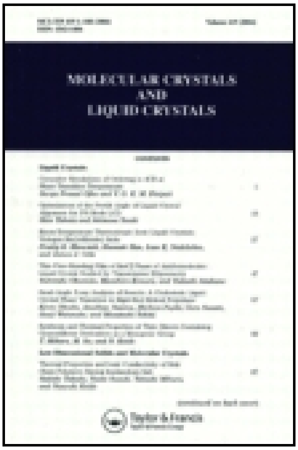

Molecular Crystals and Liquid Crystals

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Synthesis and Chromatographic Properties of Liquid Crystalline Polysiloxanes Containing Steroid Substituents

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Synthesis and Chromatographic Properties of Liquid Crystalline Polysiloxanes Containing Steroid Substituents

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A series of alkenyl-substituted cholesterol and related steroids have been prepared. These liquid-crystalline compounds were hydrosilylated onto polyhydromethylsiloxane. The polymers have a broad range of liquid crystallinity even if the starting alkenes had a narrow range. Those polymers containing the benzoate ester linking group were not suitable for stationary phases in high temperature capillary gas chromatography because the phases were not stable at temperatures above 250°–270°C. A capillary column coated with a polymer containing a phenyl group directly attached to the steroid proved to be effective in separating certain PAH isomers.

Keywords: liquid crystals, polysiloxanes, capillary gas chromatography, steroidal substituents, stationary phases, synthesis

INTRODUCTION

There has been a considerable amount of recent interest in the preparation of polysiloxane stationary phases containing liquid-crystalline side chains.[1–7] It is clear that polycyclic aromatic hydrocarbons (PAH) are separated on liquid crystalline phases mainly according to molecular geometry (i.e., length/breadth ratio).[1–11] Liquid crystalline phases with chiral mesomorphic groups such as the steroids, comprise a specific group of phases which shows promise for separating enantiomers according to molecular shape (stereochemistry). Some liquid crystalline chiral phases have shown resolving power which declines at higher temperatures when the phase becomes isotropic.[12,13]

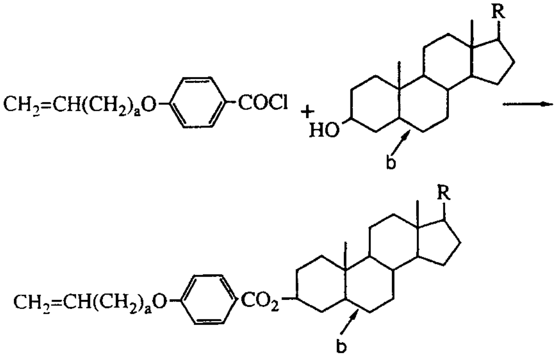
Some chiral nematic (cholesteric) phases have been tested as chiral phases in packed-column gas chromatography.[8,14] Unfortunately, the phases tested separate molecules strictly according to their length/breadth ratios and not according to their 3-dimensional orientations. This may be due to the fact that the nematic phases has a lower degree of order than the smectic phase. Indeed, the best liquid crystalline phases previously mentioned contained *smectic* liquid crystalline side groups. Since the liquid crystalline polysiloxanes are often smectic (apparently due to restricted translational freedom imposed by attachment to the polymer[15–18]), there remains some hope that steroid-substituted polysiloxane phases may prove useful for chiral separations.

This paper reports the synthesis of new alkene-substituted steroid compounds. These new liquid crystalline molecules were attached to a polysiloxane backbone. Several of these polymers were tested as stationary phases for gas chromatography. Preliminary results show that methionine methyl ester enantiomers were not resolved, but one phase did separate PAH isomers as expected for a liquid-crystalline phase.

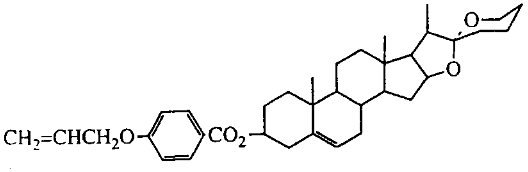
RESULTS AND DISCUSSION

Sterol esters are well known liquid crystals which also possess several chiral centers.[19] Janini and his coworkers have prepared a sterol ester mesomorph grafted onto a polysiloxane backbone and they have demonstrated its liquid crystallinity.[11] An understanding of steroid mesomorphs with slight variations in the sterol portion of the mesomorph may be possible by studying the polysiloxanes containing these modified steroids. It is possible that these slight modifications could allow us to maximize the range of liquid crystallinity and thus the range of temperatures useful for gas chromatographic separations. Esters of the commercially available sterols cholesterol, dihydrocholesterol, β-sitosterol, stigmasterol, and diosgenin, as well as the readily accessible 5-pregnen-3β-ol[20] were used to prepare the alkene-substituted steroids (see Figure 1). Compound 1 and its polysiloxane adduct (1a) were reported by Janini and coworkers,[11] although no details other than phase transitions were given by them.

p-Allyloxybenzoate esters of cholesterol (1) and dihydrocholesterol (2) have wider ranges of liquid crystallinity than do the corresponding *p*-vinylbenzoate esters (8 and 9), respectively (see Table I). Additionally, polysiloxanes substituted with the *p*-alkoxybenzoate esters



