

Synthesis and Mesomorphic Behavior of Terminally Carboxyl Oligo(ethylene oxide) Monomethyl Ethers-Substituted Side Chain Liquid Crystalline Polysiloxanes. I

GOW-PYNG CHENG JENG, JEN-FENG KUO,* and CHUH-YUNG CHEN

Department of Chemical Engineering, National Cheng-Kung University, Tainan, Taiwan 70101, Republic of China

SYNOPSIS

A series of alkene monomers containing carboxyl biphenyl benzoate ester or carboxyl *p,p'*-phenyl benzoate ester based on mesogenic core with a carboxyl (\pm)-2-methyl ethylene glycol monomethyl ether group or various lengths of carboxyl oligo (ethylene oxide) monomethyl ethers as the terminal group were synthesized. And they were grafted onto the poly(methylhydrosiloxanes) (PMHS) by the platinum catalyzed hydrosilylation process. Their molecular structure, the thermal transitions temperature, and mesophase texture of monomers and of polymers were characterized using ^1H nuclear magnetic resonance, differential scanning calorimetry, and polarizing optical microscopy with hot stage. The polymers obtained all show smectic phase while their precursor monomers show both smectic and/or nematic phase, or in some cases, no mesophase. The factors governing mesophase texture and transition temperature are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Side chain liquid crystalline (LC) polymers have been extensively studied during the last decade.¹⁻⁴ Thermotropic side chain LC polymers, owing to their particular properties, have been considered as potential advanced materials for speciality applications, such as in information storage,⁵⁻⁷ in elements requiring nonlinear optical characteristics,^{8,9} and in piezo-, pyro-, and ferroelectric devices.¹⁰ Syntheses, structure-property relations, and applications were concisely reviewed by Varshney¹¹ and Gray et al.¹²

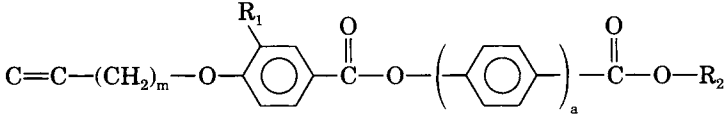
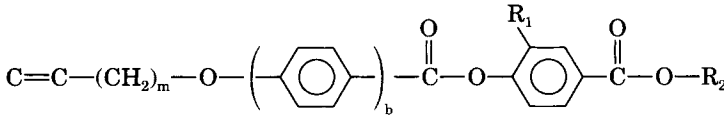
Utilizing the characteristics in the ordered arrangement of the liquid crystalline molecules, Wise et al.¹³ suggested that side chain LC polymers have potential materials as the stationary phase of gas chromatography for separation of geometrical and optical isomeric species. Aspects of side chain LC polymers as stationary phase are mostly focused on

the type of those mesophase monomer-grafted polysiloxane backbone.¹⁴⁻¹⁶ Moreover, it has been indicated that a low-order smectic phase (e.g., A and C) can provide an optimal combination of efficiency and selectivity resolution.¹⁷

Crown ether type compounds have been known to be an effective stationary phase for separation of metal ions¹⁸ and many organic compounds.¹⁹ In this study, alkene monomers with carboxyl biphenyl benzoate ester or carboxyl *p,p'*-diphenyl benzoate ester-based mesogenic group bearing oligo(ethylene oxide) monomethyl ether or (\pm) 2-methyl ethylene glycol monomethyl ether as the terminal, which have potential to form crown ether-like structures, were prepared. These monomers were grafted onto poly(methylhydrosiloxane) (PMHS) to obtain side chain LC polymers by the Pt-catalyzed hydrosilylation process. The monomers and side chain LC polymers obtained were well characterized using ^1H nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and polarizing optical microscopy with hot stage. Factors affecting the mesophases and transition temperatures were also discussed.

* To whom correspondence should be addressed.

Table I Characterization of Monomers ME1S3 ~ ME1S3KBL1

Codes	m	R_1	a	b	R_2	200 MHz $^1\text{H-NMR}$ (CDCl_3 , δ , ppm)
						 
