Examples of amphitropic polymers: monolayer film, Langmuir–Blodgett film and liquid-crystalline properties of some polymeric amphiphiles containing cholestanol moieties and those of some closely related non-polymeric amphiphiles

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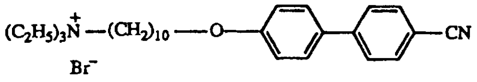
A range of alternating copolymers were prepared by free-radical-initiated copolymerizations of maleic anhydride with a series of α-alkenes containing cholestanyl moieties. Derivatives of these copolymers were prepared by reacting the anhydride residues with methanol, water, dimethylamine and/or morpholine. A related series of non-polymeric amphiphiles containing steroid moieties was also prepared. Isotherms were measured for monolayers of the various polymers and the various non-polymeric amphiphiles on water and, where possible, Langmuir–Blodgett (LB) multilayers were prepared. The majority of the materials gave good isotherms (relatively steep with collapse pressures >40 mN m^{-1}) indicating that the monolayers were ordered and, as determined by the detection of Bragg peaks by X-ray diffraction, Y-type LB films with regular layer structures. Appropriate materials were also examined, by optical microscopy and differential scanning calorimetry (DSC), for possible liquid-crystalline properties. Four polymers and one non-polymeric amphiphile exhibited smectic A mesophases. Another non-polymeric amphiphile exhibited a cholesteric mesophase. Thus, examples were found of amphitropic polymers and non-polymeric amphiphiles which can form organised molecular arrangements both because they are amphiphilic and because they contain mesogens.

There has been great interest in recent years in monolayers of amphiphiles at air–water interfaces and, in favourable cases, in the deposition of such monolayers onto solid supports (Langmuir–Blodgett films).[1–3] Often thick LB multilayers can be prepared by the repeated deposition of monolayers. Such structures are not only of interest as examples of organised systems, but they also have potential applications in microelectronics, optoelectronics and molecular electronics.[4] Although the LB films of many non-polymeric amphiphiles are highly ordered, unfortunately they are prone to molecular reorganisation.[5,6] This prompted us several years ago to study monolayers of preformed polymers and the derived LB films.[7–11] The polymeric LB films are usually more stable and physically more robust than those of non-polymeric amphiphiles. Even though in the best cases[9,10,12] polymeric LB films are generally less ordered, they can nevertheless be sufficiently ordered for many applications.

Liquid crystals, including polymeric liquid crystals,[13] are another major family of organized systems that has been studied extensively in recent years. Currently there is growing interest in compounds which have both amphiphilic character and contain mesogens, *i.e.* compounds which contain the two types of ordering effect. Such compounds have been called amphitropic[14] or amphotropic.[15] Examples are the cyanobiphenyl derivative **1**[14] and the cholesteryl derivative **2**.[15] We considered it of interest to study some amphitropic polymers which, on the basis of previous work,[9–12,16] could be expected to form excellent LB films but which also contained liquid crystal mesogens, and to determine how the interplay of the two ordering effects influences their properties. For example, do the ordering effects tend to reinforce each other or do they act in opposition? Do some polymers form ordered monolayers and LB films as well as being liquid crystals? Our initial aim is to identify amphitropic polymers which form good monolayers and LB multilayers and which are also liquid crystals.



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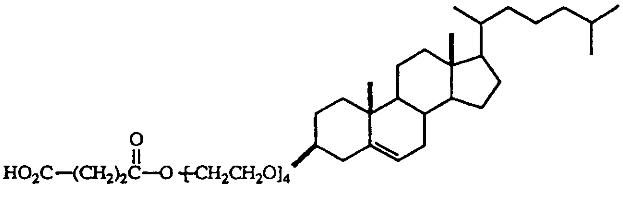

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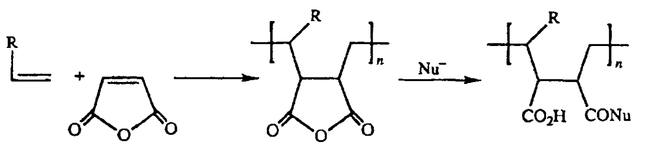
In this paper we describe the synthesis of some α-alkene–maleic anhydride copolymers and their derivatives, a type of polymer which is known to give excellent LB films in many cases,[9,11] where in the present work the α-alkene contains 5α-cholestanyl mesogens. The monolayers, LB films and liquid-crystalline properties of these amphiphilic polymers, and the same properties of some closely related non-polymeric analogues, have been studied. Monolayers of steroids at the air–water interface have been studied before on several occasions[15,17–21] but very little work has been carried out on steroidal LB films.[18,21] Such films are also of interest because Y-type LB films can be considered as assemblies of bilayers, and derivatives of cholesterol (**3**) are present in many biological bilayers.[22]

Experimental

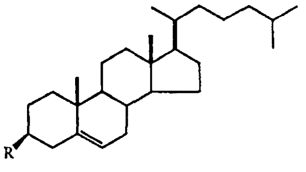
Synthesis of amphiphiles

Cholesterol (**3**), 5α-cholestane-3β-ol (**4**), cholesteryl hemisuccinate (**5**) and cholesteryl hemiphthalate (**6**) were obtained



Scheme 1

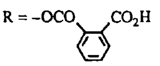
from the Aldrich Chemical Company Limited and were recrystallized before use. Other amphiphiles were prepared from compounds **3** and **4** using the reactions described below. The key synthetic steps are outlined in Scheme 1. Tetrahydrofuran (THF) and benzene were dried by distillation over calcium hydride. Organic solutions were dried over sodium sulfate. Mps were determined using a Kofler hotstage apparatus and are uncorrected. IR spectra were measured for KBr discs (unless indicated otherwise) using a Nicolet MX1 instrument. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz instrument for solutions in deuteriochloroform containing tetramethylsilane as an internal standard. High-pressure liquid chromatography (HPLC) was carried out using Waters 6000A equipment with a R401 refractive index detector, a silica column coated with octadecylsilane and THF as the eluent.



