Synthesis of a New Side-Chain Liquid Crystalline Polymer with a Polynorbornene Main Chain by Ring-Opening Metathesis Polymerization

Sung-Hyun Kim, Hyung-Jong Lee, Sung-Ho Jin, Hyun-Nam Cho,[†] and Sam-Kwon Choi[*]

Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong Yusung-Gu, Daejon, Korea

Received June 19, 1992
Revised Manuscript Received October 16, 1992

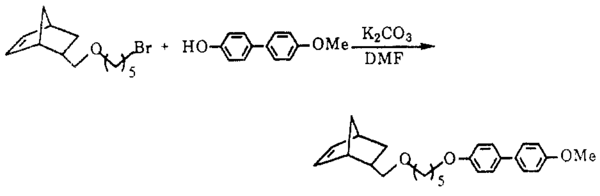
Introduction

In recent years considerable effort has been directed to the synthesis of novel side-chain liquid crystalline (LC) polymers because of a variety of applications, especially in the field of electrooptics.[1] Side-chain liquid crystallinity generally requires a molecular structure in which a flexible polymer chain, or flexible connector group between the mesogen and backbone, provides sufficient conformational freedom to allow the rigid mesogenic units to form stacks or organized domains.[2,3] The types of polymer backbones used for the synthesis of side-chain LC polymers have been limited to polysiloxanes,[4,5] polyacrylates,[6,7] and polymethacrylates.[8,9] There are only a few examples in which other main-chain structures like polyolefin,[10] poly(vinyl ether),[11,12] polyphosphazene,[13,14] or polyoxetane[15] are used.

We have been interested in the effects of the structure of the main chain, the length of the spacers, and the structure of the mesogenic group on the liquid crystalline phase exhibited. In our previous work we reported a novel thermotropic side-chain LC polymer with electrical conductivity synthesized by transition metal catalyst systems.[16] In this paper, we report a new example of an LC polymer that has a polynorbornene main chain and a methoxy-substituted biphenyl mesogenic group.

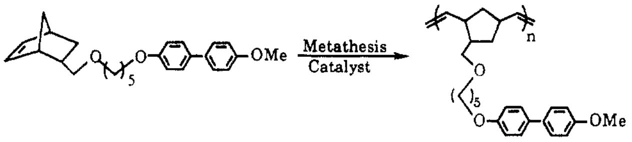
Experimental Section

Monomer. The monomer 5-{[[5-[(4-methoxybiphenyl-4′-yl)-oxy]pentyl]oxy]methyl}-2-norbornene was synthesized by the reaction of the 4-methoxy-4′-hydroxybiphenyl mesogenic group with an exo,endo mixture of 5-((5-bromopentoxy)methyl)-2-norbornene in the presence of K_2CO_3 using DMF as solvent: yield 86%.



The structure of the product was identified by elemental analysis, MS, IR, and ^{1}H NMR, and ^{13}C NMR. Elemental anal. Calcd for $C_{26}H_{32}O_3$: 79.56; H, 8.22. Found: C, 79.38; H, 8.03. MS: *m/e* 392 (parent), 200 (base). IR: 3057 (HC═, vinylic), 1568 (CH═CH, vinylic), 1606, 1475 (C═C, aromatic), 824, 807 (aromatic para substitution), 717 cm^{-1} (cis arrangement of double bond). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.2–1.8 [m, 10 H, $(CH_2)_3$, CH_2], [2.25 (m), 2.71 (br d), 2.83 (br d), 2.94 (t), 3.06 (dd), 3 H, the nonolefinic norbornene protons], 3.3–3.4 (m, 4 H, CH_2OCH_2), 3.76 (s, 3 H, OCH_3), 3.92 (t, 2 H, CH_2OAr), [5.85 (dd), 6.05 (dd), olefinic methine of the endo isomer], 6.01 (m, olefinic methine of the exo isomer), 6.87 (dd, 4 H, aromatic), 7.39 (dd, 4 H, aromatic). ^{13}C NMR ($CDCl_3$): δ (ppm) 55.2 (OCH_3), 132.4 (C(2)), 139.6 (C(3)), 158.1 and 158.6 (alkoxy-substituted 4,4′-aromatic carbons). The ratio of endo to exo isomers calculated from the ratio of the corresponding olefinic resonances is 79:21.

