Synthesis and Characterization of Side-Chain Liquid-Crystalline Polymers Containing a Poly(1,6-heptadiyne) Derivative

In recent years considerable effort has been directed to the synthesis of novel liquid-crystalline side-chain polymers and their characterization.

In the case of liquid-crystalline (LC) polymers containing mesogens as side groups, systematic investigations became possible only after Finkelmann and Ringsdorf[1,2] had demonstrated that a flexible spacer has to be inserted between the main chain and the mesogens. The spacer is introduced in order to decouple the motions of the polymer main chain from that of the side groups in the liquid state.

The types of polymer backbones used for the synthesis of side-chain LC polymers have been limited to polymethacrylates,[3,4] polysiloxanes,[5,6] and polyphosphazene.[7,8,9]

Very little, if any, work has been done on liquid-crystalline monoacetylenics.[10] Such monomers are very interesting as sources of novel structures with a rigid backbone containing conjugated double bonds which can be generated through γ-rays.

There are numerous examples of side-chain LC polymers prepared by radical, cationic, and group-transfer polymerization; however, a metathesis polymerization technique to synthesize LC polymers has not been used. Furthermore, no systematic studies to prepare the side-chain LC polymers with electrical conductivity have been reported yet.

This paper presents our results on the synthesis of a novel class of side-chain thermotropic LC polymer with electrical conductivity, namely, poly[4-methoxy-4′-(hexyloxy)biphenyl dipropargylacetate].

Monomer. The monomer 4-methoxy-4′-(hexyloxy)biphenyl dipropargylacetate was synthesized by reacting the mesogenic spacer group with dipropargylacetyl chloride in the presence of triethylamine using THF as solvent: yield 76% (Scheme I).

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

Elem anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.23. Found: C, 77.35, H, 7.18. IR: 1726 (C=O), 3285 cm^{-1} ($\equiv$CH). ^{1}H NMR ($CDCl_3$): 1.4–1.9 (m, $-(CH_2)_4-$), 2.1 (t, $\equiv$CH), 2.7 (d, $CH_2C\equiv C$), 2.9 (>CH), 3.9 (s, $-OCH_3$), 6.9–7.5 ppm (m, phenyl rings). MS: *m/e* 418 (parent), 200 (base). ^{13}C MNR ($CDCl_3$): 19.9 ($CH_2C\equiv$), 43.0 (>CH), 70.4 ($C\equiv CH$), 80.4 ($-C\equiv CH$), 172.4 ($-CO_2-$).

Figure 1 shows the DSC curves obtained for consecutive heating and cooling cycles on the monomer. In the second heating, two prominent endotherms are observed at T_m = 75 °C and T_i = 106 °C. There is a slight shoulder on the isotropization peak between 103 and 105 °C. Figure 2 shows the photomicrographic property of the liquid-crystalline state of the monomer. The mesophase found for the monomer in the region 75–106 °C (69–96 °C on cooling) was characterized by the following observation through the polarizing optical microscope. The mesophase found for the monomer is probably a smectic form.

Scheme II outlines the cyclopolymerization of the monomer with transition-metal catalysts.

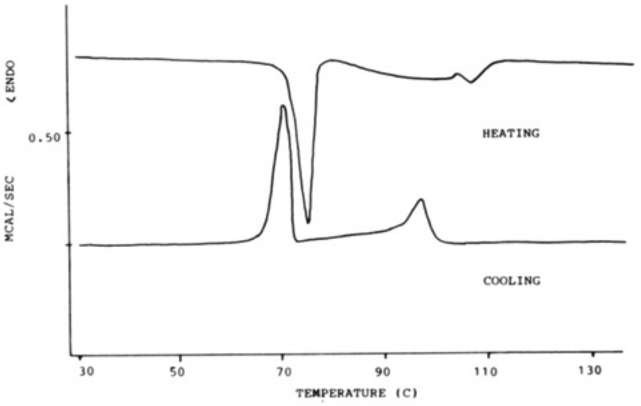


Figure 1. DSC thermogram of the monomer (scanning rate = 10 °C).