(3) R = –OH

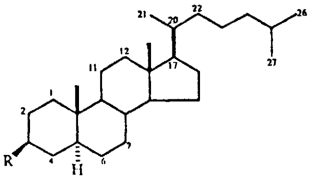
(5) R = –OCO(CH₂)₂CO₂H

(6) R = –OCO CO₂H



$-OCO-C_6H_4-CO_2H$

(7) R = $-OCO.CH\overset{c}{=}CH.CO_2H$



(4) R = –OH

(16) R = –O(CH₂)₉CO₂H

Cholesterol hemimaleate (7). A mixture of cholesterol (**3**) (5.02 g; 13.0 mmol), sodium hydride (80% in mineral oil, 0.50 g; 16.6 mmol) and maleic anhydride (5.01 g; 51.1 mmol) in dry benzene (25 ml) was stirred vigorously and heated under reflux. After 2 days the mixture was cooled and treated carefully with water (2 ml). The solvents were evaporated off and the residue recrystallized from aqueous ethanol. Yield 3.98 g (64%), mp 130–132 °C. Satisfactory IR and ^1H NMR spectra were obtained. Found: C, 76.6; H, 9.8. Calc. for $C_{31}H_{48}O_4$: C, 76.8; H, 10.0%.

Allyl 5α-cholestan-3β-yl ether (8). A two-phase mixture of 5α-cholestan-3β-ol (**4**) (12.26 g; 31.54 mmol), allyl chloride (96.85 g; 1.23 mol), an aqueous solution of sodium hydroxide (40 g of a 50% solution) and tetrabutylammonium hydrogen sulfate (2.47 g; 7.22 mmol) was stirred vigorously under reflux for 12 h. Excess allyl chloride was then distilled off, water (150 ml) was added and the mixture extracted with diethyl ether. The extracts were washed with saturated brine (2 × 150 ml), dried and the solvent evaporated. The residue was recrystallized from hot ethanol to give the desired product **8** (12.5 g, 93%), mp 67–68.5 °C (lit.,[23] 62 °C); IR ν_{max} (Nujol mull)/cm^{-1} 1635; ^1H NMR δ: 0.7–2.4 (46 H, m, steroid nucleus), 4.51 (2 H, m, $=CHCH_2O-$), 3.60 (1 H, m, 3α-H), 5.08 (2 H, m, vinyl CH_2), 5.84 (1 H, m, vinyl CH).

5α-cholestan-3β-yl undec-10-enyl ether (9). Undec-10-en-1-ol (17.03 g; 0.10 mol), pyridine (40 ml) and toluene-*p*-sulfonyl chloride (20.97 g; 0.11 mol) were stirred together at 15 °C for 1 h, then at ambient temperature for 1 h. The mixture was added to ice and concentrated hydrochloric acid (40 ml). After the mixture reached ambient temperature it was extracted with diethyl ether (2 × 50 ml). The extracts were washed successively with dilute hydrochloric acid (50 ml of 5%), aqueous sodium hydrogen carbonate (50 ml of 5%), water (2 × 50 ml), dried and then the solvent evaporated off. Distillation of the oily residue at 0.2 mmHg gave undec-10-en-1-yl tosylate (29.53 g; 91%) as an oil. A satisfactory ^1H NMR spectrum was obtained.

A suspension of sodium hydride (0.31 g; 12.9 mmol) in dry THF (20 ml) was prepared. 5α-Cholestan-3β-ol (**4**) (2.00 g; 5.15 mmol) was added. When effervescence of hydrogen ceased the above tosylate (2.00 g; 6.16 mmol) in THF (10 ml) was added to the mixture. It was then heated under reflux for 24 h, cooled and added to water (100 ml) acidified with hydrochloric acid. The product was extracted with diethyl ether–light petroleum [bp 40–60 °C; 2 × 50 ml (1 : 15 v/v)]. The extracts were washed with hydrochloric acid (25 ml of 5%), dried and the solvent evaporated off. Recrystallization of the residue from acetone gave the desired product **9** (1.20 g; 43%), mp 42.5–44 °C; IR ν_{max}/cm^{-1} 1638; ^1H NMR δ: 0.7–2.4 (62 H, m, steroid nucleus and 8 side-chain CH_2), 3.62 (1 H, m, 3α-H), 4.55 (2 H, m, CH_2O), 5.09 (2 H, m, vinyl CH_2), 5.90 (1 H, m, vinyl CH). Found: C, 84.6; H, 12.9. Calc. for $C_{38}H_{68}O$: C, 84.4; H, 12.7%.

5α-cholestan-3β-yl 2-(prop-2-enyl)ethyl ether (10). A mixture of ethylene glycol (81.0 g; 1.31 mol), potassium carbonate (18.0 g; 0.13 mol) and allyl chloride (15.0 g; 0.2 mol) was stirred and heated at 100 °C for 8 h. Fractional distillation of the mixture at 0.2 mmHg gave 2-(prop-2-enyloxy)ethanol (12.1 g; 60% yield) with a satisfactory ^1H NMR spectrum. This was converted into the corresponding tosylate (47% yield) which was then reacted with sodium hydride and 5α-cholestan-3β-ol (**4**) using the reaction procedures described previously for the preparation of compound **9**. This gave the desired product **10** (46% yield), mp 45–46 °C; IR ν_{max}/cm^{-1} 1642; ^1H NMR δ: 0.7–2.4 (46 H, m, steroid nucleus), 3.55 (1 H, m, 3α-H), 3.60 (4 H, s, OCH_2CH_2O), 4.22 (2 H, m, $=CHCH_2O$), 5.25 (2 H, m, vinyl CH_2), 5.80 (1 H, m, vinyl CH). Found: C, 81.0; H, 11.7. Calc. for $C_{32}H_{56}O_2$: C, 81.3; H, 12.0%.

5α-cholestan-3β-yl 1,4,7,10,13-pentaoxahexadec-15-enyl ether (11). Tetraethylene glycol was converted into the corresponding monoallyl ether (40% yield), which was converted into the corresponding tosylate (63% yield) and this was then reacted with 5α-cholestan-3β-ol (**4**) using the reaction procedures described for the preparation of compounds **9** and **10**. This gave the target compound **11** (81% yield) as a pale yellow viscous oil. IR ν_{max}/cm^{-1} 1637; a satisfactory ^1H NMR spectrum was obtained. Found: C, 75.1; H, 11.0. Calc. for $C_{38}H_{68}O_5$: C, 75.4; H, 11.3%.