Compd	a	b	R
1	1	C=C	$CH(CH_3)(CH_2)_3CH(CH_3)_2$
2	1	sat	$CH(CH_3)(CH_2)_3CH(CH_3)_2$
3	9	sat	$CH(CH_3)(CH_2)_3CH(CH_3)_2$
4	1	C=C	C_2H_5
5	1	C=C	$CH(CH_3)(CH_2)_2CH(C_2H_5)CH(CH_3)_2$
6	1	C=C	$CH(CH_3)CH{=}CHCH(C_2H_5)CH(CH_3)_2$



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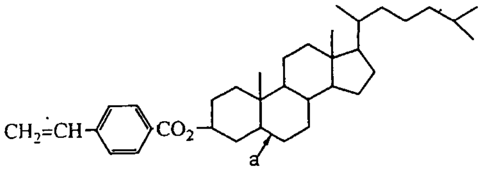
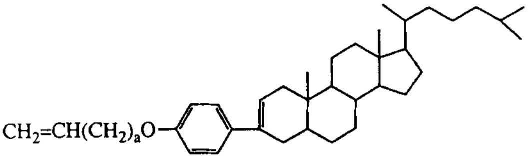


8, a= C=C
9, a= sat



10, a= 1
11, a= 9

FIGURE 1 New steroidal alkenes.

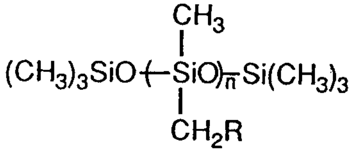
TABLE I

Phase transition temperatures (°C) of sterol esters and polymers

Compound	Alkene	50% Polymer
1	k 124 n* 226 i	k 95 s 272 i
2	k 100 n* 226 i	g 101 s 230 i
3	k 108 n* 183 i	g 94 s 206 i
4	k 109 n* 210 i	g 130 s 229 d
5	k 135 n* 139 i	g 100 s 292 i
6	k 143 n* 150 i	g 99 s 291 i
7	k 178 n* 205 i	g 146 s 314 d
8	k 169 n* 203 i	g 130 s 269 d
9	k 100 n* 157 i	g 116 s 254 i

(1a and 2a) (prepared by a hydrosilylation reaction) (see Figure 2) were more thermally stable (see Table II) than were those substituted with the *p*-alkylbenzoate analogues (8a and 9a). These stability results were determined by coating capillary columns with the various polymers and subjecting the columns to high temperatures in a gas chromatograph. The *p*-alkylbenzoate polymers, 8a and 9a, produced serious bleed when the capillary columns were heated only to 220°C, while the alkyloxybenzoate polymer (1a) could be used up to 250°C. For this reason, the remaining sterols were all esterified with *p*-allyloxybenzoyl chloride[3] and then hydrosilylated onto 50% polyhydromethylsiloxane (where each siloxane unit has one methyl group and one hydrogen atom).

The esters containing ether moieties should be less stable, since these materials are prone to air oxidation. Also, polysiloxanes containing phenoxypropyl substituents were found to be less stable than those without an oxygen in the linking unit.[22] The results show that the alkoxy polymers are, in fact, the most stable as reported above. Mass spectrometry of the effluents from the heated columns showed that the major breakdown product from these sterol phases was 3,5-cholestadiene and not products of air oxidation. Thus, the primary decomposition pathway for these polymeric esters probably involves a concerted ester elimination (E_i mechanism[23]). Such eliminations are known to occur *via* a concerted 6-membered transition state, with some polar character being developed. Apparently, some positive charge develops at sterol carbon 3, while at the same time, partial negative charge develops in the carboxylate group. The increased electron-donating character of the *p*-alkoxy group destabilizes the



$$(CH_3)_3SiO\!\left(\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2R}{\overset{|}{\underset{|}{Si}}}}O\right)_{\overline{n}}Si(CH_3)_3$$

1a, R = $-(CH_2)_2O-PhCO_2-$cholesteryl

2a, R = $-(CH_2)_2O-PhCO_2-$cholestanyl

3a, R = $-(CH_2)_{10}O-PhCO_2$cholestanyl

4a, R = $-(CH_2)_2O-PhCO_2-$(5-pregen-3β-yl)

5a, R = $-(CH_2)_2O-PhCO_2$(β-sitosteryl)

6a, R = $-(CH_2)_2O-PhCO_2-$stigmasteryl

7a, R = $-(CH_2)_2O-PhCO_2-$diosgeninyl

8a, R = $-CH_2-PhCO_2-$cholesteryl

9a, R = $-CH_2-PhCO_2-$cholestanyl

10a R = $-(CH_2)_2O-Ph-$(cholest-2-enyl)

11a, R = $-(CH_2)_{10}O-Ph-$(cholest-2-enyl)

12a, R = 50% $-(CH_2)_2O-PhCO_2-$cholestanyl (from 2)

R = 50% $-(CH_2)_2O-PhCO_2-$cholestanyl (from 3)

FIGURE 2 Steroidal polysiloxanes.

developing negative charge relative to the *p*-alkyl substituent, thus increasing the stability of the alkoxy polymers.

This hypothesis could also explain why the polymer from dihydrocholesteryl *p*-allyloxybenzoate, 2a, decomposed at an even higher temperature (270°C). The presumed cholesteryl ester transition state must involve syn elimination of the 4-β-hydrogen. As the hydrogen leaves, a *p*-orbital develops at carbon 4 which can be stabilized by overlap with the adjacent pi-bond on carbon 5. This stabilization would reduce the energy of activation. There is no π bond on carbon 5 of 2a so that this sort of stabilization is unavailable and, therefore, polymer 2a would be more stable.

