

Synthesis and Mesomorphic Behavior of Terminal Oligo(ethylene glycol) Monomethyl Ether-Substituted Low Molecular Weight Thermotropic Liquid Crystals

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SYNOPSIS

A number of alkenyl monomers containing biphenyl benzoate-based on a mesogenic core with various lengths of oligo(ethylene glycol) monomethyl ether as the terminal group were synthesized. The purity, the thermotropic transition temperature, and the mesomorphic texture were investigated with ¹H-nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and optical polarized microscopy with a hot stage. The monomers studied in this project showed predominately nematic phases, whereas those with ester-linked derivatives studied in our previous work were able to present both nematic and smectic phases. They also exhibited higher isotropic transition temperatures than those of the ester-linked derivatives. The factors governing mesophase texture and transition temperature are discussed thoroughly. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Side-chain liquid crystal polymers (LCPs) have been extensively studied during the last decade.¹⁻⁴ Thermotropic side-chained LCPs, owing to their particular properties, have been considered as potential materials for various kinds of special applications, such as in information storage⁵⁻⁷ and ferroelectric devices.⁸ The synthesis, structure-property relation, and application of this kind of thermotropic liquid crystals were reviewed by Varshney⁹ and Gray et al.¹⁰ In the application of the chromatographic technique, a biphenyl benzoate-based liquid crystal was found to be an efficient stationary phase in the GC capillary column for the purpose of separation of polycyclic aromatic hydrocarbons (PAHs) and for some optical isomeric species.¹¹ To increase the thermostability of this sort of packing materials in the high-temperature operating GC oven, it is necessary to increase the mesophase temperature with a higher isotropic change

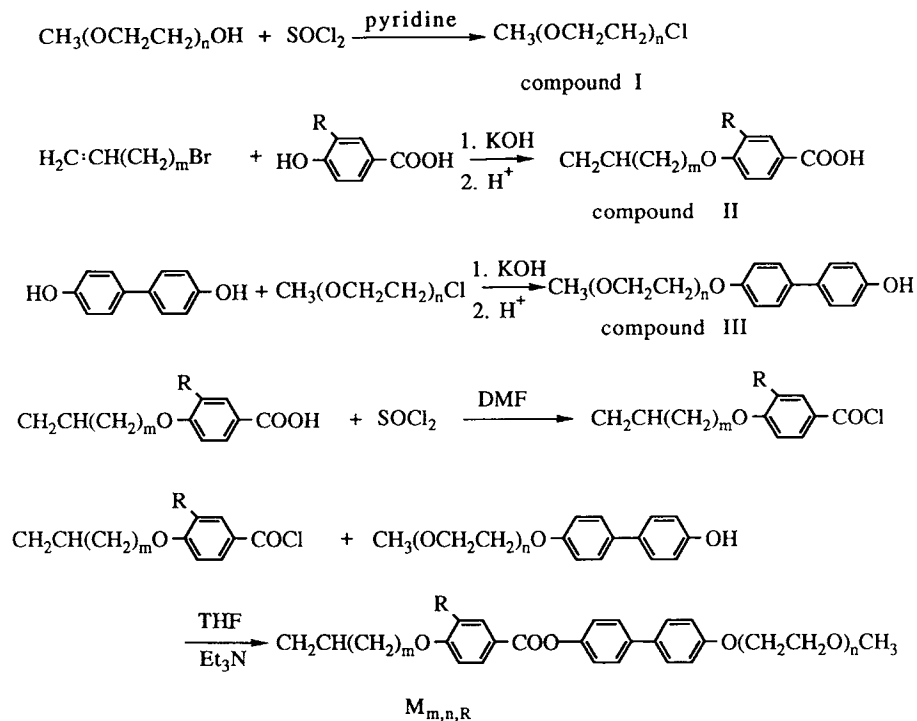
for the liquid crystals. Crown ether-type compounds have been reported to be an effective stationary phase for separating metal ions¹² and many heterocyclic organic compounds.¹³ In this study, we prepared a series of alkenyl monomers with a biphenyl benzoate bearing oligo(ethylene glycol monomethyl ether) as the quasi-crown ether-type terminal group, which are ready to graft onto the poly(methyl hydrogen siloxane) backbone. These alkenyl monomers are found to exhibit long-range nematicity with high temperatures that fitted our aim. The structure and properties were characterized by proton nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry, and optical polarized microscopy with a hot stage. Factors affecting the mesomorphic phase and the transition temperatures will be investigated.

EXPERIMENTAL

Material

4,4'-Biphenol, mono-, di-, and triethylene glycol monomethyl ether, 4-hydroxybenzoic acid, 5-bromo-1-pentene, and 9-decenol (from Aldrich Chemical

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m : 1,3,8
 n : 1,2,3
 R : H, OCH₃

Scheme 1 Procedure of preparing low molecular-weight liquid crystal $M_{m,n,R}$.

Co.), thionyl chloride, allyl bromide, and triethylamine (from R.D.H. Co.), and *N,N*-dimethylformamide, *p*-toluenesulfonyl chloride, and potassium hydroxide (from Merck Co.) were used as received. Anhydrous tetrahydrofuran (THF) was first refluxed over sodium and then distilled under a nitrogen atmosphere.

Technique

¹H-NMR spectra were recorded on a Bruker AC200 spectrometer (200.13 MHz) with deuterated chloroform as the lock solvent. Tetramethylsilane (TMS) was used as an internal standard. The phase transitions of the resulting monomers were determined by a differential scanning calorimeter (Perkin-Elmer DSC-7). The DSC measurements were carried out with a cooling and heating rate of 10°C per min. The anisotropic texture of the compounds was obtained by an Olympus BH-2 optical polarized microscope with a Linkam THMS 600 hot stage and a TMS 91 central processor.

Synthesis of the Intermediates

Compound I was prepared by the procedure of Edward et al.¹⁴ Compound II was prepared by the procedure of Ringsdorf and Schneller.³ Compound III was synthesized by the nucleophilic attack of 4,4'-biphenol onto compound I in the presence of a base. An example is the following: 0.16 mol of 4,4'-biphenol, 0.16 mol 2-chloroethyl methyl ether, and 0.18 mol KOH were refluxed in ethanol in the presence of KI at 78°C in a 100 mL round-bottom flask. After stirring 24 h, the solution was treated with 6*N* HCl and filtered. The precipitate was saved and purified by column chromatography with an eluent system of dichloromethane/*n*-hexane (8 v/2 v). Finally, 12.1 g (0.049 mol) 4-(2-methoxyethoxy)-4'-hydroxybiphenyl, with melting point 153°C, was obtained (yield 35%).