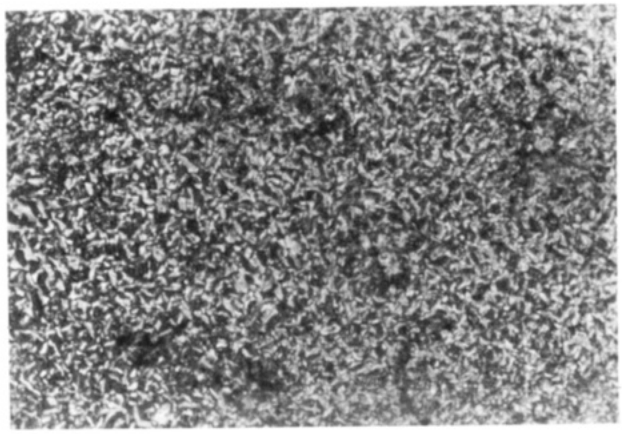
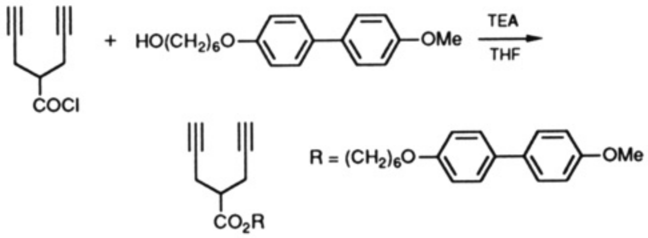
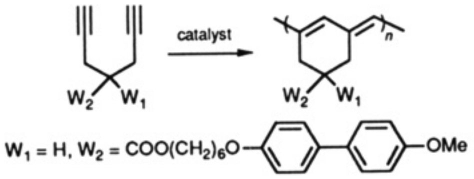


Figure 2. Microphotograph of the monomer, taken at 80 °C.

Scheme I



Scheme II



catalyst: $MoCl_5$, WCl_6, $PdCl_2$
cocatalyst: $(n\text{-Bu})_4Sn$, Ph_4Sn, $EtAlCl_2$

Polymer. Catalyst preparation and polymerization were carried out under dry-nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent to make 0.2 M solutions before 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 the cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, the monomer solution was injected into a polymerization ampule. After the reaction mixture was allowed to react at 60 °C for 24 h, polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in 1,4-dioxane and precipitated upon addition of a large excess of hexane. The polymer was filtered and dried under vacuum at 40 °C for 24 h. The polymer yield was determined by gravimetry. In Table I, the results for the cyclopolymerization of the monomer by various catalyst systems are listed. The catalytic activity of $MoCl_5$ is greater than that of WCl_6. When the mole ratio of the monomer to the catalyst was

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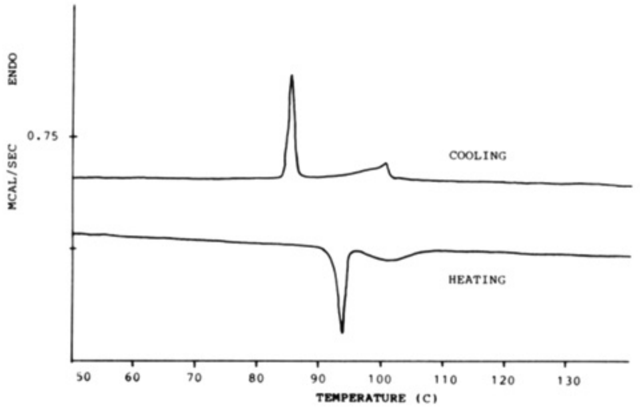

Figure 3. DSC thermogram of the polymer (scanning rate = 10 °C) [sample: exp. no 4 in Table I].

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

exp. no.	catalyst syst[b] (mole ratio)	M/C[c]	$[M]_0$[d]	polym yield,[e] %	$\bar{M}_n/10^4$[f]	$\bar{M}_w/\bar{M}_n$[f]
1	$MoCl_5$	50	0.125	86		
2	$MoCl_5$	100	0.125	56	8.0	2.1
3	$MoCl_5$	50	0.25	80	9.2	1.9
4	$MoCl_5$–(*n*-Bu)$_4$Sn (1:1)	50	0.25	95	10.5	2.7
5	$MoCl_5$–$EtAlCl_2$ (1:1)	50	0.25	90	10.0	2.4
6	WCl_6	50	0.25	trace		
7	WCl_6–(*n*-Bu)$_4$Sn (1:1)	50	0.25	trace		
8	WCl_6–$EtAlCl_2$ (1:1)	50	0.25	10		
9	$PdCl_2$[g]	50	0.25	60		

[a] Polymerization was carried out at 60 °C for 24 h in dioxane. [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 at 90 °C for 24 h in dioxane.

Table II
Thermal Transition Temperatures and Enthalpies for Monomer and Polymer

sample	phase transitions (°C) and corresponding enthalpy changes (cal/g): heating	phase transitions (°C) and corresponding enthalpy changes (cal/g): cooling
monomer	K 75 (7.32) S 106 (4.97) i	i 96 (3.81) S 69 (6.84) K
polymer	K 92 (2.11) S 105 (0.66) i	i 101 (1.08) S 85 (2.5) K

relatively low, a high yield was obtained. As shown in Table I, (*n*-Bu)$_4$Sn is an excellent cocatalyst for the polymerization of this monomer. The highest number-average molecular weight of the polymer obtained was ca. 10.5 × 10^4 (with $MoCl_5$–(*n*-Bu)$_4$Sn as a catalyst). These results are similar to those reported for the polymerization of dipropargylmalonate.[11,12]

Figure 3, 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 major endothermic transition (melting) is found; the corresponding enthalpies ΔH_m are 2.11 J/g.

