tert-butyl-2-methylcyclohexanone and methyl vinyl ketone as described previously.[5] The ^{13}C and ^{1}H NMR data are summarized in Tables I and III, respectively.

6α-*tert*-Butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (6) and 6β-*tert*-Butyl-9β-hydroxy-10β-methyl-2-decalone (7). To 5.00 g (29.7 mol) of 4-*tert*-butyl-2-methylcyclohexanone at 0 °C was added 1 mL of 3.5 M ethanolic sodium ethoxide followed by the dropwise addition of 2.52 g (36 mol) of freshly distilled methyl vinyl ketone. A second 1 mL of 3.5 M sodium ethoxide was then added, followed by the dropwise addition of an additional 0.5 g of methyl vinyl ketone and the reaction mixture was allowed to stand at −13 °C for 72 h. After warming to ambient temperature, the reaction mixture was partitioned between ether and saturated aqueous NH_4Cl. The aqueous phase was extracted with ether, and the combined etheral extracts were washed with brine and dried and the solvent was removed to give 6.73 g of a viscous oil. Flash chromatography[26] on silica gel with ether–hexanes as eluent gave 0.246 (4%) of 6α-*tert*-butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (**6**) as a colorless oil which was homogeneous to GLC, but which slowly decomposed on standing: IR 1668, 1620 cm^{-1}; UV λ_{max} 238 (log ϵ 4.10); mass spectrum *m/e* (relative intensity) 220 (100), 205 (13), 192 (28), 178 (30, 164 (53), 163 (50); ^{1}H NMR δ 0.80 (s, 9 H, $C(CH_3)_3$), 1.15 (s, 3 H, CH_3), 5.64 (s, =CH). The ^{13}C NMR data and the balance of the ^{1}H data are summarized in Tables I and II, respectively.

The semicarbazone formed white crystals from methanol, mp 204–206 °C. Anal. Calcd for $C_{16}H_{26}N_3O$: C, 69.28; H, 9.81; N, 15.15. Found: C, 69.07; H, 9.83; N, 15.07.

The more polar material from the original reaction mixture was dissolved in ethyl acetate–benzene (5:95) and chromatographed on silica gel. Elution with ethyl acetate–benzene (3:7) gave, after recrystallization from hexanes, 0.794 g (11%) of ketol **7**. The analytical sample: mp 139–141 °C crystallized from hexanes; IR 3496, 1701 cm^{-1}; H NMR δ 0.86 (s, 9 H, $C(CH_3)_3$, 1.20 (s, 3 H, CH_3); mass spectrum *m/e* (relative intensity) 238 (5), 220 (2), 168 (100), 126 (24), 125 (24), 112 (19). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.62; H, 11.02.

6β-*tert*-Butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (5). To a solution of 0.067 g of NaOH in 7 mL of water and 14 mL of methanol was added 0.400 g of ketol **7** in 27 mL of methanol and the mixture was heated at reflux under N_2 for 23 h. The cooled reaction mixture was diluted with brine, concentrated in vacuo, and extracted with ether. The ethereal extracts were washed with brine and dried and the solvent was removed at reduced pressure to give 0.420 g of a yellow oil. Distillation (140 °C (air bath), 2.4 mm) followed by chromatography on silica gel and elution with ether–hexanes gave 0.300 g (81%) of octalone **5** contaminated with 15% of the β,γ-isomer **8**. For octalone **5**: IR 1651 cm^{-1}; UV λ_{max} 240 nm (log ϵ 4.02); ^{1}H NMR 0.79 (s, 9 H, $C(CH_3)_3$), 1.18 (s, 3 H, CH_3), 5.76 (s, 1 H, =CH). The balance of the ^{1}H NMR and ^{13}C NMR data are summarized in Tables III and I, respectively. Mass spectrum, *m/e* (relative intensity) 220 (66), 205 (7), 192 (28), 178 (19), 164 (38), 163 (54), 149 (37), 136 (53), 123 (54), 122 (58), 121 (100).

The 2,4-dinitrophenylhydrazone formed orange crystals from ethanol–ethyl acetate, mp 160–162 °C. Anal. Calcd for $C_{21}H_{18}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 62.73; H, 7.24; N, 12.68.

Nonconjugated enone **8**: IR 1710 cm^{-1}; ^{1}H NMR 80.84 (s, 9 H, $C(CH_3)_3$), 130 (s, 3 H, CH_3); mass spectrum, *m/e* (relative intensity) 220 (100), 205 (14), 192 (20), 165 (31), 164 (62), 163 (50), 149 (48), 147 (18), 146 (18), 145 (33).