Synthesis of Monomer $M_{m,n,R}$

All compounds were synthesized by the same procedure (Scheme 1). An example is demonstrated by

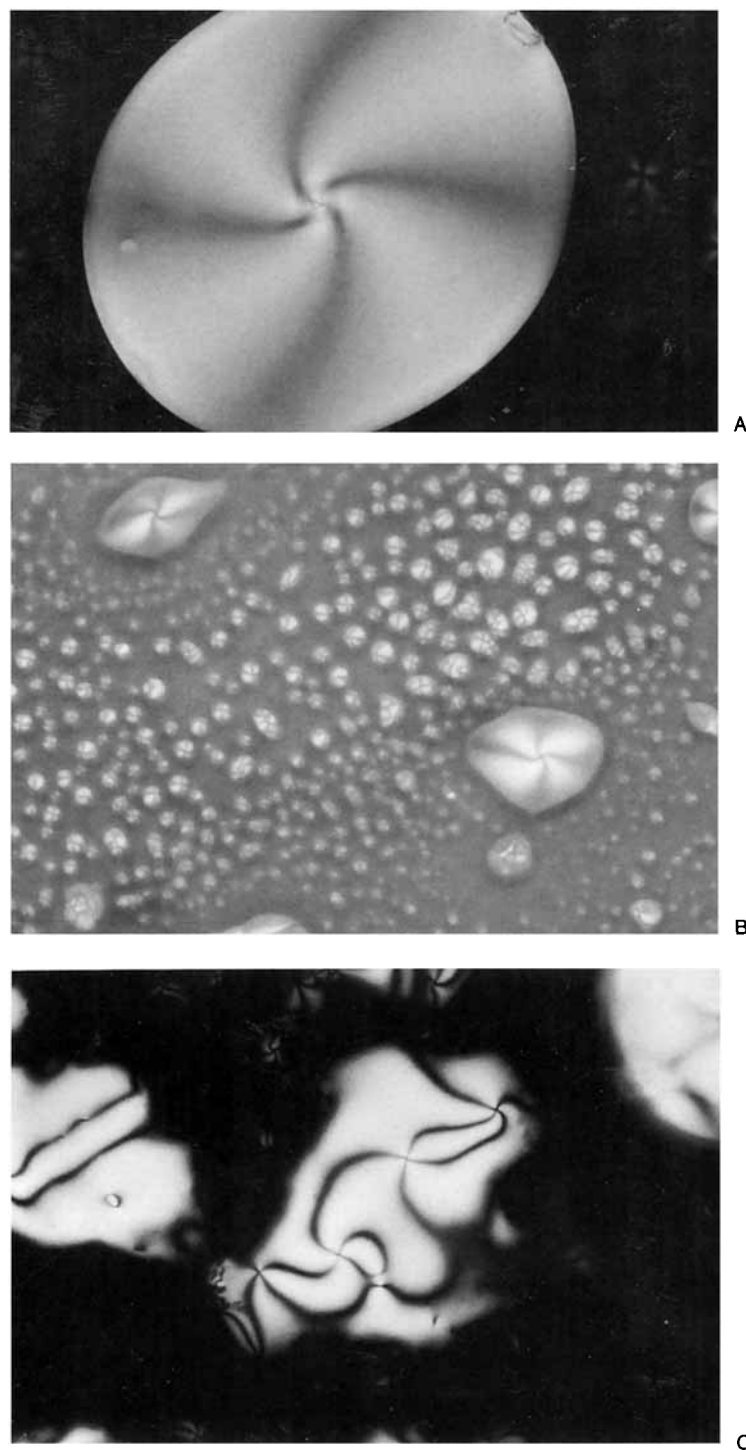


Figure 1 Mesomorphic textures of the monomers at various temperatures. Nematic phases for (A) $M_{1,1,H}$ at 222°C, (B) $M_{3,1,H}$ at 210°C, (C) $M_{8,1,H}$ at 180°C, (D) $M_{1,1,H}$ at 218°C, (E) $M_{1,2,H}$ at 150°C, (F) $M_{1,3,H}$ at 110°C, (G) $M_{1,1,OCH_3}$, at 140°C, (H) $M_{1,2,OCH_3}$ at 80°C, and (I) $M_{1,3,OCH_3}$ at 65°C.

