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SYNTHESIS AND CHROMATOGRAPHIC PROPERTIES OF POLYSILOXANE STATIONARY PHASES CONTAINING BIPHENYLCARBOXYLATE ESTER LIQUID-CRYSTALLINE SIDE GROUPS

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SUMMARY

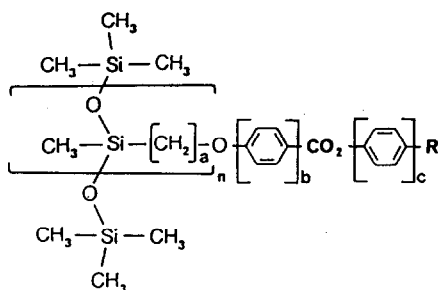
Ten new liquid-crystalline alkene compounds based on the biphenylcarboxylate ester have been prepared. Some of these alkenes, along with liquid-crystalline alkenes previously reported, were attached to polysiloxane polymers and tested as stationary phases in capillary column gas chromatography. The phase containing nearly 50% substitution with the biphenylcarboxylate ester side groups which were each separated from the polysiloxane backbone by a three-carbon and an ether-oxygen spacer proved to have the best chromatographic properties.

INTRODUCTION

Stationary phase containing liquid-crystalline functional groups provide unique selectivity for the gas chromatographic separations of many types of compounds. Until quite recently, the liquid-crystalline phases were inefficient and unstable at high temperatures. Previous studies of these types of phases up to 1984 have been reviewed¹⁻⁴.

Modern synthetic methods⁵ have allowed the preparation of polysiloxanes containing liquid crystal substituents which are both efficient and stable at relatively high temperatures. The first polysiloxane liquid-crystalline stationary phase (polymer 1, Fig. 1), named MEPSIL (mesomorphic polysiloxane) by Laub and co-workers^{2,6}, was found to be stable up to 300°C, and it was used to separate the 1- to 6-methylchrysenes according to length-to-breadth (*L/B*) ratio⁷. This polymer was prepared by hydrosilylating a polyhydromethylsiloxane with an alkene-containing liquid-crystalline compound using a platinum catalyst^{2,6}. Jones *et al.*¹ prepared a series of mesomorphic polysiloxanes based on biphenylcarboxylate ester liquid crystals (polymers 2-10, Fig. 1). These polymers proved to have mainly high order smectic liquid-crystalline characteristics. Indeed, a polymer prepared from equal amounts of two liquid-crystalline alkenes (polymer 10) gave better resolution of methyl dibenzothiophenes in the smectic region than in the nematic¹.

Some of the polymers shown in Fig. 1 have proven to be excellent stationary phases for the separation of a variety of materials. Apfel *et al.*² have shown that

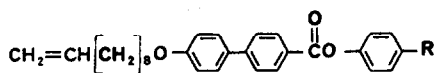
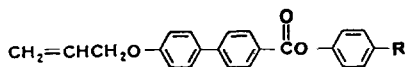


Compound	a	b	c	R
1	3	1	2	OCH ₃
2	3	2	1	OCH ₃
3	5	2	1	OCH ₃
4	3	2	2	OCH ₃
5	3	1	2	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
6	3	2	1	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
7	3	2	2	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
8	5	2	1	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
9	5	2	2	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
10	50% 3	1	2	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
	50% 3	2	1	CO ₂ CH ₂ C [*] H(CH ₃)CH ₂ CH ₃
11	50% 3	2	1	OCH ₃
	50% 5	2	1	OCH ₃

Fig. 1. Structures of reported liquid-crystalline polysiloxane stationary phases.

polymer 1 effectively separates three-, four- and five-ring polynuclear aromatic hydrocarbons (PAHs). Polymer 10 separated the isomers of dimethyldibenzothiophene with almost baseline resolution¹. Polymer 11 with a smectic range of 100 to 300°C showed unsurpassed selectivity for various isomeric polycyclic aromatic compounds including the methylphenanthrenes, methylchrysenes, hydroxydibenzothiophenes, aminophenanthrenes, three-ring nitrogen heterocycles and four-ring PAHs³. A real-world separation of PAHs in a coal tar sample using polymer 11 which contained 75% methyl and 25% of a 50:50 mixture of liquid crystal substituents, showed much improved resolution of the various PAHs over separations exhibited by SE-54⁴. Thus, continued work with these improved liquid-crystalline phases is important.

This paper reports the synthesis of additional liquid-crystalline alkenes based on the biphenylcarboxylate ester or amide structures (Fig. 2). More importantly, the properties of polysiloxanes prepared from these new liquid crystals as well as from the previously reported liquid-crystalline alkenes¹ are reported. Polymer 2, containing 48% of the liquid crystal, has been shown to possess the best chromatographic properties of any liquid-crystalline phase we have tested.