ME1S3	1	H	2		$(\text{C}_2\text{H}_4\text{O})\text{CH}_3$	3.38 (s, $-\text{OCH}_3$); 3.69–3.78 (m, $-\text{CH}_2\text{O}-$, 2H); 4.42 (q, $-\text{COO}-\text{CH}_2$); 4.67–4.75 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.34–5.55 (3m, $\text{CH}_2=\text{C}-$); 5.95–6.31 (m, $\text{C}=\text{CH}-$); 7.10–8.20 (4m, 12 aromatic protons)
ME2S3	1	H	2		$(\text{C}_2\text{H}_4\text{O})_2\text{CH}_3$	3.30 (s, $-\text{OCH}_3$); 3.53–3.89 (m, $-\text{CH}_2\text{O}-$, 6H); 4.47 (q, $-\text{COO}-\text{CH}_2$); 4.64–4.75 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.21–5.55 (3m, $\text{CH}_2=\text{C}-$); 5.90–6.30 (m, $\text{C}=\text{CH}-$); 7.10–8.17 (4m, 12 aromatic protons)
ME3S3	1	H	2		$(\text{C}_2\text{H}_4\text{O})_3\text{CH}_3$	3.27 (s, $-\text{OCH}_3$); 3.49–3.90 (m, $-\text{CH}_2\text{O}-$, 10H); 4.50 (q, $-\text{COO}-\text{CH}_2$); 4.69–4.74 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.20–5.61 (3m, $\text{CH}_2=\text{C}-$); 5.95–6.35 (m, $\text{C}=\text{CH}-$); 6.95–8.15 (4m, 12 aromatic protons)
ME1S5	3	H	2		$(\text{C}_2\text{H}_4\text{O})\text{CH}_3$	1.89–2.13 (m, $-(\text{CH}_2)_2-$); 3.45 (s, $-\text{OCH}_3$); 3.73–3.77 (m, $-\text{CH}_2\text{O}-$); 4.48–4.53 (q, $-\text{COO}-\text{CH}_2$); 4.04–4.10 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.01–5.1 (3m, $\text{CH}_2=\text{C}-$); 5.77–5.94 (m, $\text{C}=\text{CH}-$); 6.96–8.17 (4m, 12 aromatic protons)
ME1S10	8	H	2		$(\text{C}_2\text{H}_4\text{O})\text{CH}_3$	0.97–2.03 (m, $-(\text{CH}_2)_7-$); 3.44 (s, $-\text{OCH}_3$); 3.75–3.79 (m, $-\text{CH}_2\text{O}-$); 4.48–4.53 (q, $-\text{COO}-\text{CH}_2$); 4.02–4.08 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.05–5.1 (3m, $\text{CH}_2=\text{C}-$); 5.80–5.84 (m, $\text{C}=\text{CH}-$); 6.95–8.17 (4m, 12 aromatic protons)
ME1S5L1	3	OCH_3	2		$(\text{C}_2\text{H}_4\text{O})\text{CH}_3$	1.82–2.32 (m, $-(\text{CH}_2)_2-$); 3.95 (s, $-\text{Ph}-\text{OCH}_3$); 3.42 (s, $-\text{OCH}_3$); 3.74–3.76 (m, $-\text{CH}_2\text{O}-$); 4.48–4.83 (q, $-\text{COO}-\text{CH}_2$); 4.10–4.16 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.34–5.55 (3m, $\text{CH}_2=\text{C}-$); 5.95–6.31 (m, $\text{C}=\text{CH}-$); 7.10–8.21 (5m, 11 aromatic protons)
ME1S3KA	1	H	2		$\text{C}^*\text{H}(\text{CH}_3)\text{CH}_2\text{OCH}_3$	3.42 (s, $-\text{OCH}_3$); 3.55–3.62 (m, $-\text{CH}_2\text{O}-$); 5.49–5.50 (q, $-\text{COO}-\text{CHCH}_3$); 1.37–1.40 (m, $-\text{COO}-\text{CHCH}_3$); 4.62–4.65 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.31–5.49 (3m, $\text{CH}_2=\text{C}-$); 6.09–6.10 (m, $\text{C}=\text{CH}-$); 6.99–8.19 (4m, 12 aromatic protons)
ME1S3KB	1	H	2		$\text{C}^*\text{H}(\text{CH}_3)\text{CH}_2\text{OCH}_3$	3.41 (s, $-\text{OCH}_3$); 3.49–3.65 (m, $-\text{CH}_2\text{O}-$); 5.48–5.50 (q, $-\text{COO}-\text{CHCH}_3$); 1.26–1.39 (m, $-\text{COO}-\text{CHCH}_3$); 4.59–4.62 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.30–5.41 (3m, $\text{CH}_2=\text{C}-$); 6.04–6.16 (m, $\text{C}=\text{CH}-$); 7.00–8.26 (4m, 12 aromatic protons)
ME1S3KBL1	1	OCH_3	2		$\text{C}^*\text{H}(\text{CH}_3)\text{CH}_2\text{OCH}_3$	3.41 (s, $-\text{OCH}_3$); 3.50–3.66 (m, $-\text{CH}_2\text{O}-$); 3.96 (s, $-\text{OCH}_3$); 5.47–5.50 (m, $-\text{COO}-\text{CHCH}_3$); 1.25–1.37 (m, $-\text{COO}-\text{CHCH}_3$); 4.61–4.63 (m, $-\text{CH}_2-\text{O}-\text{Ph}-$); 5.31–5.42 (3m, $\text{CH}_2=\text{C}-$); 6.04–6.16 (m, $\text{C}=\text{CH}-$); 6.98–8.28 (5m, 11 aromatic protons)

