Synthesis and characterization of new side chain liquid crystalline polymers based on poly(dipropargylamine) main chain

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SUMMARY

A new thermotropic side-chain liquid crystalline polymers based on poly (dipropargylamine) backbone were prepared by metathesis polymerization with transition metal catalysts. It was found that the $MoCl_5$-$EtAlCl_2$ catalyst system were very effective for the cyclopolymerization of presently investigated monomers. Resulting polymers were soluble in common organic solvents such as THF, chloroform, etc. The number-average molecular weight ($\overline{M}n$) values of the polymers were in the range of 6.49×10^3 - 11.6×10^3, relative to polystyrene standard by GPC.

Thermal properties of the monomers and the polymers synthesized were examined by differential scanning calorimetry (DSC) and cross-polarized optical microscopy. Both monomer and polymer displayed enantiotropic liquid crystallinity showing the reversible phase transition.

INTRODUCTION

Recently, a large variety of side-chain liquid crystalline (LC) polymers has been extensively investigated, which has become of increasing interest because of their theoretical and technological significances (1-4). In order to obtain the mesophases of these polymers, the introduction of flexible spacer groups between the polymer main chain and the mesogenic side chain is necessary to decouple the motions of the backbone component from those of the anisotropically oriented mesogenic group. Most of the studies reported the side-chain LC polymers to date have been concerned with materials in which the mesogenic groups are attached to the flexible polymer backbone such as polysiloxanes, polyacrylates, and polymethacrylates, etc.

However, to our knowledge there are only few reports in the literature concerning the use of rigid polymer backbone for side-chain LC polymers. Furthermore, systematic studies to prepare the side-chain LC polymers with electrically conductive system by metathesis polymerization have been far less studied (5,6). In the previous paper (7), we reported the synthesis and characterization of a thermotropic side-chain LC polymer based on poly (dipropargylamide) backbone which was prepared by transition metal catalyst system. In this paper, we describe the results on the preparation and properties of another series of a novel side-chain LC monomers, and their polymers with a new type of highly conjugated backbone, poly(dipropargylamine).

EXPERIMENTAL
Materials.   Tungsten (VI) and molybdenum (V) chlorides (Aldrich Chemical Co., resublimed, 99.9 %) were used without further purification. 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. 4-Aminobenzoic acid, 4-aminophenol, 1,6-dibromohexane, and dipropargylamine (all from Aldrich Chemicals) were used without further purification. 4-Cyano-4'-hydroxybiphenyl was obtained from Tokyo Kasei and was used as received.

Instruments. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with the use of a Bruker AM-300 spectrometer and chemical shifts were reported in ppm unit with tetramethylsilane as an internal standard. Infrared spectra were measured as neat oil or as KBr pellets on a Bomen spectrometer and frequencies were given in reciprocal centimeter. Shimadzu UV-3100S spectrometer was used for UV spectral data. The number average molecular weight ($\overline{Mn}$) and polydispersities were determined in THF solvent by Waters GPC-150C calibrated with polystyrene standards. Perkin Elmer DSC-4 thermal analyzer was used to obtain the DSC thermograms with heating rates of 10 °C/min in nitrogen atmosphere. Leitz Ortholux-II optical microscope equipped with Mettler FP-80 hot stage was used in cross-polarized mode for visual observation of thermotropic behavior and optical texture of the monomers and polymers.

Synthesis of Monomer. Scheme I describes the synthesis of the monomer.

