Design and Synthesis of a New Side-Chain Liquid Crystalline Polymer by Metathesis Polymerization

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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] So far, most of the studies of side-chain LC polymers have been concerned with materials in which the mesogenic groups are attached to the flexible polymer backbone such as polyacrylates, polymethacrylates,[3,4] and polysiloxanes,[5,6] etc. It has been well-known that there are numerous examples of side-chain LC polymers prepared by various methods such as radical, cationic, group-transfer, and also ring-opening metathesis polymerizations in recent years.[7-9] However, to our knowledge there are very few reports in the literature concerning the use of a rigid polymer backbone for side-chain LC polymers.[10-13] Furthermore, systematic studies to prepare the side-chain LC polymers with an electrically conductive system have been far less studied.[12]

In our previous works, we reported the synthesis and characterization of some thermotropic side-chain LC polymers based on a poly(1,6-heptadiyne) backbone by transition-metal catalyst systems.[12,14] In this paper, we describe the results of the preparation and properties of a novel side-chain LC polymer with a new type of highly conjugated backbone, poly(dipropargylamine).

Experimental Section. Scheme I outlines the synthesis of monomer.

Synthesis of 11-Bromo-*N,N*-dipropargylundecaneamide (A). 11-Bromoundecanoic acid (5.3 g, 20 mmol) was dissolved in thionyl chloride (about 17 mL). The solution was evaporated to dryness by means of an evaporator. The product was dissolved in 50 mL of dry tetrahydrofuran (THF) and added to a mixed solution of dipropargylamine (2 mL, 20 mmol) and triethylamine (about 2.8 mL) in 100 mL of dry THF at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed, and the residue was diluted with dichloromethane; the organic layer was washed with water, followed by drying over magnesium sulfate. After evaporating the solvent, the crude products were purified by column chromatography (silica gel; hexane–ethyl acetate (8:2) eluent). Yield: 83%.

Monomer. The monomer 11-(4-cyanobiphenylyl)oxy-*N,N*-dipropargylundecaneamide was synthesized by the reaction of the 4-cyano-4′-hydroxybiphenyl mesogenic group with the compound **A** in the presence of K_2CO_3 using DMF as solvent. Yield: 90%.

The structure of the product was identified by elemental analysis, MS, IR, and ^1H and ^{13}C NMR.

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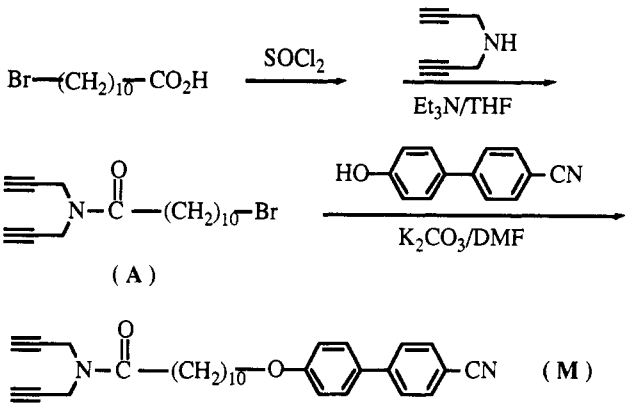
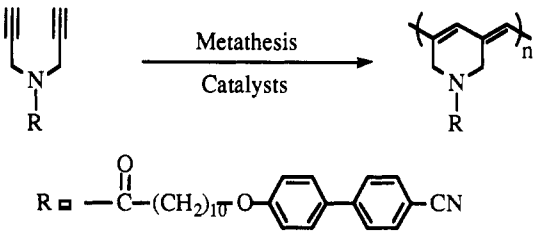
Scheme I