received. Toluene, used in the hydrosilylation reaction, was first refluxed over sodium and then distilled under nitrogen stream.

Techniques

$^1\text{H-NMR}$ spectra were recorded on a Bruker AC200 (200.13 MHz) from CDCl_3 solution with tetramethylsilane (TMS) as internal standard. The phase transition temperatures of monomers and polymers were studied with a DuPont 910 differential scanning calorimeter (DSC) with a liquid nitrogen cooling accessory. A 9900 computer system was used to read the temperatures and heat effects where the thermal transitions occurred. The anisotropic textures of the monomers and polymers were obtained using an Olympus BH-2 polarizing optical microscopy as well as a LINKAM THMS 600 hot stage and a TMS 91 central processor.

Synthesis of Monomers (Scheme 1)

Compound 1 was prepared using the procedure of Ringsdorf and Schneller.³ 4-(4-Hydroxyphenyl) benzoic acid was prepared according to the four-step procedure of Gray and co-workers.²⁰

Compound 2 was synthesized by esterification of the corresponding mono, di, triethylene glycol monomethyl ether with 4-(4-hydroxyphenyl) benzoic acid. An example is: 0.023 mole 4-(4-hydroxyphenyl) benzoic acid, 0.069 mole diethylene glycol monomethyl ether, and 20 g proton catalyst resin (Dow Chemical HCR-W2-H resin) in 30 mL of sodium-dried benzene were carried out in a 100 mL round flask reactor equipped with a water separator for about three days. The catalyst resin was filtered

off. Ethyl ether 100 mL was added into the filtrate, and the solution was extracted with 100 mL saturated sodium bicarbonate solution twice, and washed with water twice, and subsequently dried over anhydrous magnesium sulfate (MgSO_4). The MgSO_4 was filtered off and the filtrate was further concentrated on a rotary evaporator. The crude product obtained was purified through a silica gel-packed column, and ethyl acetate/*n*-hexane (7v/3v) was used as the mobile phase. Finally 5.24 g (yield 72%) diethylene glycol monomethyl ether 4-(4-hydroxyphenyl)benzoate, melting point 84°C, was obtained.

Synthesis of Monomers ME1S3 ~ ME1S3KBL1

All the monomers listed in Table I were synthesized by the same procedure. As shown by the codes given in Table I, the alkene monomers were obtained as follows: MEiSj, ME1S3KA, ME1S3KB, and ME1S3KBL1. According to the characteristic groups of the alkene monomers, in the MEiSj, M denotes monomer, Ei the terminal carboxyl ethylene glycol monomethyl group with i's oligo (ethylene oxide) units, and Sj the alkenyloxy spacer with j's carbons. ME1S3KA is similar to ME1S3 except that there is a chiral methyl group (K) in the terminal of the carboxyl ethylene glycol monomethyl ether group. Whereas ME1S3KB is similar to ME1S3KA except biphenyl benzoate ester being replaced by *p,p'*-phenyl benzoate ester. ME1S5L1 and ME1S3KBL1 are, respectively, similar to ME1S5 and ME1S3KB except that there is a lateral methoxy group on the mesogenic core.

An example of ME2S3 is: 0.021 mole 4-allyloxybenzoic acid and 12 mL thioyl chloride containing a drop of dimethyl formamide (DMF) was reacted

Table II Thermal Transition Temperatures (°C) and Thermodynamic Parameters for Monomers

