

Synthesis and Characterization of Side-Chain Liquid Crystalline Polysiloxanes Containing 4-Alkanyloxyphenyl *trans*-4-Alkylcyclohexanoate Side Groups

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SYNOPSIS

The synthesis and characterization of nine polysiloxanes containing 4-alkanyloxyphenyl *trans*-4-*n*-alkylcyclohexane side groups are described. Six monomers which contain a pentyloxy or a hexyloxy flexible spacer display a nematic mesophase, while the other three monomers which contain an undecyloxy flexible spacer display nematic, smectic A and smectic E mesophases. All synthesized polymers present two smectic mesophases except one containing 4-hexanyloxyphenyl *trans*-4-*n*-butylcyclohexanoate side groups presents one smectic mesophase and one containing 4-undecanyloxyphenyl *trans*-4-*n*-pentyloxyphenyl *trans*-4-*n*-hexanoate side groups presents three smectic mesophases. *Trans*-*cis* isomerization of mesogens and side chain crystallization did not occur for any of the synthesized polymers.

INTRODUCTION

Side-chain liquid crystalline polymers (LCPs) are of both theoretical and practical interest because they combine the anisotropic properties of liquid crystals with the polymeric properties and have the potential of being used for some new applications.¹⁻¹⁰ Over the past few years, Percec et al. and we reported on systematic investigations concerning the replacement of aromatic structures from the mesogenic side groups of side-chain LCP by heterocycloalkane units, e.g., the 1,3-dioxane rings.¹¹⁻¹⁸ We have demonstrated that mesogenic units based on *trans*-1,3-dioxane ring can be used to synthesize non-crystallizable side-chain LCPs even when the polymers contain up to 11 methylene in the spacers. The conformational isomers of *trans*-1,3-dioxane based mesogens are in a dynamic equilibrium and this depresses their crystallization when they are attached as polymeric side chains. However, the *trans*-1,3-dioxane based mesogens are not very stable and undergo a thermal induced *trans*-*cis* isomerization at high temperatures. The mesophases of the polymers are destroyed because the *cis* isomers present no liquid crys-

talline properties.¹⁶ This disadvantage could be improved if cyclohexane rings are used instead of 1,3-dioxane rings.

Since Demus et al.¹⁹ reported the nematic cyclohexane carboxylate in 1973, several kinds of low molar mass liquid crystals containing a cyclohexane ring have been synthesized.²⁰⁻²⁵ These liquid crystals, which exhibit low viscosity and nematic mesophase near room temperature, are suitable for twisted nematic (TN) display devices.

To our best knowledge, there is only one report in the literature concerning the characterization of a side-chain liquid crystalline polymer containing a *trans*-cyclohexane based mesogen.²⁶ The goal of this study is to present the synthesis and characterization of a series of side-chain liquid crystalline polysiloxanes containing 4-alkanyloxyphenyl *trans*-4-*n*-alkylcyclohexanoate side groups. The effects of spacer length as well as terminal alkyl length on the properties of mesophases exhibited by the synthesized polymers are discussed.

EXPERIMENTAL

Materials

Poly(methylhydrogensiloxane) ($\bar{M}_n = 2270$) was obtained from Petrarch System, Inc. and was used

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as received. *trans*-4-*n*-Propylcyclohexanoic acid, *trans*-4-*n*-butylcyclohexanoic acid, *trans*-4-*n*-pentylcyclohexanoic acid, and *p*-benzyloxyphenol were obtained from Tokyo Kasei, Inc. and were used as received. Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen. Dicyclopentadienyplatinum (II) chloride catalyst was synthesized as previously described.¹² 10-Undecen-1-yl tosylate was prepared according to a literature procedure.¹⁵

Techniques

¹H-NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. Heating and cooling rate were 10°C/min. Thermal transitions reported were collected during the second heating and cooling scans. A Nikon Microphot-FX optical polarized microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Preparative gel permeation chromatography (GPC) was run on a Waters 510 LC instrument equipped with a 410 differential refractometer and a preparative GPC column (22.5 mm × 60 cm) supplied by American Polymer Standard Co.

