are in the 3.5 to 26 × 10^4 range relative to polystyrene standards by GPC. The ^{1}H-, ^{13}C-NMR, and IR spectra of the resulting polymers indicate that side-chain liquid crystal polymers with a 1,6-heptadiyne backbone possess a polyene structure, presumably with cyclic recurring units in the polymer backbone. Thermal behaviors, morphology, and electrical conductivities are investigated by using differential scanning calorimetry, cross-polarized optical microscopy, and an LCR meter. **M-1** and **P-1** displayed enantiotropic liquid crystallinity showing reversible phase transition. **M-2** and **P-2** displayed no mesophase. The electrical conductivities of the film-type polymers are in the 10^{-4} to 10^{-2} S/cm range.

INTRODUCTION

Liquid crystalline (LC) polymers are currently the focus of intensive fundamental and applied research [1]. Several merits of these materials, including a self-assembly tendency, render them attractive in the development of novel liquid crystal devices and telecommunication techniques. The types of polymer backbone used for the synthesis of side-chain LC polymers have been limited to polysiloxanes [2, 3], polyacrylates [4, 5], and polymethacrylates [6, 7]. There are only a few examples in which other main chain structures like polyolefin [8], poly(vinyl ether) [9, 10], polyphosphazene [11, 12], or polyoxetane [13] are used.

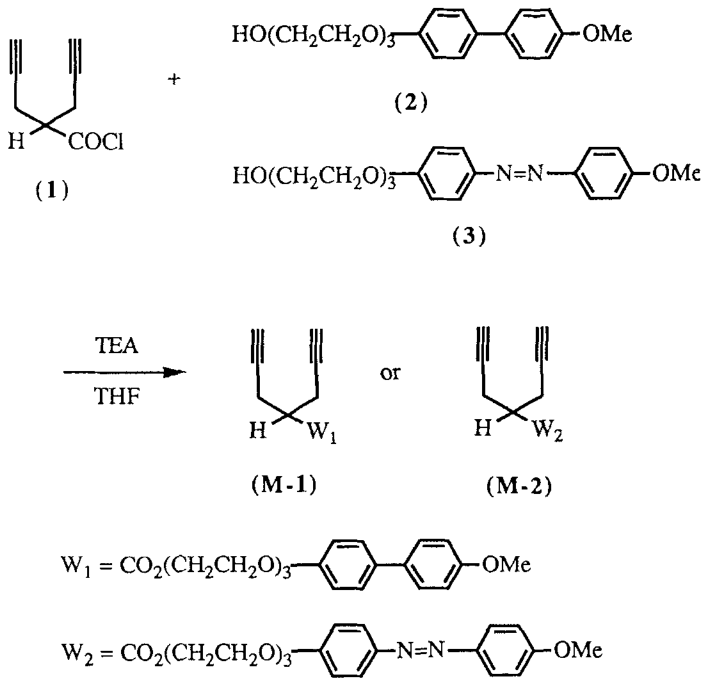
We have been interested in the effects of the structure of main chains, the length of spacers, and the structure of mesogenic groups on the characteristics of LC polymers. In several previous papers we presented the first examples of thermotropic side-chain LC polymers with electric conductivity by transition metal catalysts [14–16].

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

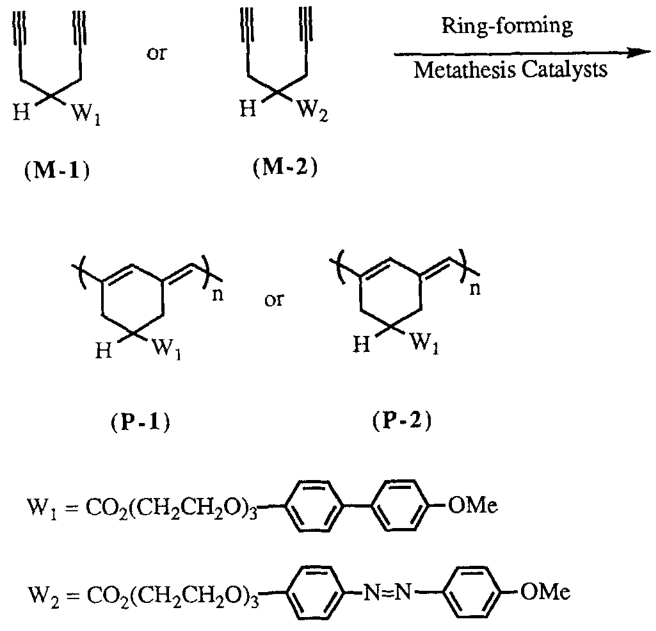
EXPERIMENTAL

Materials

Solvents were purified by normal procedures and handled under moisture-free conditions. The polymerization solvent, 1,4-dioxane, was distilled from calcium



SCHEME 1.