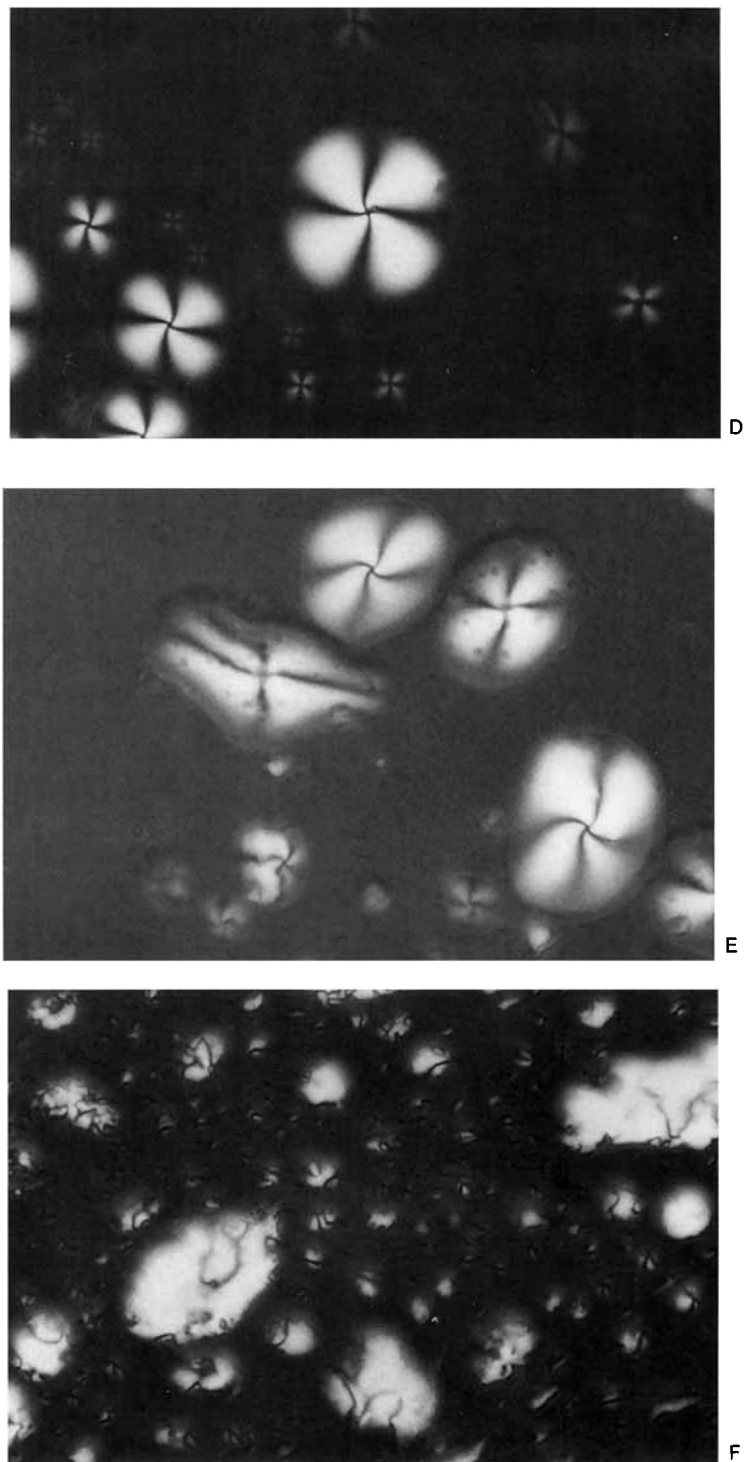


Figure 1 (Continued from the previous page)

$M_{1,1,H}$: 0.021 mol 4-allyloxybenzoic acid and 12 mL thionyl chloride containing 1 drop of *N,N*-dimethylformamide (DMF) was reacted at 60°C for 2 h. The excess thionyl chloride was removed by a vac-

uum rotary evaporator to obtain yellow viscous 4-allyloxybenzoyl chloride. The acid chloride was then dissolved in 5 mL anhydrous THF and then added slowly to a solution of 0.019 mol 4-methoxyethoxy-

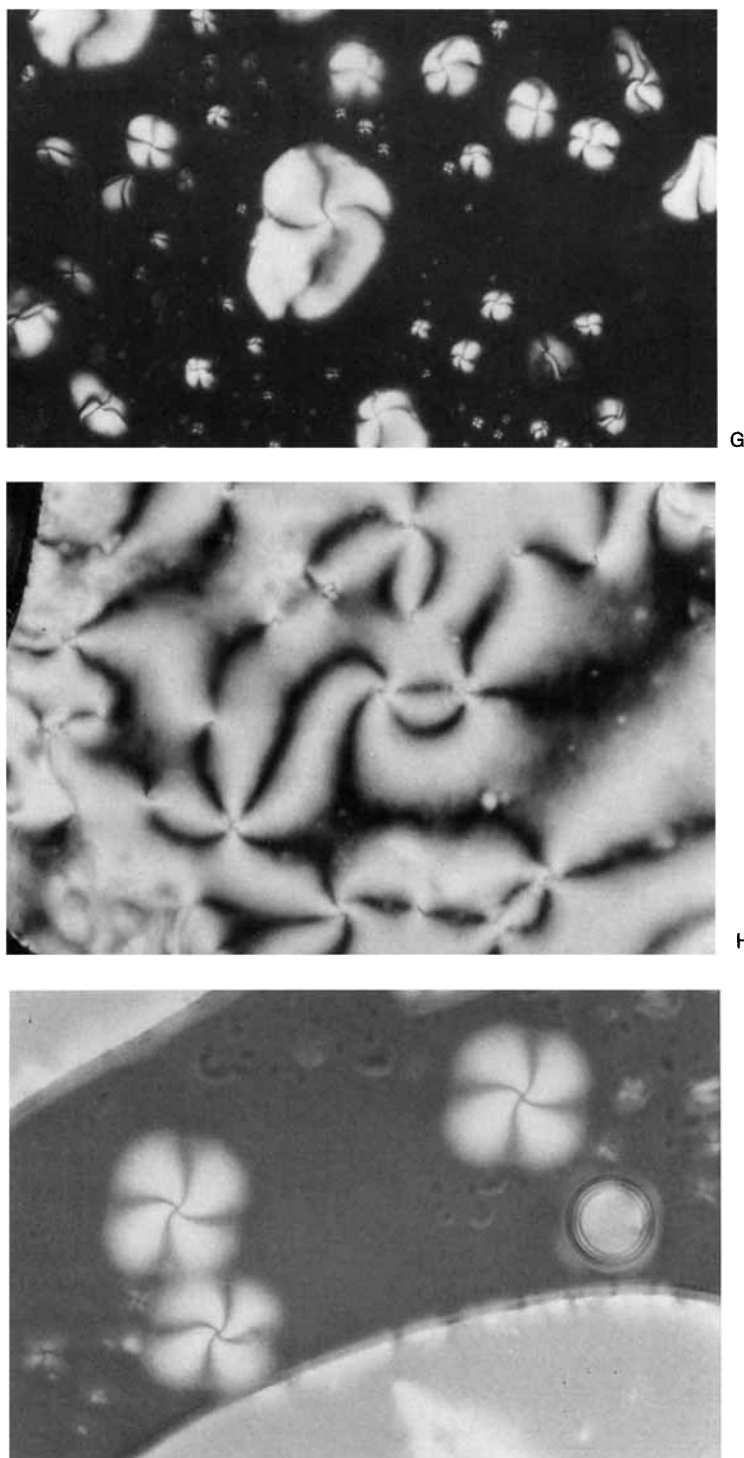


Figure 1 (Continued from the previous page)

4'-hydroxybiphenyl containing excess dried triethylamine and 5 mL anhydrous THF in an ice bath. After 4 h stirring, THF and Et_3N were removed with a rotary evaporator. The residue was dissolved in 50 mL CH_2Cl_2 and successfully extracted twice with

saturated sodium bicarbonate, 6N HCl, and water. The organic layer was then dried with MgSO_4 and the solvent was evaporated off after filtration. The crude product was further purified by column chromatography, with an eluent system of dichloro-

methane/*n*-hexane (7 v/3 v). Finally, 4.44 g (0.011 mol) product, with a melting point of 146°C, was obtained (yield 58%).