Deuterium Labeling Procedures. Labeling under basic conditions was carried out using NaOD in D_2O/dioxane as described previously.[1] Labeling under acidic conditions was carried out using DCl or D_2SO_4 in diglyme also using previously described procedures.[1]

Acknowledgment. The JEOL FX-90Q NMR spectrometer was obtained through an NSF Support of Research Equipment Grant. We wish to thank R. Frank Pittman and Rod Boston for carrying out the mass spectral determinations. We especially thank Dr. David J. Goldsmith of Emory University for his assistance in obtaining the 360-MHz spectra.

Supplementary Material Available: Table II, ^{13}C chemical shifts of enones **3–6** at +50 and −50 °C, ORTEP structures of the ring B chair conformer of enone **3** and enone **5** (Figures 1 and 2), and the experimental details for the preparation of 4-*tert*-butyl-2-methylcyclohexanone (4 pages). Ordering information is given on any current masthead page.

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Synthesis of Smectic Liquid-Crystalline Polysiloxanes from Biphenylcarboxylate Esters and Their Use as Stationary Phases for High-Resolution Gas Chromatography

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Eight new liquid-crystalline compounds based on the 4-(4-hydroxyphenyl)benzoate ester have been prepared. These compounds all exhibit liquid-crystalline characteristics. The new compounds all contain an olefinic group needed for attachment to a siloxane polymer. The polysiloxanes prepared by a hydrosilylation reaction also exhibited liquid-crystalline characteristics. A copolymer prepared from equal molar amounts of two of the liquid-crystalline alkenes was found to have unique separating properties when used as a stationary phase in high-resolution gas chromatography.

A large number of polymers containing mesogenic side chains and a polysiloxane backbone have been prepared and characterized.[1-6] The use of a flexible spacer to decouple the motions of the mesogenic groups from the polymer main chain has allowed the preparation of thermotropic liquid crystals exhibiting both smectic and ne-

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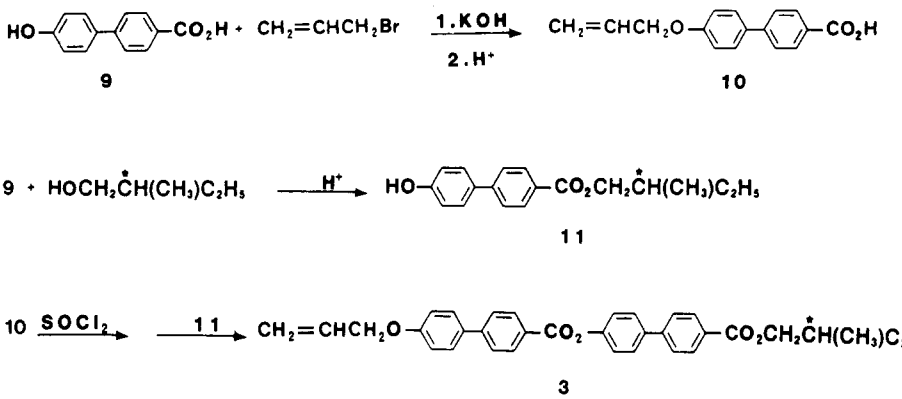
Scheme I. Preparation of Liquid-Crystalline Alkenes



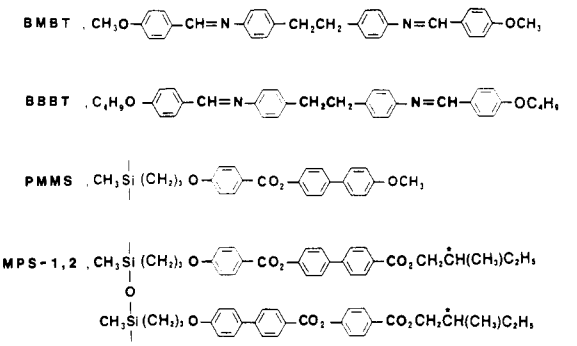
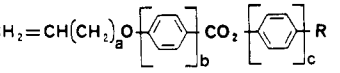


Figure 1. Liquid-crystalline stationary phases.

matic phases.[1,2] Chiral mesogens have yielded polymers showing cholesteric phases.[2,6,7] Most attempts at preparing cholesteric homopolymers have met with failure as they nearly always gave only smectic phases.[6] It was believed that chiral monomers should not exhibit the liquid-crystalline state in order to obtain cholesteric polymers from them. The first example of a cholesteric polymer was based on alkoxybenzoate esters of optically active 2-methyl-1-butanol.[6] Two cholesteric polymers were obtained, the first having transitions from 2 to 13 °C and the second from 17 to 37.5 °C.[6] The second also showed a smectic range at lower temperatures. These liquid-crystalline polysiloxane materials have not yet been used as stationary phases for gas chromatography.