12, R - OCH₃13, R - CO₂CH₂C^{*}H(CH₃)CH₂CH₃14, R - CO₂PC₆H₄OCH₃

15, R - CN

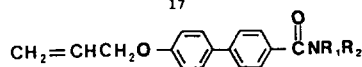
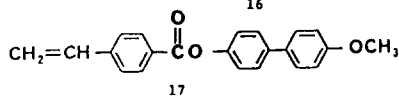
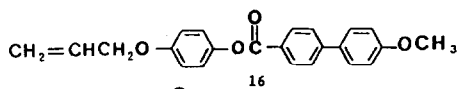
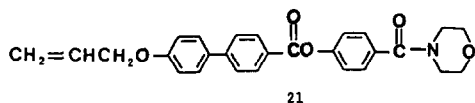
18, R₁ - H, R₂ - pC₆H₄OCH₃19, R₁ - C₂H₅, R₂ - pC₆H₄OCH₃20, R₁ - CH₃, R₂ - C₆H₅

Fig. 2. New liquid crystalline alkenes prepared in this study.

EXPERIMENTAL

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 with cross polarizers. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter. Carbon and hydrogen analyses were performed by MHW Labs. (Phoenix, AZ, U.S.A.). Gel permeation chromatography with Ultra Styragel (10⁶-10⁷ Å) columns (Waters Assoc., Milford, MA, U.S.A.) was used to determine the molecular weight distribution of the polymers and for fractionation/purification. Chemicals were purchased from Aldrich except as indicated. The 4-[4-(9-decenyloxy)phenyl]benzoic acid⁴, (S)-2-methyl-2-butyl-4-hydroxybenzoate¹, 4-(4-allyloxyphenyl)benzoic acid¹, 4-(4-methoxyphenyl)benzoic acid⁸ and 4-vinylbenzoic acid⁹ starting materials were prepared as reported. The 20 000 $\overline{\text{MW}}$ 25% hydro-containing polymethylhydrosiloxane used in this study was prepared as reported⁴. The 2270 $\overline{\text{MW}}$ 50% hydro-containing polymethylhydrosiloxane was purchased from Petrarch and used

without purification. The 5000 $\overline{\text{MW}}$ 50% hydro-containing polymer was obtained by dissolving 20 g of the Petrarch 2270 $\overline{\text{MW}}$ polymer in 40 ml of benzene and precipitating the polymer with 75 ml of methanol. The resulting polymer was dissolved in benzene and precipitated with methanol two or three more times. The 1000 $\overline{\text{MW}}$ 25% hydro-containing polymer was purchased from Petrarch. Other starting materials were prepared as outlined below.

*4'-Methoxyphenyl 4-hydroxybenzoate*¹⁰. A mixture of 4.9 g (36 mmol) of 4-hydroxybenzoic acid, 4.96 g (40 mmol) of 4-methoxyphenol, ten drops of sulfuric acid, and 20 ml of benzene was refluxed for six days. Water was removed with a Dean Stark trap. The reaction was monitored by thin-layer chromatography, and when the 4-hydroxybenzoic acid was reacted, the solid product was filtered from the mixture. The crude product dissolved in 250 ml of diethyl ether was washed with saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Then 150 ml of ether were slowly distilled while 100 ml of hexane were added to give 7.58 g (86%) of white crystals: m.p. 190–193°C; IR (KBr) 3390, 1700 cm^{-1} ; NMR (DMSO- d_6) δ 3.18 (s, 1H, OH), 3.57 (s, 3H, CH₃), 6.6–7.1 (m, 6H, ArH), 7.65–7.9 (m, 2H, ArH). This material was used to prepare compound 14 without further purification.

4-Allyloxyphenol. Hydroquinone (11.0 g, 0.1 mol) was dissolved in 100 ml of acetone, then potassium carbonate (13.8 g, 0.1 mol) and allylbromide (8.65 ml, 0.1 mol) were added. The mixture was stirred at room temperature for 2.5 days, then it was diluted with 100 ml of water and the acetone was evaporated under vacuum. A solution of 6 g of sodium hydroxide in 200 ml of water was added and the mixture was extracted with two 40-ml portions of methylene chloride. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with four 30-ml portions of methylene chloride. The extracts were washed with brine, dried over magnesium sulfate, decolorized with Norite, filtered, and the solvent was evaporated. The crude product was chromatographed on 15 g of silica gel with diethyl ether–hexane (1:2) to give 2.47 g (16.5%) of a light brown solid: m.p. 31–38°C (lit.¹¹ m.p. 43°C); NMR (C²HCl₃) δ 4.46 (d, t, $J = 5.5/1.5$ Hz, 2H, CH₂O), 5.12 (s, 1H, OH), 5.1–5.2 (m, 2H, CH₂=C), 6.02 (d, d, t, $J = 17.5/10/5.5$ Hz, 1H, CH=C), 6.64–6.88 (m, 4H, ArH). This material was used without further purification for the synthesis of compound 16.