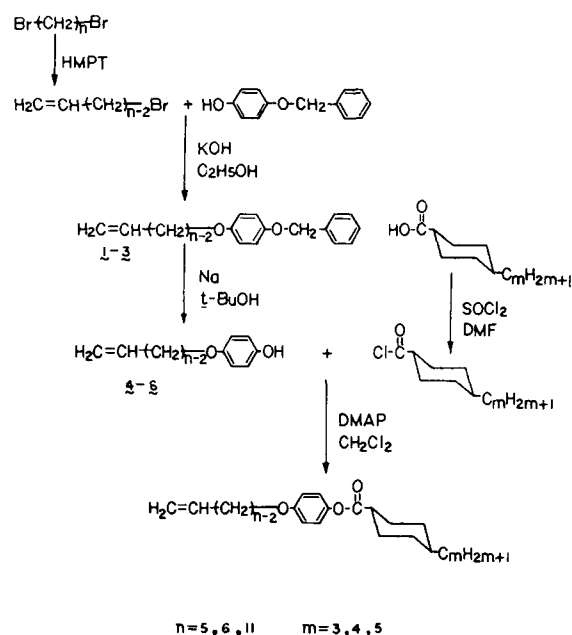
Synthesis of Monomers and Polymers

The synthesis of the cyclohexane containing monomers is outlined in Scheme 1.

p-(1-Pentenyl-5-oxy)phenyl Benzyl Ether (1), *p*-(1-Hexenyl-6-oxy)phenyl Benzyl Ether (2), *p*-(1-Undecenyl-11-oxy)phenyl Benzyl Ether (3)

Compounds 1–3 were prepared by the same method. The synthesis of compound 3 is described below.

p-Benzyloxyphenol (5 g, 0.025 mol) was added to a solution of 1.82 g (0.032 mol) of potassium hydroxide in 120 mL (90%) of ethanol. Sodium iodide (0.1 g) was added and the solution was heated to reflux temperature for 1 h. 10-Undecen-1-yl tosylate (9.72 g, 0.03 mol) was slowly added and the solution was refluxed overnight. The solution was cooled and the solid salt was removed by filtration and ethanol was removed on a rotavapor. The remaining solid was recrystallized from a mixture of methanol and water to yield 7.5 g (85%) of white crystals; mp = 71°C. ¹H-NMR (CDCl₃, δ, ppm): 1.27–2.10 (m,



Scheme 1. Synthesis of 4-alkenyloxyphenyl *trans*-4-*n*-alkylcyclohexanoates.

16H, $-(\text{CH}_2)_8-$), 3.90 (t, 2H, $-\text{CH}_2-\text{O}-\text{Ph}$), 4.97 (m, 2H, $=\text{CH}_2$), 5.02 (s, 2H, $-\text{O}-\text{CH}_2-\text{Ph}$), 5.81 (m, 1H, $-\text{CH}=\text{}$), 6.88 (2d, 4H, $-\text{O}-\text{C}_6\text{H}_4-\text{O}-$), 7.40 (m, 5H, $-\text{O}-\text{CH}_2-\text{C}_6\text{H}_5$).

p-(1-Pentenyl-5-oxy)phenol (4), *p*-(1-Hexenyl-6-oxy)phenol (5), *p*-(1-Undecenyl-11-oxy)phenol (6)

Compounds 4–6 were prepared by the same method. The synthesis of compound 6 is described below.

Sodium, 2.3 g (0.1 mol) was added rapidly but in small pieces to a hot solution of 3.52 g (0.01 mol) of *p*-(1-undecenyl-11-oxy)phenyl benzyl ether in 70 mL of anhydrous *t*-BuOH. The solution was heated to reflux for 10 h. After the sodium had all reacted, a small amount of cold water was added, followed by the addition of a cold, dilute hydrochloric acid solution. The *t*-BuOH was removed on a rotavapor and the residue was extracted with ethyl acetate. The collected ethyl acetate solution was washed with water, dried over anhydrous MgSO₄, and then evaporated to dryness. The obtained product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 : 5 as eluent) to yield 2.3 g (87%) of white crystals; mp = 65°C. ¹H-NMR (CDCl₃, δ, ppm): 1.27–2.10 (m, 16H, $-(\text{CH}_2)_8-$), 3.90 (t, 2H, $-\text{CH}_2-\text{O}-$), 4.53 (s, 1H, $-\text{Ph}-\text{OH}$), 4.97 (m, 2H, $=\text{CH}_2$), 5.81 (m, 1H, $-\text{CH}=\text{}$), 6.78 (2d, 4 aromatic protons).