The liquid crystal to isotropic transition occurs at temperatures well above 100 °C and is very broad. This relatively broad isotropization temperature range is probably due to the high viscosity and the polydispersity of the polymeric product.[8] On the cooling cycle, the mesophase region is broadened with exotherms at 101 and 85 °C. On the cooling cycle, the isotropization enthalpy from the smectic to the isotropic phase is in the range 1.08 J/g. The typical texture for the polymer is presented in Figure 4. Upon cooling the temperature of the isotropic liquid, a mesophase begins to form at 105 °C, in the form of "spherulites" (Figure 4A) which, after further cooling to 103 °C within 30 min (Figure 4B), grow, coalesce, and reorganize their shape until a final texture is established at ca. 101 °C (Figure 4C), suggesting the existence of a smectic mesophase. The transition temperatures and enthalpies measured by DSC for the monomer and polymer are summarized in Table II. Careful ^1H 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 5), an acetylenic proton peak at 2.0 ppm disappeared and a new vi-

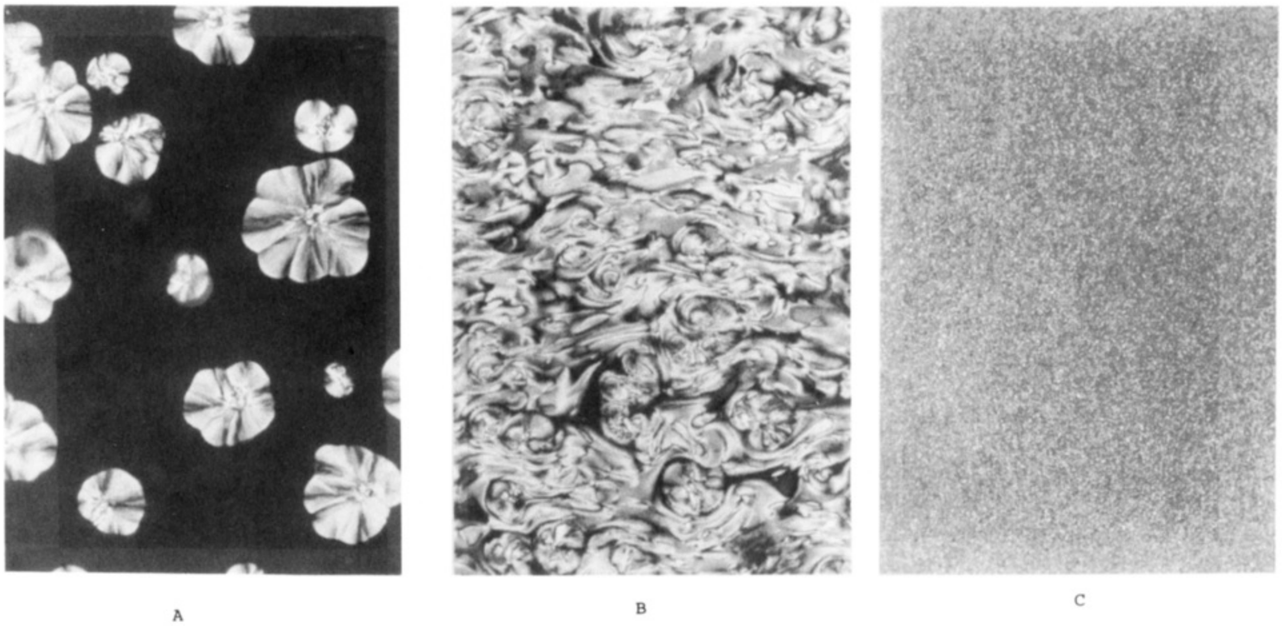

Figure 4. Effect of temperature on the microscopic morphology of the polymer [sample: exp. no. 4 in Table I]: (a) annealing time, t_a = 1 h, taken at 105 °C; (b) t_a = 1 h, taken at 103 °C; (c) t_a = 1 h, taken at 101 °C.