The properties and the analytical data of the eight monomers are listed as follows:

• M_{1,1,H}

Mp: 146–147°C; IR (KBr): 1731 ($\nu_{C=O}$) cm⁻¹; ¹H-NMR (CDCl₃) δ : 3.47 (s, 3H, OCH₃); 3.76–3.81 (m, 2H, CH₂OCH₃); 4.15–4.20 (m, 2H, CH₂OAr); 4.63–4.65 (m, 2H, CH₂=CHCH₂); 5.31–5.49 (m, 2H, CH₂=CH); 6.00–6.15 (m, 1H, CH₂=CH); 6.96, 7.23, 7.51, 7.58 (4d, J = 8.4 Hz, 8H, aromatic protons); 7.00, 8.17 (2d, J = 9 Hz, 4H, aromatic protons); EIMS (70 eV) *m/e*: 404 (M⁺, 31); 302(0.2); 243(4); 185(5); 161(100); 139(2); 121(10); 59(9); 41(15); HRMS Calcd for C₂₅H₂₄O₅: 404.1624, Obs: 404.1625.

• M_{1,2,H}

Mp: 110–112°C; IR (KBr): 1731 ($\nu_{C=O}$) cm⁻¹; ¹H-NMR (CDCl₃) δ : 3.41 (s, 3H, OCH₃); 3.57–3.62 (m, 2H, CH₂OCH₃); 3.73–3.77 (m, 2H, ArOCH₂CH₂); 3.87–3.92 (m, 2H, CH₂CH₂OCH₃); 4.17–4.22 (m, 2H, ArOCH₂CH₂O); 4.63–4.66 (m, 2H, CH₂=CHCH₂); 5.32–5.50 (m, 2H, CH₂=CH); 5.99–6.15 (m, 1H, CH₂=CH); 7.00, 7.24, 7.51, 7.58 (4d, J = 8.4 Hz, 8H, aromatic protons); 7.01, 8.17 (2d, J = 9 Hz, 4H, aromatic protons); EIMS (70 eV) *m/e*: 448 (M⁺, 26); 408(0.2); 390(0.5); 360(0.2); 288(4); 186(4); 161(100); 139(2); 131(1); 121(7); 105(4); 59(11); 41(9); HRMS Calcd for C₂₇H₂₈O₆: 448.1886, Obs: 448.1884.

• M_{1,3,H}

Mp: 94–95°C; IR (KBr): 1731 ($\nu_{C=O}$) cm⁻¹; ¹H-NMR (CDCl₃) δ : 3.39 (s, 3H, OCH₃); 3.54–4.21 (4m, 12H, ethylene glycolic protons); 4.62–4.66 (m, 2H, CH₂=CHCH₂); 5.31–5.50 (m, 2H, CH₂=CH); 5.97–6.17 (m, 1H, CH₂=CH); 6.98, 7.24, 7.50, 7.58 (4d, 8H, aromatic protons); 7.01, 8.16 (2d, J = 8.8 Hz, 4H, aromatic protons); EIMS (70 eV) *m/e*: 492 (M⁺, 33); 452(2); 373(1); 332(11); 288(0.5); 186(13); 161(100); 139(6); 121(16); 105(5); 57(33); HRMS Calcd for C₂₉H₃₂O₇: 492.2148, Obs: 492.2146.

• M_{3,1,H}

Mp: 141–143°C; IR (KBr): 1731 ($\nu_{C=O}$) cm⁻¹; ¹H-NMR (CDCl₃) δ : 1.93 (p, J = 6 Hz, 2H, CH₂=CHCH₂CH₂); 2.27 (q, J = 7 Hz, 2H, CH₂=CHCH₂); 3.47 (s, 3H, OCH₃); 3.76–3.81 (m,

2H, CH₂OCH₃); 4.07 (t, J = 6.4 Hz, 2H, CH₂=CH(CH₂)₂CH₂); 4.15–4.20 (m, 2H, CH₃OCH₂CH₂); 5.01–5.13 (m, 2H, CH₂=CH); 5.76–5.94 (m, 1H, CH₂=CH); 6.98, 7.24, 7.49, 7.59 (4d, J = 8.2 Hz, 8H, aromatic protons); 7.01, 8.16 (2d, J = 9 Hz, 4H, aromatic protons); EIMS (70 eV) *m/e*: 432 (M⁺, 28); 243(4); 189(100); 186(3); 185(5); 139(2); 121(46); 76(1); 69(3); 41(8); HRMS Calcd for C₂₇H₂₈O₅: 432.1937, Obs: 432.1938.

• M_{8,1,H}

Mp: 125–126°C; IR (KBr): 1731 ($\nu_{C=O}$) cm⁻¹; ¹H-NMR (CDCl₃) δ : 1.21–1.58 (m, 10H, OCH₂-CH₂(CH₂)₅); 1.81 (p, J = 6.6 Hz, 2H, CH₂-CH₂CH₂O); 2.05 (q, J = 7 Hz, 2H, CH₂=CHCH₂); 3.46 (s, 3H, OCH₃); 3.74–3.80 (m, 2H, CH₂OCH₃); 4.04 (t, J = 6.6 Hz, CH₂CH₂CH₂O); 4.14–4.19 (m, 2H, PhOCH₂); 4.90–5.03 (m, 2H, CH₂=CH); 5.71–5.91 (m, 1H, CH₂=CH); 6.96, 7.22, 7.49, 7.56 (4d, J = 8.4 Hz, 8H, aromatic protons); 6.99, 8.14 (2d, J = 8.9 Hz, 4H, aromatic protons); EIMS (70 eV) *m/e*: 502 (M⁺, 25); 364(0.6); 348(0.5); 333(0.4); 304(0.2); 259(100); 244(11); 186(15); 139(2); 121(59); 77(2); 69(7); 59(16); HRMS Calcd for C₃₂H₃₈O₅: 502.2719, Obs: 502.2718.