Table I. Characterization of Monomers IM-IXM

Monomer	Yield (%)	300 MHz ¹ H-NMR (CDCl ₃ , δ, ppm)
IM	89	0.85-2.23 (m, 20H, $\text{-(CH}_2\text{)}_2\text{-}$ and $\text{C}_3\text{H}_7\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.92 (t, 2H, $\text{-CH}_2\text{-O-}$), 5.02 (m, 2H, =CH_2), 5.82 (m, 1H, -CH=), 6.89 (m, 4H, 4 aromatic protons).
IIM	79	0.85-2.23 (m, 22H, $\text{-(CH}_2\text{)}_2\text{-}$ and $\text{C}_4\text{H}_9\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.92 (t, 2H, $\text{-CH}_2\text{-O-}$), 5.02 (m, 2H, =CH_2), 5.82 (m, 1H, -CH=), 6.89 (m, 4H, 4 aromatic protons).
IIIM	71	0.85-2.23 (m, 24H, $\text{-(CH}_2\text{)}_2\text{-}$ and $\text{C}_5\text{H}_{11}\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.92 (t, 2H, $\text{-CH}_2\text{-O-}$), 5.02 (m, 2H, =CH_2), 5.82 (m, 1H, -CH=), 6.89 (m, 4H, 4 aromatic protons).
IVM	86	0.85-2.20 (m, 22H, $\text{-(CH}_2\text{)}_3\text{-}$ and $\text{C}_3\text{H}_7\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.93 (t, 2H, $\text{-CH}_2\text{-O-}$), 5.00 (m, 2H, =CH_2), 5.82 (m, 1H, =CH-), 6.89 (m, 4H, 4 aromatic protons).
VM	91	0.85-2.20 (m, 24H, $\text{-(CH}_2\text{)}_3\text{-}$ and $\text{C}_4\text{H}_9\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.93 (t, 2H, $\text{-CH}_2\text{-O-}$), 5.00 (m, 2H, =CH_2), 5.82 (m, 1H, =CH-), 6.89 (m, 4H, 4 aromatic protons).
VIM	86	0.85-2.20 (m, 26H, $\text{-(CH}_2\text{)}_3\text{-}$ and $\text{C}_5\text{H}_{11}\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.93 (t, 2H, $\text{-CH}_2\text{-O-}$), 5.00 (m, 2H, =CH_2), 5.82 (m, 1H, =CH-), 6.89 (m, 4H, 4 aromatic protons).
VIIM	70	0.80-2.23 (m, 32H, $\text{-(CH}_2\text{)}_8\text{-}$ and $\text{C}_3\text{H}_7\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, $\left(\begin{array}{c} \text{O} \\ \\ \text{tt, 1H, -O-C-CH} \end{array} \right)$, 3.90 (t, 2H, $\text{-CH}_2\text{-O-}$), 4.95 (m, 2H, =CH_2), 5.80 (m, 1H, =CH-), 6.89 (m, 4H, 4 aromatic protons).

Table I. Continued

Monomer	Yield (%)	300 MHz ¹ H-NMR (CDCl ₃ , δ, ppm)
VIIIM	86	0.80–2.23 (m, 34H, $\text{-(CH}_2\text{)}_8$ and $\text{C}_4\text{H}_9\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, 2.43 (tt, 1H, -O-C(=O)-CH $\left\langle \right\rangle$), 3.90 (t, 2H, $\text{-CH}_2\text{-O-}$), 4.95 (m, 2H, =CH_2), 5.80 (m, 1H, =CH-), 6.89 (m, 4H, 4 aromatic protons).
IXM	74	0.80–2.23 (m, 36H, $\text{-(CH}_2\text{)}_8$ and $\text{C}_5\text{H}_{11}\text{-CH}$ $\left\langle \begin{array}{l} \text{CH}_2\text{-CH}_2\text{-} \\ \text{CH}_2\text{-CH}_2\text{-} \end{array} \right\rangle$, 2.43 (tt, 1H, -O-C(=O)-CH $\left\langle \right\rangle$), 3.90 (t, 2H, $\text{-CH}_2\text{-O-}$), 4.95 (m, 2H, =CH_2), 5.80 (m, 1H, =CH-), 6.89 (m, 4H, 4 aromatic protons).