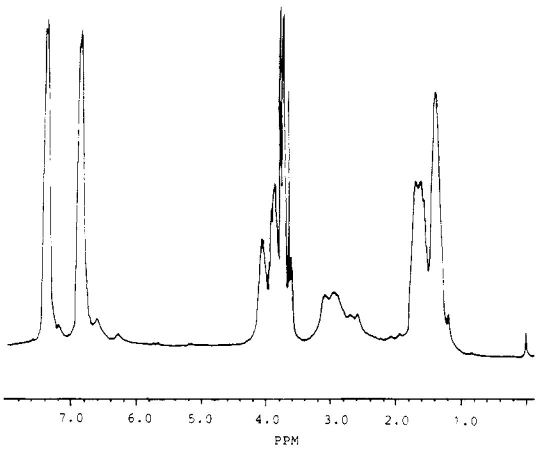

Figure 5. ^1H NMR spectrum of the polymer in $CDCl_3$ [sample: exp. no. 4 in Table I].

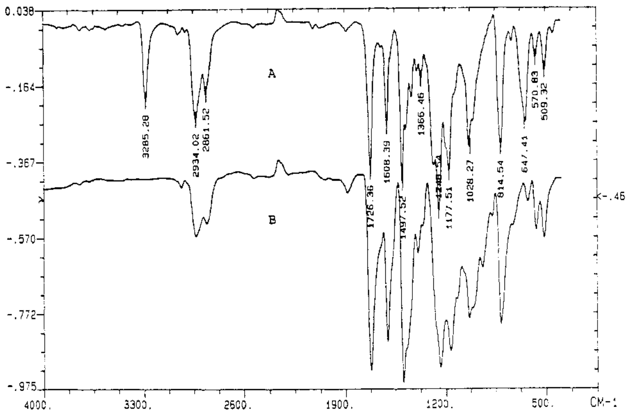

Figure 6. IR spectrum of the monomer (A) and polymer (B) [sample: exp. no. 4 in Table I, KBr pellet].

nylic proton peak at 6.8–7.2 ppm appeared. Figure 6 shows the IR spectra for the monomer and polymer. The IR spectrum of the polymer shows no absorption at 3285 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. The development of the band characteristic of conjugated –C═C– sequences unfortunately cannot be clearly identified, due to the interference in the region of 1650–1550 cm^{-1} of benzene ring absorption bands dominating the weight of the molecule. Figure 7 exhibits the ^{13}C NMR of the monomer and the polymer. The monomer gave acetylenic carbon peaks at 71 and 80 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 140 ppm in the polymer. The peak of the methylene carbon adjacent to the polymer backbone shifted from 20 to 43 ppm on polymerization. The obtained polymer is completely soluble in various organic solvents such as chloroform, methylene chloride, THF, 1,4-dioxane, toluene, DMF, and pyridine and easily cast on glass plates to give a black, 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 ideal six-membered cyclic backbone structures.[11-13]

Room-temperature conductivities of the polymers undoped and doped with I_2 were found to be 6.3×10^{-11} and 10^{-2} S/cm, respectively. Research for other poly(dipropargyl derivatives) with various paired mesogenic groups and some novel LC polymers with electrical conductivity is in progress.

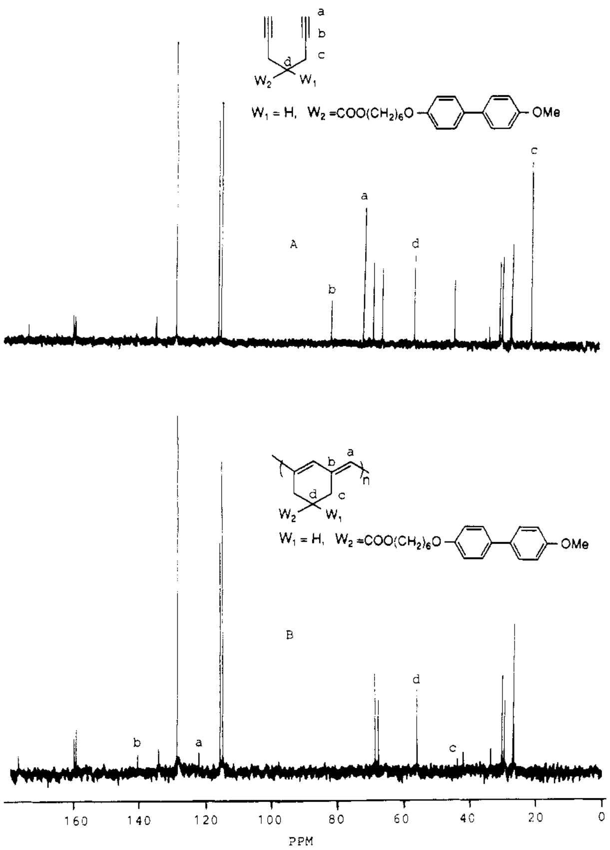

Figure 7. ^{13}C NMR spectrum of the monomer (A) and polymer (B) [sample: exp. no. 4 in Table I].

Acknowledgment. We gratefully acknowledge the support of this work by the Korea Science and Engineering Foundation.

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Received May 23, 1991
Revised Manuscript Received August 14, 1991