Catalyst: $MoCl_5$, WCl_6, $PdCl_2$

Cocatalyst: $(n\text{-}Bu)_4Sn$, $EtAlCl_2$

SCHEME 2.

hydride. Diethyl malonate, 6-chloro-1-hexanol, and 2-[2-(2-chloroethoxy)ethoxy]-ethanol (Aldrich Chemicals) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried over calcium hydride and fractionally distilled. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemicals, resublimed, 99+ %) were used without further purification. Organotin compounds, such as tetrabutylin and tetraphenyltin, and organoaluminum compounds, such as $EtAlCl_2$, were used without further purification.

Techniques

^1H- and ^{13}C-NMR spectra were recorded with a Bruker AM 300 spectrometer, and the chemical shifts were reported in ppm units with tetramethylsilane as internal standard. Infrared spectra were measured with a KBr pellet on a Bomen spectrometer, and the frequencies are given in reciprocal centimeters. The weight-average molecular weights ($\overline{M}_w$) and polydispersity ($\overline{M}_w/\overline{M}_n$) were determined in THF solvent with a GPC-150C Waters by using polystyrene standards. A Perkin-Elmer DSC-4 thermal analyzer was used to obtain DSC thermograms with a heating rate of 10°C/min under nitrogen atmosphere except where noted. A polarizing microscope equipped with a Mettler FP-80 hot stage was used for visual observation of thermotropic behaviors and optical textures of monomers and polymers. The electrical conductivity was measured at a frequency of 100 Hz with an applied voltage of 1 V with an Ando AG-430 LCR meter.

Synthesis of Dipropargyl Acetyl Chloride (1) and Side Chain Mesogenic Alcohols (2, 3)

The synthesis, purification, and characterization of dipropargyl acetyl chloride (**1**), 4-methoxy-4′-[2-bis(ethyleneoxy)ethanol]biphenyls (**2**), and 4-[(4-methoxy phenyl)azo-4′-{2-bis(ethyleneoxy) ethanol}]phenyl (**3**) were according to literature procedures [12, 14, 15, 17].

Synthesis of 4-Methoxy-4′-[2-bis(ethyleneoxy) Ethanol] Biphenyl Dipropargyl Acetate (M-1)

A series of 4-substituted-1,6-heptadiyne monomers were synthesized as outlined in Scheme 1. Compound **2** (5 g, 0.014 mol) was dissolved in dried THF and 4 g (0.04 mol) of TEA (distilled from KOH). The solution was cooled in an ice water bath to 0°C, and 3.1 g (0.02 mol) dipropargyl acetyl chloride (**1**) was added dropwise. The reaction 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 it through a column of silica gel using ethyl acetate and hexane (1:10) as the eluent. It was further purified by

TABLE 1. Polymerization of **M-1** with Various Transition Metal Catalysts[a]

Expt.	Catalyst system,[b] mole ratio	M/C[c]	$[M]_0$[d]	Polymer yield, %[e]	GPC[f]	
					$\overline{M}_w/10^4$	$\overline{M}_w/\overline{M}_n$
1	$MoCl_5$	25	0.25	96	14.0	3.5
2	$MoCl_5$	50	0.125	84	9.8	2.3
3	$MoCl_5$	50	0.25	85	17.3	2.9
4	$MoCl_5/(n\text{-}Bu)_4Sn$ (1/1)	50	0.25	100	26	3.7
5	$MoCl_5/EtAlCl_2$ (1/1)	50	0.25	90	19	3.4
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	–	–
9	$PdCl_2$[g]	50	0.25	70	3.7	2.5

[a] Polymerization was carried out at 60°C for 24 hours in dioxane.

[b] Mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 minutes 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 standards calibration.

[g] Polymerization was carried out 90°C for 24 hours in dioxane.