p-(1-Pentenyl-5-oxy)phenyl *trans*-4-*n*-Propylcyclohexanoate (IM), *p*-(1-Pentenyl-5-oxy)phenyl *trans*-4-*n*-Butylcyclohexanoate (IIM), *p*-(1-Pentenyl-5-oxy)phenyl *trans*-4-*n*-Pentylcyclohexanoate (IIIM), *p*-(1-Hexenyl-6-oxy)phenyl *trans*-4-*n*-Propylcyclohexanoate (IVM), *p*-(1-Hexenyl-6-oxy)phenyl *trans*-4-*n*-Butylcyclohexanoate (VM), *p*-(1-Hexenyl-6-oxy)phenyl *trans*-4-*n*-Pentylcyclohexanoate (VIM), *p*-(1-Undecenyl-11-oxy)phenyl *trans*-4-*n*-Propylcyclohexanoate (VIIM), *p*-(1-Undecenyl-11-oxy)phenyl *trans*-4-*n*-Butylcyclohexanoate (VIIM), *p*-(1-Undecenyl-11-oxy)phenyl *trans*-4-*n*-Pentylcyclohexanoate (IXM)

The monomers IM–IXM were synthesized by the same method. The preparation of monomer VIIIM is described below.

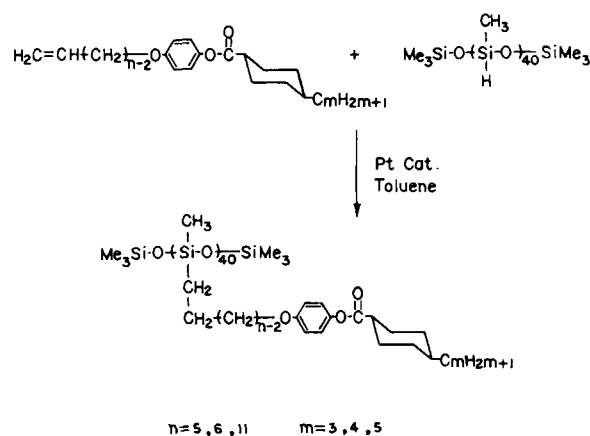
0.8 g (4.34 mmol) of *trans*-4-*n*-butylcyclohexanoic acid was reacted at room temperature with excess thionyl chloride containing a drop of dimethylformamide and 7 mL of methylene chloride for 2 h. The solvents were removed under reduced pressure to give the crude acid chloride. The product was dissolved in 10 mL of methylene chloride and slowly added to a cold solution of 1.25 g (4.77 mmol) of *p*-(1-undecenyl-11-oxy)phenol and 0.7 g of 4-dimethylaminopyridine in 100 mL of methylene chloride. The solution was allowed to stand at room temperature for 2 h and then the solvent was removed by heating over a boiling water bath. The obtained crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane

= 1 : 10 as eluent) to yield 1.6 g (86%) of white crystals. Table I summarizes the yields and ¹H-NMR chemical shifts of all synthesized monomers.

Synthesis of Polysiloxanes

The synthesis of liquid crystalline polysiloxanes is outlined in Scheme 2. A general synthetic procedure is described below.

0.8 g (10 mol % excess versus the Si–H groups present in polysiloxane) of the olefinic derivative was dissolved in 80 mL of dry, freshly distilled toluene together with the proper amount of poly(methylhydrogensiloxane). The reaction mixture



Scheme 2. Synthesis of polysiloxanes containing 4-alkanyloxyphenyl *trans*-4-*n*-alkylcyclohexanoate side groups.

was heated to 110°C under nitrogen and 100 μg of dicyclopentadienylplatinum(II) chloride catalyst was then injected with a syringe as solution in methylene chloride (1 mg/mL). The reaction mixture was refluxed (110°C) under nitrogen for 24 h. After this reaction time the FT-IR analysis showed that the hydrosilation reaction was complete. The polymers were separated and purified by several reprecipitations from tetrahydrofuran solution into methanol and further purified by preparative GPC, and then dried under vacuum.

RESULTS AND DISCUSSION

The synthetic routes used for the preparation of monomers **IM–IXM** are outlined in Scheme 1. Direct monoetherification of hydroquinone with alkenyl halides usually gives very low yields and we had difficulties on the purification of the final products. Therefore, we used 4-benzyloxyphenol as the starting material. It was etherified with alkenyl ha-

lides to give alkenyloxyphenyl benzyl ethers which were debenzylated²⁷ to form 4-alkenyloxyphenols. 4-Alkenyloxyphenols obtained by this improved method were always white, pure, and were obtained with high yields. The monomers which were prepared by esterification of 4-alkenyloxyphenol with *trans*-4-alkylcyclohexanoic acid, were obtained with pretty high yields and high purity as determined by thin layer chromatography and ¹H-NMR spectroscopy. Table I summarizes the ¹H-NMR chemical shifts of all synthesized monomers. The cyclohexane ring's methine proton, which is next to the carbonyl group, shows a resonance at 2.43 ppm. This peak is splitted as a triplet of triplets and the coupling constant ($J_{\text{axial-axial}}$) is ca. 30 Hz. This means that the methine proton is at an axial position. Since the formation of a mesophase required elongated molecular shape, all monomers should be in the equatorial *trans* form.