Interesting trends of transition temperatures versus substitution are seen in Table I. The nature of the alkyl substituent on the steroid (*R*

TABLE II

Gas chromatographic performance of selected steroidal polysiloxanes

		Chromatographic properties at 150°C		Thermostability [Column bleed, (pA)]	
Polymer	% Substitution	Selectivity[a] $\alpha_{phen/ant}$	Efficiency[b]	220°C	250°C
1a	50	1.17	3,980	10	20
2a	50	1.12	3,556	0	13
8a	25	1.09	2,774	20	45
10a	50	1.17	2,680	2	10

[a]phen = phenanthrene and ant = anthracene.

[b]measured at a capacity factor (k^1) > 10.

k^1 = the retention time of a solute relative to the retention time of an unretained material such as methane gas.

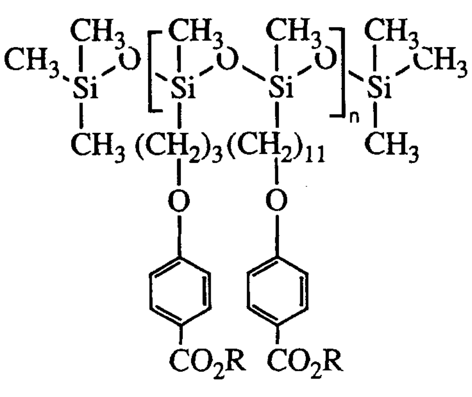
in Figure 1) has a considerable effect on phase transition temperatures in the monomer, but relatively little effect in the polymer. For example, alkenes 5 and 6 have a higher solid transition and lower isotropic point than 1, but the transition temperatures of polymers (5a and 6a) are very similar to that of 1a. Perhaps the additional ethyl groups in 5 and 6 disrupt mesophase stability by reducing the planarity of the steroid, while the polymers containing 5 and 6 causes the steroid systems to observe a higher degree of order. This effect of broadening of the liquid crystalline range for steroids which are grafted onto polysiloxane chains is also observed for alkene 7 which has a liquid crystal range of only 27°C, while the polymer, 7a, has a liquid crystal range of nearly 170°C (see Table I). It is likely that the spiroketal functionality of 7 distorts the shape of diosgenin from planarity, giving a rather narrow range of liquid crystallinity. Thus, as is apparent from the data in Table I, a polymer with a liquid crystalline steroid side group will generally have a large mesophase range, even if the starting steroid compound has a somewhat narrow range.

The sterol esters reported here also show the effects of unsaturation on liquid crystallinity. In general, ring unsaturation increases the crystalline to nematic transition temperature of the starting ester by varying amounts. This is apparent with alkenes 1 and 8 versus alkenes 2 and 9, where 2 and 9 have lower k to n* transitions. This result may be due to increased rigidity of the alkene and thus crystallinity of the mesomorph. These unsaturation effects were not observed in the polymers.

The effects of polar groups are also apparent in these liquid crystalline alkene-esters. As previously noted, *p*-allyloxyesters 1 and 2 have a wider range of liquid crystallinity than do *p*-vinyl esters 8 and 9. Current theory suggests that of the two main attractive forces operative in liquid crystals, dispersive (lipophilicity) and polar, the polar effects are more important in promoting high smectic or nematic to isotropic phase transitions, and polar substituents increase the mesophase range to a greater extent.[15–19] The allyloxy groups of 1 and 2 are more polar than the vinyl groups of 8 and 9, so that 1 and 2 have the wider range of liquid crystallinity. Polar effects may also explain the high isotropic temperature observed for the diosgenin polymer, 7a (see Table I), where dipoles at both ends of the mesogen could make some contribution.

The effects of increasing the spacer between the mesogen and the polysiloxane backbone are interesting. Increasing the length of spacer to the dihydrocholesteryl ester mesomorph (2a versus 3a) somewhat decreases the range of liquid crystallinity in the polymer (see Table I). This is opposite to what has been observed with other liquid crystal polymers.[15–19] The polymers developed from 3-(*p*-alkoxy)cholesterol discussed in the next section are like the normal polymers containing liquid-crystalline side groups, in that 11a with a longer spacer has a larger mesophase range than 10a (Table IV).

Finkelmann and his coworkers have postulated that polymers with two liquid-crystalline side groups with widely varying spacers will have greater translational freedom in the liquid crystal portion of the polymer, and, therefore, nematic rather than smectic transition states would be obtained.[18] Polymer 12a prepared from equimolar amounts of 2 and 3 did not have properties



12a, R = Cholesteryl

in compliance with Finkelmann's postulation. Polymer 12a had a narrow range of liquid crystallinity (*g* 93 s 179 *i*) and a lower isotropic point that either polymer 2a or 3a (Table I). Also, polymer 12a had a smectic rather than nematic transition state. Finkelmann's polymers had a larger variation in the spacers (2/12) than that in 12a (3/11). Perhaps the greater variation is necessary to have nematic states in a polymeric material.

The phase transitions for three polymers prepared from mixtures of alkenes 1 and 8 are given in Table III. The mesophase ranges of the mixed polymers 13a, 14a and 15a (Table III) are similar to that for 1a. Even though the difference in spacer length is small (ethyl versus propoxy), these results again fail to confirm Finkelmann's hypothesis that polymers with varying side chain liquid crystals should be nematic.