Mesogenic (nematic liquid–crystalline) stationary phases which provide separations based on molecular geometry have been shown to be highly selective for polycyclic aromatic compounds (PAC).[8-11] Janini and co-workers showed that *N,N'*-bis(*p*-methoxybenzylidene)-α,α'-bi-*p*-toluidine (BMBT, see Figure 1) exhibited unique solute separations based on differences in the molecular length-to-breadth (L/B) ratio of solute geometric isomers.[8] Haky and Muschik reported the gas chromatographic properties of smectic and nematic liquid crystals in packed columns; however, these liquid crystals were not polymeric and therefore exhibited high volatility and poor column efficiencies.[11] Laub and co-workers overcame these limitations by blending liquid–crystalline compounds (BBBT, for example, Figure 1) with SE-52.[12] These materials could be used in open tubular capillary columns of concomitant high efficiency and high and adjustable selectivity. These mixed phases, however, were not useful at elevated temperatures, and the solid to nematic transition temperature was not reduced. A poly(mesogen/methyl)siloxane (PMMS) prepared by Laub and co-workers[13] with a nematic temperature range of 70–300 °C was found to separate the 1- to 6-methylchrysenes based on the L/B ratios.[14] A smectic poly(mesogen/methyl)siloxane phase has not been reported.

Table I. Alkene Liquid-Crystalline Compounds



no.	*a*	*b*	*c*	R
1	1	1	2	$COOCH_2C^*H(CH_3)CH_2CH_3$
2	1	2	1	$COOCH_2C^*H(CH_3)CH_2CH_3$
3	1	2	2	$COOCH_2C^*H(CH_3)CH_2CH_3$
4	1	2	1	OCH_3
5	1	2	2	OCH_3
6	3	2	1	$COOCH_2C^*H(CH_3)CH_2CH_3$
7	3	2	2	$COOCH_2C^*H(CH_3)CH_2CH_3$
8	3	2	1	OCH_3

It is known that the phenyl moiety stabilizes the rod-like structures necessary to compounds exhibiting liquid-crystalline behavior. Further stabilization is given by the biphenyl group.[7] In this paper we present our extension of the work of Finkelmann and Rehage[6] using biphenyl carboxylate esters as mesogenic precursors and report on a number of homopolymers showing cholesteric transitions above 200 °C. These polymers were derived from mesogenic alkenes which also exhibited liquid crystallinity. A polymer composed of two different liquid-crystalline moieties (PMPS-1,2, see Figure 1) was found to have a wide smectic range. This material was found to separate efficiently and selectively certain polycyclic aromatic compounds. The separation of other materials including chiral compounds will be reported later.

Results and Discussion

The mesogenic siloxane polymers used in this study were prepared by platinum-catalyzed alkylation of poly[oxy(methylsilylene)] with mesogenic olefins as previously reported.[1] The olefins (see Table I) were based on the 4-(4-hydroxyphenyl)benzoate moiety (**9**) prepared by the four-step procedure of Gray and co-workers.[15] The flexible

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Table II. Phase Transitions for Liquid-Crystalline Alkenes and Their Corresponding Siloxane Polymers

	phase transitions (°C)[a]	
no.	alkene	polymer
1	k 100 s 150 n* 188 i	g 130 s 214 n* 226 i
2	k 118 s 198 n* 213 i	g 190 s 235 n* 248 i
3	k 152 s 240 n* 278 i	g 149 s 254 n* 291 i
4	k 137 n 243 i	g 98 s 258 i
5	k 214 n 290 i	
6	k 105 s 198 i	g 113 s 200 i
7	k 135 s 295 n* 315 i	g 114 s 350 d
8	k 133 s 172 n 253 i	g 109 s 295 i

[a] k = crystalline; s = smectic; n = nematic; n* = cholesteric; i = isotropic; g = glassy, d = decomposition.

spacer was attached by a base-catalyzed alkylation of the phenolic oxygen with allyl bromide or 5-bromopentene (compound **10**, for example, see Scheme I). Esterification was accomplished via the acyl halide by treatment first with thionyl chloride and then with a phenol. (*S*)-2-Methyl-1-butanol esters were prepared by an acid-catalyzed reaction with phenyl and biphenyl carboxylates[6] (compound **11**, Scheme I). Specific compounds prepared are shown in Table I. Each olefin exhibited liquid-crystalline phases on melting. Transition temperatures of each alkene and its corresponding siloxane polymer are listed in Table II.

Minor variations in olefin structure such as the sequence of phenyl and biphenyl groups in **1** and **2** can cause considerable differences in transition temperatures. These variations can be seen in Table II where the transition to the smectic phase took place at 100 °C for **1** and 118 °C for **2**. The other phase transitions (to cholesteric and to isotropic) were also very different (see Table II). The phase transitions of the corresponding polysiloxane polymers were likewise very different (Table II).