Copolymerizations. Alkenes **8**, **9**, **10** and **11** were separately copolymerized with maleic anhydride in anhydrous THF at 60° using azoisobutyronitrile as the initiator and the products were isolated and characterized using the procedures given previously for the copolymerization of hexadec-1-ene and maleic anhydride.[9] This gave copolymers **12a**–**15a**, respectively, in yields of 45–70%. All of these polymers gave satisfactory IR spectra, *i.e.*, they had bands at ν_{max} 1850 (m) and 1780 (s) cm^{-1} characteristic of carbonyl groups in five-membered ring anhydrides and they had no carbonyl bands due to maleic anhydride, a possible impurity. By gel permeation chromatography (GPC), using the methods given before,[9] **12a** had $\bar{M}_n = 4800$, $\bar{M}_w = 8600$; **13a** had $\bar{M}_n = 5100$, $\bar{M}_w = 9700$; **14a** had $\bar{M}_n = 3400$, $\bar{M}_w = 6800$; **15a** had $\bar{M}_n = 4300$, $\bar{M}_w = 7400$. There was no evidence for non-polymeric impurities.

Derivatives of copolymers. The following procedures are typical. Long reaction times were used simply to ensure virtually quantitative reactions.

Half methyl ester **12b**. Polymer **12a** (1.00 g) was treated with methanol (50 ml) at reflux temperature for 14 days. Excess methanol was then evaporated off and the residue dissolved in a minimum of THF (10 ml). The solution was added slowly to ice-cold light petroleum (100 ml) to precipitate the polymer. The polymer was collected and dried (0.84 g, 79%); IR ν_{max} 1728 and 1711 cm^{-1}, no carbonyl bands attributable to anhydride residues were detected. Found: C, 77.2; H, 10.5%. Calc.: C, 77.5; H, 10.8%.

The half methyl esters **14b** and **15b** were prepared similarly from the appropriate anhydride copolymers.

Diacid **12c**. Polymer **12a** (1.60 g) was treated with sodium hydroxide (2.0 g) in water (50 ml) for 1 week at reflux temperature. The cooled solution was then added to aqueous hydrochloric acid (2 mol l^{-1}, 500 ml). The precipitate was collected, dissolved in THF, and reprecipitated into water (500 ml). The polymer was collected, washed with water and dried (1.20 g, 72%); IR ν_{max}/cm^{-1} 3800–2200 (br), and 1708, no carbonyl bands attributable to anhydride residues were detected. Found: C, 76.5; H, 10.4%. Calc.: C, 77.2; H, 10.7%.

The anhydride residues of polymers **13a**, **14a** and **15a** were hydrolysed to the corresponding diacid derivatives by allowing monolayers on the water surface at a surface pressure of 20 mN m^{-1} to stand for 20 h at 20 °C.[9]

Acid–dimethylamide **12d**. Polymer **12a** (0.50 g) was dissolved in a solution of dimethylamine in ethanol (33%, 50 ml), and the mixture was heated under reflux for 4 days. The cooled mixture was acidified (2 mol l^{-1} HCl). This precipitated the polymer, which was collected and reprecipitated into water and then into light petroleum. The dried product (0.33 g, 61%) gave IR ν_{max}/cm^{-1} 1709 (strong, carboxy), 1652 (strong, amide), no bands attributable to anhydride residues were detected. Found: C, 77.4; H, 11.5; N, 2.4%. Calc.: C, 77.8; H, 11.1; N, 2.5%.

The acid–amides **15d**, **12e** and **14e** were prepared similarly from the appropriate anhydride copolymers.

10-(5α-cholestan-3β-yloxy)decanoic acid (16). A mixture of ether **9** (2.50 g; 4.63 mmol), potassium permanganate (2.46 g; 15.57 mmol), water (26.3 ml), benzene (26.3 ml), tetrabutylammonium hydrogen sulfate (13 mg; 3.83×10^{-2} mmol) and acetic acid (4.66 ml) was stirred vigorously at 0 °C in a conical flask for 5 h. Sodium sulfate (2.10 g; 16.67 mmol), hydrochloric acid (2.1 ml; 12 mol l^{-1}) and water (2.1 ml) were added, and the dark colour rapidly disappeared. The mixture was then extracted with diethyl ether (2 × 75 ml). The combined extracts were washed with water (2 × 10 ml), dried and evaporated to dryness. Recrystallization of the residue from pentane gave the desired product **16** (1.51 g; 46%), mp 85–100 °C (see Table 3; later). Satisfactory IR and ^1H NMR spectra were obtained. Found: C, 79.8; H, 11.7. Calc. for $C_{37}H_{66}O_3$: C, 79.5; H, 11.9%.

Langmuir isotherms and film deposition

Isotherms of monolayers and, in appropriate cases, their deposition properties were studied for compounds **3–7** and **16** and for polymers **12a–12e**, **13a** and **13c**, **14a–14c** and **14e**, and **15a–15d**. All the non-polymeric amphiphiles were shown by HPLC analysis to be >99.5% pure.

Isotherms were measured for monolayers on water at pH 5.4–5.6 with no added ions using the apparatus and procedures described previously.[9] For the non-polymeric amphiphiles, the spreading solvent was ethyl acetate, while for the polymers a mixture of ethyl acetate and THF (9:1 v/v), or a mixture of chloroform and THF (9:1 v/v) proved to be satisfactory (see Table 2; later). LB films were deposited onto hydrophobic[18] silicon wafers from over water containing $CdCl_2$ (2.5×10^{-4} mol l^{-1}) using the apparatus and procedures described previously.[9] The presence of the $CdCl_2$ did not noticeably affect the isotherm. In general, transfer was carried out at a surface pressure of 30 mN m^{-1} and at a dipping speed of 8 mm min^{-1}. The results are summarized in Tables 1 and 2.

X-Ray studies

These were carried out as described previously.[9] The results are summarised in Tables 1 and 2.

Studies of polymerization of Langmuir–Blodgett multilayers

These studies were carried out using the procedure as previously described for crosslinking LB multilayers.[10]

Liquid crystal studies

The thermal properties of the various samples were examined using a Nikon Optiphot-2 optical microscope equipped with a hot stage controlled by a Mettler FP80 HT apparatus. The results are summarised in Table 3. Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC4 instrument linked to a data station with heating and cooling rates of 5 °C min^{-1}.