Polymer. 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 a 0.2 M solution 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 50 °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 reaction mixture was dropped into methanol with rapid stirring, and the precipitate separated from the solution and was washed twice with methanol. The polymer was filtered and dried under vacuum at 40 °C for 2 days. The polymer yield was determined by gravimetry.



Catalyst : $MoCl_5$, WCl_6, $WCl_4(OAr)_2$

Cocatalyst : $EtAlCl_2$, Et_3Al, $PbEt_4$

Results and Discussion

In Table I the results for the ring-opening metathesis polymerization of the monomer by various catalyst systems are listed. $MoCl_5$ and WCl_6 alone give very low polymer yields. However, when $EtAlCl_2$ or Et_3Al was used as cocatalyst, the polymer yield increased. When the mole ratio of monomer to catalyst was relatively low, the yield was improved. The $WCl_4(O\text{-}2,6\text{-}C_6H_3X_2, X = Ph)_2$ catalyst system,[17] which is well known to have a good tolerating property to polar functional groups in metathesis reactions, was found to be effective. In this system, it was found that $PbEt_4$ is an excellent cocatalyst.

It was shown that the resulting polymers with relatively high number-average molecular weights exhibit good solubility in common organic solvents such as THF, chloroform, toluene, DMF, etc. However, in certain catalyst system (nos. 6 and 7 in Table I), we obtained high molecular weight polymers which were just swelled in the above organic solvents.

Careful ^{1}H NMR, ^{13}C NMR, and IR analyses were carried out to prove the chemical structure of the polymer. As the polymerization proceeded (Figure 3), the vinylic proton peaks at 5.85 and 6.04 ppm disappeared. The ^{1}H NMR spectrum of the polymer shows new vinyl protons as broad signals between 5.15 and 5.26 ppm in the ratio of approximately 6:4. These broad signals correspond to the vinyl protons of the cis and trans double bond of the ring-opened polymer, respectively. One of the main differences between the IR of the monomer and that of the polymer is that there is a strong band at 719 cm^{-1} in the monomer but a very weak band at 710 cm^{-1} and a broad band at 970 cm^{-1} in the polymer. The strong band about 719 cm^{-1} is due to the cis arrangement about a double bond in which the ═CH bond can undergo an out-of-plane bending vibration, while a trans double bond usually absorbs near 970 cm^{-1} in such a vibration mode. The above IR information also supports that the ring-opened polynor-

---

[*] To whom correspondence should be addressed.

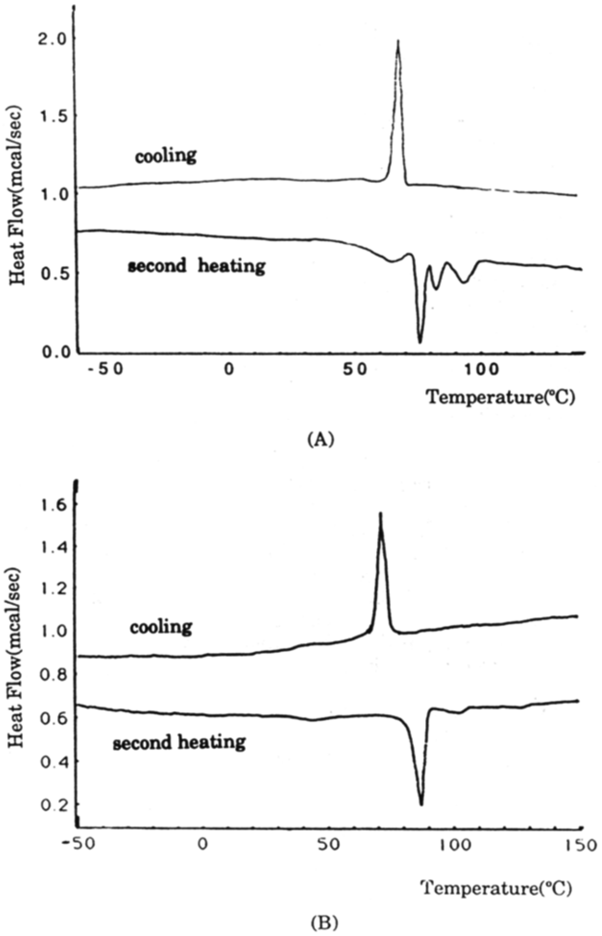
[†] Polymer Materials Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheangyangri, Seoul, Korea.