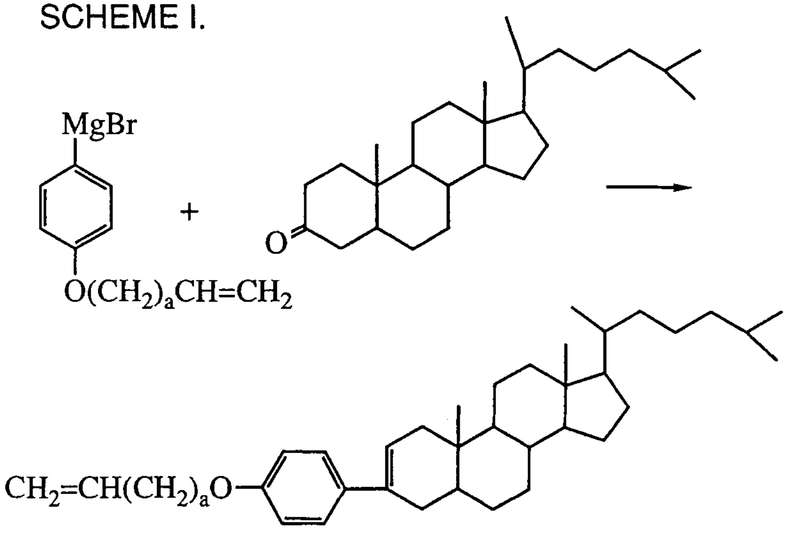
As noted above, liquid crystal phases derived from the sterol esters are thermally unstable at higher temperatures (250°C for 1a, 270°C for 2a). Even so, these materials could be used for stationary phases for capillary gas and supercritical fluid chromatography. As can be seen from Table II, the geometric isomers, phenanthrene and anthracene, are well separated, with for example an α value of 1.17 on a capillary column coated with polymer 1a. In an effort to prepare more thermally stable polymers, we have prepared liquid-crystalline alkenes 10 and 11 (Figure 1) *via* a Grignard reaction of *p*-alkoxyphenylmagnesium halide with cholestanone and subsequent dehydration[24] (Scheme 1). Hydrosilylation of 10 and 11 onto a polyhydromethylsiloxane would yield a liquid crystalline phase which no longer contained a labile ester group. As can be seen from Table II, phase 10a was the most thermally stable of all steroid phases tested. The range of liquid crystallinity for 10 and 11 are quite narrow (see Table IV). The polymers 10a and 11a prepared by a hydrosilylation

TABLE III

Phase transitions for mixed polymers prepared from 1 and 8

Polymer	1(%)	8(%)	Phase Transition (°C)
1a	50	0	k 95 s 272 i
13a	35	15	g 97 s 276 i
14a	30	20	g 97 s 268 i
15a	25	25	g 100 s 275 i
8a	0	50	g 130 s 269 i

SCHEME I.



10, a= 1
11, a= 9

TABLE IV

Phase transition temperatures (°C) of 3-arylcholestenes and polymers

Compound	Monomer	Polymer
10	k 101 n* 164 i	g 104 s 283 n* 303 i
11	k 55 n* 88 i	g 74 s 339 n* >360
10 + 11 (1:1)	—	g 79 s 306 i

reaction exhibited very wide ranges of liquid crystallinity as expected (Table IV).

Polymers 10a and 11a were insoluble in methylene chloride or other volatile solvents that are suitable for static coating. Polymer 10a was therefore statically coated from a solution in benzene and at a temperature of 65°C. A somewhat lower coating efficiency resulted from not using an appropriate solvent for the static coating procedure (Table II). Chromatographic efficiency was found to be strongly dependent on k' and elution temperature which indicates that bulky highly ordered steroid substituents supress mobility in the polysiloxane backbone and diffusion in the stationary phase.