Results and discussion

Synthesis of amphiphiles

We have previously shown[9] that the amphiphilic polymers obtained (see Scheme 1) by (*a*) the copolymerization of equimolar amounts of long-chain vinyl compounds such as hexadec-1-ene with maleic anhydride, followed by (*b*) reaction of the anhydride residues in the products with nucleophiles such as water, methanol or small amines, give excellent monolayers on water and good Y-type LB multilayers which display up to three orders of Bragg peaks in X-ray reflection experiments. In the present work, polymers of the same general family have been prepared using vinyl compounds containing cholestanyl

Table 1 Properties of monolayers at air–water interface and Langmuir–Blodgett films of the non-polymeric amphiphiles **3–7** and **16**

	monolayer area per molecule/Å^2 [a]			X-ray data		
compound	at 0 mN m^{-1} [b]	at 30 mN m^{-1}	collapse pressure, π_c/mN m^{-1}	number of layers in LB film[c]	number of Bragg peaks	*d*-spacing per bilayer/Å
3	47	43.0	37	—	—	—
4	46	42.0	39	—	—	—
5	50	42.0	39	282	3	42.5
6	62	47.0	32	220	1	44.6
7	43	39.0	44	242	3	45.5
16	41	34.5[d]	29	25	3	41.7

[a] Monolayers prepared using solutions of the amphiphiles in ethyl acetate. [b] By extrapolation of the 'solid' section of the isotherm to zero pressure. [c] Transferred onto hydrophobic silicon at a surface pressure of 30 mN m^{-1} from over water containing $CdCl_2$ (2.5×10^{-4} mol l^{-1}). Deposition occurred on both up and down strokes with a deposition ratio of 0.95–1.05. [d] At 20 mN m^{-1}.

Table 2 Properties of monolayers at air–water interface and Langmuir–Blodgett films of the amphiphilic polymers

polymer	monolayer area per repeat unit/Å^2 at 0 mN m^{-1}[a]	monolayer area per repeat unit/Å^2 at 30 mN m^{-1}	collapse pressure, π_c/mN m^{-1}	X-ray data: number of layers in LB film[b]	X-ray data: number of Bragg peaks	X-ray data: *d*-spacing per bilayer/Å
12a[c]	50	39.0	53	—	—	—
12b[d]	47	41.3	55	100	1	43.1
12c[c]	45	40.0	54	100	4	45.6
12d[d]	45	40.8	57	100	1	44.0
12e[c]	63	50.1	38	100	1	41.7
13a[c]	48	40.2	54	—	—	—
13c[c]	56	47.6	50	50	1	50.0
14a[c]	52	44.5	53	—	—	—
14b[c]	54	47.2	52	100	2	49.3
14c[c]	57	40.2	48	50	2	48.6
14e[c]	50	44.2	49	100	2	50.4
15a[c]	62	43.5	48	—	—	—
15b[c]	52	49.0	45	—	2	54.1
15c[c]	62	50.3	43	30	2	55.7
15d[c]	41	34.1	47	100	2	56.6

[a] See footnote *b* in Table 1. [b] See footnote *c* in Table 1. [c] Monolayers prepared using solutions of the amphiphiles in a mixture of chloroform–THF 9:1 v/v. [d] Monolayers prepared using solutions of the amphiphiles in a mixture of ethyl acetate–THF (9:1 v/v).

Table 3 Liquid-crystalline properties of various amphiphiles[a] determined using DSC

compound to polymer	glass to liquid crystal[c] *T*/°C	glass to liquid crystal[c] Δ*H*/kJ mol^{-1}	transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) determined by DSC[b]	liquid crystal[c] to isotropic liquid *T*/°C	liquid crystal[c] to isotropic liquid Δ*H*/kJ mol^{-1}
6	95[d]	0.75		155[d]	0.38
16	68	1.00		85	14.65
12a			decomposed at 235 °C		
12d			clearing point 295 °C		
12e			decomposed at 260 °C		
13a	137	0.38		194	3.16
14a	125	0.27		163	1.17
14e			decomposed at 250 °C		
15a	142	0.03		252	0.12
15d	69	17.12		173	39.42

[a] No liquid-crystalline phase observed for either of compounds **5** and **7**. [b] Cooling rate 5 °C min^{-1}. [c] Except where indicated otherwise the mesophase was smectic A as determined by optical microscopy. [d] Cholesteric mesophase as determined by optical microscopy.

moieties. The products are a series of amphiphilic polymers containing cholestanyl moieties which differ in the head groups and the type and length of the 'spacer' unit linking the mesogen to the polymer backbone.

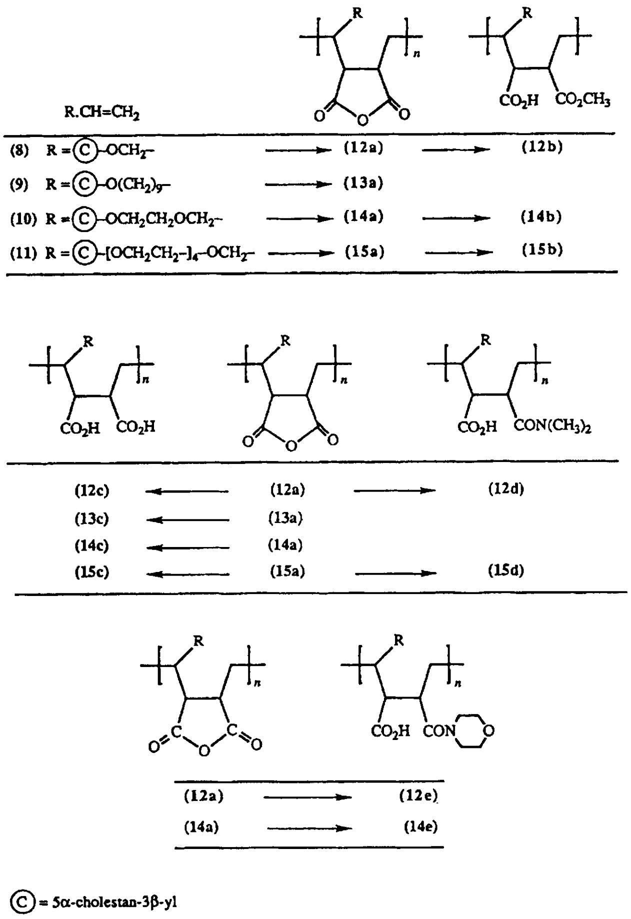
Vinyl compounds **8–11** were prepared by reacting the appropriate chloride or tosylate with the sodium alkoxide of 5α-cholestan-3β-ol (**4**). Each vinyl compound in THF was then copolymerized with an equimolar amount of maleic anhydride using azoisobutyronitrile as the free-radical initiator (see Scheme 1). This gave polymers **12a–15a**. Their molecular masses were estimated by GPC (relative to polystyrene standards) and were found to be in the range $\bar{M}_n$=4300–5100. Polydispersities were in the range 1.7–2.0. The anhydride copolymers were reacted with appropriate nucleophiles[9] to give acid–methyl ester derivatives **12b**, **14b** and **15b**, the diacid derivatives **12c–15c**, acid–dimethylamides **12d** and **15d**, and **12e** and **14e** (see Scheme 2). For the synthesis of the diacid derivatives **13c–15c** the anhydride residues were hydrolysed by leaving monolayers of the corresponding anhydride copolymers on the water surface for 20 h.[9]

Oxidation of vinyl compound **9** with potassium permanganate gave 10-(5α-cholestan-3β-yloxy)decanoic acid (**16**). Reaction of cholesterol (**3**) with maleic anhydride gave the half maleate **7**.