N-Ethyl-4-methoxyaniline. Finely ground *p*-anisidine (10 g, 81.3 mmol) was slowly added to 60 ml of acetic anhydride in an ice bath. The mixture was stirred for 2 h at room temperature and then poured into 600 ml of brine. This mixture was stirred until the brown oil dissolved and grey crystals were obtained. The product was filtered, washed with water, dried, and recrystallized from ethanol–diethyl ether to give 13.4 g (90+%) of light grey crystals: m.p. 124–126°C; IR (KBr) 1640, 1650 cm^{-1} ; NMR (C²HCl₃) δ 2.10 (s, 3H, CH₃CO), 3.76 (s, 3H, CH₃O), 6.7–6.9 (m, 2H, ArH), 7.25–7.45 (m, 2H, ArH), 8.04 (s, broad, 1N, NH). This amide was reduced according to the procedure described by Wilson and Stenberg¹² to give the product aniline as a light yellow oil (57%): b.p. 138–139°C/14 mmHg; NMR (C²HCl₃) δ 1.18 (t, $J = 7$ Hz, 3H, CH₃), 3.06 (q, $J = 7$ Hz, 2H, CH₂), 3.23 (s, broad, 1H, NH), 3.70 (s, 3H, CH₃O), 6.4–6.82 (m, 4H, ArH). This material was used without further purification to prepare compound 19.

*4-Hydroxybenzomorpholide*¹³. *n*-Butyllithium (16.9 ml, 2.60 *M* in hexane, 44

mmol) was added to an ice cold solution of 4.2 ml (48 mmol) of morpholine in 40 ml of tetrahydrofuran. A slightly yellow precipitate formed. The mixture was stirred for 0.5 h at 0°C, then a solution of 3.04 g (44 mmol) of methyl 4-hydroxybenzoate in 20 ml of tetrahydrofuran was added dropwise. The white suspension thus obtained was stirred at room temperature for 1 h and then poured into 50 ml of 2 *M* hydrochloric acid. The organic layer was washed with brine, and the water phase was extracted twice with methylene chloride. The combined organic phases were dried over magnesium sulfate, decolorized with Norite, filtered, and concentrated. The light yellow solid product was recrystallized from methylene chloride and diethyl ether to give 3.21 g (78%) of white crystals: m.p. 144–146°C; IR (KBr) 3200 (broad), 1610 cm^{-1} ; NMR (C^2HCl_3) δ 3.68 (s, 8H), 6.74 (d, $J=8.5$ Hz, 2H), 7.24 (d, $J=8.5$ Hz, 2H), 9.03 (s, 1H). Analytically calculated for $\text{C}_{11}\text{H}_{13}\text{NO}_3$: C, 63.76; H, 6.32. Found: C, 63.66; H, 6.51.

General procedure for the preparation of liquid-crystalline alkene esters or amides (12–21)

The appropriately substituted biphenylcarboxylic acid (20 mmol), one drop of dimethylformamide, and 15 ml of distilled thionylchloride were stirred at room temperature for 3–4 h giving a clear light yellow solution. The excess thionylchloride was removed under vacuum. Toluene (20 ml) was added and then removed under vacuum to remove any residual thionylchloride. The white or slightly colored acid chloride was dissolved in 50 ml of dry methylene chloride and added dropwise to an ice cooled solution of 20 mmol of the substituted phenol or aniline and 30 mmol of triethylamine in 50 ml of dry methylene chloride under a nitrogen atmosphere. The reaction mixture was stirred at 0°C for 1 h and then washed with 2 *M* hydrochloric acid followed by a saturated sodium bicarbonate solution. The aqueous phases were extracted with two portions of methylene chloride. The combined organic phases were dried over anhydrous magnesium sulfate and decolorized with Norite. The resulting product was recrystallized. Specific details are given for each product.

4-Methoxyphenyl 4-[4-(9-decenyloxy)phenyl]benzoate (12). 4-[4-(9-Decenyloxy)phenyl]benzoic acid⁴ (2.91 g) and 1.03 g of 4-methoxyphenol were used. The product was recrystallized from methylene chloride–methanol to give 2.84 g (75%) of white crystals: m.p. 88°C to smectic, 158°C to nematic, 187°C to isotropic; IR (KBr) 1737 cm^{-1} ; NMR (C^2HCl_3) δ 1.15–2.2 [m, 14H, $(\text{CH}_2)_7$], 3.84 (s, 3H, OCH_3), 4.03 (t, $J=5.5$ Hz, 2H, $\text{CH}_2\text{-O}$), 4.85–5.15 (m, 2H, vinyl H), 5.6–6.1 (m, 1H, vinyl H), 6.8–7.3 (m, 6H, ArH), 7.45–7.8 (m, 4H, ArH), 8.05–8.4 (m, 2H, ArH). Analytically calculated for $\text{C}_{30}\text{H}_{34}\text{O}_4$: C, 78.57; H, 7.47. Found: C, 78.69; H, 7.66.