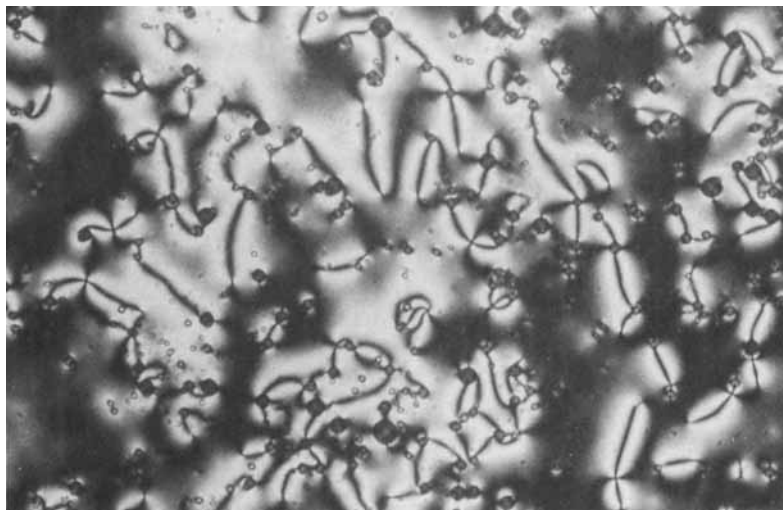
The thermal behavior of all monomers is reported in Table II. All monomers synthesized display me-

Table II. Phase Transitions and Phase Transition Enthalpies of Monomers **IM–IXM**

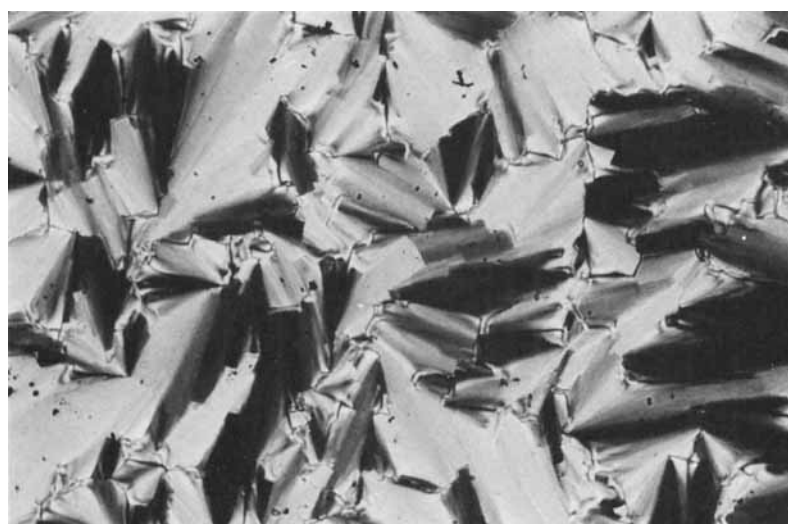
Monomer	n^a	m^a	Phase Transitions, °C (Corresponding Enthalpy Changes, kcal/mru) ^b	
			Heating	Cooling
IM	5	3	K 35(4.75) N 63(0.24) I	I 63(0.27) N 2(3.90) K
			K 32(4.48) N 63(0.24) I	I 63(0.22) N 2(3.85) K
IIM	5	4	K 41(7.14) N 75(0.31) I	I 73(0.31) N 18(4.02) K
			K 30(5.06) N 51(0.19) I	I 51(0.21) N 2(3.58) K
IVM	6	3	K 12(3.23) N 51(0.23) I	I 51(0.22) N 5(0.89) K ₁ - 31(0.94) K ₂
			K 20(4.38) N 63(0.20) I	I 63(0.27) N 18(0.26) K ₁ 3(2.22) K ₂
VM	6	4	K 37(10.31) N 62(0.34) I	I 62(0.38) N 43(0.14) S _A 28(0.64) S _E 5(6.13) K
			K 36(6.34) S _E 45(0.69) S _A 56(0.31) N 66 (0.34) I	I 65(0.38) N 55(0.33) S _A 44(0.83) S _E 18(2.49) K
VIM	6	5	K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
			K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
VIIIM	11	3	K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
			K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
VIIIM	11	4	K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
			K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
IXM	11	5	K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K
			K 35(6.22) S _E 56(0.92) S _A 66(0.38) N 73(0.39) I	I 72(0.42) N 66(0.38) S _A 55(0.96) S _E 15(2.39) K

^a According to Scheme 1.