• M_{1,1,OCH₃}

Mp: 131–133°C; IR (KBr): 1731 ($\nu_{C=O}$) cm⁻¹; ¹H-NMR (CDCl₃) δ : 3.47 (s, 3H, OCH₃); 3.73–3.85 (m, 2H, CH₂OCH₃); 3.97 (s, 3H, Ar-OCH₃); 4.12–4.23 (m, 2H, ArOCH₂); 4.76 (d, J = 6.2 Hz, 2H, CH₂=CHCH₂); 5.32–5.51 (m, 2H, CH₂=CH); 5.96–6.21 (m, 1H, CH₂=CH); 6.96 (d, J = 8.4 Hz, 1H, aromatic proton *meta* to OCH₃); 7.01, 7.23, 7.51, 7.58 (4d, J = 8.6 Hz, 8H, aromatic protons on biphenyl); 7.69 (d, J = 1.8 Hz, 1H, aromatic proton *ortho* to OCH₃); 7.87 (dd, J = 8.4, 1.8 Hz, 1H, aromatic proton *para* to OCH₃); EIMS (70 eV) *m/e*:

Table I Thermal Transition Temperature (°C) and Thermodynamic Properties for the Monomers

Code	Heating	Cooling
M1,1,H	K146N227(4.9/9.8)**I	I220N109K
M1,2,H	K111N183(2.1/4.6)**I	I156N81K
M1,3,H	K94N147(1.5/3.6)**I	I141N75I
M3,1,H	K149N218(2.2/4.5)**I	I217N120K
M8,1,H	K125N187(1.8/3.9)**I	I185N97K
M1,1,OCH ₃	K135N154(1.9/4.4)**I	I147N101K
M1,2,OCH ₃	K99I	I93(1.0/3.0)**N52K
M1,3,OCH ₃	K78I	I78(0.8/2.3)**N51K

K, crystalline; N, nematic; I, isotropic. Thermodynamic properties; $\Delta H = J/g$; $\Delta S = 10^{-3} J/g$.

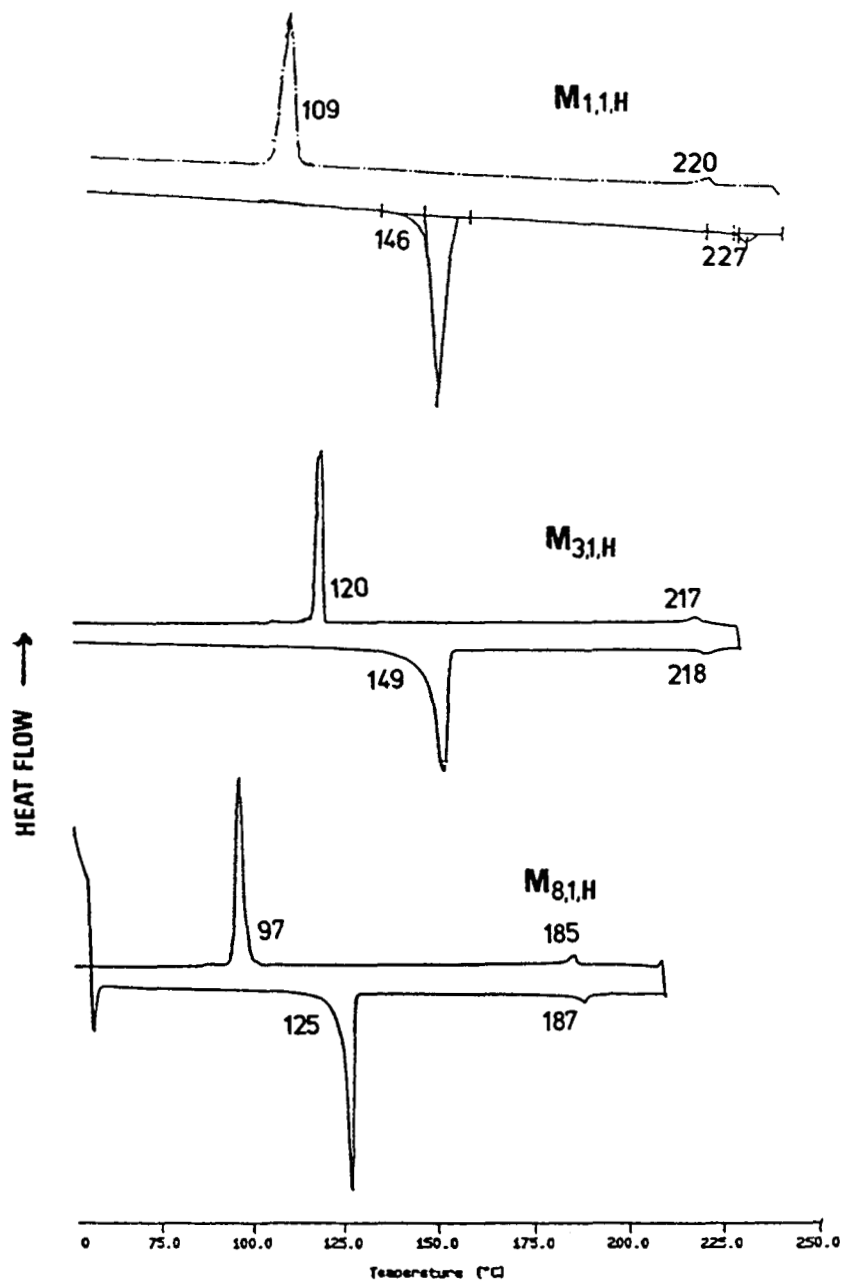


Figure 2 DSC thermograms of $M_{1,1,H}$, $M_{3,1,H}$, and $M_{8,1,H}$; scanning rate = $10^{\circ}\text{C}/\text{min}$. Endothermal peaks (heating process) and exothermal peaks (cooling process) are given in $^{\circ}\text{C}$.

434(M^+ , 29); 374(2); 244(9); 151(14); 135(3); 122(13); 59(15); HRMS Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_6$: 434.1729, Obs: 434.1730.

• $M_{1,2,\text{OCH}_3}$

Mp: $98\text{--}99^{\circ}\text{C}$; IR (KBr): $1731 (\nu_{\text{C}=\text{O}}) \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3) δ : 3.40 (s, 3H, CH_2OCH_3); 3.56–3.63 (m, 2H, CH_2OCH_3); 3.69–3.76 (m, 2H, Ar-

OCH_2CH_2); 3.85–3.91 (m, 2H, $\text{CH}_2\text{CH}_2\text{OCH}_3$); 3.96 (s, 3H, ArOCH_3); 4.15–4.21 (m, 2H, $\text{ArOCH}_2\text{CH}_2$); 4.68–4.72 (m, 2H, $\text{CH}_2=\text{CHCH}_2$); 5.30–5.49 (m, 2H, $\text{CH}_2=\text{CH}$); 6.03–6.17 (m, 1H, $\text{CH}_2=\text{CH}$); 6.94 (d, $J = 8.5 \text{ Hz}$, 1H, aromatic proton *meta* to OCH_3); 6.98, 7.23, 7.50, 7.58 (4d, $J = 8.7 \text{ Hz}$, 8H, aromatic protons on biphenyl); 7.69 (d, $J = 1.9 \text{ Hz}$, 1H, aromatic proton *ortho* to OCH_3); 7.84 (dd, $J = 8.5, 1.9 \text{ Hz}$, 1H, aromatic proton *para* to OCH_3);

Table II Comparison Between Ether and Ester Linkage Monomers of Different Lengths of Alkenyloxy Groups

Code	Heating	Cooling
M1,1,H	K146N227(4.9/9.8)**I	I220N109K
@ME1S3	K107S151(1.6/3.8)**N180(0.6/1.4)**I	
M3,1,H	K149N218(2.2/4.5)**I	I217N120K
@ME1S5	K91S171(4.4/9.9)**N181(0.7/1.6)**I	
M8,1,H	K125N187(1.8/3.9)**I	I185N97K
@ME1S10	K72S153(4.5/10.5)**I	

@, ester linkage monomers; ME, unit of the ethylene glycolic group; S, length of the alkenyloxy group.