Codes	Heating	Cooling
ME1S3	K107S _A 151(1.62)N 180(0.63)i	i 173(0.56)N 144(1.53)S _A 79 K
ME2S3	K 91S _A 146(2.57)N 157(0.51)i	i 155(0.51)N 143(2.33)S _A 65 K
ME3S3	K 73S _A 125(7.80)*N 128(—)i	i 124(—)N 119(6.72)*S _A 48 K
ME1S5	K 91S _B 171(4.37)N 181(0.73)i	i 177(0.64)N 167(4.29)S _B 64 K
ME1S10	K72S _A 153(4.48)i	i 147(4.21)S _A 55 K
ME1S5L1	K102i	i 75 K
ME1S3KA	K 92S _A 150(9.21)i	i 148(8.81)S _A 54 K
ME1S3KB	K112S ₇ 195(8.92)i	i 189(8.22)S ₇ 74 K
ME1S3KBL1	K 68i	i 44 K

* Overlapped transition $\Delta H = \Delta H(S_A) + \Delta H(N)$; LC texture determined by polarizing optical microscopy; K-crystalline, S_A-smectic A; S_B-smectic B, S₇-unknown smectic; N-nematic. Thermodynamic parameters (ΔH) are shown in parentheses as J/g.

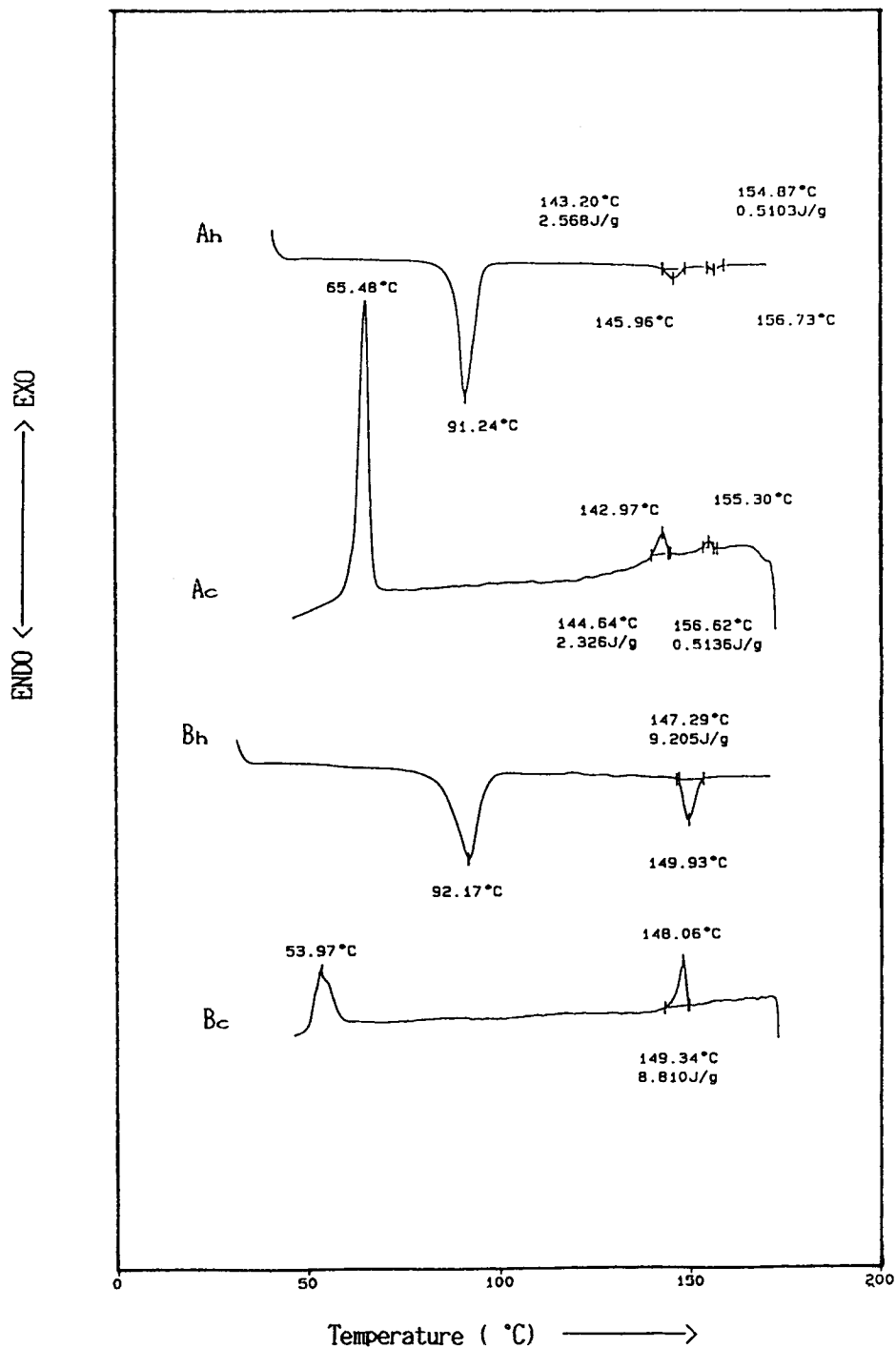
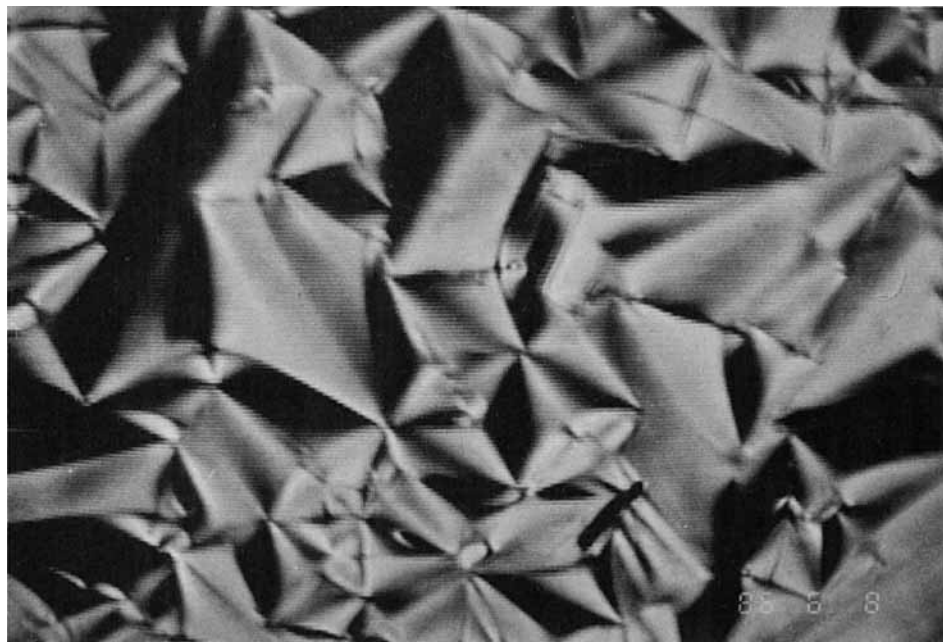