The chiral alkenes having cholesteric regions had smectic phases at lower temperatures. Those alkenes with two biphenyl groups and their derived polymers had higher transition temperatures (as would be predicted) when compared with their analogues with only one biphenyl group (see Table II). As has been observed previously,[2,4-7] increasing the length of the flexible spacer (Table I) produced polymers with the more ordered smectic structures (compare **3** and **7**, Table II). Coupling of the alkenes to the polymer backbone stabilized the liquid-crystalline state, giving compounds with higher isotropic transitions than the uncoupled precursors (Table II). Polymers from **1–3** are the first examples of cholesteric homopolymers with transitions above 200 °C.

A wider range between transitions may be obtained with polymers made by blending two of these alkenes with an appropriate poly[oxy(methylsilylene)]. Such a copolymer (PMPS-1,2, Figure 1) was synthesized. This material exhibited the following phase transformations: 130 °C glass transition, 219 °C smectic to nematic transition, 235 °C nematic to isotropic transition. The polymer was tested as a stationary phase for high-resolution gas chromatography. A summary of those results are given here. A more detailed account will be given elsewhere.

Most chromatographic separations using a liquid-crystal stationary phase have been reported in the nematic range. Since both the nematic and smectic regions lead to order in the liquid crystal, with the smectic region possessing the highest order, it was decided to study the resolution of closely related polycyclic aromatic compound isomers in both regions. Figure 2 shows a plot of log α vs. temperature

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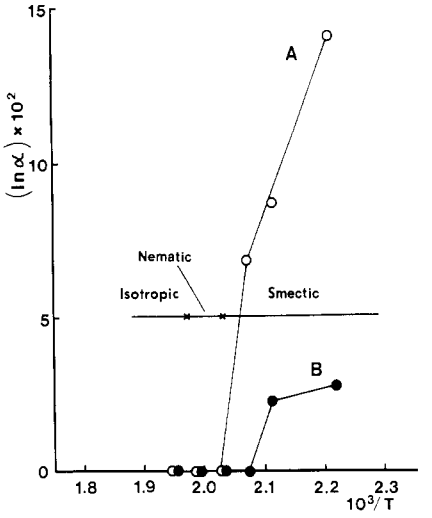

Figure 2. Dependence of separation factor (α) on column temperature (K) for separation f (A) 3-methyldibenzothiophene/1-methyldibenzothiophene and (B) 2-methyldibenzothiophen/8-methylnaphtho[1,2-*b*]thiophene on PMPS-1,2.

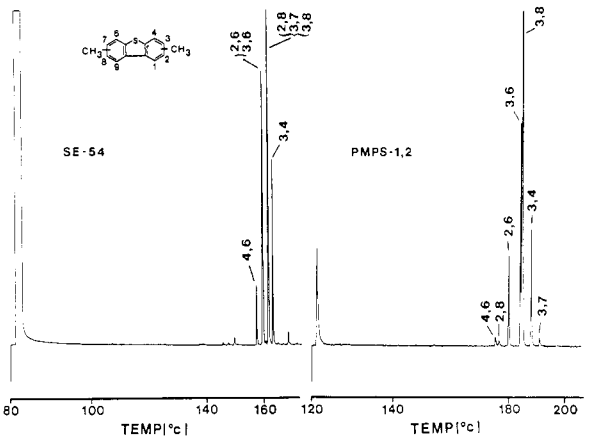

Figure 3. Chromatograms of isomeric dimethyldibenzothiophenes on SE-54 (FID) and PMPS-1,2 (FPD). Temperature was programmed from 80 °C (SE-54) and 120 °C (PMPS-1,2) at 4 °C min^{-1} with a 2-min initial isothermal period. Hydrogen gas at 100 cm/s was used as the carrier gas.

for two pairs of isomeric sulfur heterocycles, where α is the relative retention or separation number of the pair. Clearly, the separation is greatly improved by performing the chromatography within the lower temperature smectic region.

Figure 3 shows chromatograms of a number of dimethyldibenzothiophene isomers on capillary columns coated with either a nonpolar methylphenylpolysiloxane stationary phase (SE-54) or with the PMPS-1,2 polymer. The resolution is much superior when the liquid crystal polymer is used. This is a result of both the high selectivity of the column and its demonstrated high chromatographic efficiency. Columns can be easily coated with the PMPS-1,2 polymer to produce efficient columns that lead to narrow chromatographic peaks. This is a distinct advantage of this polymer over other nonpolymeric liquid-crystal stationary phases.

Additional studies are presently underway to improve the characteristics of this type of stationary phase. Different monomers are being attached to the polysiloxane backbone to broaden the smectic range of the polymer. While size and shape of the solute molecules greatly affect their separation on these phases, there is presently no clear correlation. However, these liquid-crystalline polymers appear to offer unique separations that cannot be obtained

by using any other type of stationary phase.