EIMS (70 eV) m/e : 478(M^+ , 23); 390(1); 288(15); 191(100); 186(10); 151(21); 122(8); 79(3); 59(22); HRMS Calcd for $C_{28}H_{30}O_7$: 478.1992, Obs: 478.1992.

• $M_{1,3,OCH_3}$

Mp: 69–70°C; IR (KBr): 1728($\nu_{C=O}$) cm^{-1} ; 1H -NMR ($CDCl_3$) δ : 3.39 (s, 3H, CH_2OCH_3); 3.53–4.21 (4m, 12H, ethylene glycolic protons); 3.97 (s, 3H, $ArOCH_3$); 4.71–4.74 (m, 2H, $CH_2=CHCH_2$); 5.81–5.83 (m, 2H, $CH_2=CH$); 6.02–6.21 (m, 1H, $CH_2=CH$); 6.95 (d, $J = 8.4$ Hz, 1H, aromatic proton *meta* to OCH_3); 6.99, 7.25, 7.51, 7.54 (4d, $J = 7.0$ Hz, 8H, aromatic protons on biphenyl); 7.69 (d, $J = 2.0$ Hz, 1H, aromatic proton *ortho* to OCH_3); 7.84 (dd, $J = 8.4, 2.0$ Hz, 1H, aromatic proton *para* to OCH_3); EIMS (70 eV) m/e : 522(M^+ , 20); 482(6); 403(0.5); 332(29); 288(3); 212(4); 191(100); 169(3); 151(31); 135(3); 122(6); 59(44); HRMS Calcd for $C_{28}H_{30}O_7$: 522.2254, Obs: 522.2257.

RESULTS AND DISCUSSION

Differential scanning calorimetric and optical polarized microscopic methods were used to investigate the liquid crystallinity of the monomers and the correlations between them and the chemical structures.

The eight monomers discussed here were modified by the terminal groups (alkenyloxy group with three to 10 methylene units and oligo(ethylene glycol) monomethyl ether with one to three repeated ethylene glycols) and a lateral group (hydrogen or methoxy group). The codes $M_{m,n,R}$ represent the length of these three substituents, where m, n, and

R are the length of alkenyloxy, oligo(ethylene glycol) monomethyl ether, and the lateral group, respectively. Table I shows the phase-transition temperatures and the thermodynamic properties of the monomers synthesized in this work. Figure 1 shows the texture of the monomers under an optical polarized microscope at various temperatures. Their influences exerted on the liquid crystalline properties of the monomers are discussed as follows:

The monomers $M_{1,1,H}$, $M_{3,1,H}$, and $M_{8,1,H}$ are specified by the length of their alkenyloxy groups attached to the mesogens. The decrease of the melting point, the isotropic transition, and the thermodynamic properties with increasing length of the alkenyloxy group were observed in the thermograms (Fig. 2). The results show that the spacer length does not change the melting points significantly. In other words, the long saturated methylene chain may not be as flexible as to hinder the molecules to maintain the lattice. In comparison to the ester linkage analogous derivatives, these three ether linkage monomers showed higher melting points and isotropic transition temperature. The comparative values, including the thermal transition temperatures and the thermodynamic properties, are listed in Table II. The texture of the three monomers suggests a four-thread windmill-like nematic phase under an optical polarized microscope, as illustrated in Figure 1(A)–(C). The fact that liquid crystalline molecules usually show a large smectic range and the phase transition enthalpy with increasing length of the free substituents on the mesogens was described elsewhere.¹⁵ The three monomers synthesized in this work behave in an opposite manner, especially for the one with the longest methylene chain containing 10 carbons. This phenomenon may be due to the disturbance of the large flexibility of the ether linkage terminal group. Because of the

Table III Comparison Between Ether and Ester Linkage Monomers of Different Lengths of Terminally Ethylene Glycolic Groups

Code	Heating	Cooling
M1,1,H	K146N227(4.9/9.8)**I	I220N109K
@ME1S3	K107S151(1.6/3.8)**N180(0.6/1.4)**I	
M1,2,H	K111N183(2.1/4.6)**I	I156N81K
@ME2S3	K91S146(2.6/6.1)**N157(0.5/1.2)**I	
M1,3,H	K94N147(1.5/3.6)**I	I141N75K
@ME3S3	K73S125(7.8/19.3)**I	

@, ester linkage monomers; ME, unit of the ethylene glycolic group; S, length of the alkenyloxy group.