(S)-4-[(2-Methyl-1-butoxy)carbonyl]phenyl 4-[4-(9-decenyloxy)phenyl]benzoate (13). 4-[4-(9-Decenyloxy)phenyl]benzoic acid⁴ (1.30 g) and 0.77 g of (*S*)-2-methyl-1-butyl 4-hydroxybenzoate¹ were used. The product was recrystallized from methylene chloride–methanol to give 1.81 g (90%) of white waxy crystals: m.p. 46°C to smectic, 168°C to isotropic; IR (KBr) 1719, 1735 cm^{-1} ; NMR (C^2HCl_3) δ 0.96 (t, $J=6.5$ Hz, 3H, CH_3), 1.03 (d, $J=7$ Hz, 3H, CH_3), 1.2–2.2 [m, 17H, $(\text{CH}_2)_7$ and CH-CH_2], 4.03 (t, $J=6.5$ Hz, 2H, $\text{CH}_2\text{-O}$), 4.05–4.30 (m, 2H, CH_2O), 4.84–5.16 (m, 2H, vinyl H), 5.84 (d, d, t, $J=10/12/7$ Hz, 1H, vinyl H), 7.02 (d, $J=8.5$ Hz, 2H, ArH), 7.33 (d, $J=9$ Hz, 2H, ArH), 7.61 (d, $J=8.5$ Hz, 2H, ArH), 7.73 (d, $J=8.5$ Hz, 2H, ArH), 8.16 (d, $J=9$ Hz, 2H), 8.26 (d, $J=8.5$ Hz, 2H, ArH); $[\alpha]_D^{25} + 2.4$ (c

0.5, chloroform). Analytically calculated for $C_{35}H_{42}O_5$: C, 77.46; H, 7.80. Found: C, 77.29; H, 7.85.

4-(4-Methoxyphenoxy)phenyl 4-[4-(allyloxy)phenyl]benzoate (14). 4-(4-Allyloxyphenyl)benzoic acid¹ (2.54 g) and 2.44 g of 4'-methoxyphenyl 4-hydroxybenzoate¹⁰ were used. The product was recrystallized from methylene chloride-methanol to give 4.2 g (87%) of white crystals, which were not quite pure: m.p. 158°C to smectic, 210°C to nematic, >350°C to isotropic; IR (KBr) 1740, 1602, 1510 cm^{-1} ; NMR (C^2HCl_3) δ 3.84 (s, 3H, CH_3), 4.62 (dxt, $J=5.5/1.5$ Hz, 2H, CH_2), 5.2-5.6 (m, 2H, vinyl H), 6.08 (d, d, t, $J=17/10.5/5$ Hz, 1H, vinyl H), 6.96 (d, $J=9$ Hz, 2H, ArH), 7.04 (d, $J=8$ Hz, 2H, ArH), 7.15 (d, $J=9$ Hz, 2H, ArH), 7.39 (d, $J=8.5$ Hz, 2H, ArH), 7.62 (d, $J=8$ Hz, 2H, ArH), 7.72 (d, $J=8.5$ Hz, 2H, ArH), 8.26 (d, $J=8.5$ Hz, 2H, ArH), 8.30 (d, $J=8.5$ Hz, 2H, ArH).

4-Cyanophenyl 4-[4-(allyloxy)phenyl]benzoate (15). 4-(4-Allyloxyphenyl)benzoic acid¹ (1.78 g) and 0.88 g of 4-cyanophenol were used. The product was recrystallized from methylene chloride-methanol and then from toluene to give 1.9 g (76%) of white crystals: m.p. 159-160°C to nematic, 249°C to isotropic; IR (KBr) 2234, 1736 cm^{-1} ; NMR (C^2HCl_3) δ 4.60 (d, t, $J=5/1.5$ Hz, 2H, CH_2), 5.2-5.6 (m, 2H, vinyl H), 6.08 (d, d, t, $J=17/10/5$ Hz, 1H, vinyl H), 6.90-7.15 (m, 2H, ArH), 7.25-7.47 (m, 2H, ArH), 7.47-7.85 (m, 6H, ArH), 8.10-8.30 (m, 2H, ArH).

4-Allyloxyphenol 4-[4-(methoxy)phenyl]benzoate (16). 4-(4-Methoxyphenyl)benzoic acid⁸ (3.42 g) and 2.33 g 4-allyloxyphenol² were used. The product was recrystallized from methylene chloride-methanol to give 4.42 g (82%) of white plates: m.p. 123°C to smectic, 130°C to nematic, 236°C to isotropic; IR (KBr), 1729 cm^{-1} ; NMR (C^2HCl_3) δ 3.85 (s, 3H, CH_3), 4.53 (d, t, $J=5/1.5$ Hz, 2H, CH_2), 5.15-5.55 (m, 2H, vinyl H), 6.03 (d, d, t, $J=17.5/10/5$ Hz, 1H, vinyl H), 6.80-7.20 (m, 6H, ArH), 7.45-7.75 (m, 4H, ArH), 8.05-8.30 (m, 2H, ArH). Analytically calculated for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.45; H, 5.71.