TABLE 2. Polymerization of **M-2** with Various Transition Metal Catalysts[a]

Expt.	Catalyst system,[b] mole ratio	M/C[c]	$[M]_0$[d]	Polymer yield, %[e]	GPC[f] $\overline{M}_w/10^4$	GPC[f] $\overline{M}_w/\overline{M}_n$
1	$MoCl_5$	25	0.25	60	8.1	3.0
2	$MoCl_5$	50	0.125	Trace	–	–
3	$MoCl_5$	50	0.25	75	6.9	2.5
4	$MoCl_5$	12.5	0.25	85	7.4	2.8
5	$MoCl_5/(n\text{-}Bu)_4Sn$ (1/1)	50	0.25	50	4.0	3.6
6	$MoCl_5/EtAlCl_2$ (1/1)	50	0.25	35	3.5	1.9
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	Trace	–	–

[a] Polymerization was carried out at 60°C for 24 hours in dioxane.

[b] Mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 minutes 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 standards calibration.

[g] Polymerization was carried out 90°C for 24 hours in dioxane.

recrystallization from methanol to yield 4.6 g (68%) of a white powder. M/S: *m/e* 450 (parent), 200 (base).

Synthesis of 4-[(4-Methoxyphenyl) Azo-4′-{2-bis(ethyleneoxy) Ethanol}]phenyl Dipropargyl Acetate (M-2)

The synthetic routes for **M-2** are illustrated in Scheme 1. **M-2** was prepared by the same procedure as described for the preparation of **M-1**. Yield: 75%. M/S: *m/e* 478 (parent), 200 (base).

Polymerization of Monomers

Polymerization was carried out under nitrogen atmosphere because the active species of the catalysts are very sensitive to oxygen and moisture. Transition metal halides and organometallic compounds were dissolved in each solvent to make 2.0 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 minutes. Finally, the monomer dissolved in each solvent was injected into the polymerization ampule. After the mixture was allowed to react at 60°C for 24 hours, 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