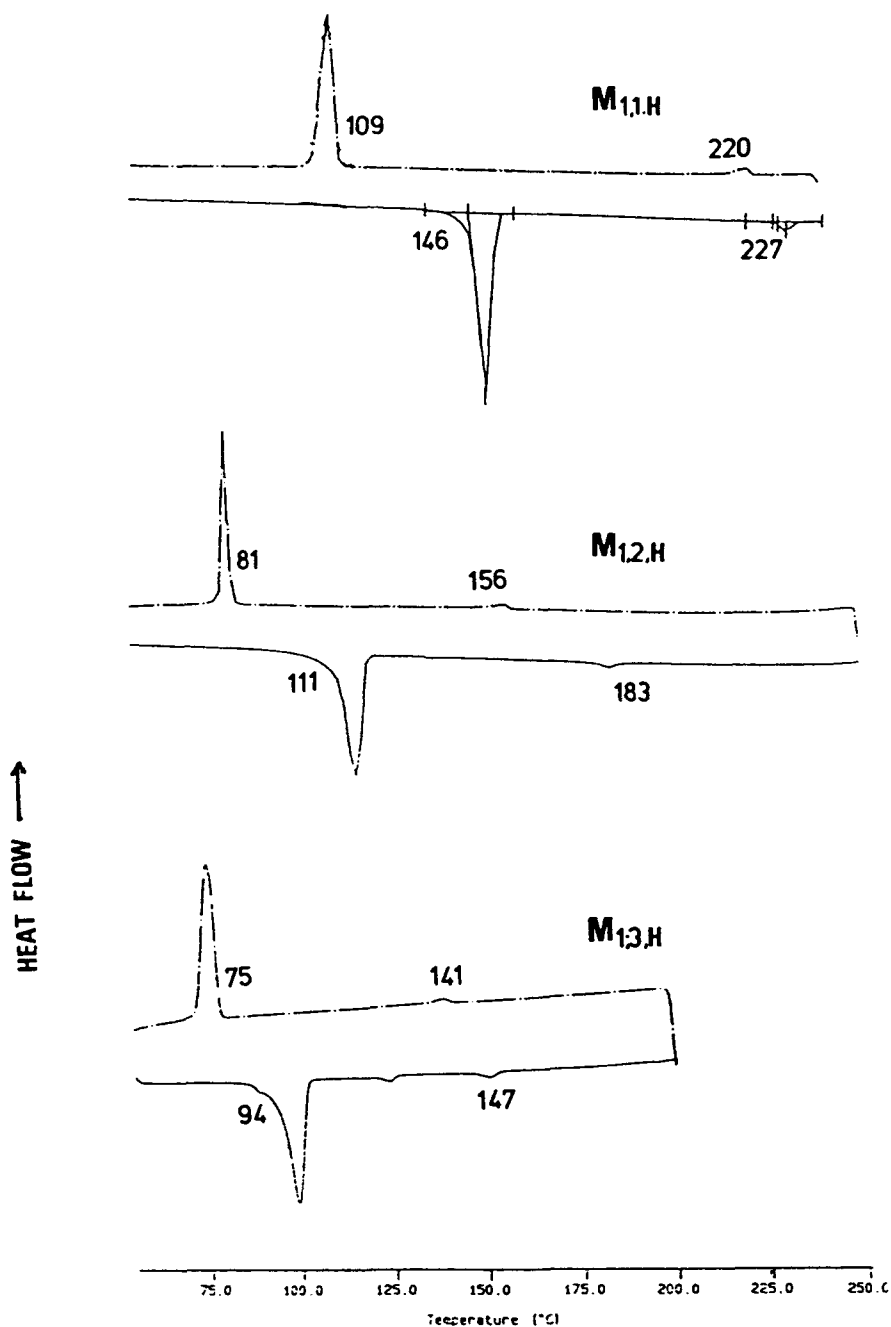


Figure 3 DSC thermograms of $M_{1,1,H}$, $M_{1,2,H}$, and $M_{1,3,H}$; scanning rate = $10^{\circ}\text{C}/\text{min}$. Endothermal peaks (heating process) and exothermal peaks (cooling process) are given in $^{\circ}\text{C}$.

motion of the flexible terminal segment, mesogens are restricted to arrange themselves in a nematic mesophase instead of a more ordered smectic phase.

Monomers $M_{1,1,H}$, $M_{1,2,H}$, and $M_{1,3,H}$ are specified by the length of the oligo(ethylene glycol)-monomethyl ether terminals. These monomers also showed only a nematic phase under the optical po-

larized microscope [Fig. 1(D)–(F)]. The corresponding thermograms are shown in Figure 3. The thermograms of $M_{1,2,H}$ and $M_{1,3,H}$ showed intermediate transitions between melting and isotropic temperatures. However, no peaks were observed in the cooling process; the two transitions are proven to be fake ones from the microscopic pictures at