Figure 1 DSC thermograms of monomers. ME2S3: (Ah) Heating (10°C/min), (Ac) Cooling (2°C/min); ME1S3KA: (Bh) Heating (10°C/min), (Bc) Cooling (2°C/min)

until the solution became clear (ca 3 h). The excess thioyl chloride in it was removed by a vacuum rotary evaporator to obtain yellow viscous 4-allyloxybenzoyl chloride. The acid chloride was dissolved in 5 mL CH_2Cl_2 , and slowly added to a solution of 0.019

mole diethylene glycol monomethyl ether 4-(4-hydroxyphenyl) benzoate containing excess mole ratio dry triethylamine in 50 mL of CH_2Cl_2 in an ice water bath to incur reaction. CH_2Cl_2 and triethylamine in the reaction solution were removed by the rotary



(A)



(B)

Figure 2 Polarizing optical micrographs of monomers ME1S3KA and ME1S3KB. (A) Smectic A texture for ME1S3KA at 132°C; (B) Smectic ? texture for ME1S3KB at 172°C.

evaporator under reducing pressure. The residue material was dissolved in 100 mL CH_2Cl_2 . It was extracted with 100 mL of saturated sodium bicarbonate solution twice, then washed with 6N HCl

solution, and with water twice, and then dried over MgSO_4 . The MgSO_4 was filtered off, and the filtrate was concentrated on a rotary evaporator. Finally, the crude product was purified through a silica gel-

packed column and $\text{CH}_2\text{Cl}_2/n$ -hexane/methanol (20v/5v/1v) was the mobile phase to obtain a pure product 6.88 g (yield 76%), *mp* 91°C. The characteristic chemical shifts of the monomers obtained are shown in Table I.

Synthesis of Polymers PE1S3 ~ PE1S3KBL1

ME2S3, 1 g, and 0.136 g poly(methylhydrosiloxane) were dissolved in 10 mL of sodium-dried toluene. Next, 30 μL of 7.5×10^{-3} M chloroplatinic acid isopropanol solution was added to the above solution. Temperature was kept at 80°C. The reaction was followed by monitoring the disappearance of Si—H IR band at 2165 cm^{-1} . They were purified by the following procedure; methanol precipitation and CH_2Cl_2 redissolution, several times. And then dried under vacuum at room temperature.