Scheme I
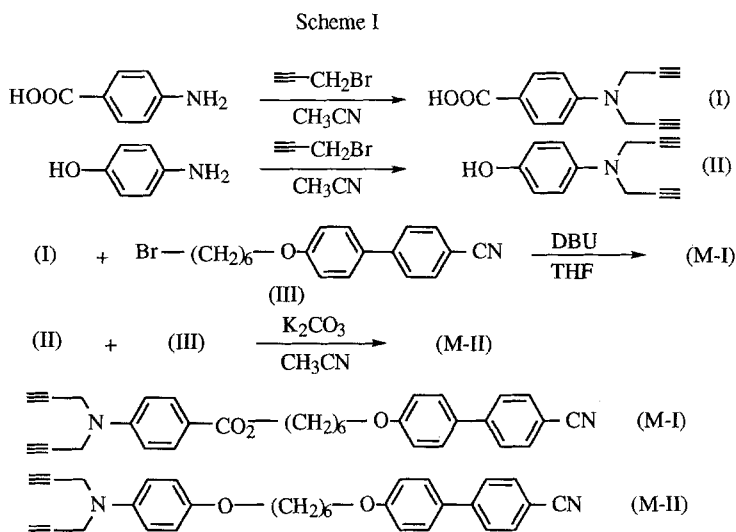
Synthesis of 4-Dipropargylaminobenzoic Acid (I). 4-Aminobenzoic acid (10 g, 73 mmol) and propargyl bromide (44 g, 0.27 mol) were stirred in CH$_3$CN (150 mL) at reflux condition for 24 h. The reaction mixture was cooled and poured into exess water to precipitate the product. The precipitated solid was collected by filteration, washed throughly with water and recrystallized from ethanol and ethyl acetate (2 : 1). Yield; 30%
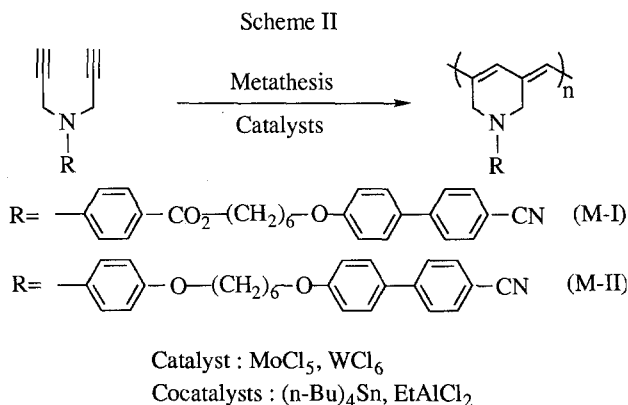
Synthesis of 4-Dipropargylaminophenol (II). 4-Aminophenol (5 g, 46 mmol) and propargyl bromide (30 g, 0.2 mol) were stirred in CH$_3$CN (150 mL) at reflux condition for 20 h. The reaction mixture was washed with water and extracted with methylene chloride. The solvent was removed with a rotatory evaporator and the crude product was purified by column chromatography on silica gel with ethyl acetate and hexane (1 : 2) as eluent. Yield;

40%

4-Cyano-4'-hexyloxybiphenyl Dipropargylamino Benzoate (M-I).   The compound (III) (8) (3.6 g, 10 mmol) in THF (about 20 mL) was added to a solution of 4-dipropargylaminobenzoic acid (I) (2 g, 9.4 mmol) and DBU (1.4 g, 9.4 mmol) in THF (20 mL), and the mixture was refluxed with stirring for 10 h. The reaction was monitored by TLC. After cooling, the mixture was diluted with ethyl acetate (50 mL), and the precipitate was filtered and washed with ethyl acetate. The filtrate was purified by column chromatography using 10 : 1 mixture of hexane and ethyl acetate as eluent, which was further purified by recrystallized from ethanol. Yield; 30%. IR: 3262 cm^{-1} ($\equiv$CH); 2150 cm^{-1} (C$\equiv$C). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.4~1.6 (m, -(CH$_2$)$_2$-), 1.6~1.9 (m, -(CH$_2$)$_2$-), 2.2 (t, $\equiv$CH), 4.0 (t, -OCH$_2$-), 4.2 (d, -CH$_2$C$\equiv$), 4.3 (t, -OCH$_2$-), 6.8~7.0 (dd, aromatic protons), 7.5~7.7 (m, aromatic protons), 7.9 (m, aromatic protons).