Monolayer and LB film properties of compounds 3–7 and 16

Monolayers of compounds **3–7** and **16** were prepared (by using solutions in ethyl acetate) on a subphase of water at pH 5.4–5.6 at 20 °C and their isotherms were recorded. These are shown in Fig. 1 and 2. When possible the monolayers were transferred onto hydrophobic silicon wafers[24] by vertical dipping and the multilayers were studied by X-ray reflectometry. The results obtained are summarized in Table 1.

The isotherms of cholesterol (**3**) and cholestanol (**4**) are very similar to those reported previously.[1] They have a good shape with collapse pressures, $\pi_c > 35$ mN m^{-1} and, by extrapolation of the 'solid' portion of the isotherm to zero pressure, cross-sectional areas, A_0 of 47 Å^2 and 46 Å^2, respectively. CPK molecular models of these steroids have cross-sectional areas of *ca.* 40 Å^2. All attempts to prepare LB multilayers from these two alcohols failed. The monolayers deposited well on the down strokes but they rapidly transferred back to the water surface on the upstrokes. Langmuir *et al.* reported similar problems with these two compounds but found that cholestanol (**4**) could be deposited as Y-type films on a base of barium stearate.[18] On the same base, however, cholesterol (**3**) only deposited as an X-type film and even then only for a few layers, but it did deposit Y-type if the subphase contained cupric chloride.[18]



Scheme 2

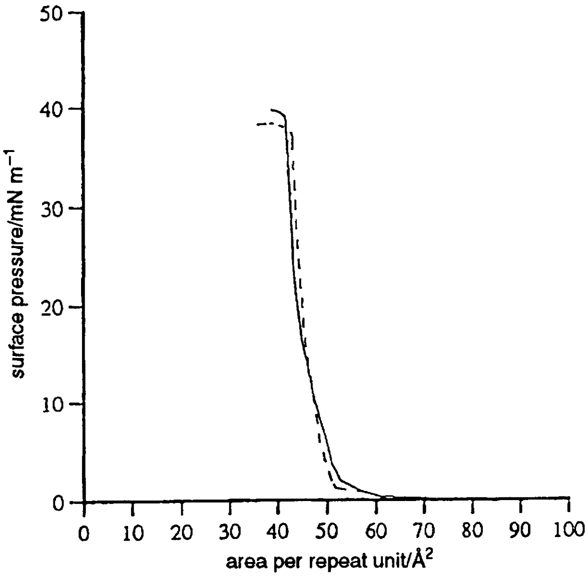


Fig. 1 Isotherms of cholesterol (**3**) (– – –) and cholestanol (**4**) (—) measured at 20 °C and pH 5.3–5.6

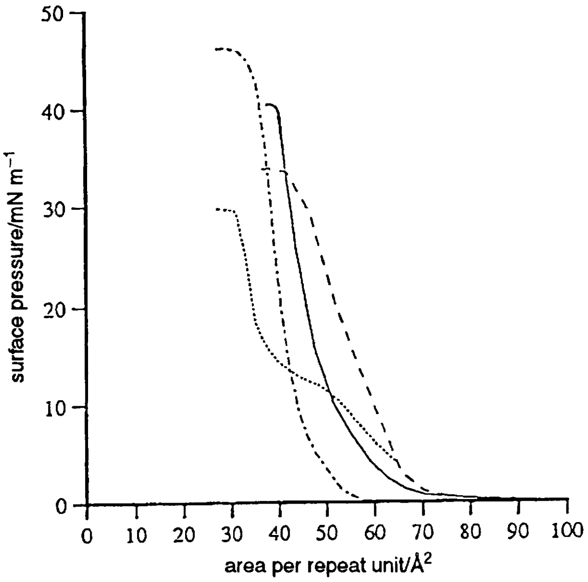


Fig. 2 Isotherms of various non-polymeric amphiphiles. All isotherms were measured at 20 °C and pH 5.3–5.6. Cholesteryl hemisuccinate (**5**) (—); cholesteryl hemiphthalate (**6**) (– – –); cholesteryl hemimaleate (**7**) (–·–·–) and compound **16** (······).

The half esters **5**–**7** gave good isotherms (see Fig. 2), though they were less satisfactory than those of the steroidal alcohols **3** and **4**. Thus, the isotherms either had lower collapse pressures, were less steep, and/or showed a more gradual transition from the 'gaseous' to the 'solid' region. The isotherm of the phthalate **6** was, not surprisingly in view of the relative bulk of the head group, the least satisfactory. All the half esters **5**–**7** could be deposited readily from a subphase of 2.5×10^{-4} mol l^{-1} aqueous $CdCl_2$ solution. The multilayers of half esters **5** and **7** each showed three orders of Bragg peaks whilst that of the half phthalate showed only one. Given that stearic acid multilayers usually show at least 12 orders,[25] it is evident that the present LB multilayers are not particularly well ordered. However, it is important to note that these simple cholesterol derivatives readily give LB multilayers whereas cholesterol (**3**) itself does not. Using CPK molecular models the maximum lengths of the half esters **5**, **6** and **7** are 25 Å, 27 Å and 23 Å, respectively. This, and the *d*-spacings given in Table 1, suggest that the molecules in the bilayers are probably in a simple Y-type pattern and tilted from the normal by 32°, 22° and 5°, respectively.