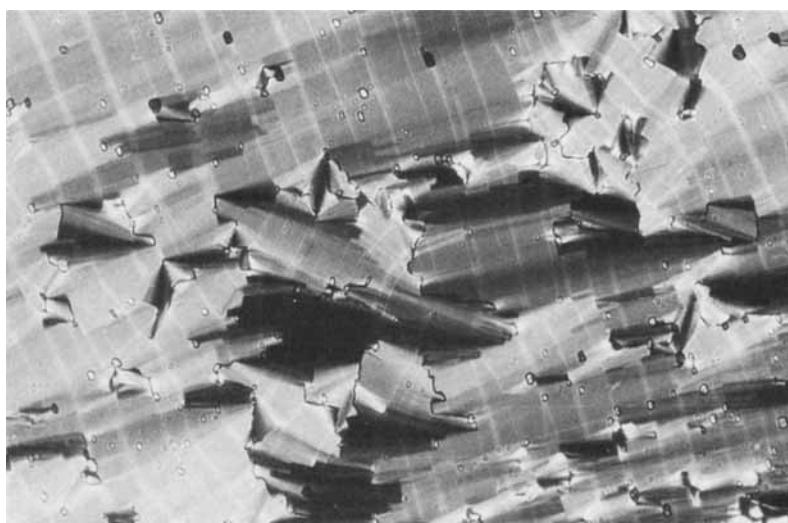
^b K = crystalline, N = nematic, S = smectic, I = isotropic.



A



B



C

Figure 1. Optical polarized micrographs displayed by monomer IXM (80 \times): (A) Nematic schlieren texture obtained after cooling to 68 $^{\circ}$ C, (B) focal-conic texture of the smectic A phase obtained after cooling to 61.0 $^{\circ}$ C, (C) arced focal-conic texture of the smectic E phase obtained after cooling to 51.7 $^{\circ}$ C.

sophases. The monomers **IM** to **VIM** exhibit an enantiotropic nematic mesophase. They displayed respectively a characteristic schlieren nematic texture. Monomer **VIIM** displays an enantiotropic nematic phase and two monotropic smectic mesophases (S_A and S_E), while monomers **VIIIM** and **IXM** display enantiotropic nematic, S_A and S_E phases. Optical polarizing microscope observation revealed very characteristic textures for these three mesophases. Figure 1 presents three representative textures exhibited by monomer **IXM**. Texture A which was obtained after cooling from isotropic phase to 68°C, is a typical schlieren nematic texture. Texture B which was obtained after cooling from nematic phase to 61°C, is a typical focal-conic texture of the smectic A phase. Texture C which was obtained after cooling from smectic A phase to 51.7°C, is an arced focal-conic texture. The lines of the arcs are very clear and the bands are unbroken. This texture is very

characteristic of the smectic E phase. No other phase shows this type of texture, except the smectic G phase formed on cooling smectic B phase. In this case, the arcs are seen, but they are dissimilar to those of the smectic E phase because they are broken.²⁸ Some conclusions can be obtained from the data reported in Table II. Nine monomers can be separated into three groups, i.e., **IM–IIIM**, **IVM–VIM** and **VIIM–IXM**. The difference among three groups of monomers is due to the length of the flexible alkenyl spacers. In each group, the difference among three monomers is on the length of the terminal alkyl chains. As can be seen from the table, the tendency toward smectic mesomorphism increases with increasing spacer length. The isotropization temperature first decreases, and then increases with increasing spacer length. In each group, when the length of a terminal alkyl group increases from propyl to pentyl, it does not affect the type of