4-Cyano-4'-hexyloxybiphenyl Dipropargylaminophenyl Ether (M-II).   A mixture of 4-dipropargylaminophenol (II) (3 g, 16.2 mmol), compound (III) (5.8 g, 16.2 mmol) and anhydrous potassium carbonate (5 g) in 150 mL CH$_3$CN was refluxed with stirring for 24 h. The reaction was checked by TLC. After cooling, the salt was filtered. The filtrate was purified by column chromatography on silica gel using a 35 : 65 mixture of ethyl acetate and hexane as eluent, which was further purified by recrystallization from ethanol. Yield; 83%. IR: 3280 cm^{-1} ($\equiv$CH); 2225 cm^{-1} (CN). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.4~1.7 (m, -(CH$_2$)$_2$-), 1.7~1.9 (m, -(CH$_2$)$_2$-), 2.2 (t, $\equiv$CH), 3.9 (t, -OCH$_2$-), 4.0 (d, -CH$_2$C$\equiv$), 4.0 (t, -OCH$_2$-), 6.8~7.0 (m, aromatic protons), 7.5~7.7(m, aromatic protons).

Polymerization.   The polymerization was carried out with MoCl$_5$- and WCl$_6$-based catalyst systems (9). Scheme II outlines the polymerization of the monomer with transition metal catalysts.

Scheme II

R= —⟨◯⟩—CO$_2$—(CH$_2$)$_6$—O—⟨◯⟩—⟨◯⟩—CN   (M-I)

R= —⟨◯⟩—O—(CH$_2$)$_6$—O—⟨◯⟩—⟨◯⟩—CN   (M-II)

Catalyst : MoCl$_5$, WCl$_6$

Cocatalysts : (n-Bu)$_4$Sn, EtAlCl$_2$

RESULTS AND DISCUSSION.

The polymerization of M-I was carried out with MoCl$_5$- and WCl$_6$- based catalysts and their results are summarized in Table I. The catalytic activity of MoCl$_5$ was greater than that of WCl$_6$. As shown in Table I, EtAlCl$_2$ exhibited excellent cocatalyst activity compared with (n-Bu)$_4$Sn for the polymerization of M-I. The number-average molecular weights and the polydispersities of the polymers obtained are also listed in Table I. Table II lists the results of the polymerization of M-II by various catalyst systems. These results are similar to those for the polymerization of M-I. When the polymerization by MoCl$_5$ with EtAlCl$_2$ as cocatalyst,

the P-II yield was quantitative.

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

Exp. No	Catalyst System[b] (mole ratio)	M/C[c]	$[M]_o$[d]	Polymer Yield (%)[e]	$\overline{M}nx10^{-3f}$	$\overline{M}w/\overline{M}n$[f]
1	MoCl$_5$	50	0.25	95	7.5	2.7
2	MoCl$_5$	100	0.25	82	8.0	2.1
3	MoCl$_5$	50	0.5	100	7.8	2.5
4	MoCl$_5$-(n-Bu)$_4$Sn (1:4)	50	0.25	90	10.5	3.0
5	MoCl$_5$-EtAlCl$_2$ (1:4)	50	0.25	100	11.6	2.4
6	WCl$_6$	50	0.25	trace		

[a]Polymerization was carried out in THF at 60 °C for 24 h.
[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 standards calibration.

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

Exp. No	Catalyst System[b] (mole ratio)	M/C[c]	$[M]_o$[d]	Polymer Yield (%)[e]	$\overline{M}nx10^{-3f}$	$\overline{M}w/\overline{M}n$[f]
1	MoCl$_5$	50	0.25	95	7.7	2.7
2	MoCl$_5$	100	0.25	76	7.2	2.8
3	MoCl$_5$	50	0.5	90	7.8	3.1
4	MoCl$_5$ — (n-Bu)$_4$Sn (1:4)	50	0.25	80	6.7	3.0
5	MoCl$_5$ — EtAlCl$_2$ (1:4)	50	0.25	100	6.49	2.4
6	WCl$_6$	50	0.25	trace		