4'-Methoxybiphenyl-4-yl 4-vinylbenzoate (17). 4-Vinylbenzoic acid⁹ (2.22 g) and 3.0 g of 4-hydroxy-4'-methoxybiphenyl were used. The product was recrystallized from methylene chloride-methanol and then from toluene to give 3.33 g (67%) of white plates: m.p. 163°C to smectic, 295°C to isotropic; IR (KBr) 1732, 1609, 1499 cm^{-1} ; NMR (C^2HCl_3) δ 3.84 (s, 3H, CH_3), 5.40 (d, d, $J=11/0.7$ Hz, 1H, vinyl H), 5.88 (d, d, $J=18/0.7$ Hz, 1H, vinyl H), 6.77 (d, d, $J=18/11$ Hz, 1H, vinyl H), 6.85-7.05 (m, 2H, ArH), 7.10-7.33 (m, 2H, ArH), 7.35-7.65 (m, 6H, ArH), 8.0-8.25 (m, 2H, ArH). Analytically calculated for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.80; H, 5.51.

N-(4-Methoxyphenyl) 4-[4-(allyloxy)phenyl]benzamide (18). 4-(4-Allyloxyphenyl)benzoic acid¹ (2.38 g) and 1.23 g of 4-methoxyaniline were used. The solvents were distilled from the reaction mixture, then the solid product was washed with three 200-ml portions of water, dried, and the product was recrystallized from dimethylformamide to give 2.7 g (80%) of beige crystals. This compound could not be further purified because of its slight solubility in any solvent: m.p. 235°C to nematic, 256°C to isotropic; IR (KBr) 1638 cm^{-1} ; NMR (DMSO- d_6) δ 3.33 (s, 1H, NH), 3.76 (s, 3H, CH_3), 4.50-4.70 (m, 2H, CH_2), 5.15-5.55 (m, 2H, vinyl H), 6.03 (d, d, t, $J=17/10.5/5$ Hz, 1H, vinyl H), 6.77-7.16 (m, 4H, ArH), 7.50-7.85 (m, 6H, ArH), 7.85-8.10 (m, 2H, ArH).

N-Ethyl-N-(4-methoxyphenyl)-4-[4-(allyloxy)phenyl]benzamide (19). 4-(4-

Allyloxyphenyl)benzoic acid¹ (0.72 g) and 0.46 g of N-ethyl-4-methoxyaniline were used. The product was recrystallized from benzene-hexane to give 0.53 g (49%) of white crystals. An analytically pure sample was obtained by sublimation (150°C, 0.05 Torr): m.p. 88–89°C to smectic, 90.5°C to isotropic; IR (KBr) 1630 cm⁻¹; NMR (C²HCl₃) δ 1.20 (t, $J=7$ Hz, 3H, CH₃), 3.72 (s, 3H, CH₃), 3.94 (q, $J=7$ Hz, 2H, CH₂), 4.45–4.66 (m, 2H, CH₂), 5.15–5.55 (m, 2H, vinyl H), 6.04 (d, d, t, $J=17/10.5/5$ Hz, 1H, vinyl H), 6.62–7.10 (m, 6H, ArH), 7.15–7.60 (m, 6H, ArH). Analytically calculated for C₂₅H₂₅NO₃: C, 77.49; H, 6.50. Found: C, 77.65; H, 6.70.

N-Methyl-N-phenyl-4-[4-(allyloxy)phenyl]benzamide (20). 4-(4-Allyloxyphenyl)benzoic acid¹ (0.76 g) and 0.32 g of N-methylaniline were used. The product was recrystallized from toluene-hexane to give 0.85 g (83%) of white crystals: m.p. 115–120°C to smectic, 121°C to isotropic; IR (KBr) 1630 cm⁻¹; NMR (C²HCl₃) δ 3.50 (s, 3H, CH₃), 4.44–4.6 (m, 2H, CH₂), 5.16–5.54 (m, 2H, vinyl H), 6.0 (d, d, t, $J=17.3/10.2/5.1$ Hz, 1H, vinyl H), 6.8–7.6 (m, 13H, ArH and NH). Analytically calculated for C₂₃H₂₁NO₂: C, 80.44; H, 6.16. Found: C, 80.69; H, 6.35.

4-(4-Morpholinylcarbonyl)phenyl 4-[4-(allyloxy)phenyl]benzoate (21). 4-(4-Allyloxyphenyl)benzoic acid¹ (0.76 g) and 0.62 g of 4-hydroxybenzomorpholide were used. The product was recrystallized from methylene chloride-ethanol to 1.23 g of white crystals: m.p. 176°C to nematic, 207°C to isotropic; IR (KBr) 1720, 1618 cm⁻¹; NMR (C²HCl₃) δ 3.68 (s, 8H, morpholinyl H), 4.5–4.7 (m, 2H, CH₂), 5.2–5.6 (m, 2H, vinyl H), 5.85–6.35 (m, 1H, vinyl H), 7.02 (d, $J=9$ Hz, 2H, ArH), 7.2–7.85 (m, 8H, ArH), 8.25 (d, $J=8.5$ Hz, 2H, ArH). Analytically calculated for C₂₇H₂₅NO₅: C, 72.12; H, 5.68. Found: C, 72.22; H, 5.71.