Chromatographic selectivity of polymer 10a is illustrated in Figure

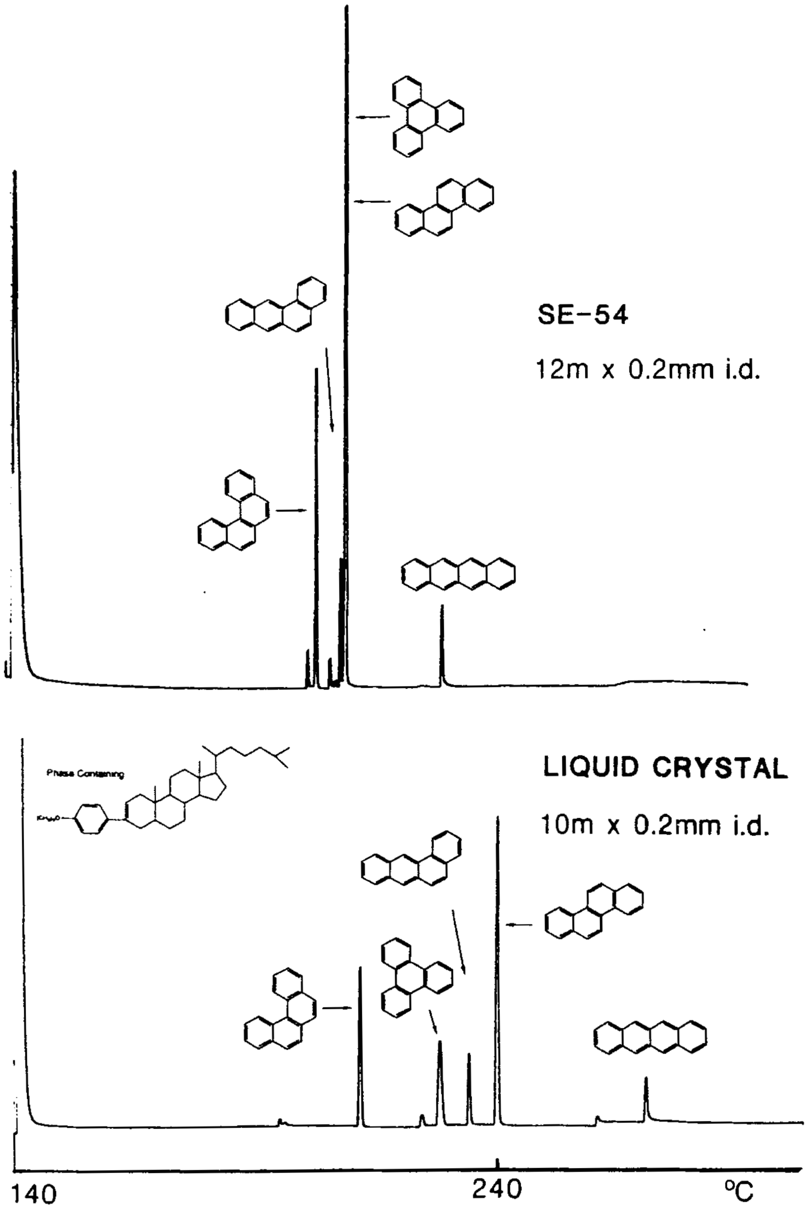


FIGURE 3 Gas chromatogram of four-ring PAH isomers on A, a nonpolar phase and B, a liquid crystalline steroid phase (10a). Conditions: 10 m × 200 μm i.d. fused silica coated with 0.15 μm stationary phase film.

3 with the separation of 4-ring PAH isomers. Complete separation of all five isomers according to length to breadth ratio emphasizes a strong liquid crystalline separation mechanism.

EXPERIMENTAL

Infrared (IR) spectra were obtained on a Beckman Acculab 2 spectrometer. Nuclear Magnetic Resonance (NMR) spectra were recorded on a JEOL FX-90Q spectrometer. Phase transitions were obtained using a Thomas-Kofler hot stage microscope with cross polarizers. The melting of the alkenes changed the material to a layered thread-like structure indicative of the nematic phase. This thread-like structure became a liquid at the isotropic temperature. The glass to smectic phase transition of the polymers was accompanied by the material becoming highly ordered and colored. The material changed to a liquid at the isotropic temperature. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter. Carbon and hydrogen analyses were done by MHW Labs, Phoenix, Arizona.

PREPARATION OF STEROL ALKENES

Synthesis of cholesteryl 4'-allyloxybenzoate, 1: 4-Allyloxybenzoyl chloride[3] (2.58 g, 13.1 mmol) and 5.32 g (13.8 mmol) of cholesterol (recrystallized from ethanol and dried at 80°C under vacuum for 16 h) were mixed with 25 mL of methylene chloride, and the suspension was cooled in an acetone/ice bath. Anhydrous pyridine (5.3 mL, 66 mmol, distilled from calcium hydride and stored over potassium hydroxide) was added and the mixture was stirred overnight while gradually warming to room temperature. Ether (200 mL) was then added and the mixture was washed twice with 200 mL portions of 1 M aqueous hydrochloric acid and once with 200 mL of saturated aqueous sodium bicarbonate. The ether phase was then dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was recrystallized from ethyl acetate/ethanol (1:1) to give 1 as white crystals, 5.14 g (72%); k 124 n* 226 i; $[\alpha]_D$ $-2.6°$ ($c=1.007$, chloroform); NMR (δ): 7.97 (2H, d, $J=10$ Hz), 6.91 (2H, d, $J=10$ Hz), 6.28 – 5.81 (1H, m), 5.55 – 5.19 (3H, m), 5.02 – 4.66 (1H, m), 4.58 (2H, d, $J=6$ Hz), 2.43 (2H, d, $J=10$ Hz), 1.05 (3H, s, 19 – Me), 0.85 (6H, d, $J=6$ Hz, 26,27 – Me_2), 0.67 (3H, s, 18 – Me). Anal. Calcd. for $C_{37}H_{54}O_3$: C, 81.27; H, 9.95. Found: C, 81.20; H, 10.14.

Synthesis of dihydrocholesteryl 4′-allyloxybenzoate, 2: Dihydrocholesterol (7.00 g, 18.0 mmol) was esterified as above for 1 to give 2 as white crystals, 4.50 g (48%); k 100 n* 226 i; $[\alpha]_D$ +20.4° (c = 0.997, chloroform); NMR (δ): 7.95 (2H, d, J = 10 Hz), 6.88 (2H, d, J = 10 Hz), 6.29 – 5.17 (3H, m), 5.07 – 4.66 (1H, m), 4.56 (2H, d, J = 6 Hz), 0.86 (3H, s, 19 – Me), 0.67 (6H, d, J = 7 Hz, 26, 27 – Me_2), 0.65 (3H, s, 18 – Me). Anal. Calcd. for $C_{37}H_{56}O_3$: C, 80.97; H, 10.28. Found: C, 81.07; H, 10.12.