[a]Polymerization was carried out in THF at 60 °C for 24 h.
[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.
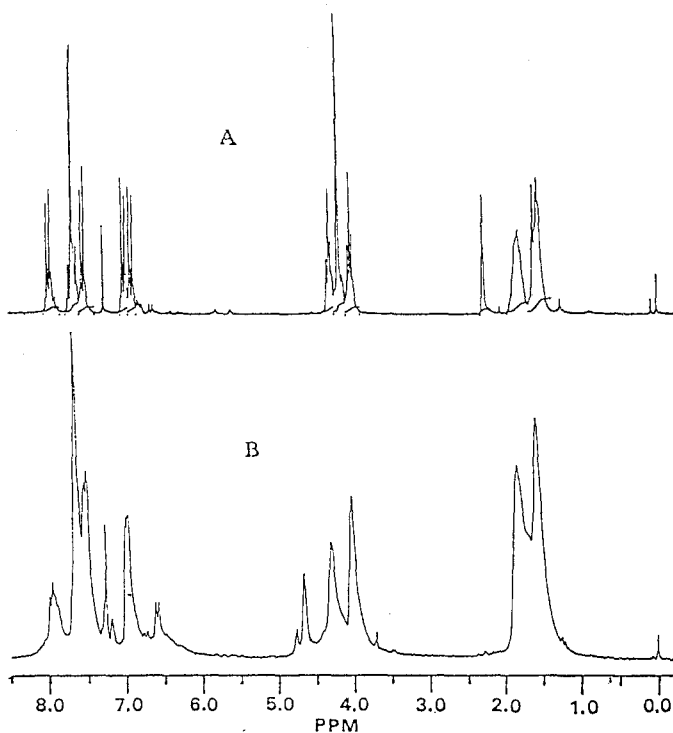[f]Values were obtained by GPC analysis with polystyrene standards calibration.

Figure 1. ^{1}H-NMR spectra of the M-I (A) and the P-I (B) in CDCl$_3$.

Careful ^{1}H-NMR, ^{13}C-NMR, UV-vis, and IR analyses were carried out for both the monomers and polymers in order to prove the chemical structure. The ^{1}H-NMR spectra of M-I and P-I are shown in Figure 1. As the polymerization proceeded, an acetylenic proton peak at 2.3 ppm disappeared and a new vinylic proton peak was observed at 6.3~6.6 ppm together with aromatic biphenyl rings. And the broad peaks at 4.7~4.8 ppm are assignable to the methylene protons on the cyclic ring. Figure 2 exhibits the ^{13}C-NMR of M-I and P-I. The monomer gave acetylenic carbon peaks at 73 and 79 ppm. On the other hand, the polymer did not show any of these peaks. In stead, the olefinic carbon peaks of the polymer backbone appeared at about 123 and 138 ppm. The peak of the methylene carbon adjacent to the polymer backbone shifted from 40 to 54 ppm upon polymerization. Also, the IR spectrum of the polymer shows no absorption at 3262 or 2150 cm^{-1} which are expected to be present for the acetylenic hydrogen stretching and the carbon-carbon triple bond stretching of the monomer, respectively. UV-visible spectra of all monomers and polymers were obtained in CHCl$_3$. The spectra of the polymers exhibited the characteristic broad peak of 400~650 nm that was due to the π–π^* transition of the conjugated polyenes.

The obtained polymers were soluble in various organic solvents such as chloroform, THF, etc. and insoluble in n-hexane, acetone, diethyl ether, and ethyl acetate. From the above spectral and solubility data, the polymer structure was believed to be the cyclized form as described in Scheme II (9, 10).
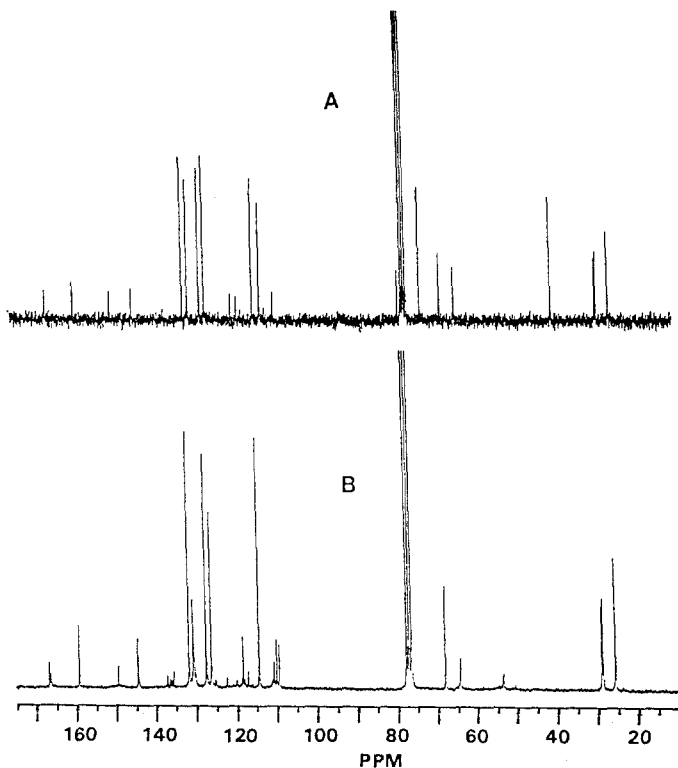
Figure 2. ^{13}C-NMR spectra of the M-I (A) and the P-I (B) in CDCl$_3$.

