

# Synthesis of Liquid Crystalline Polysiloxanes and Polymethacrylates with Broad Temperature Ranges of the Chiral Smectic C Phase

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**ABSTRACT:** The synthesis of side-chain liquid crystalline polysiloxanes and polymethacrylates containing oligooxyethylene spacers and 4-(*S*)-2-methyl-1-butyl [(4-hydroxybiphenyl-4'-yl)carbonyl]oxybenzoate mesogenic side groups is presented. Differential scanning calorimetry, optical polarizing microscopy, and X-ray diffraction measurements reveal chiral smectic mesomorphism for all polymers. All three polysiloxanes present enantiotropic smectic A and chiral smectic C phases. The chiral smectic C phase covers a very broad temperature range (about 200 °C). Among polymethacrylates prepared in this study, the polymethacrylate which contains three oxyethylene units in its spacer is the only one revealing smectic A and chiral smectic C phases. The results seem to demonstrate that the tendency toward a chiral smectic C phase increases with increasing the flexibility of the polymer backbone and the oligooxyethylene spacer can increase dramatically the thermal stability of the chiral smectic C phase.

## Introduction

The potential application of ferroelectric liquid crystals (FLCs) in fast-switching, high-resolution electrooptical devices is well documented.<sup>1-3</sup> Besides low molar mass FLCs, a number of ferroelectric liquid crystalline side-chain polymers have been successfully prepared during the past few years.<sup>4-27</sup> These polymers are interesting because of their ferroelectric properties.<sup>17-26</sup> This field has been reviewed by LeBarney and Dubois.<sup>28</sup> However, the detailed structure-property relationship of ferroelectric liquid crystalline polymers (LCPs) has not been very clear up until now. It seems necessary to introduce additional functional groups into the mesogenic units, spacers, and polymer backbone of side-chain liquid crystalline polymers to create some new property combinations in order to achieve these goals.

In this study, a series of new chiral smectic liquid crystalline polysiloxanes and polymethacrylates containing oligooxyethylene spacers and 4-(*S*)-2-methyl-1-butyl [(4-hydroxybiphenyl-4'-yl)carbonyl]oxybenzoate mesogenic side groups are synthesized. Their characterizations by differential scanning calorimetry, optical polarizing microscopy, and X-ray diffraction have been presented.

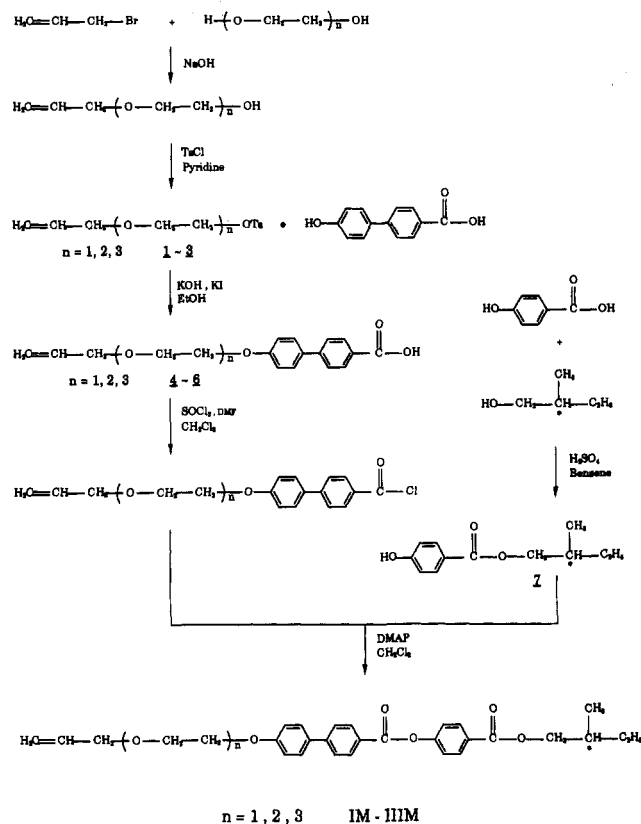
## Experimental Section

**A. Material.** Poly(methylhydrogensiloxane) ( $\bar{M}_n = 2270$ ) and divinyltetramethyldisiloxane platinum catalyst were obtained from Petrarch Systems (Bristol, PA) and used as received.

*S*-(*-*)-2-Methyl-1-butanol,  $[\alpha]_D = -6.5^\circ$  (from Merck), 2-(allyloxy)ethanol, 4-hydroxybiphenyl-4'-carboxylic acid (from Tokyo Kasei Co.), and all other reagents (from Aldrich) were used as received. Toluene used in the hydrosilation reaction and 1,3-dioxane were first refluxed over sodium and then distilled under nitrogen. 2,2'-Azobis(isobutyronitrile) (AIBN; from Fluka) was freshly recrystallized from methanol.

**B. Techniques.** <sup>1</sup>H-NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. FT-IR spectra were measured on a Nicolet 520 FT-IR spectrometer. Polymer samples

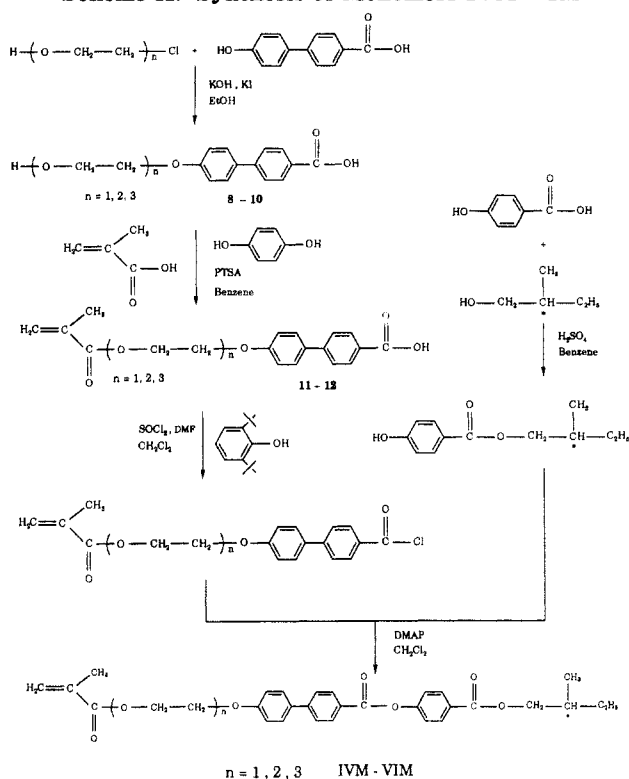
## Scheme I. Synthesis of Monomers IM-IIIIM