General procedure for the synthesis of liquid-crystalline polysiloxanes

The liquid-crystalline alkene (1.1 mmol) and the appropriate hydrosiloxane polymer were dissolved or suspended in 5 ml of 1,2-dichloroethane in a PTFE vial. Dicyclopentadienylplatinum(II) chloride² (0.5 mg) (or 0.1 ml of a freshly prepared 0.1% solution of the catalyst in methylene chloride) was added, and the vial was filled with argon gas. The mixture was heated to 80°C for 16 h. The polymers were precipitated with 15 ml of methanol and the solvents were removed by centrifugation. The solid polymers were dissolved in 5 ml of methylene chloride, precipitated with 15 ml of methanol, and the solvents were again removed by centrifugation. This process was then repeated again. The polymer was dissolved in methylene chloride, filtered (5–10 μ m pore size), precipitated with methanol, centrifuged, and dried in vacuum. Table I lists the physical data for various liquid-crystalline polymers. Alkenes 1–4 and 6 were reported previously¹.

Preparation of capillary columns

Fused-silica capillaries (10 m \times 200 μ m I.D., Hewlett Packard, Avondale, PA, U.S.A.) were used as column material to test the performance of the liquid-crystalline stationary phases prepared in this study. The fused-silica capillaries were purged with dry nitrogen gas at 250°C for 2 h before use. Each mesomorphic polymer evaluated was dissolved in methylene chloride (35°C) at a concentration of 2.4 mg ml⁻¹ which gave a film thickness of 0.15 μ m using the static coating procedure. Before filling the capillary, the coating solution was carefully filtered through a 2- μ m stainless-steel filter. The columns were coated and purged with nitrogen gas for 30 min, and the

TABLE I

PHASE TRANSITIONS FOR LIQUID-CRYSTALLINE ALKENES AND THEIR CORRESPONDING POLYSILOXANES

k = Crystalline; s, s', s'' = different smectic phases; n = nematic; n* = cholesteric; i = isotropic; g = glassy; d = decomposition; LC = liquid crystal.

Alkene		Polymer			
No.	Transition temp. (°C)	MW	% LC	% Si-H	Transition temp. (°C)
1*	k 100 s 150 n* 181 i	5000	50	0	g 99 s 200 n 320 i
2*	k 152 s 240 n* 278 i	20 000	22	3	k 83 g 98 s 226 i
		5000	38	<1	g 93 s 271 i
		5000	48	2	g 104 s 308 i
3*	k 133 s 172 n 253 i	20 000	22	3	g 96 s 260 i
		20 000	22.5	3.5	g 103 s 288 i
		2270	50	<1	g 125 s 328 m > 350 i
4*	k 214 n 290 i	1000	25	<1	g 195 s 266 n 307 i
12	k 88 s 158 n 187 i	20 000	25	<1	g 92 s 246 n 286 i
13	k 46 s 168 i	Only mixed polymers were formed (see below)			
14	k 158 s 210 n > 350 i	Polymer was not soluble			
15	k 160 n 249 i	5000	46	4	g 105 s 175 s' > 350 i
16	k 123 s 130 n 236 i	Only mixed polymers were formed (see below)			
17	k 163 s 295 i	5000	50**	<1	g 125 s 170 s' 296 i
18	k 235 n 256 i	No polymer was prepared			
19	k 89 s 91 i	No polymer was prepared			
20	k 115-120 s 121 i	No polymer was prepared			
21	k 176 n 207 i	No polymer was prepared			
1/2***		5000	45	5	g 95 s 306 i
		5000	48.5 [§]	1.5	g 100 s 230 s' 280 s'' 305 i
		5000	50 ^{§§}	<1	g 105 s 322 i
1/15***		5000	49	1	g 97 s 135 s' > 350
2/3***		20 000	22	3	g 118 s 229 i
		20 000	25	<1	g 120 s 260 i
		1000	22	3	g 95 s 189 n 199 i
		2270	44	6	g 120 s 297 i
		5000	43	7	g 87 s 295 i
2/12***		20 000	21.5	3.5	g 60 s 226 i
2/16***		5000	50	<1	g 80 s 235 s' 317 i
		5000	50	<1	g 105 s 220 s' 308 i
6/13***		20 000	50		g 182 s 225 i

* Alkene was previously reported in ref. 1.

** Mixture of α and β adducts (about 1:1).

*** Equal molar mixtures.

[§] Compound 1 was added after 38 h.

^{§§} Compound 1 was added after 15 h.

stationary phase was finally cross-linked using azo-*tert.*-butane as free radical initiator. Coated columns were evaluated for selectivity, efficiency, and thermostability using an HP 5890 gas chromatograph.

Selectivity was evaluated for the different stationary phases by measuring the separation factor for anthracene-phenanthrene at 120 and 150°C, and by analyzing several isomeric mixtures of polycyclic aromatic compounds. Efficiency was measured

for phenanthrene at 150°C with a hydrogen carrier gas linear velocity of 50 cm s⁻¹. A temperature program from 100°C to 300°C was applied to study the thermostability of the liquid-crystalline stationary phases.