Synthesis of 5-pregnen-3β-yl 4′-allyloxybenzoate, 4: 5-Pregnen-3β-ol[20] (1.00 g, 3.31 mmol) was esterified as above for 1 to give 4 as off-white crystals, 0.53 g (35%); k 109 n* 210 i; $[\alpha]_D$ – 8.0° (c = 1.013, chloroform); NMR (δ): 7.96 (2H, d, J = 10 Hz), 6.90 (2H, d, J = 10 Hz), 6.28 – 5.80 (1H, m), 5.54 – 5.12 (3H, m), 5.02 – 4.64 (1H, m), 4.56 (2H, d, J = 6 Hz), 2.42 (2H, d, J = 8 Hz), 1.06 (3H, s, 19 – Me), 0.58 (3H, s, 18 – Me). Anal. Calcd. for $C_{31}H_{42}O_3$: C, 80.48; H, 9.15. Found: C, 80.29; H, 9.08.

Synthesis of β-sitosteryl 4′-allyloxybenzoate, 5: β-Sitosterol (6.00 g, 1.45 mmol, recrystallized from 95% ethanol) was esterified as above for 1 to give 5 as white crystals, 4.46 g (56%); k 135 n* 139 i; $[\alpha]_D$ – 1.1° (c = 1.044, chloroform); NMR (δ): 7.97 (2H, d, J = 9 Hz), 6.91 (2H, d, J = 9 Hz), 6.26 – 5.84 (1H, m), 5.51 – 5.21 (3H, m), 5.03 – 4.66 (1H, m), 4.58 (2H, d, J = 6 Hz), 2.43 (2H, d, J = 9 Hz), 1.09 (3H, s, 19 – Me), 0.69 (3H, s, 18 – Me). Anal. Calcd. for $C_{39}H_{58}O_3$: C, 81.48; H, 10.17. Found: C, 81.36; H, 10.09.

Synthesis of stigmasteryl 4′-allyloxybenzoate, 6: 90% Stigmasterol (10.00 g, 24.2 mmol) was esterified as above for 1 to give 6 as white crystals, 8.16 g (65%); k 143 n* 150 i; $[\alpha]_D$ – 11.7° (c = 0.998, chloroform); NMR (δ): 7.99 (2H, d, J = 9 Hz), 6.92 (2H, d, J = 9 Hz), 6.24 – 5.86 (1H, m), 5.54 – 4.67 (6H, m), 4.59 (2H, d, J = 6 Hz), 2.45 (2H, d, J = 9 Hz), 1.08 (3H, s, 19 – Me), 0.72 (3H, s, 18 – Me). Anal. Calcd. for $C_{39}H_{56}O_3$: C, 81.77; H, 9.85. Found: C, 81.93; H, 9.74.

Synthesis of diosgeninyl 4′-allyloxybenzoate, 7: Diosgenin (6.11 g, 14.7 mmol) was esterified as above for 1 to give 7 as white crystals, 4.58 g (57%) (recrystallized from acetic acid); k 178 n* 205 i; $[\alpha]_D$ – 62.9° (c = 1.003, chloroform); NMR (δ): 7.96 (2H, d, J = 10 Hz), 6.90 (2H, d, J = 10 Hz), 6.26 – 5.19 (4H, m), 5.04 – 4.25 (4H, m), 3.60 – 3.15 (2H, m), 2.42 (2H, d, J = 6 Hz), 1.07 (3H, s, 19 – Me), 0.79 (3H, s, 18 – Me). Anal. Calcd. for $C_{37}H_{50}O_5$: C, 77.31; H, 8.77. Found: C, 77.13; H, 8.64.

Synthesis of 4-(10'-undecen-1'-yloxy)benzoic acid: 4-Hydroxybenzoic acid (13.81 g, 0.100 mol) was dissolved in 70 mL of 95% ethanol and 11.2 g of potassium hydroxide in 14 mL of water, a few crystals of potassium iodide and 35.69 g (0.110 mol) of 10-undecenyl tosylate (prepared from tosyl chloride and the corresponding alcohol) were added. The mixture was refluxed 48 h, after which it was allowed to cool. Water (80 mL) was added and the mixture was washed with 200 mL of ether. The aqueous layer was acidified with concentrated aqueous hydrochloric acid and was then extracted three times with 100 mL portions of methylene chloride. The combined methylene chloride extracts were dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was recrystallized from 95% ethanol to give 4-(10'-undecen-1'-yloxy)benzoic acid as white crystals, 5.89 g (20%); k 77 s 82 n 135 i; NMR (δ): 11.15 (1H, br s), 8.06 (2H, d, J = 10 Hz), 6.92 (2H, d, J = 10 Hz), 6.05 – 5.60 (1H, m), 5.11 – 4.83 (2H, m), 4.02 (2H, t, J = 7 Hz). Anal. Calcd. for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 73.84; H, 9.13.