were film cast onto a KBr tablet for the IR measurements. 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 rates were 10 °C/min. Thermal transitions reported were collected during the second heating and cooling scans. A Carl-Zeiss Axiophot 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

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## Scheme II. Synthesis of Monomers IVM-VIM



equipped with a 410 differential refractometer and a preparative GPC column (22.5 mm × 60 cm) supplied by American Polymer Standard Co. X-ray diffraction measurements were performed with nickel-filtered Cu K $\alpha$  radiation with a Rigaku powder diffractometer. Optical rotations were measured at 25 °C on a Jasco DIP-140 polarimeter with chloroform as solvent for all compounds.

**C. Synthesis of Monomers.** The synthesis of olefinic monomers IM-IIIIM for hydrosilylation reaction and methacrylate monomers IVM-VIM is outlined in Schemes I and II. 2-[2-

(Allyloxy)ethoxy]ethanol and 2-[2-[2-(allyloxy)ethoxy]ethoxy]ethanol were synthesized according to a literature procedure.<sup>29</sup>

**2-(Allyloxy)ethyl Tosylate (1), 2-[2-(Allyloxy)ethoxy]ethyl Tosylate (2), and 2-[2-[2-(Allyloxy)ethoxy]ethoxy]ethyl Tosylate (3).** All three compounds were prepared by the same method. The synthesis of compound 2 is described below. To a stirred solution of *p*-toluenesulfonyl chloride (11.7 g, 0.061 mol) in 60 mL of dried pyridine was added dropwise at 0 °C 2-[2-(allyloxy)ethoxy]ethanol (8.13 g, 0.056 mol). The reaction mixture was stirred at 4 °C overnight. The resulting solution was poured into 70 mL of ice water and extracted with diethyl ether. The ether layer was washed with 30 mL of a 6 N hydrochloric acid solution and water, dried over anhydrous MgSO<sub>4</sub>, and filtered. The diethyl ether was removed in a rotavapor, and the crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2 as eluent) to yield 12.9 g of a colorless oil.

**1:** yield 73.5%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, ppm)  $\delta$  2.45 (s, 3H, -CH<sub>3</sub>), 3.61-4.18 (m, 6H, -OCH<sub>2</sub>CH<sub>2</sub>- and =CHCH<sub>2</sub>O-), 5.18 (m, 2H, H<sub>2</sub>C=CH-), 5.82 (m, 1H, H<sub>2</sub>C=CH-), 7.33-7.81 (2d, 4 aromatic protons).

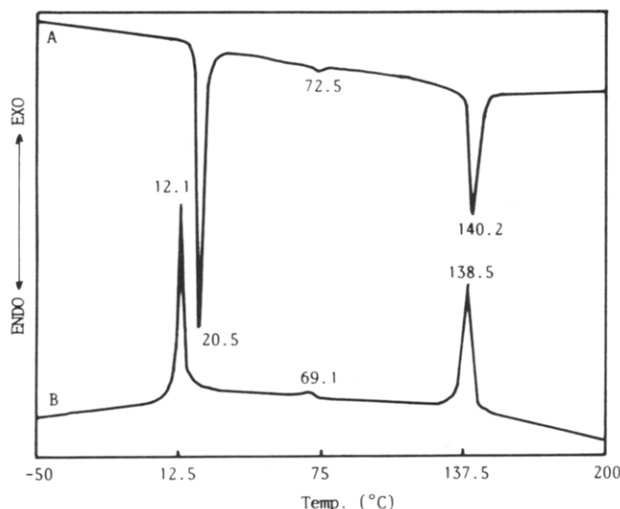
**2:** yield 63.6%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, ppm)  $\delta$  2.39 (s, 3H, -CH<sub>3</sub>), 3.46-4.12 (m, 10H, -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>- and =CHCH<sub>2</sub>O-), 5.16 (m, 2H, H<sub>2</sub>C=CH-), 5.82 (m, 1H, H<sub>2</sub>C=CH-), 7.28-7.75 (2d, 4 aromatic protons).

**3:** yield 71.5%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, ppm):  $\delta$  2.44 (s, 3H, -CH<sub>3</sub>), 3.58-4.17 (m, 14H, -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>- and =CHCH<sub>2</sub>O-), 5.19 (m, 2H, H<sub>2</sub>C=CH-), 5.89 (m, 1H, H<sub>2</sub>C=CH-), 7.33-7.80 (2d, 4 aromatic protons).

**4-[2-(Allyloxy)ethoxy]biphenyl-4'-carboxylic Acid (4), 4-[2-[2-(Allyloxy)ethoxy]biphenyl-4'-carboxylic Acid (5), and 4-[2-[2-(Allyloxy)ethoxy]ethoxy]biphenyl-4'-carboxylic Acid (6).** All three compounds were prepared by the same method. The synthesis of compound 5 is described below. 4-Hydroxybiphenyl-4'-carboxylic acid (3.06 g, 14.3 mmol), KOH (2.08 g, 37.2 mmol), and KI (0.3 g) were dissolved in 100 mL of 95% ethanol. The mixture was refluxed for 1 h, and 2-[2-(allyloxy)ethoxy]ethyl tosylate (4.70 g, 15.7 mmol) was added dropwise. The resulting solution was refluxed for 20 h, cooled to room temperature, and acidified with 6 N hydrochloric acid. The precipitated solid was filtered and recrystallized from a mixture of ethanol and water to yield 4.09 g of white crystals.