Table III. Phase Transitions and Phase Transition Enthalpies of Polymers IP–IXP

Polymer	n^a	m^a	Phase Transitions, °C (Corresponding Enthalpy Changes, kcal/mru) ^b	
			Heating	Cooling
IP	5	3	$g \rightarrow 7 S_2 \rightarrow 35(0.32) S_A \rightarrow 125(0.44) I$	$I \rightarrow 125(0.51) S_A \rightarrow 29(0.41) S_2 \rightarrow 3 g$
IIP	5	4	$g \rightarrow 3 S_2 \rightarrow 79(0.17) S_A \rightarrow 143(0.80) I$	$I \rightarrow 139(0.80) S_A \rightarrow 76(0.19) S_2 \rightarrow 0 g$
IIIP	5	5	$g \rightarrow 8 S_2 \rightarrow 102(0.23) S_A \rightarrow 152(0.97) I$	$I \rightarrow 148(0.95) S_A \rightarrow 98(0.22) S_2 \rightarrow 5 g$
IVP	6	3	$g \rightarrow -6 S_2 \rightarrow 90(0.06) 106(0.10) I$	$I \rightarrow 102(0.21) S_A \rightarrow 86(0.16) S_2 \rightarrow -11g$
VP	6	4	$g \rightarrow -12 S_A \rightarrow 108(0.66) I$	$I \rightarrow 100(0.75) S_A \rightarrow -15 g$
VIP	6	5	$g \rightarrow -6 S_2 \rightarrow 76(0.19) S_A \rightarrow 131(0.81) I$	$I \rightarrow 125(0.78) S_A \rightarrow 71(0.18) S_2 \rightarrow -10 g$
VIIIP	11	3	$S_E \rightarrow 69(0.71) S_A \rightarrow 126(1.01) I$	$I \rightarrow 121(1.00) S_A \rightarrow 64(0.85) S_E$
VIIIP	11	4	$S_E \rightarrow 82(1.04) S_A \rightarrow 141(1.17) I$	$I \rightarrow 121(1.00) S_A \rightarrow 64(0.85) S_E$
IXP	11	5	$S_3 \rightarrow 66(0.11) S_E \rightarrow 85(0.54) S_A \rightarrow 135(0.84) I$	$I \rightarrow 133(0.92) S_A \rightarrow 80(0.54) S_E \rightarrow 60(0.11) S_3$

^a According to Scheme 2.

^b mru = mole repeating units; g = glassy, N = nematic, S = smectic, I = isotropic.

mesophase formed, but does affect the isotropization temperature (T_{NI}); i.e., both monomers with a propyl or a butyl terminal group show similar T_{NI} values while the monomer with a pentyl terminal group presents a higher T_{NI} value.

The synthesis of side-chain liquid crystalline polysiloxanes is outlined in Scheme 2. Some preliminary information on the phase behavior of the polysiloxanes was obtained by DSC²⁹ and optical polarizing microscopy.²⁸ Table III summarizes the thermal transitions and thermodynamic parameters of the synthesized polymers. All polymers present smectic mesomorphism. It is well documented that in many cases the mesophase formed by a side-chain liquid crystalline polymer is more organized than the one exhibited by the corresponding monomer. Polymers **IP** to **IIIP** exhibit a glass transition and two enantiotropic mesomorphic transitions. On the optical polarized microscope, on cooling from an isotropic phase all three polymers first displayed a focal-conic texture which is characteristic of a smectic A phase. Upon further cooling from smectic A phase to the other smectic phase, the polymers became very viscous and were not able to form a characteristic texture so far. On going from **IP** to **IIIP**, the terminal alkyl chain length increases from propyl to pentyl and both the mesophase transitions shift to higher temperatures. This result demonstrates that a longer terminal alkyl group is leading to the formation of a more stable mesophase.

Figure 2 illustrates some representative DSC traces of polymers **IVP**–**VIP**. Basically the mesophase behavior of these three polymers follows the same trend as that of polymers **IP**–**IIIP** except that only a smectic A phase is observed for polymer **VP**. Polymers **VIIP**–**IXP** present very different mesomorphic behavior from the former six polymers. All three polymers show no discriminative glass transition and both polymers **VIIP** and **VIIIP** present two enantiotropic mesophase transitions, while polymer **IXP** present three enantiotropic mesomorphic transitions. On cooling from the isotropic phase on the optical polarized microscope all three polymers first displayed a focal-conic texture which is characteristic of a smectic A phase and then an arced focal-conic texture which is typical for a smectic E phase. Attempts to develop a characteristic texture of the third smectic phase upon the annealing of the polymer **IXP** was unsuccessful. Figure 3 shows the typical focal-conic texture and the arced focal-conic texture exhibited by polymer **VIIIP**.