The thermal transition temperatures of the monomers and polymers measured by DSC are summarized in Table III. Both M-I and P-I displayed no mesophase. It may be concluded that the lack of liquid crystalline phase formation for M-I and P-I can be attributed to rigidity of the polymer backbone and shorter length of the spacer. It has been generally observed that mesophase formation is facilitated by increasing the length of either the flexible spacer or the end groups or both. In contrast, M-II displays liquid crystallinity because it has more flexible ether linkage.

Figure 3 shows the photomicrographic properties of the liquid crystalline state of M-II and P-II. It was shown that the mesophase of M-II and P-II at 69 °C and 140 °C on cooling cycles, respectively. When M-II was cooled from the isotropic state, a black-and white schlieren texture formed at 75 °C, and it is characteristic of a typical nematic mesophase. Also, this nematic texture remained on cooiing to room temperature without textural change. The texture of the P-II shows an undeveloped mesophase, and the detailed studies of the structure in the X-ray analysis are in progress.
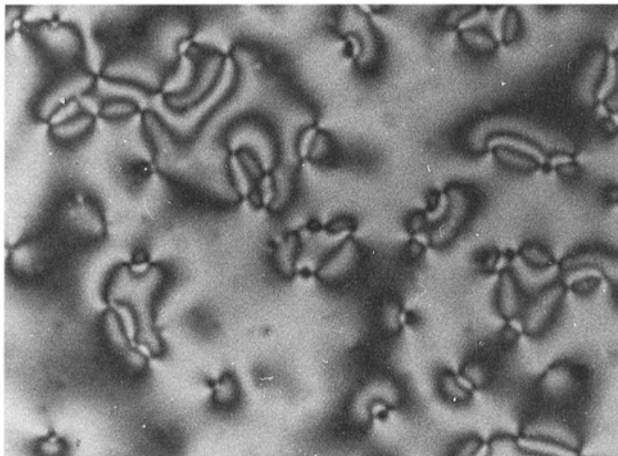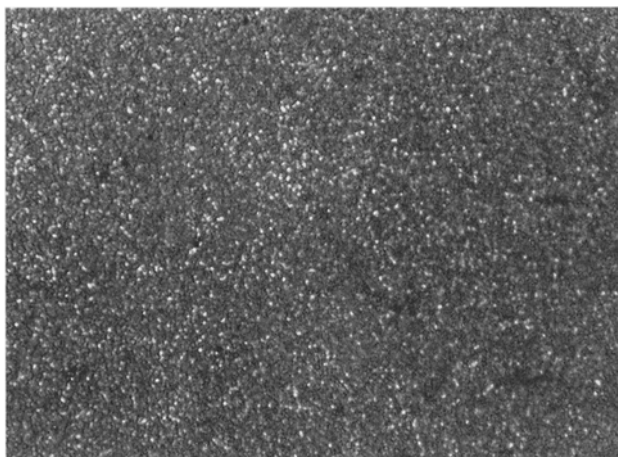
A

B

Figure 3. Microphotographs (magnification 250 x) of the M-II (A) taken at 69°C and the P-II (B) taken at 140 °C on cooling.

Table III. Thermal Transition Temperatures for the Monomers and the Polymers

Sample	Phase transition (°C)	
	Heating	Cooling
M-I	k 119 i	i 95 k
P-I	k 155 i	i 150 k
M-II	k 112 n 115 i	i 76 n 68 k
P-II	g 60 lc 147 i	i 140 lc 55 g

k; crystal   g; glassy   n; nematic   lc; liquid crystal   i; isotropic

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