Table I. Characterization of Monomers IM-VIM

monomer	yield (%)	$[\alpha]^{25}_D$	400-MHz <sup>1</sup> H-NMR (CDCl <sub>3</sub> , ppm)
IM	61.8	+6.81	0.95 (t, 3H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.01 (d, 3H, -HC(CH <sub>3</sub> )CH <sub>2</sub> -), 1.21-1.60 (m, 2H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.85 (m, 1H, -CH(CH <sub>3</sub> )-), 3.78 ~ 4.25 (m, 8H, -OCH <sub>2</sub> CH <sub>2</sub> -, -CH <sub>2</sub> CH=, and -OCH <sub>2</sub> CH(CH <sub>3</sub> )-), 5.24 (q, 2H, H <sub>2</sub> C=CH-), 5.93 (m, 1H, H <sub>2</sub> C=CH-), 6.98-8.25 (m, 12 aromatic protons)
IIIM	52.4	+7.15	0.93 (t, 3H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.01 (d, 3H, -HC(CH <sub>3</sub> )CH <sub>2</sub> -), 1.21-1.61 (m, 2H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.85 (m, 1H, -CH(CH <sub>3</sub> )-), 3.59-4.25 (m, 12H, -(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> -, -CH <sub>2</sub> CH=, and -OCH <sub>2</sub> CH(CH <sub>3</sub> )-), 5.21 (q, 2H, H <sub>2</sub> C=CH-), 5.91 (m, 1H, H <sub>2</sub> C=CH-), 6.99-8.29 (m, 12 aromatic protons)
IIIIM	61.7	+7.08	0.95 (t, 3H, -CHCH <sub>3</sub> ), 1.01 (d, 3H, -HC(CH <sub>3</sub> )CH <sub>2</sub> -), 1.21-1.59 (m, 2H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.85 (m, 1H, -CH(CH <sub>3</sub> )-), 3.58-4.25 (m, 16H, -(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> -, -CH <sub>2</sub> CH=, and -OCH <sub>2</sub> CH(CH <sub>3</sub> )-), 5.21 (q, 2H, H <sub>2</sub> C=CH-), 5.89 (m, 1H, H <sub>2</sub> C=CH-), 6.99-8.25 (m, 12 aromatic protons)
IVM	51.6	+8.35	0.94 (t, 3H, -CHCH <sub>3</sub> ), 1.00 (d, 3H, -HC(CH <sub>3</sub> )CH <sub>2</sub> -), 1.24-1.57 (m, 2H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.86 (m, 1H, -CH(CH <sub>3</sub> )-), 1.94 (s, 3H, =(C)CH <sub>3</sub> ), 4.10-4.53 (m, 6H, -OCH <sub>2</sub> CH <sub>2</sub> - and -OCH <sub>2</sub> CH(CH <sub>3</sub> )-), 5.58 and 6.14 (d, 2H, =CH <sub>2</sub> ), 7.01-8.23 (m, 12 aromatic protons)
VM	44.5	+8.07	0.95 (t, 3H, -CHCH <sub>3</sub> ), 1.01 (d, 3H, -HC(CH <sub>3</sub> )CH <sub>2</sub> -), 1.24-1.57 (m, 2H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.87 (m, 1H, -CH(CH <sub>3</sub> )-), 1.95 (s, 3H, =(C)CH <sub>3</sub> ), 3.70-4.33 (m, 10H, -(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> - and -OCH <sub>2</sub> CH(CH <sub>3</sub> )-), 5.57 and 6.13 (d, 2H, =CH <sub>2</sub> ), 7.01-8.24 (m, 12 aromatic protons)
VIM	63.7	+8.65	0.97 (t, 3H, -CHCH <sub>3</sub> ), 1.02 (d, 3H, -HC(CH <sub>3</sub> )CH <sub>2</sub> -), 1.24-1.57 (m, 2H, -CH <sub>2</sub> CH <sub>3</sub> ), 1.87 (m, 1H, -CH(CH <sub>3</sub> )-), 1.95 (s, 3H, =(C)CH <sub>3</sub> ), 3.70-4.33 (m, 14H, -(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> - and -OCH <sub>2</sub> CH(CH <sub>3</sub> )-), 5.57 and 6.13 (d, 2H, =CH <sub>2</sub> ), 7.01-8.24 (m, 12 aromatic protons)



**Figure 1.** DSC thermograms of IIM (10 °C/min): (A) heating scan; (B) cooling scan.

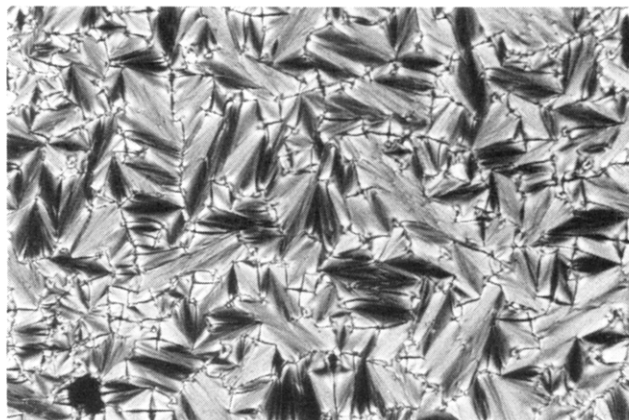
4: yield 75.6%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 3.82–4.20 (m, 6H, =CHCH<sub>2</sub>O– and –OCH<sub>2</sub>CH<sub>2</sub>–), 5.30 (m, 2H, H<sub>2</sub>C=CH–), 5.95 (m, 1H, H<sub>2</sub>C=CH–), 7.0–7.62 (m, 8 aromatic protons).