A multilayer (20 layers) of the half maleate ester **7** was deposited in the usual way. Exposure to UV irradiation through the small holes of a simple metal mask brought about polymerization.[10] A quick rinse of the exposed film in 95% ethanol resulted, due to the lower solubility of the polymer than the monomer, in the formation of the expected pattern in the films. The best results were obtained with 30 min exposure and a 10 s rinse. Longer exposures led to the polymer becoming more soluble, presumably due to chain scission and photodesorption. As a control a multilayer of the half succinate **5** was treated similarly. It did not become less soluble on irradiation, indicating that it is the maleate C=C rather than the cholesteryl C=C which polymerizes. Polymerization of ester **7** therefore provides a simple route to a polymeric LB film containing steroid moieties.

The isotherm obtained for 10-(5α-cholestan-3β-yloxy)decanoic acid (**16**), was poor (see Fig. 2). It did not display a clear 'solid' region and had a relatively low collapse pressure. Even so, the monolayer at 20 mN m^{-1} over aqueous $CdCl_2$ solution could be deposited to give a Y-type multilayer which exhibited three orders of Bragg peaks. Surprisingly, the *d*-spacing of the multilayer was slightly less than that of the multilayer of the half succinate **5**. Since the methylene chain is long and flexible it is difficult to predict with confidence how the multilayers of compound **16** are packed.

Monolayer and LB film properties of the amphiphilic polymers

Monolayers of the various polymers were prepared [by using solutions in chloroform- or ethyl acetate–THF (9:1 v/v); see Table 2] on a subphase of water at pH 5.4–5.6 at 20 °C and their isotherms were recorded. When possible the monolayers were transferred onto pieces of hydrophobic silicon wafer[24] and the multilayers obtained were studied by X-ray reflectometry. The results obtained are summarized in Table 2.

The family of amphiphilic polymers **12a**–**12e** have just one CH_2 group as a 'spacer' between the steroid moiety and the polymer backbone. As shown in Fig. 3, all these polymers give excellent isotherms. The isotherm of the parent anhydride polymer **12a** was steep, indicating that the film was well ordered. In view of the reactivity of the anhydride moieties no attempts were made to prepare LB films from this polymer. The isotherms of the half methyl ester derivative **12b**, the diacid derivative **12c** and the acid dimethylamide derivative **12d** were very similar. They all showed significant 'solid' regions, had A_0 values of *ca.* 45 Å^2, a value close to the cross-sectional area of the steroid nucleus (40 Å^2), and collapse pressures >50 mN m^{-1}. The isotherm of derivative **12e** had a lower collapse pressure and a somewhat greater value of A_0. All these polymers deposited well as Y-type multilayers which, in X-ray reflectivity studies, displayed one or more Bragg peaks corresponding to *d*-spacings of 41.7–45.6 Å. The diacid derivative **12c** was particularly well ordered and displayed four Bragg peaks, the highest number we have observed for derivatives of α-alkene–maleic anhydride copolymers. Given the data available, it is possible to suggest a likely structure for these multilayers. Thus, given: (*a*) that the experimental values for the *d*-spacings are significantly less than those expected for a Y-type multilayer in which the side chains are perpendicular to the planes of the films; (*b*) that the areas per repeat unit on the water surface and, since the deposition ratios were 1.00 ± 0.05, also in the LB films are too small (*i.e.*, $<2 \times 40$ Å^2) for a structure with fully interdigitated side chains; and (*c*) that the steroid nucleus is essentially rigid, the most likely structure is a Y-type film with the side chains essentially straight but significantly tilted and interpenetrating, if at all, only at the ends. Such an arrangement is shown schematically in Fig. 4 for polymer **12c**. Taking polymer **12c** as an example and assuming that the thickness of the 'headgroups' in the bilayer is the same (13.1 Å) as was as deduced in our earlier work,[9] then the space left for the side chains is 32.5 Å. From a CPK molecular model, the length of an entire side chain is 22.3 Å. If there is no interdigitation at all, this suggests that all the side chains are tilted from the vertical at an angle θ where $\cos\theta = [32.5/(2 \times 22.3)]$; *i.e.*, $\theta = 43°$. If the C_{20}–C_{27} side chains interdigitate, since they have a length of *ca.* 7.7 Å, and could reasonably overlap with each other by *ca.* 5.0 Å, as shown in Fig. 4, θ will be 35°.

The amphiphilic polymers **13a** and **13c** are generally similar in structure to the polymers discussed above, except that they have a much longer 'spacer' group between the steroid nucleus and the polymer backbone: ten methylene groups instead of one. The parent anhydride polymer **13a** gave a reasonably steep isotherm (see Fig. 5), indicating that the monolayer was well organised. The diacid derivatives **13c** also gave a steep isotherm (see Fig. 5), the value of A_0 being 56 Å^2. This polymer deposited to give a Y-type multilayer which displayed only one Bragg peak corresponding to a *d*-spacing of 50.0 Å. Given the presence of the long flexible 'spacer' group, it is difficult, with the data available, to suggest with confidence how the multilayer may be organised, but it could well be similar to that proposed for polymers **12c**, shown in Fig. 4, but with the side chains more tilted.

The amphiphilic polymers **14a**–**14c** and **14e** only differ from those of polymer **12a** and its derivatives in having a 'spacer' that is $-OCH_2CH_2OCH_2-$ instead of $-OCH_2-$, *i.e.* a 'spacer' that is a little larger and somewhat more flexible. The isotherm of polymer **14a** (see Fig. 6), indicates that here, as in the other series, the parent anhydride-containing polymer forms a well ordered monolayer on water. Polymers **14b**, **14c**

