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Synthesis and properties of a new side chain liquid crystalline polymer by methathesis polymerization

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SUMMARY

Novel liquid crystalline monomer, 4-methoxybiphenyloxy-(N,N'-dipropargyl)undecane amide, subjected to metathesis reaction with transition metal catalyst systems. It was found that the $MoCl_5$-$EtAlCl_2$ catalyst system was very effective for the cyclopolymerization of the monomer. Resulting polymers exhibited good solubility 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 0.98×10^4 - 1.4×10^4, relative to polystyrene standard by GPC.

Thermal properties of the monomer and the polymer synthesized were examined by differential scanning calorimetry (DSC) and cross-polarized optical microscopy. The polymer exhibited the enantiotropic liquid crystallinity and smectic mesophase.

INTRODUCTION

Finkelmann and Ringsdorf proposed the spacer concept in 1978 as a systematic method for obtaining side-chain liquid crystalline (LC) polymers, with the idea that proper spacers must be introduced to partially decouple the mobility of the main chain from that of the mesogenic pendent groups (1-4). Most of the studies reported the side-chain LC polymers 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. In the previous papers (5,6), we reported the synthesis and characterization of some thermotropic side-chain LC polymers based on poly(1,6-heptadiyne) backbone which was prepared by transition metal catalyst systems. In this paper, we describe the results on the preparation and properties of a novel side-chain LC polymer 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. 11-Bromoundecanoic acid and dipropargylamine (all from Aldrich Chemicals) were used without further purification. 4-Methoxy-4'-hydroxybiphenyl was prepared according to a literature procedure (7).

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

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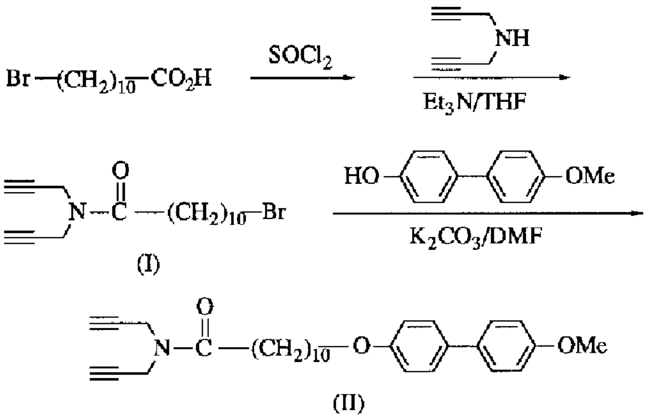
internal standard. Infrared spectra were measured as neat oil or as KBr pellets on a Bomen spectrometer and frequencies were given in reciprocal centimeter. Shimadzu UV-3100S spectrometer was used for UV spectral data. The number average molecular weight ($\overline{Mn}$) and polydispersities were determined 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



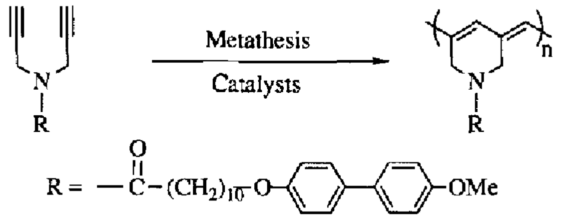
Synthesis of 11-Bromo-(N,N'-dipropargyl)undecane Amide (I). 11-Bromoundecanoic acid (5.3g, 20mmol) was dissolved in thionyl chloride (about 17 mL). The solution was evaporated to dryness by means of an evaporator. The product was dissolved in 50 mL of dry tetrahydrofuran (THF) and added to a mixed solution of dipropargylamine (2 mL, 20mmol) 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, and 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 4-methoxybiphenyloxy-(N,N'-dipropargyl)undecane amide was synythesized by the reaction of 4-methoxy-4'-hydroxybiphenyl (2g, 10mmol) with the compound (I) (3.4g, 10mmol) in the presence of potassium carbonate (4g) in dimethyl formamide (100 mL) for 24 h at 90°C. The reaction product was extracted with dichloromethane, washed with water, and dried over magnesium sulfate. After evaporating the solvent, the residue was purified by column chromatoghraphy [silica gel; hexane-ethyl acetate (8:2) eluent]. The product was further purified by recystallization from ethanol. Yield; 90%. MS: m/e 459 (parent), 199 (base). IR: 1657cm^{-1} (C=O), 3281cm^{-1} (≡CH). ^{1}H-NMR ($CDCl_3$): 1.3-1.8 (m, -$(CH_2)_8$-), 2.2-2.3 (tt, ≡CH), 2.4 (t, -$COCH_2$-), 3.8 (s, -OCH_3), 4.0

(t, -CH$_2$O-), 4.2-4.3 (dd, -CH$_2$C≡), 6.9-7.0 (dd, phenyl rings), 7.4-7.5 (dd, phenyl rings).