5: yield 83.7%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 3.56–4.20 (m, 10H, =CHCH<sub>2</sub>O– and –(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>–), 5.23 (m, 2H, H<sub>2</sub>O=CH–), 5.87 (m, 1H, H<sub>2</sub>C=CH–), 7.04–8.08 (m, 8 aromatic protons).

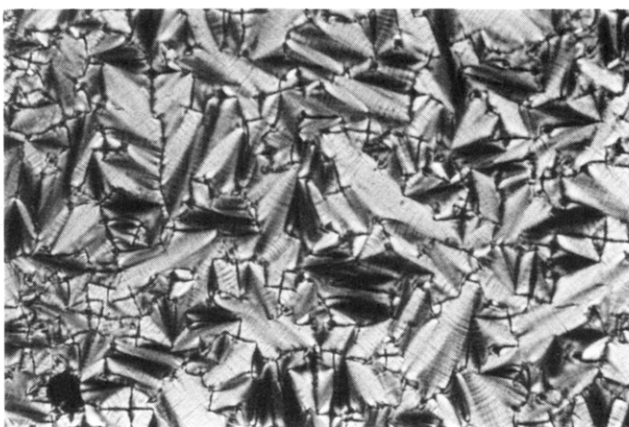
6: yield 79.3%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 3.50–4.16 (m, 14H, =CHCH<sub>2</sub>O– and –(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>–), 5.11 (m, 2H, H<sub>2</sub>C=CH–), 5.84 (m, 1H, H<sub>2</sub>C=CH–), 7.04–8.08 (m, 8 aromatic protons).

**(S)-2-Methyl-1-butyl 4-Hydroxybenzoate (7).** Compound 7 was prepared by acid-catalyzed esterification of (S)-2-methyl-1-butanol with 4-hydroxybenzoic acid in benzene. 4-Hydroxybenzoic acid (5.0 g, 0.036 mol), (S)-2-methyl-1-butanol (4.76 g, 0.054 mol), and concentrated sulfuric acid (0.2 mL) were added to 15 mL of dried benzene. The reaction mixture was refluxed until 4-hydroxybenzoic acid was completely dissolved and 0.65 mL of water was collected on a Dean–Stark trap. After cooling to room temperature, the solution was washed with a 2% aqueous solution of NaHCO<sub>3</sub> and water and dried over anhydrous MgSO<sub>4</sub>, and the solvent was removed in a rotavapor. The obtained solid was purified with column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/1 as eluent) to yield 6.96 g (93%) of white crystals: [α]<sub>D</sub><sup>25</sup> = +5.50; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, ppm): δ 0.80–1.10 (m, 6H, –CH<sub>3</sub>), 1.20–1.58 (m, 2H, –CH<sub>2</sub>–), 1.78–1.91 (m, 1H, –CH(CH<sub>3</sub>)–), 4.14 (q, 2H, –COOCH<sub>2</sub>), 6.9–7.9 (m, 4 aromatic protons).

4-(S)-2-Methyl-1-butyl [[[4-[2-(Allyloxy)ethoxy]biphenyl-4'-yl]carbonyloxy]benzoate (IM), 4-(S)-2-Methyl-1-butyl [[[4-[2-[2-(Allyloxy)ethoxy]ethoxy]biphenyl-4'-yl]carbonyloxy]benzoate (IIM), and 4-(S)-2-Methyl-1-butyl [[[4-[2-[2-[2-(Allyloxy)ethoxy]ethoxy]ethoxy]biphenyl-4'-yl]carbonyloxy]benzoate (IIIM). The olefinic monomers IM–IIIM were prepared by the esterification of (S)-2-methyl-1-butyl 4-hydroxybenzoate with the corresponding acid compounds 4–6. An example is described below. 4-[2-[2-(Allyloxy)ethoxy]ethoxy]biphenyl-4'-carboxylic acid (1.5 g, 4.38 mmol) was reacted at room temperature with excess thionyl chloride containing a drop of dimethylformamide in 7 mL of methylene chloride for 2 h. The solvent was 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 (S)-2-methyl-1-butyl 4-hydroxybenzoate (0.9 g, 4.38 mmol) and 4-(dimethylamino)pyridine (0.7 g) in 100 mL of methylene chloride. The solution was allowed to stand for 2 h, and then the solvent was removed in a rotavapor. The obtained crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/3 as eluent) to yield 1.22 g (52.4%) of white crystals. Table I summarizes the optical rotations and <sup>1</sup>H-NMR chemical shifts for monomers IM–IIIM.



A



B

**Figure 2.** Optical polarizing micrographs displayed by IIM: (A) S<sub>A</sub> texture obtained after cooling to 125 °C; (B) S<sub>C</sub>\* texture obtained after cooling to 50 °C.

4-(2-Hydroxyethoxy)biphenyl-4'-carboxylic Acid (8), 4-[2-(2-Hydroxyethoxy)ethoxy]biphenyl-4'-carboxylic Acid (9), and 4-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]biphenyl-4'-carboxylic Acid (10). The compounds 8–10 were prepared by etherification of 4-hydroxybiphenyl-4'-carboxylic acid with corresponding 2-chloroethanol, 2-(2-chloroethoxy)ethanol and 2-[2-(2-chloroethoxy)ethoxy]ethanol according to similar synthetic procedures given for compounds 4–6.

8: yield 83.7%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 4.25–4.59 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>–), 7.05–8.08 (m, 8 aromatic protons).

9: yield 52.5%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 3.59–4.20 (m, 8H, –(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>–), 7.05–8.08 (m, 8 aromatic protons).

10: yield 61.5%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 3.51–4.20 (m, 12H, –(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>–), 7.16–8.08 (m, 8 aromatic protons).