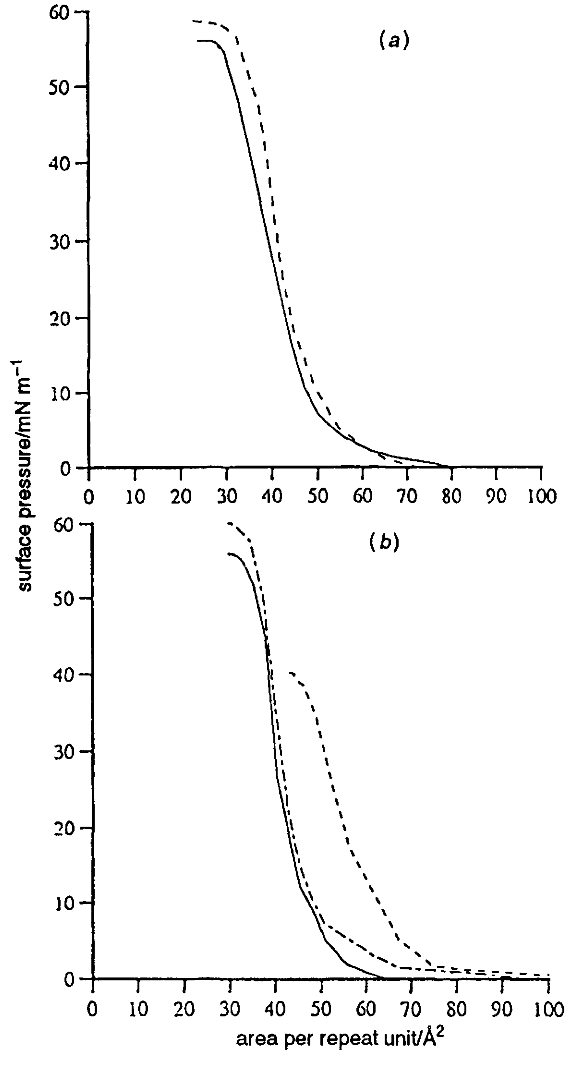


Fig. 3 Isotherms of copolymer **12a** and its derivatives measured at 20 °C and pH 5.3–5.6. (*a*) Polymer **12a** (—); polymer **12b** (– – –). (*b*) Polymer **12c** (—); polymer **12d** (–·–·–) and polymer **12e** (– – –).

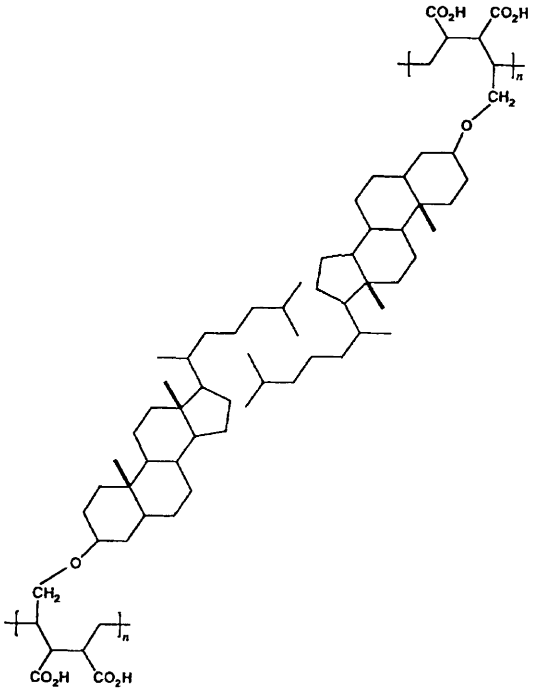


Fig. 4 Scheme showing probable arrangement of repeat units of polymer **12c** in the LB multilayer

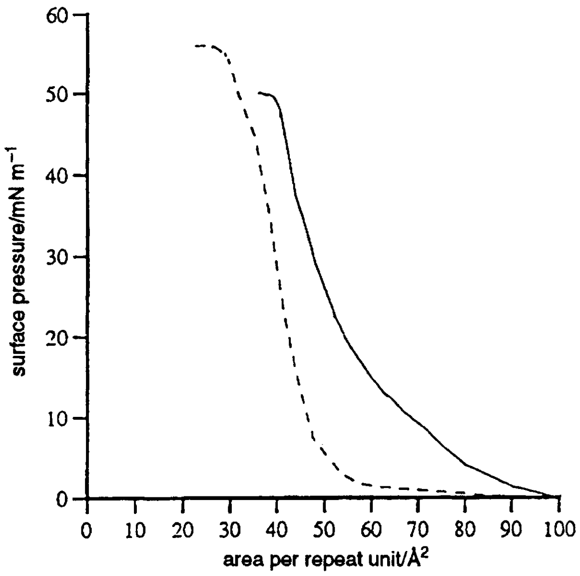


Fig. 5 Isotherms of copolymer **13a** (– – –) and its derivative polymer **13c** (—) measured at 20 °C and pH 5.3–5.6

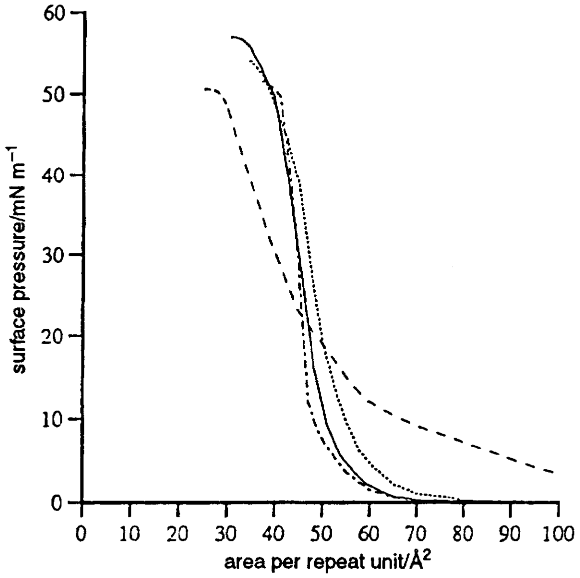


Fig. 6 Isotherms of polymer **14a** and its derivatives measured at 20 °C and pH 5.3–5.6. Polymer **14a** (—); polymer **14b** (······); polymer **14c** (– – –) and polymer **14e** (–·–·–).

and **14e** gave isotherms (Fig. 6) with A_0 values of 50–57 Å^2 and collapse pressures>48 mN m^{-1}. They deposited well to give Y-type multilayers which displayed two orders of Bragg peaks corresponding to *d*-spacings of 48.6–50.4 Å. The same arguments for the plausible structure shown in Fig. 4 for the polymers derived from polymer **12a** apply here, except that in this case the side chains are tilted a little further from the vertical. Similar calculations to those given above indicate values for θ of 39° and 45° according to whether there is or is not interdigitation, respectively.