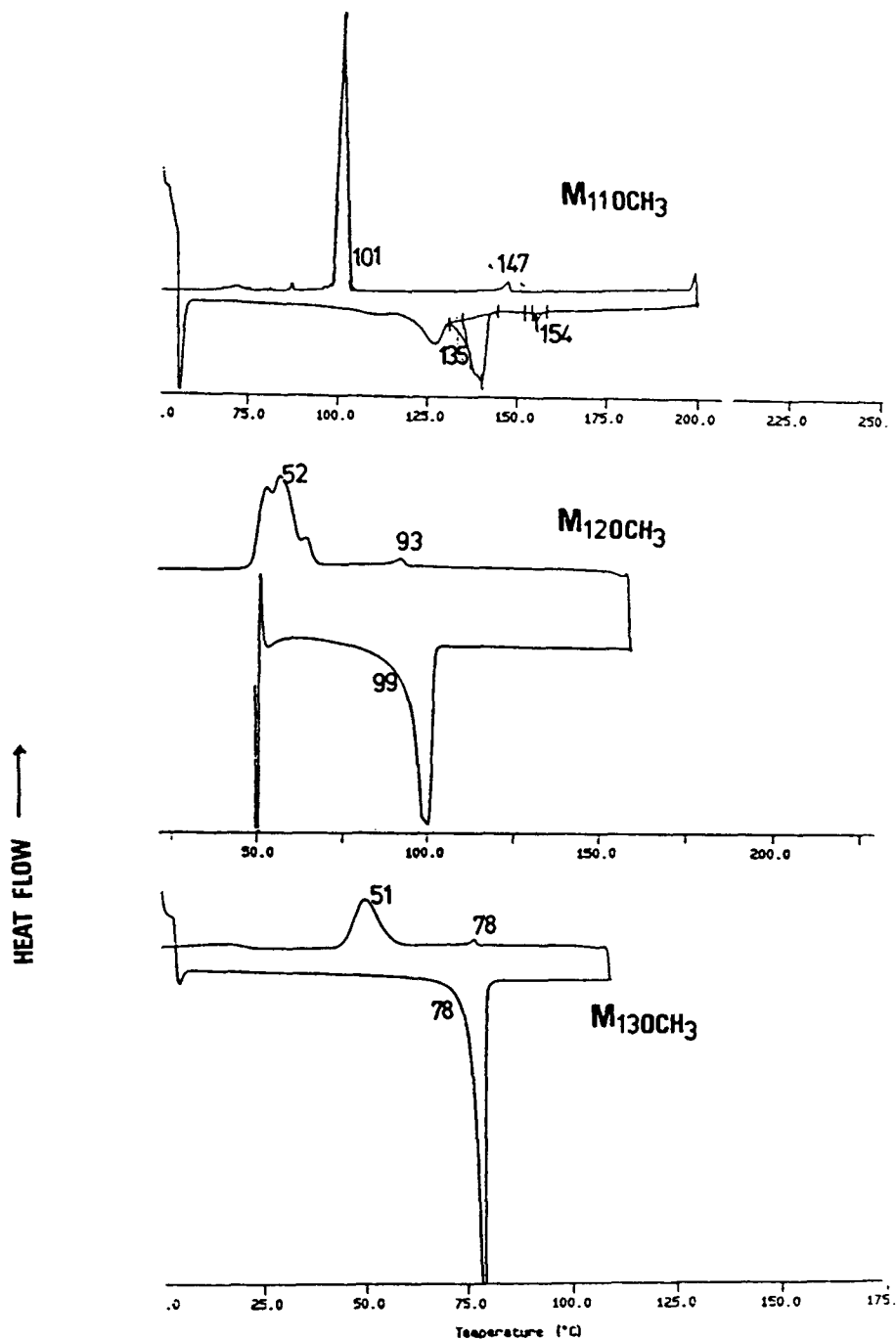


Figure 4 DSC thermograms of $M_{1,1}OCH_3$, $M_{1,2}OCH_3$, and $M_{1,3}OCH_3$; scanning rate = $10^\circ C/min$. Endothermal peaks (heating process) and exothermal peaks are given in $^\circ C$.

those temperatures. As can be seen from Figure 1 (E) for $M_{1,2,H}$ and (F) for $M_{1,3,H}$, no mesophase change between transition temperature was observed in the DSC thermograms.

In comparison with the analogous ester derivatives (Table III), the three monomers showed a rapid decrease of the enthalpy with chain length.

The same result was found in the changes of the melting and the isotropic temperatures. These facts indicate that the crystallinity of the monomers was destroyed by the increasing length of the ethylene glycolic terminal. This is probably a result of the large momentum that was accelerated by the dangling of the quasi-crown ether terminal group. The

same viewpoint can be applied to explain why there is only a nematic phase present in these types of crystalline molecules. The high flexibility of the ether-linked ethylene glycolic terminals not only reduces the thermostability of the liquid crystallinity but also inhibits the smectic arrangement of the molecules.

The chemical structures of the monomers $M_{1,1,OCH_3}$, $M_{1,2,OCH_3}$, and $M_{1,3,OCH_3}$ differ from the monomers discussed that had the additional substitution of a methoxy group on the mesogenic core. The thermograms of these monomers with lateral groups are illustrated in Figure 4. The thermogram of $M_{1,1,OCH_3}$ showed liquid crystallinity during heating as well as during cooling. However, the thermograms of the other two monomers showed a monotropic behavior. A liquid crystalline property existed only during the cooling process. The same result was obtained in an additional cycle of heating and cooling processes.

In fact, liquid crystallinity was not found in the study of the analogous ester derivatives.¹⁶ This explains why even a very small lateral group on the mesogenic core may destroy the arrangement of the mesogen; as a result, the liquid crystalline property may disappear. However, the monomers with the methoxy lateral group synthesized in this work all showed nematic liquid crystallinity. The texture of the monomers are illustrated in Figure 1(G)–(I). A reasonable explanation for this is the quasi-crown ether tail, which constitutes a looser packing between each mesogenic core. Therefore, the disturbances of the lateral group become smaller than those of the ester analogs.

CONCLUSIONS

All monomers synthesized in this work exist only in the nematic mesophase. The length of the free substituents on a mesogen determines the property and the thermal transition temperature of the liquid crystalline monomers. The influences are the following:

1. The melting point, the isotropic temperature, and the liquid crystalline region decrease with increasing length of the alkenyloxy groups.
2. The melting point, the isotropic temperature, and the liquid crystalline region decrease with increasing length of the oligo (methylene glycol) monomethyl ether terminal groups owing

to the high flexibility of the quasi-crown ether terminal; a significant loss of the thermostability was observed.

3. Monomers with a methoxy lateral group on the mesogenic core exhibit the least thermostability. Those with di- and triethylene glycol monomethyl ether showed monotropic liquid crystallinity.

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REFERENCES

1. H. Finkelmann, H. Ringsdorf, and J. H. Wendorff, *Macromol. Chem.*, **179**, 273 (1978).
2. C. S. Hsu and V. Percec, *Macromol. Chem. Rapid Commun.*, **8**, 331 (1987).
3. H. Ringsdorf and A. Schneller, *Macromol. Chem. Rapid Commun.*, **3**, 557 (1982).
4. J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci. Part A Polym. Chem.*, **25**, 2269 (1987).
5. H. J. Coles and R. Simon, *Polymer*, **26**, 1801 (1985).
6. V. P. Shibaev, Y. S. Freidzon, and N. A. Plate, *J. Eur. Polym.*, **18**, 651 (1982).
7. C. B. McArdle, M. G. Clark, G. W. Gray, C. U. Haws, D. Lacey, G. Nestor, A. Parker, K. J. Toyne, and M. C. K. Wilshire, *J. Liq. Cryst.*, **2**, 573 (1987).
8. M. S. White, G. W. Gray, and D. Lacey, in *Proceedings of the International Conference on Liquid Crystal Polymers*, Bordeaux, 1987, Abstract No. P1.
9. S. K. Varshney, *JMS-REW Macromol. Chem. Phys.*, **C26**(4), 551 (1986).
10. G. W. Gray, W. D. Hawthorne, J. S. Hill, M. S. K. Lee, G. Nestor, and M. S. White, *Polymer*, **30**, 964 (1989).
11. S. A. Wise, W. J. Bonnett, F. R. Guenther, and W. E. May, *J. Chromatogr. Sci.*, **19**, 457 (1981).
12. R. M. Izett, R. L. Bruening, M. L. Brurning, B. J. Tarbet, K. E. Krakowiak, J. S. Bradshaw, and J. J. Christensen, *Anal. Chem.*, **60**, 1825 (1988).
13. C. A. Rouse, A. C. Finlison, B. J. Tarbet, J. C. Pixton, N. M. Djordjevic, K. E. Markides, J. S. Bradshaw, and M. L. Lee, *Anal. Chem.*, **60**, 901 (1988).
14. J. D. Edward, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 377 (1957).
15. H. Finkelmann and G. Rehage, *Macromol. Chem. Rapid Commun.*, **1**, 31 (1980).
16. G. P. Chen-Jeng, Dissertation, Dept. of Chemical Engineering, National Cheng Kung University (1992); G. P. Chen-Jeng et al., *J. Appl. Polym. Sci.*, **47**, 697 (1993).

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