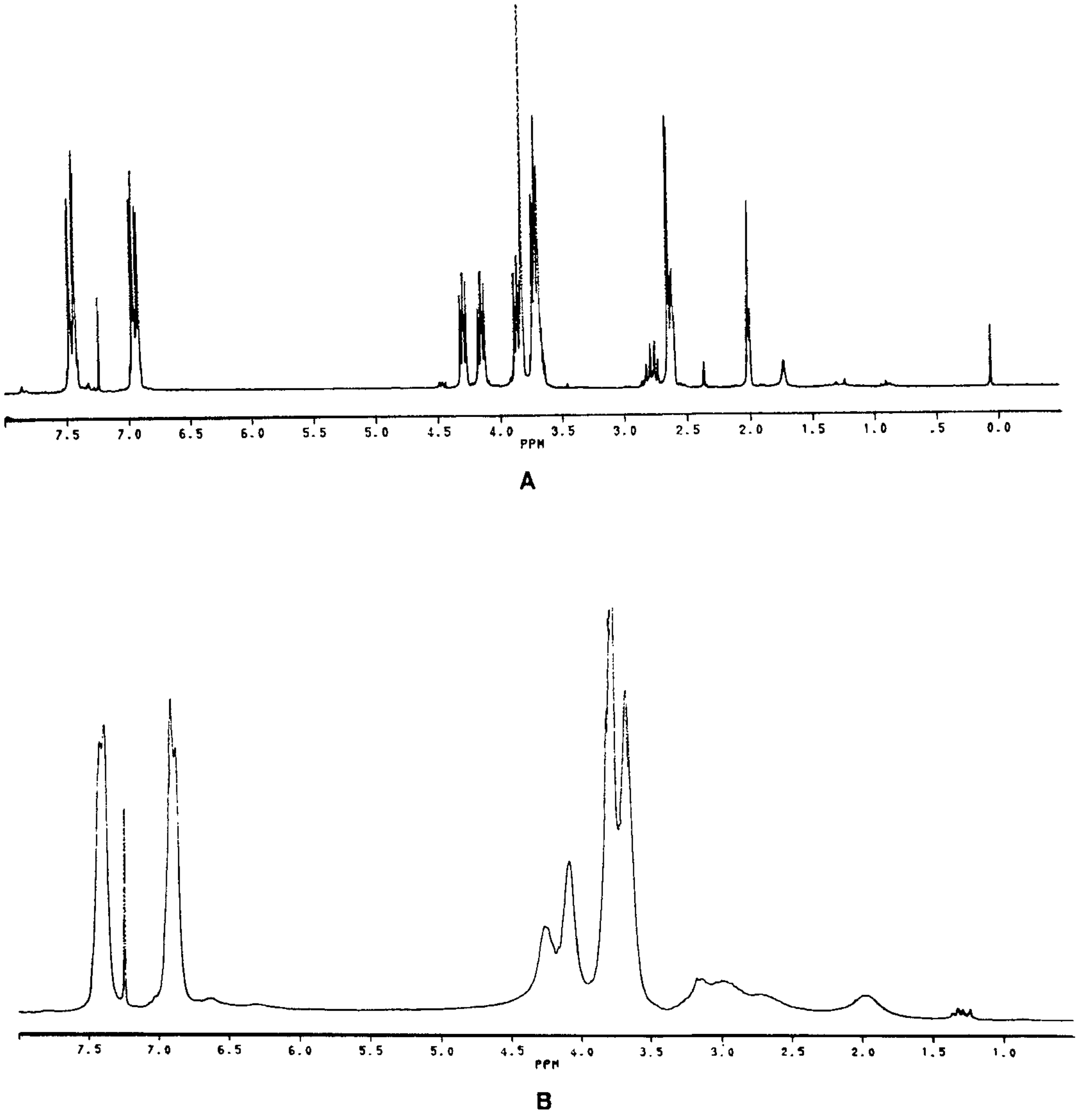


FIG. 1. ^{1}H-NMR spectrum of **M-1** (A) and **P-1** (B) in $CDCl_3$ (sample: Expt. 2 in Table 1).

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

RESULTS AND DISCUSSION

Scheme 2 outlines the polymerization of the monomers with ring-forming metathesis catalysts. The polymerization of **M-1** was carried out with transition metal catalysts, and the results are summarized in Table 1. As shown in Table 1,