Polymerization. The polymerization was carried out with MoCl$_5$- and WCl$_6$-based catalyst systems (8). Scheme II outlines the polymerization of the monomer with transition metal catalysts.

Scheme II



Catalyst : MoCl$_5$, WCl$_6$
Cocatalysts : (n-Bu)$_4$Sn, EtAlCl$_2$

RESULTS AND DISCUSSION.

In Table I, 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$_6$. As shown in Table I, EtAlCl$_2$ was an excellent cocatalyst for the polymerization of this monomer. The number-average molecular weights and the polydispersities of the polymers obtained are also listed in Table I.

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

Exp. No	Catalyst System[b] (mole ratio)	M/C[c]	[M]$_0$[d]	Polymer Yield (%)[e]	$\overline{\mathrm{Mn}}$x10^{-4}[f]	$\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$[f]
1	MoCl$_5$	50	0.25	82	1.2	2.0
2	MoCl$_5$	100	0.25	70		
3	MoCl$_5$	50	0.5	85	0.98	2.7
4	MoCl$_5$— (n-Bu)$_4$Sn (1:4)	50	0.25	72	1.1	2.3
5	MoCl$_5$– EtAlCl$_2$ (1:4)	50	0.25	100	1.4	2.2
6	WCl$_6$	50	0.25	trace		
7	WCl$_6$ – EtAlCl$_2$ (1:4)	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.

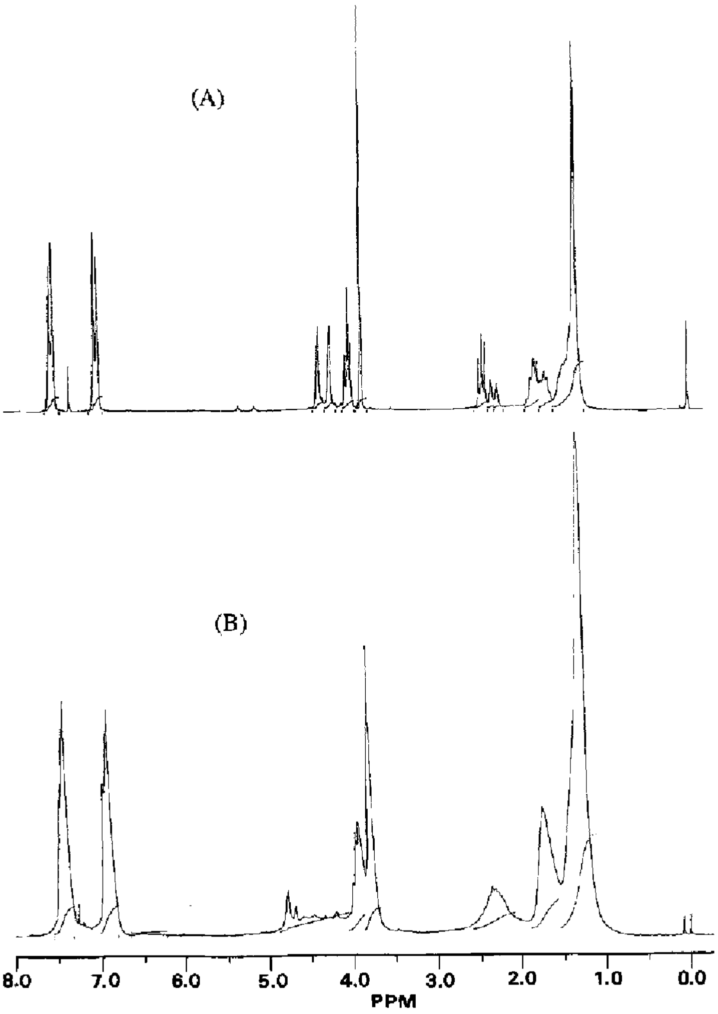


Figure 1. ^{1}H-NMR spectra of monomer (A) and polymer (B) in $CDCl_3$.

Careful ^{1}H-NMR, ^{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 aromatic region appeared. And 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.