Scheme II



Catalysts : $MoCl_5$, WCl_6, $PdCl_2$

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

Table 1. Polymerization of 11-(4-Cyanobiphenylyl)oxy-*N,N*-dipropargylundecaneamide with Various Transition-Metal Catalysts[a]

exp no.	catal syst[b] (mole ratio)	M/C[c]	$[M]_0$[d]	polym[e] yield (%)	GPC[f] $\bar{M}_n \times 10^{-4}$	GPC[f] $\bar{M}_w/\bar{M}_n$
1	$MoCl_5$	50	0.25	91	1.4	2.7
2	$MoCl_5$	100	0.25	80		
3	$MoCl_5$	50	0.5	100	1.1	2.9
4	$MoCl_5$–$(n\text{-}Bu)_4Sn$ (1:4)	50	0.25	60	1.6	2.1
5	$MoCl_5$–$EtAlCl_2$ (1:4)	50	0.25	100	1.8	2.4
6	WCl_6	50	0.25	trace		
7	WCl_6–$(n\text{-}Bu)_4Sn$ (1:4)	50	0.25	trace		
8	WCl_6–$EtAlCl_2$ (1:4)	50	0.25	trace		
9	$PdCl_2$[g]	50	0.25	15		

[a] Polymerization was carried out at 60 °C for 24 h in THF. [b] A mixture of catalyst and cocatalyst in chlorobenzene was aged at 30 °C 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. [g] Polymerization was carried out 90 °C for 24 h in DMF.

Elem anal. Calcd for $C_{30}H_{34}O_2N_2$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.14; H, 7.46; N, 6.18. IR: 1657 (C=O), 3281 cm^{-1} (≡CH). ^1H NMR ($CDCl_3$): 1.3–1.8 (m, $-(CH_2)_8-$), 2.2–2.3 (tt, ≡CH), 2.4 (t, $-COCH_2-$), 4.0 (t, $-CH_2O-$), 4.2–4.3 (dd, $-CH_2C\equiv$), 7.0–7.7 (m, phenyl rings). MS: *m/e* 454 (parent), 194 (base). ^{13}C NMR ($CDCl_3$): 36.1 ($CH_2C\equiv$), 72.1 (≡CH), 72.8 ($-C\equiv CH$), 172.4 (C=O).

Polymerization. Scheme II outlines the cyclopolymerization of the monomer with transition-metal catalysts. Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent to make 0.02 and 0.2 M solutions prior to use. A typical polymerization procedure was as follows: solvent, a catalyst solution, and, when needed, a cocatalyst solution were injected into a 20-mL ampule equipped with a rubber

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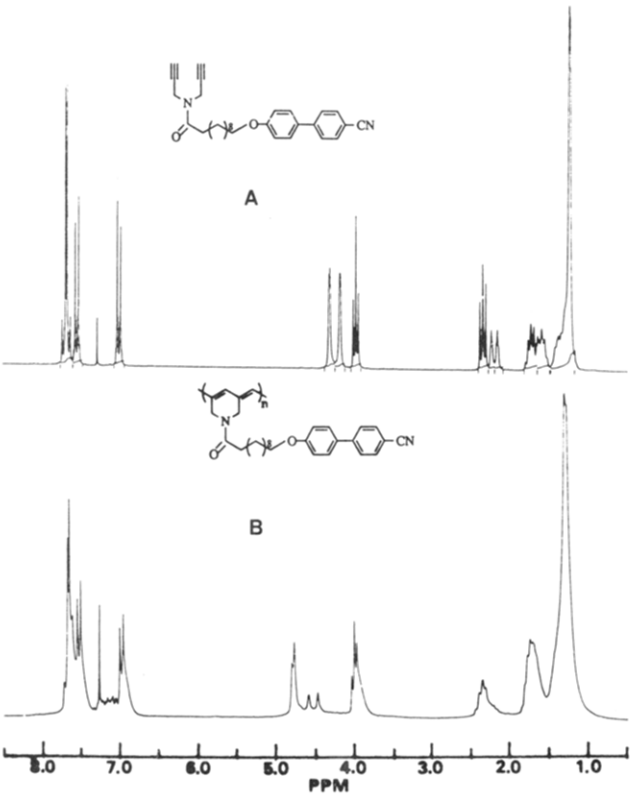

Figure 1. ^1H NMR spectrum of the monomer (A) and the polymer (B) (sample: exp no. 5 in Table 1).