RESULTS AND DISCUSSION

The liquid-crystalline alkenes (Fig. 2) used to prepare the mesomorphic polysiloxane phases were synthesized as reported in our previous paper¹. Alkenes 12 and 13 were prepared to determine if the liquid crystal which was connected to the polysiloxane by a long flexible spacer would have better separation properties. Alkene 16 is similar to that prepared by Laub and co-workers^{2,6}, except that it is a hydroquinone derivative rather than one prepared from 4-hydroxybenzoic acid. The other alkene compounds contain other polar substituents such as nitrile (15) and amide (18–21) groups.

The mesomorphic polysiloxanes were prepared by a platinum-catalyzed alkylation of the appropriate poly[oxy-(methylsilylene)] with the liquid-crystalline alkenes as reported^{1,2,14}. Table I lists the phase transitions of the alkenes and the new polysiloxane phases.

It is interesting to note that the total smectic–nematic range increases when a liquid-crystal molecule is attached to a polysiloxane chain. This change is often dramatic as shown by phase 2 (48%, 5000 MW) where the liquid-crystalline range changed from 126°C (k→i) to 204°C (k→i). In almost every case, the initial melting point was lowered and the isotropic point raised (Table I). It is also important to note that the melting point or temperature at which the phase became gummy was even lower when the phase was coated and cross-linked in the column. Thus, the 48%, 5000 MW phase 2, which has a glass to smectic phase transition temperature of 104°C, was smectic from room temperature when cross-linked, and was useable in the capillary column at temperatures from 80°C. Alkenes 18–21 had liquid-crystalline characteristics, but their phase transitions were so close together that they were not attached to polysiloxane chains.

In our efforts to create the most suitable liquid-crystalline polysiloxane stationary phase for capillary chromatography, we have studied the basic structure, including the polysiloxane backbone length, alkane spacer length, and percent mesomorphic substitution⁴. The nearly 50%-substituted polymer with mesomorphic groups decoupled from the polysiloxane chain by a three-carbon alkane spacer (polymer 2) gave good thermostability, selectivity, efficiency, and it could be synthesized reproducibly.

Stationary phases must be reproducible in composition and purity. The use of a nearly 50%-substituted polysiloxane facilitates the synthetic procedure since only one monomer (dichlorohydromethylsilane) is used to build the methylhydropolysiloxane, and only one specific liquid crystal is used to react with the hydride groups. When the hydro-containing polymer is prepared from more than one monomer, mixtures of polymers containing varying percentages of hydro groups is usually obtained. Care must also be taken to remove the platinum catalyst after the hydrosilylation reaction. It was found in this study that platinum metal can be removed from the polymer by column chromatography using a polyvinylbenzene packing material.