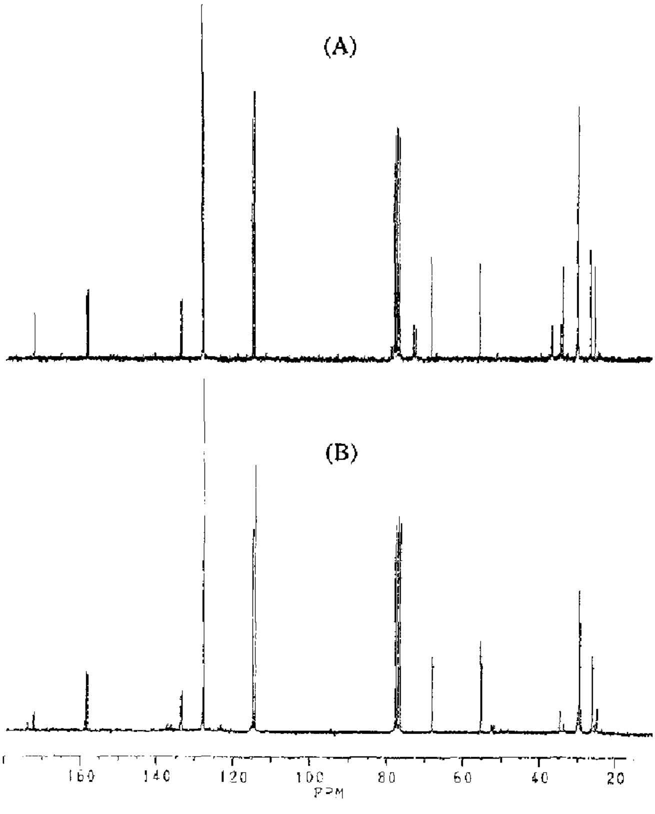
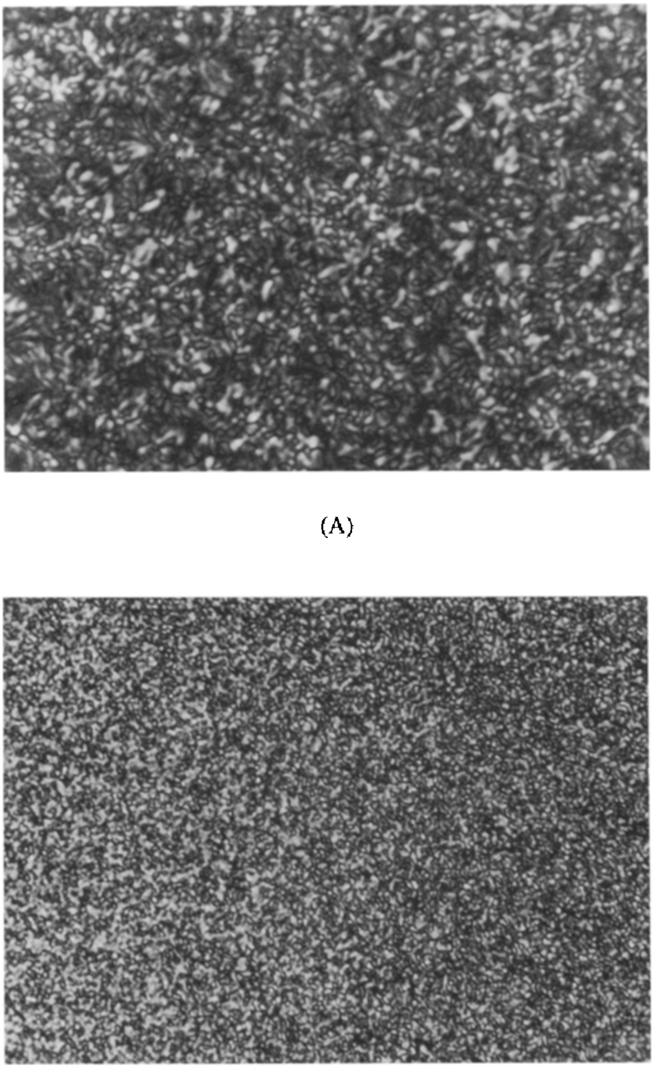


Figure 2. ^{13}C-NMR spectra of monomer (A) and polymer (B) in $CDCl_3$.

While, the polymer did not show any of these peaks. 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 upon 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.

The obtained polymer was completely soluble in various organic solvents such as chloroform, THF, 1,4-dioxane, DMF, etc. and insoluble in n-hexane, acetone, diethyl ether, and ethyl acetate. From the above spectral and solubility data, it was thought that the polymer structure was belived to be cyclized form as described in Scheme II (8,9).



(A)

(B)

Figure 3. Microphotographs of monomer (A) taken at 69°C and polymer (B) taken at 122°C on cooling.

The transition temperatures and enthalpies of the monomer and polymer measured by DSC are summarized in Table II. Figure 3(A) shows the photomicrographic property of the liquid-crystalline state of the monomer. It exhibited enantiotropic behavior, showing a stable nematic mesophase remained on cooling to room temperature. Figure 3(B) is a microphotograph of the polymer taken at 122°C. It shows a fine-grain texture, for the liquid-crystalline polymer that is consistent with smectic mesophase (10,11). The nature of the mesophase exhibited by this polymer can be greatly affected by the spacer length than the mesogenic group. In our results (12), more than 6 methylene units in a spacer length give a possibility to transform the nematic mesophase to smectic one under similar conditions.

Table II. Thermal Transition Temperatures and Enthalpies for Monomer and Polymer

Sample	Phase transition (°C) and corresponding enthalpy changes (cal/g)	
	Heating	Cooling
Monomer	N 84 I	I 70 N
Polymer	G 60 S 130 (1.76) I	I 126 (1.89) S 55 G

Research for other poly(dipropargylamine derivatives) with various mesogenic groups, spacer lengths and some novel LC polymers with electrical conductivity are in progress.

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