0024-9297/93/2226-0846$04.00/0

Table I
Polymerization of the Monomer with Various Transition Metal Catalysts

expt no.	cat. syst[a] (mole ratio)	M/C[b]	$[M]_0$[c]	polymer[d] yield (%)	$\bar{M}_n/10^3$ [e]	$\bar{M}_w/\bar{M}_n$
1	WCl_6–Et_3Al (1:4)	50	0.5	45	130	3.3
2	WCl_6–$EtAlCl_2$ (1:4)	50	0.5	40	75	2.7
3	WCl_6–$EtAlCl_2$ (1:4)	25	0.15	66	90	2.4
4	$WCl_4(OAr)_2$–$PbEt_4$ (1:2)[f]	50	0.15	62	27	4.2
5	$WCl_4(OAr)_2$–$PbEt_4$ (1:2)[f]	100	0.1	54	31	2.8
6	$WCl_4(OAr)_2$–$PbEt_4$ (1:3)[f]	50	0.5	82	g	
7	$MoCl_5$–$EtAlCl_2$ (1:4)	50	0.5	58	g	
8	$MoCl_5$	50	0.5	trace		
9	WCl_6	50	0.5	trace		

[a] A mixture of catalyst and cocatalyst in chlorobenzene was aged at 50 °C for 15 min. before use as catalyst. [b] Monomer to catalyst mole ratio. [c] Initial monomer concentration. [d] Methanol-insoluble polymer. [e] Values were obtained by GPC analysis with polystyrene standard calibration. [f] Polymerization procedure by this catalyst system proceeded as follows: 10^{-5}–10^{-4} mol of $WCl_4(O\text{-}2,6\text{-}C_6H_3X_2, X = Ph)_2$ was placed in an ampule in such a way that the catalyst concentration was 0.02 M. The solution was heated to 80 °C and $PbEt_4$ was syringed in. The resulting catalyst mixture was then transferred to another ampule with a cannula in which the monomer was kept at the reaction temperature. The ampule was maintained at 60 °C for 4 h. [g] High molecular weight polymers which were swelled in THF, toluene, chlorobenzene, DMF, chloroform, etc.