Synthesis of dihydrocholesteryl 4'-(10''-undecen-1''-yloxy)benzoate, 3. 4-(10'-Undecen-1'-yloxy)benzoic acid (2.00 g, 6.89 mmol) was suspended in 30 mL of methylene chloride and 1.8 mL (21 mmol) of oxalyl chloride and 1 drop of DMF were added. The reaction was stirred 2 h, after which the mixture was concentrated under reduced pressure and the residue was taken up in 15 mL of benzene. The benzene solution was filtered through cotton and the solid residue was washed with a further 5 mL of benzene. The combined filtrates were concentrated to dryness in vacuo to give 2.19 g of crude acid chloride, which was used without further purification. The crude acid chloride was mixed with 20 mL of methylene chloride and 2.95 g (7.59 mmol) of dihydrocholesterol, and the mixture was cooled in an acetone/icebath. Anhydrous pyridine (2.8 mL, 35 mmol) was added and the mixture was stirred overnight, while allowing the reaction to gradually warm to room temperature. Ether (100 mL) was added and the mixture was washed twice with 100-mL portions of aqueous hydrochloric acid, once with 100 mL of aqueous saturated sodium bicarbonate and once with 100 mL of aqueous saturated sodium chloride. The ether layer was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was recrystallized from 95% ethanol to give 3 as white crystals, 3.07 g (67% overall); k 108 n* 183 i; $[\alpha]_D$ + 17.1 (c = 1.022, chloroform), NMR (δ): 7.96 (2H, d, J = 10 Hz), 6.87 (2H, d, J = 10 Hz), 6.03 – 5.59 (1H, m), 5.10 – 4.70 (3H, m), 3.98 (2H, t, J = 7 Hz), 0.95 (3H, s, 19 – Me), 0.64 (3H, s, 18 – Me). Anal. Calcd. for $C_{45}H_{72}O_3$: C, 81.76; H, 10.98. Found: C, 81.50; H, 11.08.

Synthesis of cholesteryl 4'-vinylbenzoate, 8: 4-Vinylbenzoyl chloride[21] (8.78 g, 52.7 mmol) and 21.45 g (55.5 mmol) of cholesterol were mixed with 100 mL of methylene chloride and the mixture was cooled in an acetone/ice bath. Anhydrous pyridine (21.3 mL, 0.263 mol) was added and the reaction mixture was stirred overnight while gradually warming to room temperature. Benzene (400 mL) was added and the suspension was washed with 400 mL of 1 M aqueous hydrochloric acid, once with 400 mL of saturated aqueous copper sulfate and then with saturated aqueous sodium chloride. Methylene chloride (400 mL) was added to the benzene layer in order to dissolve the product and the resulting solution was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was recrystallized from benzene to give 8 as white needles, 18.17 g (67%); k 169 n* 203 i; $[\alpha]_D$ –0.2° (c = 1.002, chloroform); NMR (δ): 7.99 (2H, d, J = 9 Hz), 7.44 (2H, d, J = 9 Hz), 6.95 – 6.55 (1H, m), 5.96 – 5.24 (3H, m), 5.04 – 4.58 (1H, m), 2.44 (2H, d, J = 8 Hz), 1.05 (3H, s, 19 – Me), 0.85 (6H, d, J = 7 Hz, 26, 27 – Me_2), 0.67 (3H, s, 18 – Me). Anal. Calcd. for $C_{36}H_{52}O_2$: C, 83.67; H, 10.14. Found: C, 83.49; H, 10.01.

Synthesis of dihydrocholesteryl 4'-vinylbenzoate, 9: Dihydrocholesterol (5.00 g, 12.9 mmol) was esterified with 2.04 g (12.2 mmol) of 4-vinylbenzoyl chloride as above for 8 to give 9 as white crystals (from benzene/ethanol), 2.91 g (46%); k 100 n* 157 i; $[\alpha]_D$ +21.2° (c = 1.000, chloroform); NMR (δ): 7.98 (2H, d, J = 9 Hz), 7.42 (2H, d, J = 9 Hz), 6.90 – 6.59 (1H, m), 5.93 – 5.29 (2H, m), 5.11 – 4.65 (1H, m), 0.88 (6H, d, J = 7 Hz, 26,27 – Me_2), 0.87 (3H, s, 19 – Me), 0.66 (3H, s, 18 – Me). Anal. Calcd. for $C_{36}H_{54}O_2$: C, 83.34; H, 10.49. Found: C, 83.12; H, 10.39.

PREPARATION OF 3-(*p*-ALKENYLOXY)CHOLESTENE COMPOUNDS

Synthesis of 4-(10'-undecen-1'-yloxy)bromobenzene: 4-Bromophenol (5.25 g, 30.3 mmol) and 24.00 g (73.9 mmol) of 10-undecenyl tosylate were dissolved in 30 mL of dry acetone (dried over 4A molecular sieves) and 6.45 g (50.3 mmol) of potassium carbonate were added. The mixture was refluxed for 40 h and was then allowed to cool. Ether (200 mL) was added and the suspension was washed successively with 200 mL of water, 200 mL of 5% aqueous potassium hydroxide and then 200 mL of saturated aqueous sodium chloride. The ether phase was dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was vacuum-distilled at 64–165°C and the distillate was purified by column chromatography on 340 g of silica gel (eluent: 1% ethyl acetate in hexane) to give 4-(10′-undecen-1′-yloxy)bromobenzene as a colorless oil, 7.35 g (75%); NMR (δ): 7.36 (2H, d, J = 10 Hz), 6.77 (2H, d, J = 10 Hz), 6.06 – 4.87 (3H, m), 3.92 (2H, t, J = 7 Hz). Anal. Calcd. for $C_{17}H_{25}BrO$: C, 62.77; H, 7.75. Found: C, 62.60; H, 7.71.