Experimental Section

Infrared (IR) spectra were obtained on a Beckman Acculab 2 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded by a JEOL FX90-Q spectrometer. Phase transitions were studied by differential scanning calorimetry on a Perkin-Elmer DSC-2 apparatus or by using a Thomas-Kofler hot stage microscope using cross polarizers. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter. Carbon and hydrogen analyses were performed by MHW Laboratories, Phoeniz, AZ. Chemicals were purchased from Aldrich Chemical Company except as described below: 4-Allyloxybenzoic acid (mp 160–162 °C) was prepared by the procedure of Ringsdorf and Schneller;[4] 4-(4-hydroxyphenyl)benzoic acid (**9**, mp 293–294 °C) was prepared according to the four-step procedure of Gray and co-workers.[15]

4-[4-(Allyloxy)phenyl]benzoic Acid (10, Scheme I). 4-(4-Hydroxyphenyl)benzoic acid (**9**, 10 g, 0.047 mol) was added to a solution of 6 g of potassium hydroxide in 200 mL of ethanol. Sodium iodide (0.1 g) was added and the solution was heated to reflux temperature. Allyl bromide (6.0 g, 0.049 mol) was slowly added and the solution was refluxed overnight. The solution was cooled, poured into 400 mL of water, and acidified with concentrated hydrochloric acid. The solid carboxylic acid was removed by filtration and washed with two 200-mL portions of water. Product **10** was recrystallized from acetic acid to give 7.34 g (62%) of plates: mp 214 °C to nematic, 245 °C to isotropic; IR (KBr) 1680 cm^{-1}; NMR (Me_2SO-d_6) δ 4.62 (m, 2 H, CH_2O) 4.86–5.55 (m, 2 H, vinyl H), 5.85–6.30 (m, 1 H, vinyl H), 6.96–7.80 (m, 9 H, Ar H, COOH).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.65; H, 5.61.

4-[4-(4-Pentenyloxy)phenyl]benzoic Acid. Carboxylic acid **9** (21.4 g, 0.10 mol) and 5-bromo-1-pentene (16 g, 0.11 mol) were used as in the previous procedure to give the acid product. Recrystallization from ethanol gave white crystals: 14 g (50%); mp 206 °C to nematic, 267 °C to isotropic; IR (KBr) 1680 cm^{-1}; NMR (Me_2SO-d_6) δ 1.65–1.95 (m, 2 H, CH_2), 2.0–2.3 (m, 2 H, CH_2), 4.00 (t, 2 H, CH_2O), 5.0–5.2 (m, 2 H, vinyl H), 5.6–6.1 (m, 1 H, vinyl H), 6.8–8.1 (m, 9 H, Ar H, COOH).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.38; H, 6.49.

(*S*)-2-Methyl-1-butyl 4-Hydroxybenzoate. This compound was prepared according to the procedure of Finkelmann and Rehage[6] using 4.9 g (0.036 mol) of 4-hydroxybenzoic acid, 8.1 g (0.092 mol) of (*S*)-2-methyl-1-butanol, and 0.18 mL of sulfuric acid in 5.4 mL of benzene. The mixture was refluxed until the acid dissolved (about 16 h). The resulting solution was added to 100 mL of ether and extracted with aqueous sodium bicarbonate. The dried ether layer was evaporated to give 6.5 g (93%) of the ester product: bp 170 °C (0.6 mm); $[\alpha]^{25}_D$ +5.50° (*c* 0.03 chloroform); IR (neat) 1680 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.1 (m, 6 H, CH_3), 1.1–2.0 (m, 3 H, CH_2), 4.14 (AB-d, 2 H, $COOCH_2$), 6.9–7.9 (m, 4 H, Ar H), 7.25 (s, 1 H, OH).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.15; H, 7.68.

(*S*)-2-Methyl-1-butyl 4-(4-Hydroxyphenyl)benzoate (11, Scheme I). This compound was prepared as above by using 8.1 g (37.8 mmol) of acid **9**, 10 g (113 mmol) of (*S*)-2-methyl-1-butanol, 0.18 g of sulfuric acid, and 8 mL of benzene refluxed through a water separator. After 2 days, 100 mL of ether was added and the solution was extracted twice with 10-mL portions of 5% aqueous sodium bicarbonate. The organic phase was dried over anhydrous sodium sulfate, the ether was removed, and the product was crystallized first from heptane and then from methanol to give white needles: 8.6 g (80%), mp 112–113 °C; $[\alpha]^{25}_D$ +5.70° (*c* 0.043 chloroform); IR (KBr) 1680 cm^{-1}; NMR ($CDCl_3$) δ 0.9–1.1 (m, 6 H, CH_3), 1.1–2.0 (m, 3 H, CH, CH_2), 4.20 (AB-d, 2 H, $COOCH_2$), 5.32 (s, 1 H, OH), 6.9–8.2 (m, 8 H, Ar H).