4-[2-(Methacryloyloxy)ethoxy]biphenyl-4'-carboxylic Acid (11), 4-[2-[2-(Methacryloyloxy)ethoxy]ethoxy]biphenyl-4'-carboxylic Acid (12), and 4-[2-[2-[2-(Methacryloyloxy)ethoxy]ethoxy]ethoxy]biphenyl-4'-carboxylic Acid (13). All three compounds were prepared by esterification of methacrylic acid with corresponding compounds 8–10. The synthesis of compound 12 is described below. 4-[2-(2-Hydroxyethoxy)ethoxy]biphenyl-4'-carboxylic acid (3 g, 9.9 mmol), methacrylic acid (8.5 g, 0.099 mol), *p*-toluenesulfonic acid (0.94 g), and hydroquinone (0.44 g) were dissolved in 50 mL of dried benzene. The reaction mixture was refluxed for 40 h, and water was collected on a Dean–Stark trap. After this reaction time, benzene and excess methacrylic acid were distilled off and the crude product was dissolved in ethyl ether. The ether solution was washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed

Table II. Phase Transitions and Phase Transition Enthalpies for Monomers IM-VIM

monomer	$n^a$		phase transitions, °C (corresponding enthalpy changes, kcal/mol) <sup>b</sup>	
IM	1	heating cooling	K 95.4 (5.36) S <sub>A</sub> 171.5 (1.16) I I 168.8 (1.16) S <sub>A</sub> 76.8 (-) S <sub>C</sub> * 58.1 (1.48) K	
IIM	2	heating cooling	K 20.5 (0.99) S <sub>C</sub> * 72.5 (0.03) S <sub>A</sub> 140.2 (0.82) I I 138.5 (0.76) S <sub>A</sub> 69.1 (0.03) S <sub>C</sub> * 12.1 (0.98) K	
IIIM	3	heating cooling	K 7.6 (0.93) S <sub>C</sub> * 57.4 (0.03) S <sub>A</sub> 106.6 (0.73) I I 103.2 (0.75) S <sub>A</sub> 54.5 (0.01) S <sub>C</sub> * 1.4 (0.80) K	
IVM	1	heating cooling	K 78.0 (6.51) S <sub>A</sub> 113.8 (0.36) I I 104.7 (0.15) S <sub>A</sub> 43.0 (1.05) K	
VM	2	heating cooling	K 13.6 (0.77) S <sub>A</sub> 99.1 (0.65) I I 90.0 (0.15) S <sub>A</sub> 28.3 (1.63) K	
VIM	3	heating cooling	K 25.6 (0.65) S <sub>C</sub> * 53.5 (-) S <sub>A</sub> 75.2 (0.27) I I 69.1 (0.30) S <sub>A</sub> 45.14 (-) S <sub>C</sub> * 3.3 (0.62) K	

<sup>a</sup>  $n$  according to Schemes I and II. <sup>b</sup> K = crystalline, S<sub>A</sub> = smectic A, S<sub>C</sub>\* = chiral smectic C, N\* = chiral nematic, I = isotropic.

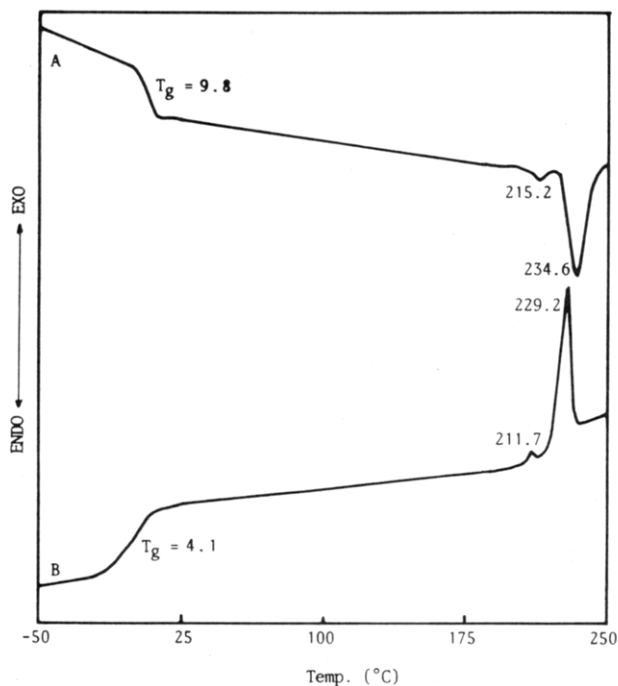
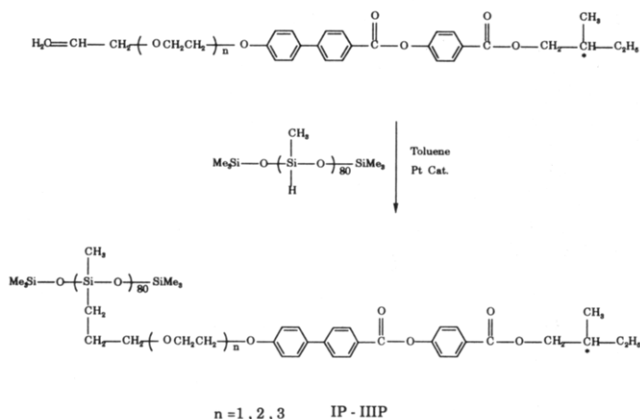


Figure 3. DSC thermograms of IP (10 °C/min): (A) heating scan; (B) cooling scan.