In order to study the thermal stability of the prepared polymers, they were heated to the temperature

above 200°C and then characterized by ¹H-NMR spectroscopy and DSC. Both the 300 MHz ¹H-NMR spectra and the DSC traces of the thermal treated samples are completely identical to those of the untreated samples. This result demonstrates that trans–cis isomerization for the cyclohexane based mesogens does not occur.

In conclusion, all the synthesized polymers show only liquid crystalline mesophases and do not undergo side chain crystallization even if very long spacers were used to connect the polymer backbone and the mesogenic units. This result could be due to the cyclohexane based mesogenic units which as illustrated in our previous studies^{11,12,16} exhibits conformational isomerism.

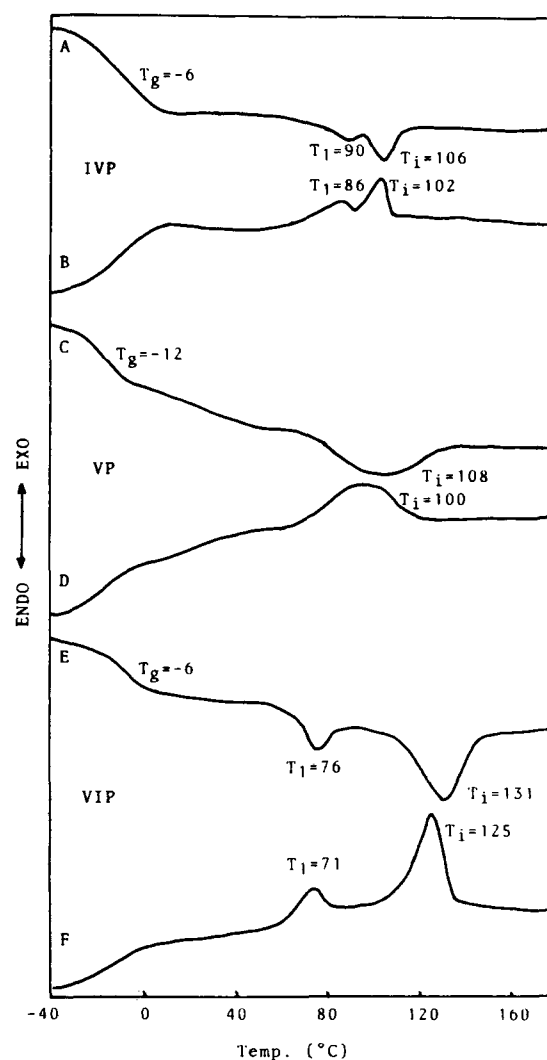
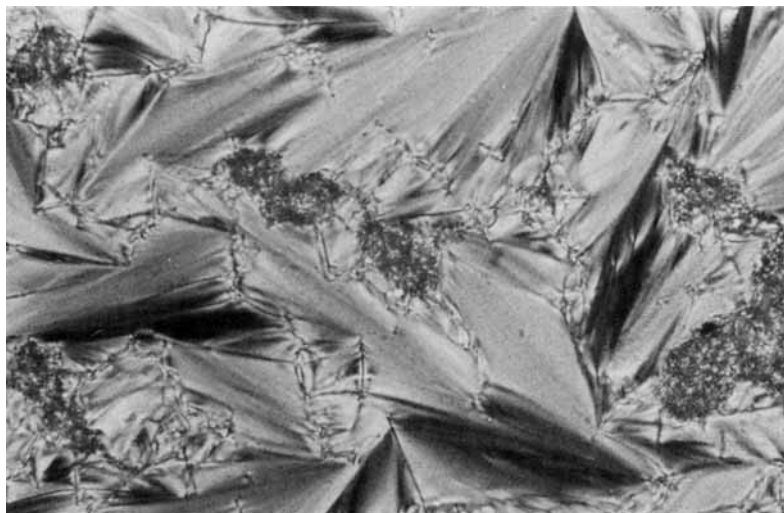


Figure 2. DSC thermograms (10°C/min): (A) **IVP**, second heating scan; (B) **IVP**, cooling scan; (C) **VP**, second heating scan; (D) **VP**, cooling scan; (E) **VIP**, second heating scan; (F) **VIP**, cooling scan.



A



B

Figure 3. Optical polarized micrographs displayed by polymer VIIIIP (400 \times): (A) focal-conic texture of the smectic A phase obtained after cooling to 114.8 $^{\circ}$ C, (B) arced focal-conic texture of the smectic E phase obtained after cooling to 63.7 $^{\circ}$ C.

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