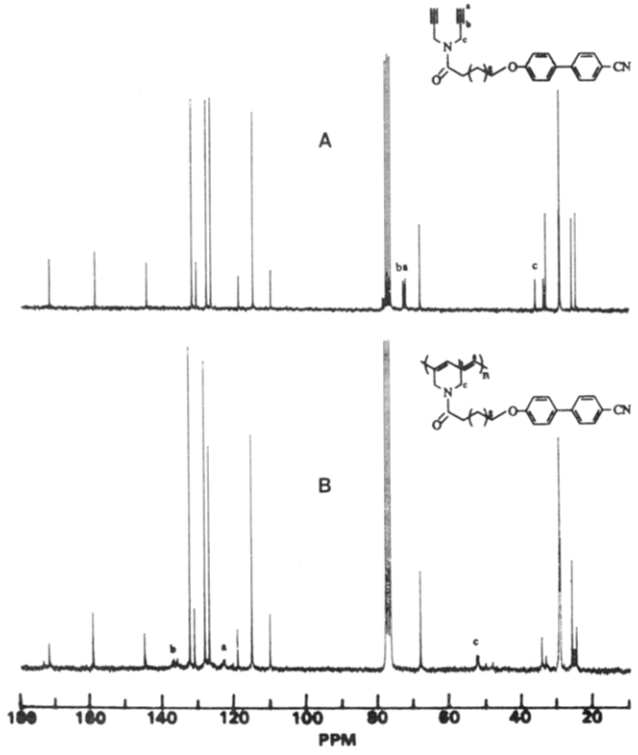

Figure 2. ^{13}C NMR spectrum of the monomer (A) and the polymer (B) (sample: exp no. 5 in Table 1).

septum in the order given. When the cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, the monomer dissolved in the same 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 $CHCl_3$ and precipitated with a large excess of methanol.

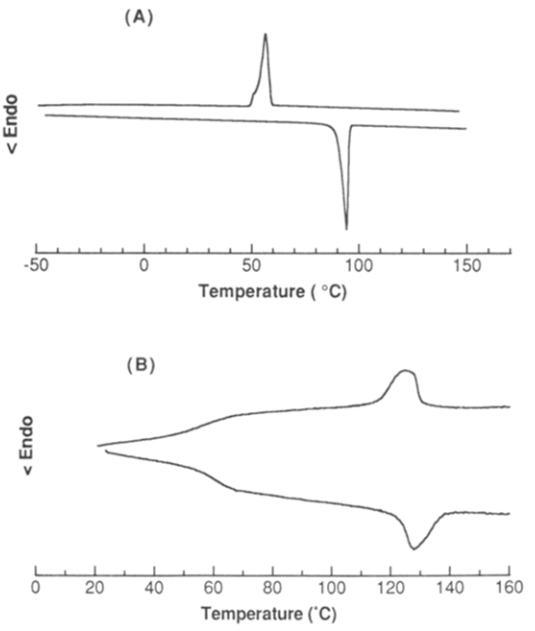

Figure 3. DSC thermograms of the monomer (A) and the polymer (B) (scanning rate = 10 °C/min) (sample: exp no. 5 in Table 1).