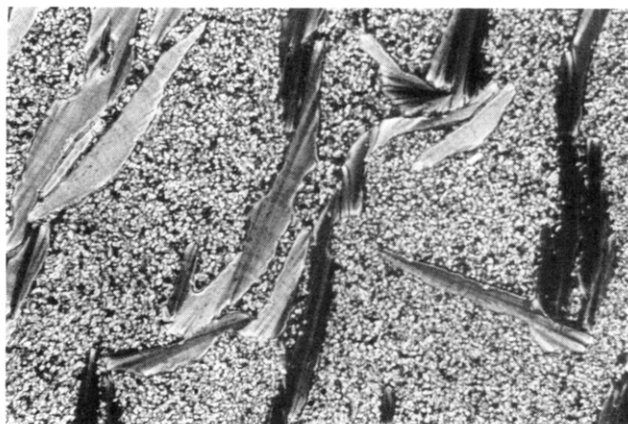
### Scheme III. Synthesis of Polysiloxanes IP-IIIIP



in a rotavapor. The obtained solid was recrystallized with a mixture of dichloromethane and *n*-hexane to yield 3.28 g of crystals.

11: yield 83.5%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 1.94 (s, 3H, =C)CH<sub>3</sub>), 4.25–4.52 (m, 4H, -OCH<sub>2</sub>CH<sub>2</sub>-), 5.58 and 6.13 (d, 2H, =CH<sub>2</sub>), 6.97–8.12 (m, 8 aromatic protons).

12: yield 89.5%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 1.92 (s, 3H, =C)CH<sub>3</sub>), 3.40–4.20 (m, 8H, -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-), 5.58 and 6.10 (d, 2H, =CH<sub>2</sub>), 6.95–8.07 (m, 8 aromatic protons).



A



B

Figure 4. Optical polarizing micrographs displayed by IP: (A) S<sub>A</sub> texture obtained after cooling to 221 °C; (B) S<sub>C</sub>\* texture obtained after cooling to 178 °C.

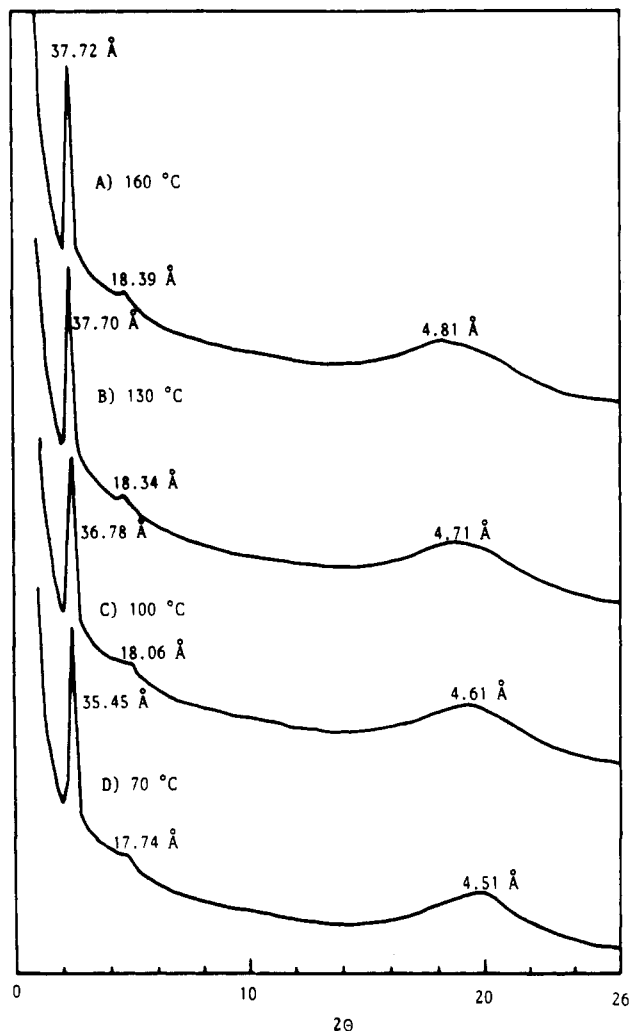
13: yield 84.3%; <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, TMS, ppm): δ 1.92 (s, 3H, =C)CH<sub>3</sub>), 3.64–4.25 (m, 12H, -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>-), 5.57 and 6.06 (2d, 2H, =CH<sub>2</sub>), 6.92–8.07 (m, 8 aromatic protons).

4-(*S*)-2-Methyl-1-butyl [[[4-[2-(Methacryloyloxy)ethoxy]biphenyl-4'-yl]carbonyl]oxy]benzoate (IVM), 4-(*S*)-2-Methyl-1-butyl [[[4-[2-[2-(Methacryloyloxy)ethoxy]ethoxy]biphenyl-4'-yl]carbonyl]oxy]benzoate (VM), and 4-(*S*)-2-Methyl-1-butyl [[[4-[2-[2-(Methacryloyloxy)ethoxy]ethoxy]biphenyl-4'-yl]carbonyl]oxy]benzoate (VIM). Monomers IVM–VIM were prepared by esterification of (*S*)-2-methyl-1-butyl 4-hydroxybenzoate with corresponding acid com-

**Table III. Phase Transitions and Phase Transition Enthalpies for Polymers IP–IIIP**

polymer	$n^a$		phase transitions, °C (corresponding enthalpy changes, kcal/mru) <sup>b</sup>
IP	1	heating	G 9.8 Sc* 215.2 (0.07) S <sub>A</sub> 234.6 (0.80) I
		cooling	I 229.2 (0.73) S <sub>A</sub> 211.7 (0.03) Sc* 4.1 G
IIP	2	heating	G -11.2 Sc* 208 (-) S <sub>A</sub> 211.8 (0.85) I
		cooling	I 212.0 (0.49) S <sub>A</sub> 206 (-) Sc* -15.0 G
IIIP	3	heating	G -25.1 Sc* 168 (-) 190.3 (0.94) I
		cooling	I 184.2 (0.98) S <sub>A</sub> 161 (-) Sc* -20.8 G

<sup>a</sup>  $n$  according to Scheme III. <sup>b</sup> mru = mole repeating unit, G = glassy, S<sub>A</sub> = smectic A, Sc\* = chiral smectic C, I = isotropic.