RESULTS AND DISCUSSION

Scheme 1 shows the preparations of the intermediates and the alkene monomers in detail. It also shows the reaction conditions for grafting the alkene monomers onto PMHS. As shown in Table I, all the chemical shifts of characteristic functional groups of the monomers were obtained as expected. The terminal group length and chirality, spacer length, mesogenic core, and lateral substituent are taken as variables for studying the properties of the LC monomers and polymers. Table II shows the transition temperatures and thermodynamic parameters of the monomers. Figure 1 illustrates the heating and cooling DSC thermograms of the monomers ME2S3 and ME1S3KA. All the monomers, except monomers ME1S3L1 and ME1S3KBL1, showed mesophase. Furthermore, the mesophase tempera-

ture and its range, the mesophase textures as well as enthalpy change (ΔH) vary significantly with the type of monomers.

The difference among ME1S3, ME2S3, and ME3S3 is the number of (ethylene oxide) in the terminal carboxyl oligo(ethylene oxide) monomethyl ether group. They show both smectic A and nematic phases. The mesophase temperature decreases with the length of terminal group increasing. The temperature range of smectic phase is nearly independent of the terminal length, and those of nematic phase became significantly narrow as the terminal group length increases. The enthalpy change of the smectic phase became larger, while that of the nematic phase became smaller.

Table II also shows the effect of alkenyloxy length on the texture and properties of mesophase. ME1S3, ME1S5, and ME1S10 have the number of methylene in the alkenyloxy group being 3, 5, and 10, respectively. ME1S3 presents enantiotropic smectic A and nematic, and ME1S5 smectic B and nematic phase; however, ME1S10 is only smectic A phase. Obviously, as the length of alkenyloxy group increases to 10 methylene units, the nematic phase disappears. It also indicates that for the smectic phase the longer the length of alkenyloxy group, the lower the isotropic temperature and the wider the temperature range, while for the nematic phase, the longer the length of alkenyloxy group, the narrower the temperature range.

In this study, the monomer containing a carboxyl (\pm) 2-methyl ethylene glycol monomethyl ether group as terminal, ME1S3KA, was also prepared. It finds that the chiral structure in the terminal group only presents smectic phase but not nematic or cholesteric phase. It might be attributed to the chiral compound not a (–) or (+) one. It significantly lowers the melting point, but increases the

Table III Thermal Transition Temperatures (°C) and Thermodynamic Parameters for Polymers PE1S3 ~ PE1S3KBL1

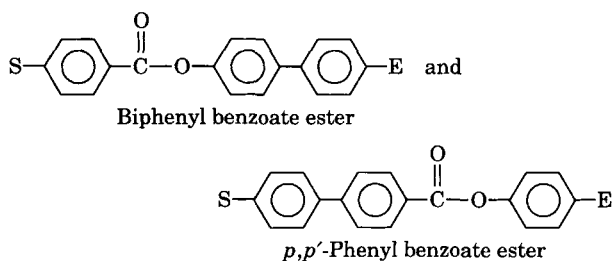
Codes	Heating ^{a,b}	Cooling
PE1S3	g 29 S 251 (2.29) i	i 248 (1.80) S 24 g
PE2S3	g 22 S 187 (2.21) i	i 184 (2.30) S 21 g
PE3S3	g 12 S 136 (—) i	i 130 (1.65) S 8 g
PE1S5	g 24 K 89 S 258 (2.68) i	i 254 (3.07) S 79 K 22 g
PE1S10	g 16 K 55 S 261 (5.64) i	i 253 (4.75) S 52 K 14 g
PE1S5L1	g 24 K 69 S 170 (1.06) i	i 163 (1.03) S 59 K 21 g
PE1S3KA	g 29 S 181 (2.45) i	i 147 (2.28) S 24 g
PE1S3KB	g 25 S 225 (—) i	i 208 (2.31) S 21 g
PE1S3KBL1	g 26 S 167 (1.60) i	i 158 (1.52) S 21 g

^a K, crystalline; S, smectic.

^b Thermodynamic parameters (ΔH) are shown in parentheses as J/g.

temperature range of smectic phase and the enthalpy change.

The molecular structure of ME1S3KA and ME1S3KB is as follows, respectively.



Where S and E denote spacer and terminal groups, respectively. Obviously, the order of phenyl and biphenyl of the mesogenic unit in ME1S3KA is the reverse of ME1S3KB. The latter presents a higher melting temperature and a higher smectic phase transition temperature than the former. However, as shown in Figure 2, the mesophase textures are quite different. The former shows the typical smectic A texture. While the latter shows a smectic-like texture (S_2) which appears as a maltese cross pattern, cone-like with rings.