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.28; H, 7.10.

General Procedure for Esterification To Form the Liquid-Crystalline Alkenes (Scheme I). The carboxylic acid was reacted at room temperature with excess thionyl chloride containing a drop of dimethylformamide until a clear solution remained. The solvents were removed under reduced pressure to give the crude acid chloride. The product was dissolved in 25 mL of methylene chloride and slowly added to a cold solution of an equimolar amount of the appropriate phenol and excess triethylamine in 150 mL of methylene chloride. The solution was allowed to stand for 2 h and then the solvent and excess triethylamine were removed by heating over a boiling water bath. The solid thus obtained was dissolved in 100 mL of methylene chloride and filtered through 50 mL of silica gel. The silica gel was washed with an additional 100 mL of methylene chloride. The filtrate and washings were combined and the solvents were removed to give the white solid product.

4-Methoxyphenyl 4-[4-(Allyloxy)phenyl]benzoate (4). 4-[4-(Allyloxy)phenyl]benzoic acid (7.1 g, 28 mmol) and 3.4 g (27.4 mmol) of 4-methoxyphenol were used in the procedure described above. The product was recrystallized from ethanol to give white crystals: 7.8 g (80%); mp 137 °C to nematic, 243 °C to isotropic; IR (KBr) 1730 cm^{-1}; NMR ($CDCl_3$) δ 3.81 (s, 3 H, OCH_3), 4.5–4.7 (m, 2 H, CH_2), 5.2–5.6 (m, 2 H, vinyl H), 5.9–6.3 (m, 1 H, vinyl H), 6.9–8.3 (m, 12 H, Ar H).

Anal. Calcd for $C_{23}H_{20}O_3$: C, 76.65; H, 5.59. Found: C, 76.49; H, 5.63.

4′-Methoxybiphenyl-4-yl 4-[4-(Allyloxy)phenyl]benzoate (5). 4-[4-(Allyloxy)phenyl]benzoic acid, 4.0 g (16 mmol), and 3.1 g (16 mmol) of 4-(4-methoxyphenyl)phenol were used in the procedure described above. The product was recrystallized from toluene (with difficulty because of its slight solubility) to give white flakes which were not quite pure: 5.9 g (86%); mp 214 °C to nematic, 290 °C to isotropic; IR (KBr) 1730 cm^{-1}; NMR ($CDCl_3$) δ 3.83 (s, 3 H, OCH_3), 4.6 (m, 2 H, OCH_2), 5.2–5.5 (m, 2 H, vinyl H), 5.9–6.3 (m, 1 H, vinyl H), 6.9–8.3 (m, 16 H, Ar H).

Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.96; H, 5.69.

4-Methoxyphenyl 4-[4-(4-Pentenyloxy)phenyl]benzoate (8). 4-[4-(4-Pentenyloxy)phenyl]benzoic acid, 3 g (10.6 mmol), and 1.32 g (10.6 mmol) of 4-methoxyphenol were used in the procedure described above. The product was recrystallized from methanol to give 3.1 g (75%): mp 133 °C to smectic, 172 °C to nematic, 253 °C to isotropic; IR (KBr) 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.4 (m, 4 H, CH_2), 3.81 (s, 3 H, OCH_3), 4.02 (t, 2 H, OCH_2), 4.9–5.2 (m, 2 H, vinyl H), 5.6–6.1 (m, 1 H, vinyl H), 6.8–8.3 (m, 12 H, Ar H).

Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.46; H, 7.22.

(*S*)-4′-[(2-Methyl-1-butoxy)carbonyl]biphenyl-4-yl 4-(Allyloxy)benzoate (1). 4-(Allyloxy)benzoic acid, 4.81 g (27 mmol), and 7.68 g (27 mmol) of (*S*)-2-methyl-1-butyl 4-(4-hydroxyphenyl)benzoate were used in the procedure described above. The product was recrystallized from methanol to give plates: 10 g (83%); mp 100 °C to smectic, 150 °C to cholesteric, 188 °C to isotropic; $[\alpha]^{25}_D$ +3.4° (*c* 0.5, chloroform); IR (KBr) 1700, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.1 (m, 6 H, CH_3), 1.1–2.0 (m, 3 H, CH, CH_2), 4.21 (AB-d, 2 H, $COOCH_2$), 4.6–4.7 (m, 2 H, OCH_2), 5.2–5.6 (m, 2 H, vinyl H), 5.9–6.3 (m, 1 H, vinyl H), 6.9–8.3 (m, 12 H, Ar H).