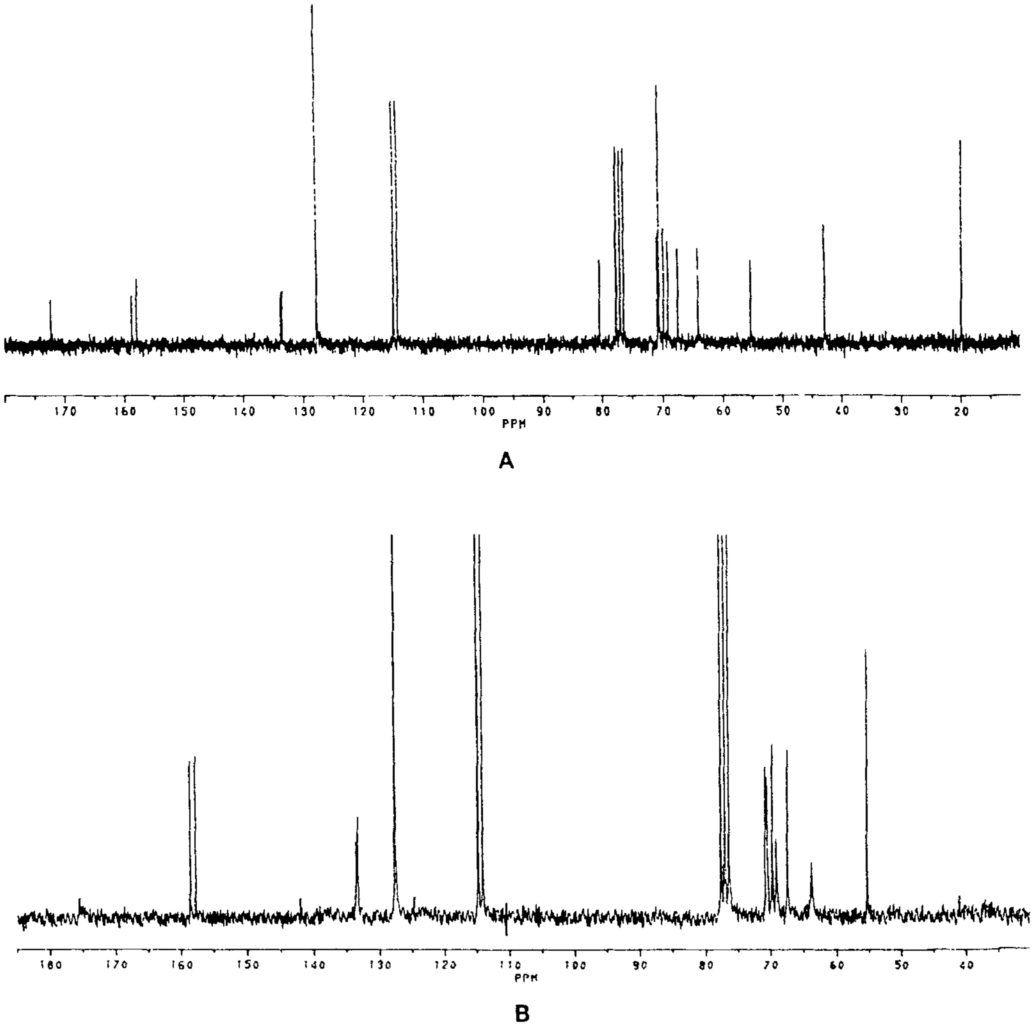


FIG. 2. ^{13}C-NMR spectrum of **M-1** (A) and **P-1** (B) in $CDCl_3$ (sample: Expt. 2 in Table 1).

with polymerization by $MoCl_5$ and $(n\text{-Bu})_4Sn$ as a cocatalyst, the **P-1** yield was quantitative. These results are similar to those reported for the polymerization of dipropargyl malonate [18, 19]. The weight-average molecular weights ($\overline{M}_w$) of **P-1** were in the 3.7 to 26 × 10^4 range with polystyrene standards. The polydispersities ($\overline{M}_w/\overline{M}_n$) of the resulting polymer, **P-1**, were in the 2.3 to 3.7 range.

Table 2 shows the results for the polymerization of **M-2** by using transition metal catalysts. In this monomer, the polymer yield was relatively low. The low catalytic activity may be due to the interaction of a heteroatom (azo unit of the mesogenic group) with the catalyst, thus hindering triple bond coordination. $MoCl_5$

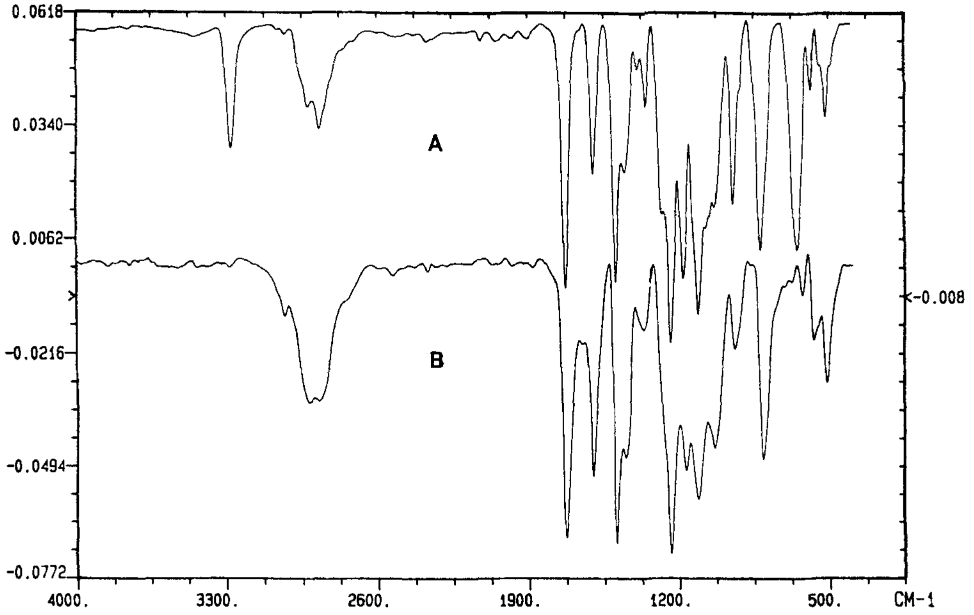


FIG. 3. IR spectrum of **M-1** (A) and **P-1** (B) in $CDCl_3$ (sample: Expt. 2 in Table 1).

alone catalyzes the polymerization of **M-2** more efficiently than $MoCl_5$-cocatalyst systems. The weight-average molecular weights ($\overline{M}_w$) and polydispersities ($\overline{M}_w/\overline{M}_n$) of **P-2** were in the 3.5 to 8.1 × 10^4 and 1.9 to 3.6 ranges, respectively.