All the monomers shown in Table II were grafted onto PMHS by the pt-catalyzed hydrosilylation

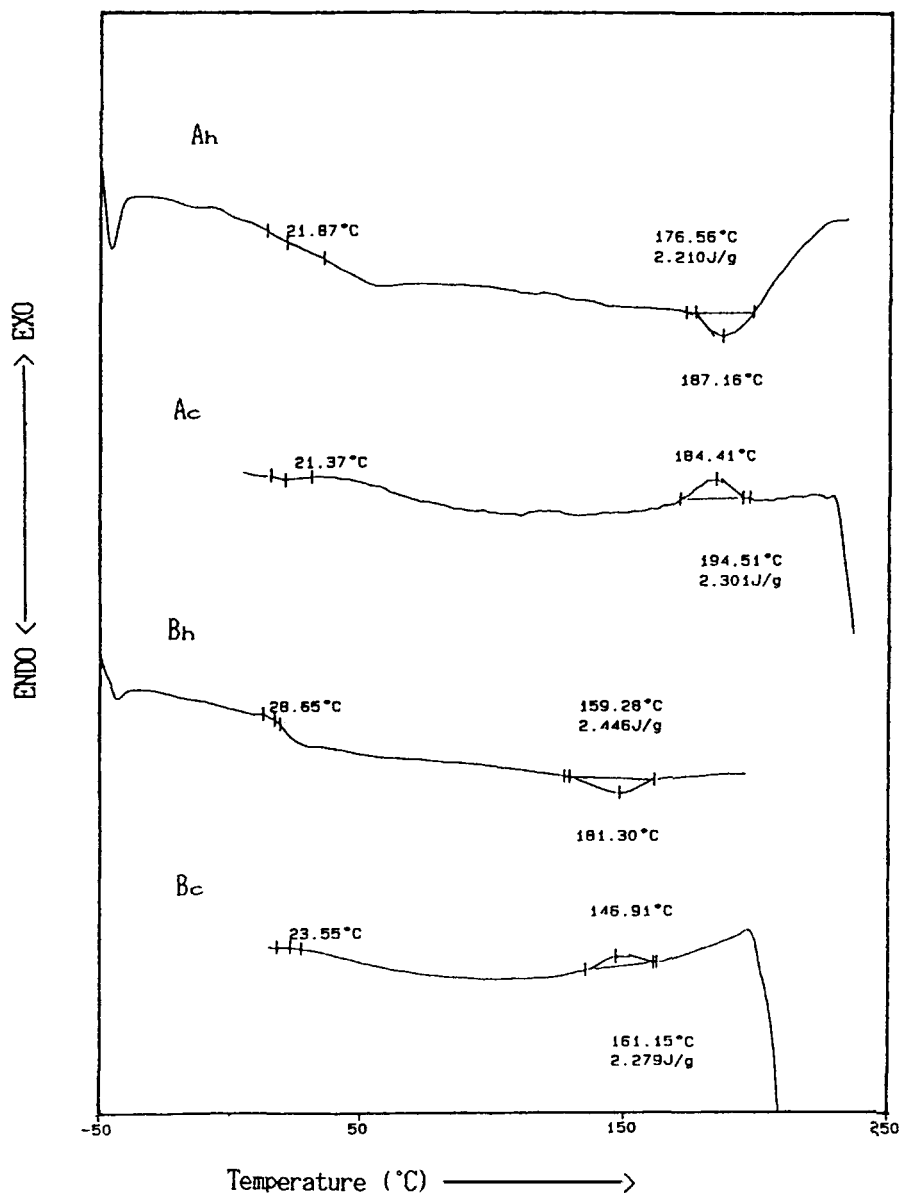
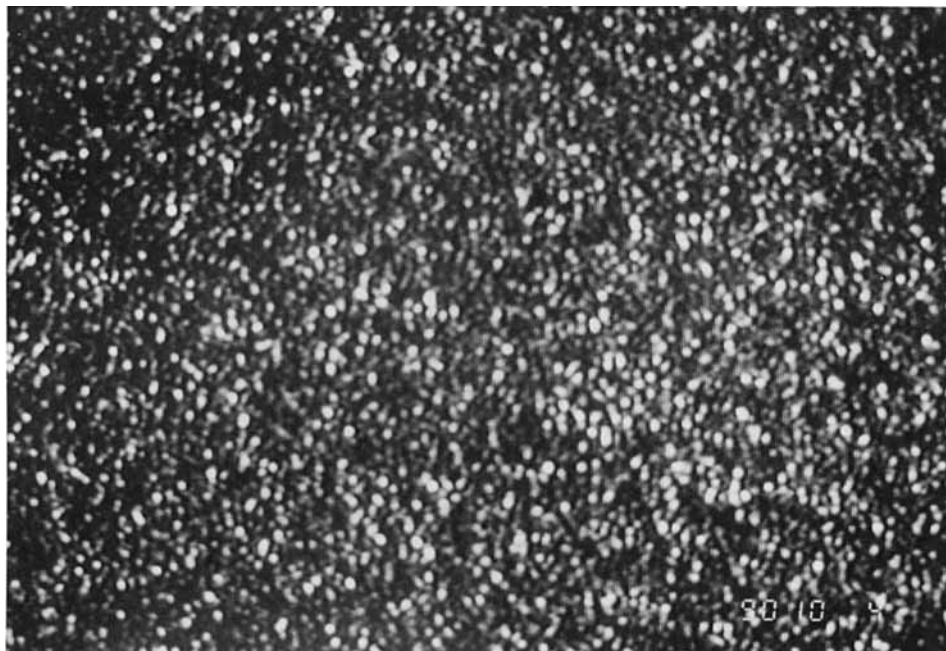