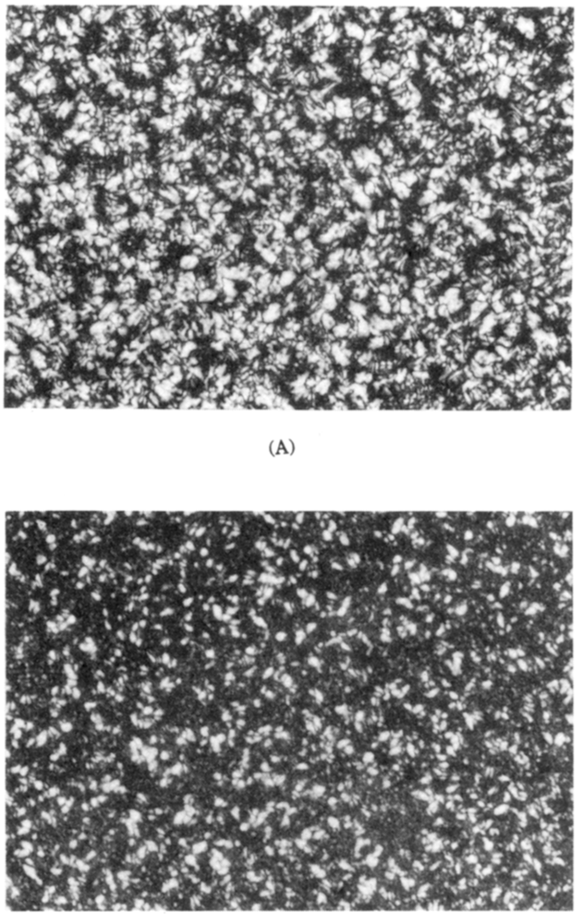


(A)

(B)

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

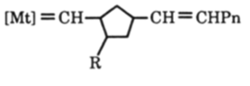
bornene main chain has both cis and trans double bonds. In the ^{13}C NMR spectroscopy, the monomer gave vinylic carbon peaks at 132.4 and 136.9 ppm. On the other hand, the polymer did not show these peaks; instead, the various vinylic carbon peaks of the ring-opened polymer backbone appeared between 130 and 135 ppm. The olefinic carbon chemical shift depends not only upon the nature of the double bond (cis or trans) but also on the arrangements of the two repeat units from which the double bond is derived, i.e., HH, HT (TH), or TT. It should be noted that in the polymerization of substituted norbornens there are two types of propagating species, represented by 1 and 2.



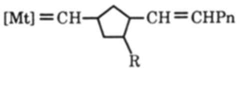
(A)

(B)

Figure 2. Microphotographs of the monomer (A) taken at 60 °C and the polymer (B) taken at 70 °C (sample: no. 4 in Table I).



1



2

1 can add monomer to give HH or HT structures while 2 can add monomer to give TH or TT structures (H = head, T = tail). Therefore, owing to the above two reasons, such various vinylic carbon peaks appeared in the ^{13}C NMR spectrum of the polymer.

Figure 1A shows the DSC traces obtained for consecutive heating and cooling cycles on the monomer. The large

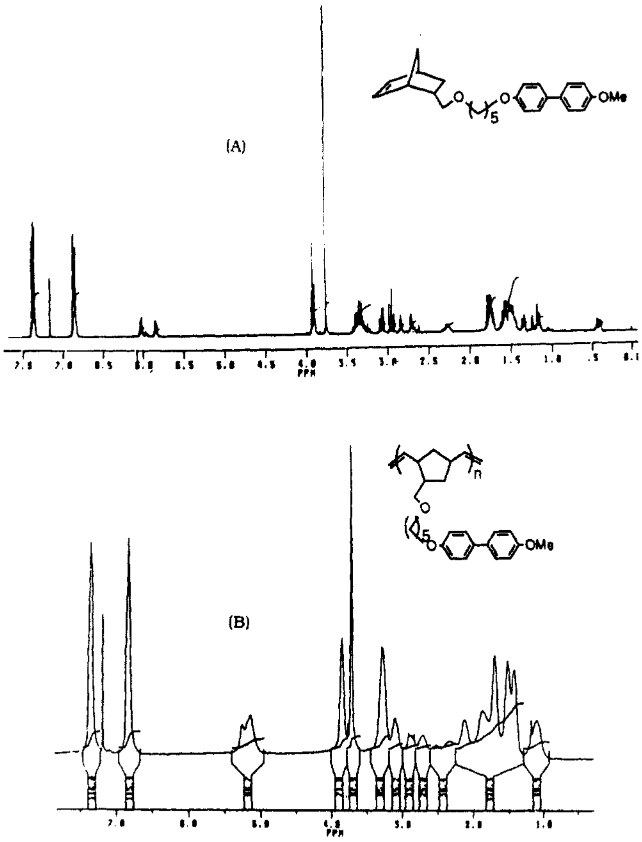


Figure 3. ^1H NMR spectra ofthe monomer (A) and the polymer (B) (sample: no. 4 in Table I).