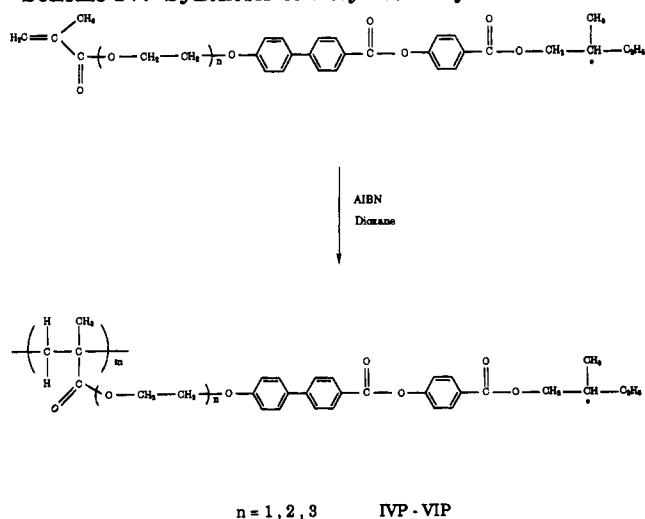
**Figure 5.** Temperature-dependent X-ray measurements for polymer IIP at (A) 160, (B) 130, (C) 100, and (D) 70 °C.

pounds 11–13 according to similar synthetic procedures given for monomers IM–IIIM. The yields, optical rotations, and <sup>1</sup>H-NMR chemical shifts of monomers IVM–VIM are also summarized in Table I.

**D. Synthesis of Polysiloxanes IP–IIIP.** The synthesis of liquid crystalline polysiloxanes is outlined in Scheme II. A general synthetic procedure is described below.

The olefinic derivative (1.0 g, 10 mol % excess versus the Si–H groups present in polysiloxane) was dissolved in 100 mL of dry, freshly distilled toluene together with the proper amount of poly(methylhydrogensiloxane). The reaction mixture was heated to 110 °C under nitrogen, and 100 μg of divinyltetramethyldisiloxane platinum catalyst was then injected with a syringe as a solution in toluene (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, purified by several reprecipitations

**Scheme IV. Synthesis of Polymethacrylates IVP–VIP**



from a tetrahydrofuran solution into methanol and further purified by preparative GPC, and then dried under vacuum.

**E. Synthesis of Polymethacrylates IVP–VIP.** The radical polymerizations of the monomers were carried out in Schlenk tubes equipped with septa, under argon. The polymerization tube containing the dioxane solution of the monomer (10%, w/v) and the initiator (AIBN, 1 wt % vs monomer) was first degassed by several freeze–pump–thaw cycles under vacuum and then filled with argon. All polymerizations were carried out at 60 °C for 15 h. After the polymerization time, the polymers were precipitated into methanol, filtered, and purified by reprecipitation from THF solutions into methanol. The polymerization results have been summarized in Table IV.

## Results and Discussion

The synthetic route used for the preparation of monomers IM–IIIM is outlined in Scheme II. The chiral group was inserted into these mesogenic compounds starting with the commercially available (*S*)-(-)-2-methyl-1-butanol. This was done by a sequence of reactions which avoided its racemization. Three monomers were characterized by differential scanning calorimetry and optical polarizing microscopy. Representative DSC traces of monomer IIM are presented in Figure 1. Monomer IIM exhibits a melting transition at 20.5 °C, a chiral smectic C to smectic A phase transition at 72.5 °C, and a smectic A to isotropic phase transition at 140.2 °C on the heating scan (curve A). Crystallization temperature is more supercooled on the cooling scan (curve B) than the other two-phase transition temperatures. Parts A and B of Figure 2 display respectively the typical smectic A and chiral smectic C textures exhibited by IIM. Table II summarizes the thermal transitions and corresponding enthalpy changes of monomers IM–VIM. Monomer IM exhibits an enantiotropic smectic A phase and a monotropic chiral smectic C phase, while both monomers IIM and IIIM present enantiotropic smectic A and chiral smectic C phases. As can be seen from the data listed in Table II, the isotropization temperature, melting temperature, and chiral smectic C to smectic A phase temperature decrease by increasing the length of the oligooxyethylene spacer.

The synthesis of polymers IP–IIIP is described in Scheme III. An excess amount of olefinic monomers was usually used to carry the hydrosilation reaction to completion. The unreacted monomers were removed by several reprecipitations from THF solution into methanol and by preparative GPC. Therefore the polymers were isolated with high purity. The polymers were characterized by differential scanning calorimetry and optical polarizing

Table IV. Phase Transitions and Phase Transition Enthalpies for Polymers IVP-VIP

polymer	$n^a$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	phase transitions, °C (corresponding enthalpy changes, kcal/mru) <sup>b</sup>	
					heating	cooling
IVP	1	10 386	16 872	1.62	G 35.3 S <sub>A</sub> 159.4 (0.26) I	I 139.2 (0.25) S <sub>A</sub> 35.2 G
VP	2	12 382	19 083	1.54	G 17.8 S <sub>A</sub> 130.6 (0.39) I	I 127.8 (0.51) S <sub>A</sub> 21.8 G
VIP	3	11 957	19 480	1.63	G -7.7 S <sub>C</sub> * 120 (-) S <sub>A</sub> 154.8 (1.15) I	I 133.1 (0.78) S <sub>A</sub> 114 (-) S <sub>C</sub> * -10.6 G

<sup>a</sup>  $n$  according to Scheme IV. <sup>b</sup> mru = mole repeating unit, G = glassy, S<sub>A</sub> = smectic A, S<sub>C</sub>\* = chiral smectic C, I = isotropic.