Figure 3 DSC thermograms (10°C/min) of polymers. PE2S3: (Ah) Heating, (Ac) Cooling; PE1S3KA: (Bh) Heating, (Bc) Cooling.



(A)



(B)

Figure 4 Polarizing optical micrographs of polymer, (A) PE2S3 at 177°C; (B) PE1S3KA at 145°C.

process. Table III summarizes the mesophase transition temperatures and thermodynamic parameters of the obtained side chain LC polysiloxane polymers.

Figure 3 illustrates the heating and cooling DSC thermograms for PE2S3 and PE1S3KA. All the polymers show liquid crystalline characteristics.

They appear in the smectic phase at much lower temperatures and over a much wider temperature range of mesophase as well as higher isotropic temperatures than would their precursors.

The textures of the smectic polymers cannot develop as well as those of their respective low molar mass smectic materials do. Figure 4 illustrates the smectic textures for PE2S3 and PE1S3KA. No trace of a typical fan-shaped texture can be obtained on annealing the smectic polymer close to T_{Si} , even for long time annealing. The PEiS3 series and PE1S5 show only smectic enantiotropic phase, regardless of their precursor monomers showing both smectic and nematic phases. The PEiS3 series all have the same spacer length and mesogenic core, but a different terminal. Table III also indicates that as the length of terminal group increases, the glass transition temperature and the isotropic temperature decreases.

PE1S3, PE1S5, and PE1S10 have the same terminal length and mesogenic core but are different in spacer length. The longer the spacer length, the lower the transition temperature, and the higher the isotropic temperature.

As suggested by H. Finkelmann et al.,¹ the spacer is prerequisite for the preparation of side chain LC polymers. The aim of the spacer is to decouple the motions of the mesogenic moieties and the backbone. It is interesting to find that both PE1S5L1 and PE1S3KBL1, which have a lateral methoxy-substituted mesogenic core, exhibit smectic phase. However, their corresponding low mass materials show no mesophase. The occurrence of liquid crystal in both PE1S5L1 and PE1S3KBL1 might be induced by the viscosity of polymer matrix as well as the significant reduction of the degree of freedom for the motions of translation and rotation of mesogenic moieties due to the linkage of mesogenic moieties with the spacer which is supposed to decouple the motions of polymer chain and mesogenic core.

Summarizing the above discussion, one finds that the side chain LC polysiloxanes based on carboxyl oligo (ethylene oxide) monomethyl ethers as the terminal all show smectic phase. The smectic phase is known to be more organized, with mesomorphic molecular packings in layers than the other types of mesophases.²¹ Therefore, the smectic mesophase in all the side chain LC polysiloxanes obtained are favorable for the terminal group to be arranged to be a crown ether-like structure.

We thank Dr. Shiun Maa, and Miss Ru-Zong Wu for their help in carrying out the ^1H NMR spectrum measurements. We are grateful to the National Science Council of The Republic of China for financial support for this work (NSC-80-0405-E006-19). We are also indebted to Prof. Chain S. Hsu for gifts of undecenyl alcohol.

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Received December 19, 1991

Accepted March 9, 1992