transition peak at 67 °C on the cooling scan is thought to be due to the isotropic liquid–smectic mesophase transition. The transition enthalpy from the isotropic phase to the LC phase is 9.95 cal/g on the cooling scan. On the second heating scan, multiple melting endothermic peaks which were not detected during the cooling scan were observed between 55 and 97 °C, which are attributed to the endo/exo isomeric mixture. Figure 2A shows the photomicrographic properties of the LC state of the monomer which indicated that the first peak and the last peak on the heating scan were due to a solid–smectic liquid crystal transition and a complete isotropization, respectively. Figure 1B presents the cooling and the second heating DSC traces of the polymer. In the heating part of the DSC curves, a prominent endothermic transition (isotropization) is found: the corresponding enthalpy ΔH_m is 3.96 cal/g. This relatively large enthalpy of isotropization is attributable to the transition from the highly ordered state to the isotropic liquid state. Figure 2B is a microphotograph of the polymer taken at 70 °C. On the cooling scan from the isotropic state, batonnets began to appear on the dark background at 71 °C, growing gradually, and finally a fanlike texture was observed. The mesophase found for the polymer is supposed to be a smectic mesophase because of both the large enthalpy of isotropization and the batonnets and fanlike textures observed by polarized optical microscopy.

In addition to research on the effect of the length of the spacers and the structure of the mesogenic group on the liquid crystalline phase exhibited, studies to increase the types of main chains are in progress.

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

References and Notes

(1) (a) Finkelmann, H.; Keichle, U.; Rehage, G. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 3453. (b) Coles, H. J.; Simon, R. In *Recent Advances in Liquid Crystalline Polymers*; Chapoy, L. L., Ed.; Elsevier Applied Science: New York, 1985; Chapter 22.
(2) Finkelmann, H.; Ringsdorf, H.; Wendroff, J. H. *Makromol. Chem.* **1978**, *179*, 273.
(3) Finkelmann, H.; Happ, M.; Portugall, M.; Ringsdorf, H. *Makromol. Chem.* **1978**, *179*, 2541.
(4) Skibaev, V. P.; Plate, N. A. *Adv. Polym. Sci.* **1984**, *60/61*, 173.
(5) Finkelmann, H.; Rehage, G. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 31.
(6) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
(7) Decobert, G.; Soyer, F.; Dubois, J. C. *Polym. Bull.* **1985**, *14*, 179.
(8) Finkelmann, H.; Rehage, G. *Adv. Polym. Sci.* **1984**, *60/61*, 99.
(9) Zentel, R.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 393.
(10) Mallon, J. J.; Kantor, S. W. *Macromolecules* **1989**, *22*, 2070.
(11) Sagane, T.; Lenz, R. W. *Polym. J.* **1988**, *20*, 923.
(12) Percec, V.; Lee, M. *Macromolecules* **1991**, *24*, 1017.
(13) Singler, R. E.; Willingham, R. A.; Lenz, R. W.; Furukawa, A.; Finkelmann, H. *Macromolecules* **1987**, *20*, 1728.
(14) Allcock, H. R.; Kim, C. *Macromolecules* **1990**, *23*, 3881.
(15) Kawakami, Y.; Takahashi, K.; Hibino, H. *Macromolecules* **1991**, *24*, 4531.
(16) Jin, S. H.; Kim, S. H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1991**, *24*, 6050.
(17) Quignard, F.; Leconte, M.; Basset, J. M. *Inorg. Chem.* **1987**, *26*, 4272.