Careful ^{1}H-, ^{13}C-NMR, and IR analyses were carried out for both monomers and polymers in order to prove the chemical structures of the polymers. The ^{1}H-NMR spectra of **M-1** (A) and **P-1** (B) are shown in Fig. 1. As polymerization proceeded, an acetylenic proton peak at 2.0–2.2 ppm disappeared, but a new vinylic proton peak appeared broadly in the 6.8–7.2 ppm range. Since the new peak is relatively weaker than the aromatic biphenyl rings and those two peaks are superposed, it is hard to separate them clearly. The broad peaks at 2.6 and 3.4 ppm are assignable to the methylene protons and methine proton on the ring, respectively. Figure 2 exhibits the ^{13}C-NMR of **M-1** (A) and **P-1** (B). The monomer has acetylenic carbon peaks at 70 and 82 ppm. On the other hand, **P-1** does not show these peaks. Instead, the olefinic carbon peaks of the **P-1** backbone appear at 123 and 141 ppm. The peak of the methylene carbon adjacent to the polymer backbone is shifted from 20 to 43 ppm on polymerization. Figure 3 shows the IR spectrum of **M-1** (A) and **P-1** (B). The IR spectrum of **P-1** shows no absorption peak at 3300 or 2150 cm^{-1}, which were expected to be present for acetylenic hydrogen stretching and carbon—carbon triple bond stretching of **M-1**, respectively. The development of the band characteristic of conjugated —C=C— sequences unfortunately cannot be clearly identified. The strong bands at 1726 and 814 cm^{-1} are attributed to the —C=O stretching of ester and C—H out-of-plane bending vibrations for para-disubstituted benzene rings. ^{1}H-, ^{13}C-NMR, and IR data of **M-2** and **P-2** are similar to those of **M-1** and **P-1**. The polymers obtained are completely dissolved by various organic solvents such as chloroform, methylene chloride, THF, 1,4-dioxane, and

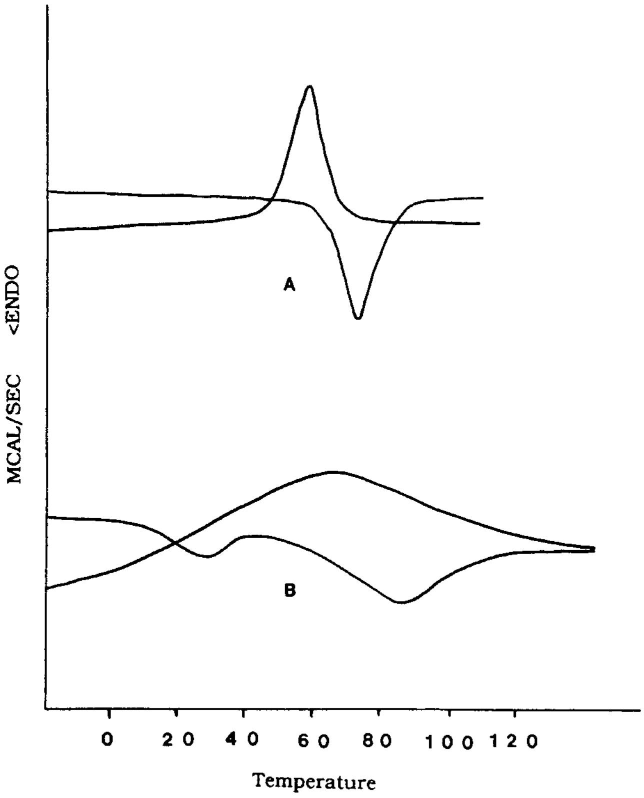


FIG. 4. DSC thermogram of **M-1** (A) and **P-1** (B) in $CDCl_3$ (scanning rate = 10°C) (sample: Expt. 2 in Table 1).

TABLE 3. Thermal Transition Temperatures for the Monomers and Polymers

	Phase transition, °C	
Sample	Heating	Cooling
M-1	S 68 i	i 60 S
P-1	g 30 S 83 i	$T = 65$
M-2	K 60 i	i 58 K
P-2	K 109 i	i 103 K