The final series of polymers studied, polymers **15a**, **15c** and **15d**, differ from the series prepared from polymer **12a** in that they have as a 'spacer' the moiety $-(-CH_2CH_2O-)_4-$. This 'spacer' was the longest used in the present work and it has substantial hydrophilic character. Of this series, polymers **15a**, **15b** and **15d** gave good isotherms (see Fig. 7). The values of A_0 were 41–62 Å^2. Polymers **15b**–**15d** deposited well to give Y-type multilayers which displayed two Bragg peaks corresponding to *d*-spacings of 54.1–55.7 Å. The structure of the

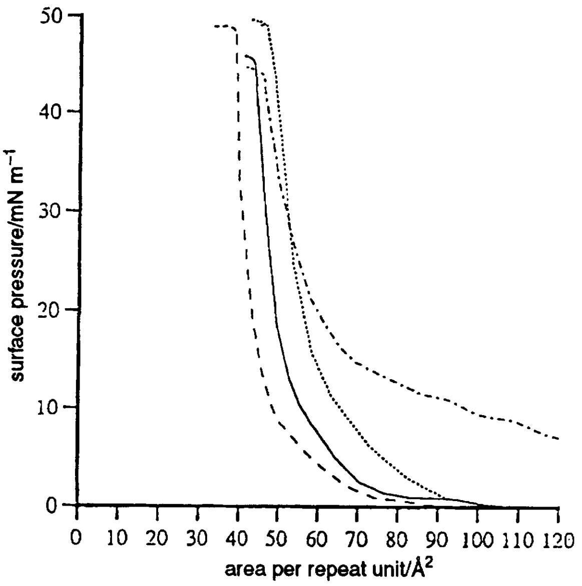


Fig. 7 Isotherms of polymer **15a** and its derivatives measured at 20 °C and pH 5.3–5.6. Polymer **15a** (······); polymer **15b** (—); polymer **15c** (–·–·–) and polymer **15d** (– – –).

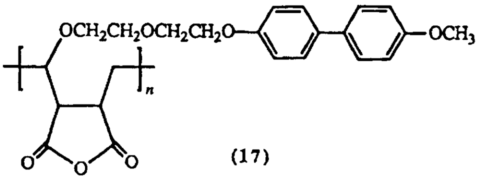
LB multilayers might well be a more highly tilted analogue of that shown for polymer **12c** in Fig. 4.

Investigation of various amphiphiles for liquid-crystalline properties

Several of the amphiphiles were investigated by optical microscopy and DSC for their liquid-crystalline properties. The results are summarised in Table 3.

As expected, neither of the half esters **5** and **7** displayed a liquid-crystalline phase. However, the half phthalate **6** displayed a smectic A phase and the long-chain acid **16** a cholesteric phase.

Investigation of the anhydride copolymers revealed that copolymer **12a**, with only a $-OCH_2-$ moiety as a 'spacer' between the steroid moiety and the polymer backbone, did not display liquid-crystalline properties, but that the other anhydride copolymers **13a**–**15a**, which have longer 'spacers', all showed a smectic A phase on cooling from the liquid phase. Skoulios *et al.* previously reported that the closely related polymer **17** shows liquid-crystalline phase behaviour. On the basis of X-ray diffraction studies the phase was identified as smectic E.[26] Acid–ester derivatives formed by reacting the anhydride residues of polymer **17** with alcohols also showed liquid-crystalline phases.[27]



(17)

The acid–methyl ester (series **b**) and diacid (series **c**) amphiphilic polymer derivatives were not studied for their liquid-crystalline properties in the present work because these derivatives begin to revert to the parent anhydride copolymers on heating to *ca.* 150–200 °C. This is, however, not a problem with the acid–*N*,*N*-dimethylamide derivatives **12d** and **15d** and the acid–morpholinoamide derivatives **12e** and **14e** because they contain tertiary-amide moieties. In the event neither polymer **12d**, polymer **12e** nor polymer **14e** displayed liquid-crystalline properties. In the first two cases, this is not surprising in view of the fact that the parent anhydride copolymer **12a** is not a liquid crystal, but in the case of polymer **14e** it suggests that when mesogenic properties are desired the acid–tertiary-amide head group is not as satisfactory as an anhydride head group. The final polymer of this set investigated, **15d**, proved to be a liquid crystal and to exhibit a smectic A phase.

Conclusions

Although cholesterol (**3**) and cholestanol (**4**) give isotherms which indicate that the monolayers are well ordered, it is not easy to prepare LB multilayers from these compounds by the vertical lifting method. However, LB multilayers are prepared easily from the half succinate **5**, half maleate **7** and half phthalate **6** esters of cholesterol and from compound **16**, all of which contain a carboxylic acid head group. The half phthalate ester **6** and compound **16** also show liquid-crystalline behaviour. The former exhibits a smectic A mesophase, the latter a cholesteric phase.

LB multilayers of the half maleate **7** can be polymerized by UV irradiation to give a polymeric LB film.

The anhydride copolymer **12a** and the various derivatives **12b**–**12e** formed by reacting the anhydride residues with appropriate nucleophiles give well ordered monolayers and excellent LB films, but none of the polymers of this series that were investigated were liquid crystals. The LB multilayers of the various ring-opened derivatives are probably arranged essentially as shown for polymer **12c** in Fig. 4, with or without interdigitation of the steroid side chains.

The anhydride copolymers **13a**–**15a**, all of which have longer spacers than anhydride copolymer **12a**, form well ordered monolayers at the air–water interface and are also liquid crystals. The mesophases are smectic A.

The carboxylic acid–*N*,*N*-dimethylcarboxamide polymer **15d** forms well ordered monolayers, good LB multilayers (two Bragg reflections) and is also a liquid crystal, again exhibiting a smectic A structure.

The LB multilayers of the various derivatives of the anhydride copolymers **13a**–**15a** probably have a structure similar to that shown in Fig. 4 but with a larger tilt of the side chains.

Polymers **13a**–**15a** form well ordered monolayers and exhibit liquid-crystalline properties. Compound **16** forms ordered LB multilayers and exhibits liquid-crystalline properties. Polymer **15d** and compound **6** form well ordered monolayers and LB multilayers also exhibit liquid-crystalline properties. Thus, examples of amphitropic polymers and further examples of amphitropic non-polymeric amphiphiles have been found which are able to form organised molecular arrangements both because they are amphiphilic and because they contain mesogens. The results indicate that with the present materials the longer the 'spacer' moiety between the hydrophilic group(s) and the mesogenic group the more likely the materials are to exhibit amphitropic properties. However, further examples of amphitropic molecules need to be studied before the interactions, if any, between the two types of ordering effects can be fully understood. It will, for example, be interesting to determine whether there are cases where the presence of a mesogenic group actually facilitates the formation of ordered monolayers and ordered LB multilayers.

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