Synthesis of 3-(4′-allyloxyphenyl)cholest-2-ene, 10: Anhydrous tetrahydrofuran (THF, 5 mL, freshly distilled from potassium) and 0.1 mL of ethylene dibromide were added to 0.76 g (31 mg-atom) of magnesium turnings under nitrogen, after which 3.31 g (15.5 mmol) of 4-allyloxybromobenzene in 15 mL of anhydrous THF were added over a period of 25 minutes. The mixture was refluxed for 1.5 h and cholestanone (5.0 g, 12.9 mmol) in 20 mL of anhydrous THF was added over 6 minutes. The reaction was refluxed a further 24 h and was allowed to cool. Saturated aqueous ammonium chloride (10 mL), 40 mL of 1 M aqueous hydrochloric acid and 50 mL of benzene were added and the phases were separated. The organic phase was washed with 50 mL of saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was dissolved in 100 mL of benzene and a few crystals of *p*-toluenesulfonic acid were added. Water was azeotropically distilled from the solution for 2 h and the solution was then cooled, washed with 100 mL portions of saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered and concentrated to dryness under reduced pressure. The residue was purified by chromatography on 190 g of silica gel, using 5% ethyl acetate/hexane as eluent. The chromatographed product was recrystallized from ethanol/ethyl acetate to give 10 as white crystals, 3.14 g (48%); k 101 n* 164 i; $[\alpha]_D$ +62.8° (c = 1.000, chloroform); NMR (δ): 7.32 (2H, d, J = 10 Hz), 6.95 (2H, d, J = 10 Hz), 6.28 – 5.19 (4H, m), 4.55 (2H, dt, J = 6 Hz, 1 Hz), 0.92 (3H, s, 19 – Me), 0.82 (6H, d, J = 6 Hz, 26,27 – Me_2), 0.69 (3H, s, 18 – Me). Anal. Calcd. for $C_{36}H_{54}O$: C, 85.99; H, 10.82. Found: C, 85.84; H, 10.72.

Synthesis of 3-[4′-(10″-undecen-1″-yloxy)phenyl]cholest-2-ene, 11: 4-(10′-Undecen-1′-yloxy)bromobenzene (7.24 g, 22.3 mmol) and 6.90

g (17.8 mmol) of cholestanone were reacted together and purified as above for 10 to give 11 as white crystals, 7.84 g (72%); k 55 n* 88 i; $[\alpha]_D$ +49.5° (c = 1.002, chloroform); NMR (δ): 7.31 (2H, d, J = 10 Hz), 6.81 (2H, d, J = 10 Hz), 6.04–5.31 (2H, m), 5.10–4.83 (2H, m), 3.93 (2H, t, J = 7 Hz), 0.89 (3H, s, 19–Me), 0.79 (6H, d, J = 6 Hz, 26,27–Me_2), 0.66 (3H, s, 18–Me). Anal. Calcd. for $C_{44}H_{70}O$: C, 85.93; H, 11.47. Found: C, 86.09; H, 11.55.

PREPARATION OF POLYSILOXANES

Polyhydromethylsiloxane: Polyhydromethylsiloxane (2.00 g, 30 cs, 2300 MW) (purchased from Petrarch Systems, Bristol, PA) was dissolved in 2 mL of methylene chloride and 5 mL of methanol were added. The suspension was centrifuged and the supernatant was discarded. The residual polymer was purified further by repeating the process of methylene chloride dissolution/methanol precipitation 7 more times. The remaining polymer was taken up in methylene chloride, filtered and dried in vacuo to give a prepurified polysiloxane.

Hydrosilylation of dihydrocholesteryl 4'-allyloxybenzoate (2) *to form 2a:* Pre-purified polyhydromethylsiloxane (212.2 mg, 3.37 mEq of Si-H) and 2.22 g (4.04 mmol) of allyloxy ester 2 were dissolved in 10 mL of toluene in a teflon vial and a few crystals of dicyclopentadienylplatinum(II) chloride catalyst[3] were added. The vial was flushed with nitrogen for 2 minutes and the reaction mixture was then stirred at 90–95°C for 72 h. After cooling, 5 mL of methanol were added and the suspension was centrifuged. The supernatant was discarded and the residue was purified by a 3-fold methylene chloride dissolution/methanol precipitation. The residue was then dissolved in 5 mL of methylene chloride and the solution was filtered through a fine TFE millipore filter. Solvent was removed in vacuum to give liquid crystalline polymer 2a, 1.25 g; g 101 s 230 i. An analytical gel permeation chromatographic (GPC) analysis showed the polymer to contain less than 2% of 2. An NMR spectrum of the polymer showed that there was less than 2% of Si-H units left in the finished polymer.

The other alkenes (1, 3-11) were hydrosilylated onto polyhydromethylsiloxane as in the previous paragraph. The transition temperatures for all polymers including those with mixed side chains are given in Tables I, III and IV.

Preparation and Testing of Capillary Columns

Fused silica capillaries 10 m × 200 μm i.d. (Polymicro Technologies Inc., Phoenix, AZ) were filled with a 3% solution of stationary phase 10a (Figure 2) in benzene. The coating bath was held at 65°C during the static coating procedure. The coated column was purged with nitrogen gas for 1/2 h at 40°C and conditioned from 40°C to 250°C at 1°C/min holding the upper temperature for 8 h. Stationary phases that were soluble in methylene chloride were coated at 25°C from a methylene chloride solution. The capillary columns were evaluated in gas chromatography for efficiency, temperature stability and selectivity. Phenanthrene and anthracene were used as standard solutes to compare chromatographic properties of the different phases. Polycyclic aromatic hydrocarbon four-ring compounds were used to illustrate mesomorphic selectivity in the liquid crystalline steroid stationary phase.

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