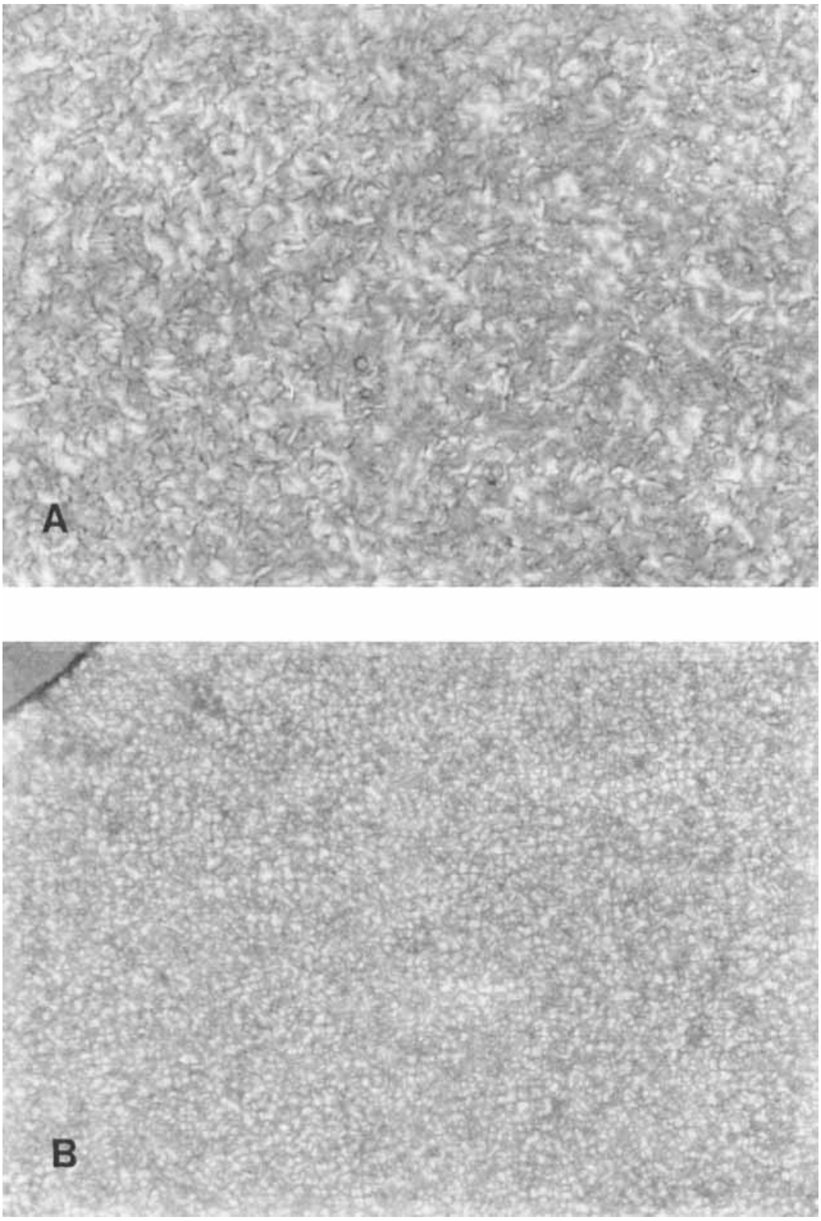


FIG. 5. Microphotographs of **M-1** (A) taken at 40°C and **P-1** (B) taken at 75°C, annealing time 1 hour (sample: Expt. 2 in Table 1).

pyridine at a concentration of 4% by weight and could be easily spin-coated on ITO glass. Such good solubility of the present polymers supports the hypothesis that these polymers are incorporated in to the cyclized form as described in Scheme 2 [14, 15].

The electrical conductivities of the film-type polymers are 10^{-4}-10^{-2} S/cm. Figure 4 shows the DSC thermograms obtained from heating and cooling of **M-1** (A) and **P-1** (B). The phase transition temperatures of the monomers and polymers are summarized in Table 3. **P-1** shows two well-separated transition regions on second heating cycles and the first cooling curve; only one broad exotherm is shown at $T = 65\,^{\circ}\mathrm{C}$. Both **M-2** and **P-2** display no mesophase. As the temperature is increased, **P-2** gradually decomposes, so the LC phase could not be detected. It has been generally observed that mesophase formation is facilitated by increasing the length of either the flexible spacer or the end of the groups or both. Figure 5 shows the photomicrographic properties of the liquid crystalline states of **M-1** (A) and **P-1** (B). The mesophases of **M-1** and **P-1** are smectic textures. In addition, we observed experimentally by optical polarized microscopy that the flow property of **P-1** was poor. Therefore, we think that **M-1** and **P-1** have mainly a smectic mesophase. Additional x-ray studies now in progress should provide more definitive information to fully characterize the liquid crystal structures involved.

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