Anal. Calcd for $C_{28}H_{28}O_5$: C, 75.66; H, 6.35. Found: C, 75.78; H, 6.37.

(*S*)-4-[(2-Methyl-1-butoxy)carbonyl]phenyl 4-[4-(Allyloxy)phenyl]benzoate (2). 4-[4-(Allyloxy)phenyl]benzoic acid, 3.0 g (12 mmol), and 2.3 g (12 mmol) of (*S*)-2-methyl-1-butyl 4-hydroxybenzoate were used in the procedure described above. The product was recrystallized from methanol to give 4.2 g (83%): mp 118 °C to smectic, 198 °C to cholesteric, 213 °C to isotropic; $[\alpha]^{25}_D$ +2.9° (*c* 0.5, chloroform); IR (KBr) 1710, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.1 (m, 6 H, CH_3), 1.1–2.0 (m, 3 H, CH, CH_2), 4.20 (AB-d, 2 H, $COOCH_2$), 4.5–4.7 (m, 2 H, OCH_2), 5.2–5.6 (m, 2 H, vinyl H), 5.9–6.3 (m, 1 H, vinyl H), 7.0–8.4 (m, 12 H, Ar H).

Anal. Calcd for $C_{28}H_{28}O_5$: C, 75.66; H, 6.35. Found: C, 75.81; H, 6.43.

(*S*)-4′-[(2-Methyl-1-butoxy)carbonyl]biphenyl-4-yl 4-[4-(Allyloxy)phenyl]benzoate (3, Scheme I). 4-[4-(Allyloxy)-phenyl]benzoic acid, 3 g (11.8 mmol), and 3.4 g (11.8 mmol) of (*S*)-2-methyl-1-butyl 4-(4-hydroxyphenyl)benzoate were used in the procedure described above. The product was recrystallized from ethanol to give 5.2 g (85%): mp 152 °C to smectic, 240 °C to cholesteric, 278 °C to isotropic; IR (KBr) 1710, 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.9–1.1 (m, 6 H, CH_3), 1.1–2.1 (m, 3 H, CH, CH_2), 4.20

(AB-d, 2 H, $COOCH_2$), 4.5–4.7 (m, 2 H, OCH_2), 5.2–5.6 (m, 2 H, vinyl H), 5.9–6.3 (m, 1 H, vinyl H), 6.9–8.3 (m, 16 H, ArH).

Anal. Calcd for $C_{34}H_{32}O_5$: C, 78.44; H, 6.20. Found: 78.62; H, 6.13.

(*S*)-4-[(2-Methyl-1-butoxy)carbonyl]phenyl 4-[4-(4-Pentenyloxy)phenyl]benzoate (6). 4-[4-(4-Pentenyloxy)phenyl]-benzoic acid, 3 g (11 mmol), and (*S*)-2-methyl-1-butyl 4-hydroxybenzoate, 2.1 g (11 mmol), were used in the procedure described above. The product was recrystallized from ethanol to give 3.8 g (75%): mp 105 °C to smectic, 198 °C to isotropic; $[\alpha]^{25}_D$ +2.6° (*c* 0.3, chloroform); IR (KBr) 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.9–1.1 (m, 6 H, CH_3), 1.1–2.4 (m, 7 H, CH, CH_2), 4.03 (t, 2 H, OCH_2), 4.17 (AB-d, 2 H, $COOCH_2$), 4.9–5.2 (m, 2 H, vinyl H), 5.6–6.1 (m, 1 H, vinyl H), 6.9–8.3 (m, 12 H, Ar H).

Anal. Calcd for $C_{30}H_{32}O_5$: C, 76.25; H, 6.83. Found: C, 76.54; H, 6.94.

(*S*)-4′-[(2-Methyl-1-butoxy)carbonyl]biphenyl-4-yl 4-[4-(4-Pentenyloxy)phenyl]benzoate (7). 4-[4-(4-Pentenyloxy)-phenyl]benzoic acid, 3 g (11 mmol), and (*S*)-2-methyl-1-butyl 4-(4-hydroxyphenyl)benzoate, 3 g (11 mmol) were used in the procedure described above. The product was recrystallized from ethanol to give 3.3 g: 57%; mp 135 °C to smectic, 295 °C to cholesteric, 315 °C to isotropic; $[\alpha]^{25}_D$ +2.7° (*c* 0.5, chloroform); IR (KBr) 1710, 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.9–1.1 (m, 6 H, CH_3), 1.1–2.4 (m, 7 H, CH, CH_2), 4.04 (t, 2 H, OCH_2), 4.21 (AB-d, 2 H, $COOCH_2$), 4.9–5.2 (m, 2 H, vinyl H), 5.7–6.1 (m, 1 H, vinyl H), 6.9–8.3 (m, 16 H, Ar H).