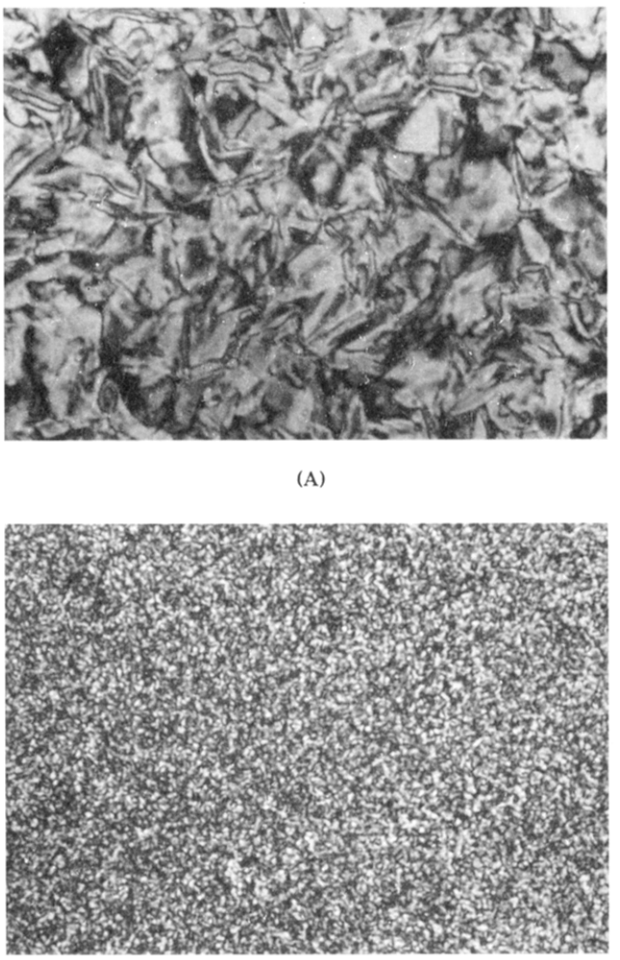

Figure 4. Microphotographs of the monomer (A) taken at 60 °C and the polymer (B) taken at 123 °C (sample: exp no. 5 in Table 1).

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

Results and Discussion. In Table 1, the results of the cyclopolymerization of the monomer by various catalyst systems are listed. The catalytic activity of $MoCl_5$ was greater than that of WCl_6. When the mole ratio of the monomer to the catalyst was relatively low and the initial monomer concentration was high, a high yield of polymer was obtained. As shown in Table 1, $EtAlCl_2$ exhibited better cocatalytic activity than $(n\text{-}Bu)_4Sn$ for the polymerization of the monomer. The highest number-average molecular weight of the polymer obtained was ca. 1.8×10^4 (with $MoCl_5$–$EtAlCl_2$ as a catalyst). The polydispersities of the resulting polymer were in the range of 2.1–2.9.

The obtained polymer was completely soluble in various organic solvents such as chloroform, MC, THF, 1,4-dioxane, DMF, etc., and films could be easily cast on glass plates to give a dark-brown, shiny thin film. It is, however, insoluble in *n*-hexane, acetone, diethyl ether, and ethyl acetate. Such a good solubility of the present cyclopolymers supports the hypothesis that these polymers possess the six-membered cyclic backbone structures.[15,16] Careful ^1H and ^{13}C NMR and IR analyses were carried out for both the monomer and polymer in order to prove the chemical structure of the polymer. As the polymerization proceeded (Figure 1), an acetylenic proton peak at 2.2–2.3 ppm disappeared and a new vinylic proton peak at 7.0–7.2 ppm appeared. The broad peaks at 4.4–4.8 ppm are assignable to the methylene protons on the cyclic ring. Figure 2 exhibits the ^{13}C NMR of the monomer and the polymer. The monomer gave acetylenic carbon peaks at 72 and 73 ppm. On the other hand, the polymer did not show these peaks. Instead, the carbon peaks of the polymer backbone appeared at about 123 and 137 ppm in the polymer. The peak of the methylene carbon adjacent to the polymer backbone shifted from 36 to 52 ppm on polymerization. Also, the IR spectrum of the polymer shows no absorption at 3281 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.

Figure 3A shows the DSC curves obtained for consecutive heating and cooling cycles on the monomer. In the second heating, the monomer exhibits a sharp single endothermic peak at $T_{SI} = 94$ °C, and there is only a slight shoulder at about 52 °C on the cooling cycle. In Figure 4A, the polarizing optical microphotograph of the monomer obtained by careful annealing at 60 °C on the cooling cycle, a rodlike texture of the monomer which is thought to be a typical smectic mesophase is shown. Figure 3B, which presents the second heating and the cooling DSC scans of the polymer, indicated two well-separated transition regions in the polymer. In the heating part of the DSC curve, a glass transition is shown at 59 °C, and smectic–isotropic transition is shown at 128 °C (125 °C on cooling); the corresponding enthalpy ΔH_1 is 1.79 cal/g. This relatively large enthalpy of isotropization is attributable to the transition from the smectic state to the isotropic liquid state. Figure 4B is a microphotograph of the polymer taken at 123 °C. It shows a fine-grain texture for the liquid-crystalline polymer that is consistent with the smectic mesophase.[17,18]

Room-temperature conductivities of the polymers undoped and doped with I_2 were found to be 6.7×10^{-11} and 8.9×10^{-3} S/cm, respectively.

Work on other poly(dipropargylamine) derivatives with various mesogenic groups and different spacer lengths is in progress.

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