microscopy. Figure 3 presents the representative DSC heating and cooling traces of polymer IP. On the heating scan (curve A), it shows a glass transition temperature ( $T_g$ ) at 9.8 °C followed by a chiral smectic C to smectic A phase transition at 215.2 °C and a smectic A to isotropic phase transition at 234.6 °C. The cooling scan (curve B) looks almost identical to the heating scan, except that a very small supercooling (less than 5 °C) is observed for both exothermic transitions. Parts A and B of Figure 4 display respectively the smectic A and chiral smectic C textures exhibited by IP. Table III summarizes the thermal transitions and corresponding enthalpy changes of polymers IP-IIIP. All the polymers present enantiotropic chiral smectic C and smectic A phases. The existence of the chiral smectic C phase for these polymers was also proved by X-ray diffraction measurements. Figure 5 presents the temperature-dependent X-ray diffraction diagrams obtained from the powder sample of IIP at 160, 130, 100, and 70 °C. Since the maximum measuring temperature for the X-ray instrument used in this study is 170 °C, it is not able to obtain the diffraction patterns of a polymer at its smectic A phase. The diffraction patterns obtained at four different temperatures look almost the same. A broad reflection at wide angles (associated with the lateral packings) and a sharp reflection at low angles (associated with the smectic layers) are respectively shown by all curves. Only their  $d$ -spacings are different. The layer spacing decreases with decreasing the measuring temperature. This indicates the existence of the chiral smectic C phase because the tilt angle of the side chains usually increases with decreasing the temperature for a chiral smectic C side-chain LCP.

The synthetic procedures for methacrylate monomers are outlined in Scheme II. Again all reaction steps were performed with retention of the configuration of the chiral end groups. The thermal transitions and thermodynamic parameters of monomers IVM-VIM are also reported in Table II. Both monomers IVM and VM show only an enantiotropic smectic A phase, while VIM presents both enantiotropic chiral smectic C and smectic A phases. The results demonstrate that the tendency toward chiral smectic C mesomorphism increases by increasing the length of the oligooxyethylene spacer for these monomers.

The synthesis of polymers IVP-VIP is described in Scheme IV. The results of the radical polymerization of the monomers are summarized in Table IV. The molecular weights of these polymers were determined by GPC using a calibration based on polystyrene standards and therefore have only a relative meaning. The thermal transitions and thermodynamic parameters of polymers IVP-VIP are also reported in Table IV. All three polymers present smectic mesomorphism. Both polymers IVP and VP show respectively a glass transition temperature at 35.3 °C and 17.8 °C and an enantiotropic smectic A phase. Polymer VIP shows a glass transition temperature at -7.7 °C and the enantiotropic chiral smectic C and smectic A phases. Upon comparison of the thermal transitions of polymethacrylates IVP-VIP with those of polysiloxanes IP-

Table V. Influence of the Polymer Backbone and Spacer on the Chiral Smectic C Temperature Breadth of Polymers

polymer	polymer backbone and spacer	temp breadth of chiral smectic C phase (°C)
IP	$\begin{array}{c} \text{CH}_3 \\   \\ (-\text{SiO}-)_n \\   \\ \text{CH}_2 \\   \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2- \end{array}$	205.4
IIP	$\begin{array}{c} \text{CH}_3 \\   \\ (-\text{SiO}-)_n \\   \\ \text{CH}_2 \\   \\ \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2 \end{array}$	239.2
IIIP	$\begin{array}{c} \text{CH}_3 \\   \\ (-\text{SiO}-)_n \\   \\ \text{CH}_2 \\   \\ \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_3 \end{array}$	193.1
IVP	$\begin{array}{c} \text{CH}_3 \\   \\ (-\text{CH}_2\text{C}-)_n \\   \\ \text{C} \\ // \quad \backslash \\ \text{O} \quad \text{OCH}_2\text{CH}_2- \end{array}$	0
VP	$\begin{array}{c} \text{CH}_3 \\   \\ (-\text{CH}_2\text{C}-)_n \\   \\ \text{C} \\ // \quad \backslash \\ \text{O} \quad (\text{OCH}_2\text{CH}_2)_2 \end{array}$	0
VIP	$\begin{array}{c} \text{CH}_3 \\   \\ (-\text{CH}_2\text{C}-)_n \\   \\ \text{C} \\ // \quad \backslash \\ \text{O} \quad (\text{OCH}_2\text{CH}_2)_3 \end{array}$	127.7

IIIP, a flexible polymer backbone can be seen here to have a tendency toward having a lower glass transition and a wider mesomorphic temperature range. The most important tendency is that the flexible polymer backbone also leads to a wider temperature range of the chiral smectic C phase. Table V presents the data illustrating the chiral smectic C temperature breadth of all polymers prepared in this study. As can be seen from the data reported in Table V, all the synthesized polysiloxanes with flexible oligooxyethylene spacers reveal a very wide temperature range of the chiral smectic C phase. Nevertheless, among the three prepared polymethacrylates with flexible oligooxyethylene spacers, VIP is the only one that presents a chiral smectic C phase and its chiral smectic C temperature range is smaller than that of its corresponding polysiloxane. The results demonstrate that the flexibility of the polymer backbone has a pronounced effect on the thermal stability of the chiral smectic C phase.

In conclusion, a series of new side-chain liquid crystalline polysiloxanes and polymethacrylates containing oligooxyethylene and 4-(*S*)-2-methyl-1-butyl [(4-hydroxybiphenyl-4'-yl)carbonyl]oxy]benzoate side groups have been prepared. All the obtained polymers exhibit smectic



mesomorphism. The nature of the flexible oligooxyethylene spacer plays a very important role in the thermal stability of the chiral smectic C phase. The flexibility of the polymer has an even more profound effect on the thermal stability of the chiral smectic C phase. A flexible polymer backbone enhances the decoupling of the motions of the side chain and main chain and therefore tends to give rise to a higher thermal stability of the mesophases, including the chiral smectic C phase.

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