Anal. Calcd for $C_{36}H_{36}O_5$: C, 78.81; H, 6.61. Found: C, 78.70; H, 6.55.

General Procedure for the Preparation of Mesogenic Polymers. Poly[oxy(methylsilylene)] (Petrarch, 2250 ave molecular weight), 50 mg (0.83 mmol of SiH), and 0.83 mmol of olefin were combined and 2 mL of toluene was added. Chloroplatinic acid, 0.2 mL (0.1 M), in 2-propanol was added, and the solution was heated at 80 °C for 16 h. The polymers were obtained by precipitation with an equal volume of methanol. The products were purified by dissolving them in 1 mL of methylene chloride and precipitating with 2 mL of methanol. This process was repeated 2 times. The product was dried at 80 °C under vacuum for 24 h. The melting characteristics of the polymers are shown in Table I. A polymer was not obtained with monomer **5** because of its limited solubility in any common solvent. A copolymer containing equal amounts of **1** and **2** substituents (PMPS-1,2) was prepared as above from equal amounts of alkenes **1** and **2** and the appropriate amount of poly[oxy(methylsilylene)]. PMPS-1,2 had the following phase transitions: 130 °C glass to smectic, 219 °C smetic to nematic, and 235 °C nematic to isotropic.

Procedure for Testing Stationary-Phase PMPS-1,2. Untreated fused silica columns, 18 m by 0.3 mm i.d. (Hewlett-Packard, Avondale, PA), were statically coated with a 0.25 μm film of SE-54 (a 5% phenyl, 94% methyl, 1% vinyl silicone) or with PMPS-1,2 as was previously described.[16] The SE-54 phase was cross-linked with azo-*tert*-butane.[17] Both columns were conditioned overnight at 280 °C under a nitrogen flow. A Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector and a flame photometric detector was used. Hydrogen gas at 100 cm s^{-1} was used as the carrier gas. The solute standards were obtained commercially or were synthesized. Figure 3 shows the chromatograms for one specific separation.

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Registry No. 1, 93001-02-6; 2, 93001-03-7; 3, 93001-04-8; 4, 93039-02-2; 5, 93001-05-9; 6, 93001-06-0; 7, 93001-07-1; 8, 93001-08-2; 9, 58574-03-1; 10, 93001-09-3; 11, 91577-91-2; allyl bromide, 106-95-6; 4-[4-(4-pentenyloxy)phenyl]benzoic acid, 93001-10-6; 5-bromo-1-pentene, 1119-51-3; (*S*)-2-methyl-1-butanol, 1565-80-6; 4-hydroxybenzoic acid, 99-96-7; 4-methoxyphenol, 150-76-5; 4-(4-methoxyphenyl)phenol, 16881-71-3; (*S*)-2-methyl-1-butyl 4-(4-hydroxyphenyl)benzoate, 91577-91-2; 3-methyldibenzothiophene, 16587-52-3; 1-methyldibenzothiophene, 31317-07-4; 2-methyldibenzothiophene, 20928-02-3; 8-methylnaphtho[1,2-*b*]thiophene, 93001-11-7.

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^{31}P NMR Study of the Mechanism of Activation and Coupling Reactions in the Synthesis of Oligodeoxyribonucleotides by the Phosphotriester Method

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The phosphotriester method provides a rapid and convenient procedure for synthesizing oligonucleotides. The mechanism has been revealed and intermediates have been identified by ^{31}P NMR methodology. It was found that reaction of a 5′-protected nucleoside 3′-(*p*-chlorophenyl phosphate) with mesitylenesulfonyl chloride (MSCl) or 1-(mesitylyl-2-sulfonyl)-3-nitro-1,2,4-triazole (MSNT) in anhydrous pyridine yields only two products within 5 min, the sulfonic acid–phosphate mixed anhydride **2** and the (3′-3′) symmetrical pyrophosphate tetraester **3** which can be isolated as a mixture. Reaction of **2** and **3** with 3′-*O*-acetylthymidine yields the phosphotriester dimer $[(MeO)_2Tr]NpTOAc$. The reaction rate and yield of dimers are closely dependent on the presence of catalysts. The reaction finished within minutes when tetrazole or 3-nitro-1,2,4-triazole was used. On the contrary, the reaction completed in hours when imidazole or 1,2,4-triazole was used as catalysts. The possible mechanisms are explored and discussed in detail.

The phosphotriester method provides a rapid and convenient procedure for the synthesis of oligonucleotides.[1-4] An important step in the synthesis of oligonucleotides by the phosphotriester approach involves activation of a phosphodiester group with a suitable condensing agent and subsequent condensation with a nucleoside 5′-hydroxyl group to form a new internucleotide linkage. Arenesulfonyl

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