The phase with an alkane spacer of five carbons to decouple the polysiloxane

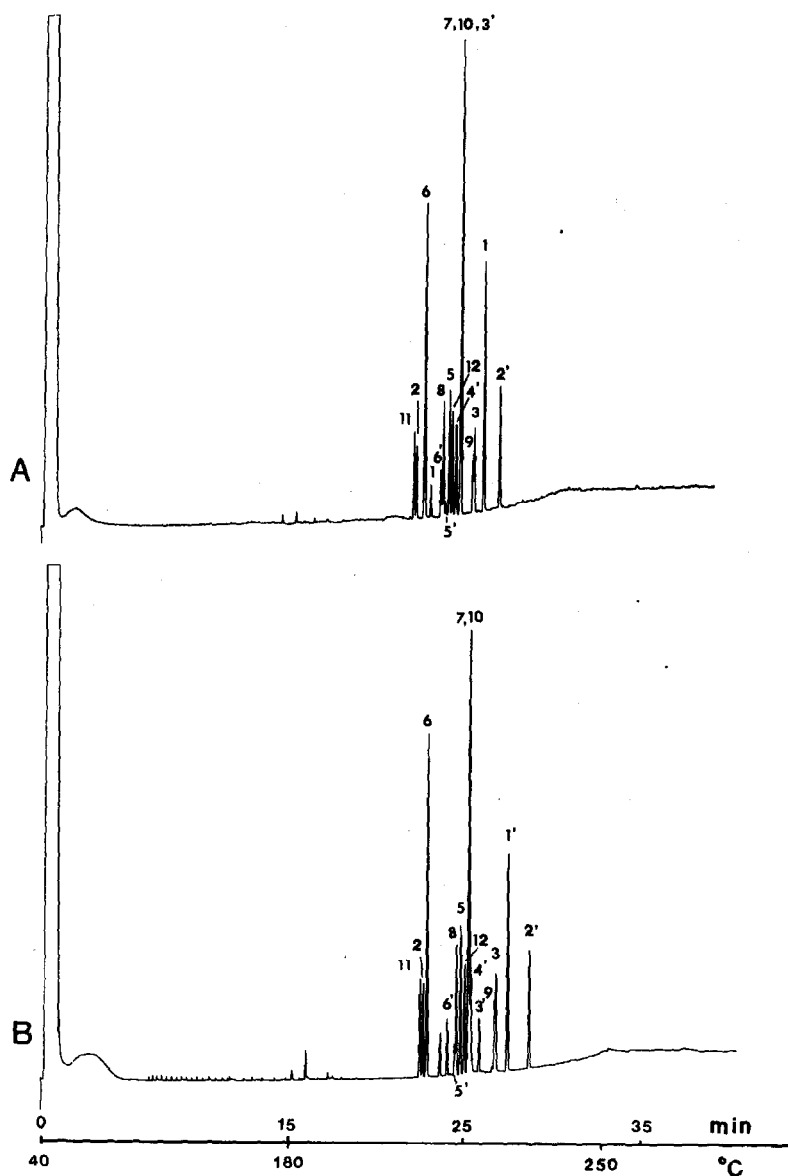


Fig. 3. Gas chromatogram of methylbenz(*a*)anthracene and methylchrysene isomers separated on approximately 50% liquid-crystalline polysiloxane stationary phases: (A) pure 48% biphenylcarboxylate phase and (B) mixed 45% biphenyl- and 5% phenylcarboxylate phase. Conditions: temperature program from 40°C to 180°C at 10°C min⁻¹ and to 250°C at 4°C min⁻¹.

from the mesomorphic groups gave excellent chromatographic properties. However, this polymer is very difficult to dissolve in solvents suitable for the static coating procedure. The corresponding polymer with a three-carbon spacer was soluble and, when coated, gave excellent separation characteristics (Fig. 3).

The chemical composition of the mesomorphic part in the liquid-crystalline polysiloxane phase was also studied in this work. Mesomorphic polysiloxanes with a biphenyl unit close to the siloxane chain (polymer 2) gave increased order to the final polymer when compared to one with a phenyl group close to the siloxane chain (polymer 1). This higher order in the polymer also resulted in superior selectivity, and there were no visible negative effects on solute diffusion into the polymer. Thus polymer 2 exhibited better separation characteristics than polymer 1. It is more difficult, however, to completely hydrosilylate with the biphenylalkene to form polymer 2 than with the phenylalkene to form 1. We were able to optimize the synthetic procedure to reduce the unreacted Si-H to <2%. The remaining Si-H would be reacted with the phenylalkene to form a polymer with no Si-H groups.

Different forms of smectic order could be seen when mixed biphenylcarboxylate and phenylcarboxylate groups were substituted in the same polymer (polymers 10 and 11, for example). Mixed polymers, however, exhibited a decreased mesomorphic selectivity and they had no better properties than the single liquid-crystalline phase. Unreacted silicon-hydride groups in the polymer could create cross-links in the phase at elevated temperatures, and they could react with silanol groups on the capillary surface. The only byproduct in these reactions is hydrogen gas. We determined that if the polymers were stored in a dry atmosphere, the 1-2% Si-H in the polymer would cause no deleterious problems. The excellent shape selectivity achieved with the nearly 50% liquid-crystalline polysiloxane containing a three-carbon spacer (polymer 2) is demonstrated in Fig. 3a, which shows the separation of seventeen isomers of methylbenz(*a*)anthracene and methylchrysene. Fig. 3b shows the same separation on a stationary phase where the remaining Si-H (*e.g.* <5%) is completely reacted with a phenylalkene as described earlier. Notice the decrease in resolution when the mixed polymer was used.

In other polymers synthesized for chromatography¹⁵, it was found that an ether-linkage close to the silicon atom was detrimental for the thermostability of those phases. The ether linkage close to the siloxane backbone had no effect on the stability of these mesomorphic phases. This is evidenced by the fact that elimination of the ether linkage between the hydrocarbon spacer and the mesomorphic molecule (phase 17) did not improve the thermal stability property of that polymer. Evidently, the liquid-crystalline moieties in these polymers are lined-up such that they are unable to take part in any elimination reactions.

An insoluble polymer resulted when the carbonyl function was turned around in the polymer (phase 16). Also, a lower selectivity was observed when this monomer was co-substituted in liquid-crystalline polymers.

Increasing the polarity of the mesomorphic endgroup by changing the methoxy to cyano (phase 15) resulted in a drastically decreased thermostability of the liquid-crystalline polysiloxane. The other nitrogen-containing liquid-crystalline alkenes (18-21) had such low liquid-crystalline transition temperatures that no phases were prepared.

Attempts to create a cholesteric polymer that separates enantiomeric isomers has not been successful so far. It can be assumed that the chiral centers in these polymers have too similar surroundings to be effective in separation of enantiomeric solutes.

In conclusion, the composition of the mesomorphic part of the liquid-crystal-

line polysiloxane can be varied in many ways without losing its liquid-crystalline character, as long as the basic structure is optimized for maximum shape-selectivity and efficiency. The basic structure includes a mesomorphic molecule coupled with a spacer between a biphenyl group and a polysiloxane backbone. The nearly 50% biphenylcarboxylate ester substituted polysiloxane with a three-carbon spacer has been found to be the most suitable shape-selective stationary phase for use in high-performance chromatography.

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