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Discotic liquid-crystalline side chain polymers with inositol derivatives as mesogens

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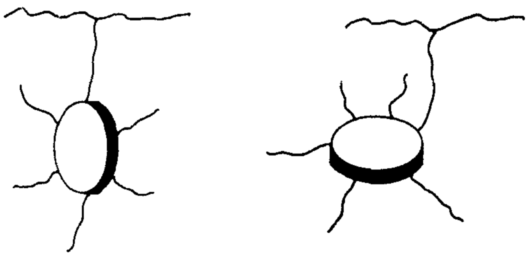
The synthesis of monofunctionalized *myo*- and *scyllo*-inositol derivatives and their attachment as side groups on a polysiloxane backbone are described. All polymers with *scyllo*-inositol mesogens show liquid-crystalline behaviour. In contrast to this the *myo*-inosital mesogens containing polymers exhibit no liquid-crystalline phases.

1. Introduction

Low molecular weight discotic liquid-crystalline compounds have been known for just ten years [1]. As the core so far used most of the discoid mesogens contain flat aromatic units with chains six or eight atoms long, e.g. alkoxy substituents [2]. The introduction of the cyclohexane ring as a non-aromatic discoid core [3, 4] opened the way to the preparation of new discotic materials with interesting properties [5–12]. In the earlier experiments [3, 4] *scyllo*-inositol derivatives, that is hexaacyloxy substituted cyclohexanes with the substituents all in the equatorial position, were synthesized and investigated. Not only did these *scyllo*-inositol derivatives show discotic mesophases but they also exhibited much broader mesophase ranges than the analogous benzene derivatives [3, 4]. In contrast the similarly functionalized *myo*-inositol, but in this case with just one acyloxy group in axial position and with five equatorially arranged substituents on the cyclohexane ring, did not possess a mesophase [8].

Investigations of liquid-crystalline polymers with rod-like mesogens as side-groups show that the tendency to form calamitic mesophases is increased by attachment to the polymer of anisometric molecules via flexible spacers [13]. In many cases liquid-crystalline polymers were found while the low molecular weight starting materials did not show mesophases. This was recently shown again for mesogens containing 1,3-dioxan units [14]. In connection with investigations of discotic side group and main chain polymers with triphenylene and benzene derivatives as the discotic mesogen [15–18] it was interesting therefore to study the influence of the attachment to the polymer of inositol derivatives. While for the *scyllo*-inositol derivatives discotic mesophases were to be expected, it had to be seen if the attachment of *myo*-inositol derivatives to a polymer backbone would also lead to mesophases. Polysiloxanes were used as the polymer main chain.

The two possibilities, namely the attachment of *scyllo*- and *myo*-inositol derivatives to a polymer chain, lead to different polymer structures and are shown



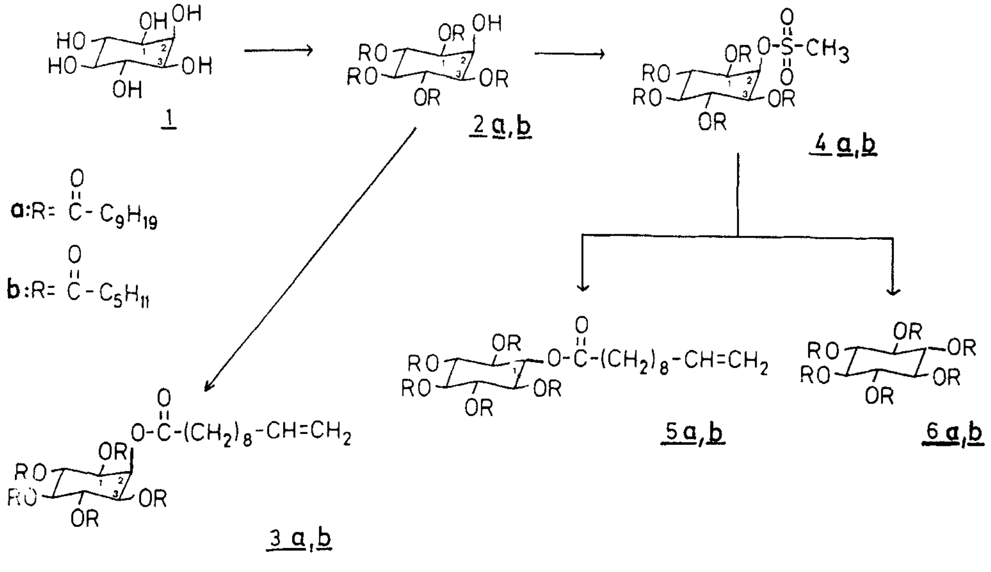
(*a*) (*b*)

Figure 1. Schematic representation of polymer attached inositol derivatives: (*a*) *scyllo*-inositol, (*b*) *myo*-inositol.

schematically in figure 1. The axial fixation (see figure 1 (*b*)) is partly comparable with the lateral attachment of rod-like mesogens in calamitic polymers [19–21].

2. Results and discussion

Starting from commercially available *myo*-inositol **1** the mono hydroxy compounds **2a** and **2b** were synthesized (see scheme 1) [8]. Esterification with 10-undecenoyl chloride leads to the *myo*-inositol derivatives **3**. Reaction of the mono hydroxy compounds **2** with methanesulphonylchloride yielded the mesylates **4**, which could be converted to the *scyllo*-inositol derivatives **5** with 10-undecenoic acid in the presence of caesium carbonate. Beside this main reaction via trans esterification the saturated hexasubstituted *scyllo*-inositols **6** are also formed. So far no possibility was found to separate these two products.



The phase behaviour of the low molar mass mesogens is summarized in table 1. The *myo*-inositol derivatives **3** were crystalline and, as expected, did not show any mesophases. In contrast the *scyllo*-inositol derivatives **5**—which were mixed with the *scyllo*-inositol derivatives **6** [3, 4, 9] (mol ratio ≈ 60 : 40)—show discotic mesophases almost in the same temperature range and of the same type as those of the pure compound **6**. The comparable mesophase behaviour of the pure compounds **6** and

Table 1. Transition temperatures of the inositol derivatives **3**, **6** and the mixtures of **5** and **6**.

No.	*R*	Transition temperatures in °C				
3a [8]	CO-C_9H_{19}	C_1	2	C_2	43	I†
3b	CO-C_5H_{11}	Oil				†
5a + **6a**	CO-C_9H_{19}	C	89	D	187	I†
5b + **6b**	CO-C_5H_{11}	C	41	D	177	I†
6a	CO-C_9H_{19}	C	84	D	189	I [3, 4]‡
6b	CO-C_5H_{11}	C	69	D	199	I [3, 4]‡

† Measured by D.S.C.
‡ Determinated by polarization microscopy.

the mixtures of **5** and **6** is understandable, because their discoidal cores are the same, they differ only slightly in the outer periphery. One of the six substituents is somewhat longer than the other five and contains a double bond. The monofunctionalized inositol derivatives **3** and **5** (the latter with the corresponding compound **6** as a non-active impurity) were the starting materials for an analogous polymer reaction with a polymethylhydrogensiloxane and a catalyst based on H_2PtCl_6. Thus the polymers **7** and **8** were synthesized; their phase behaviour is given in table 2.

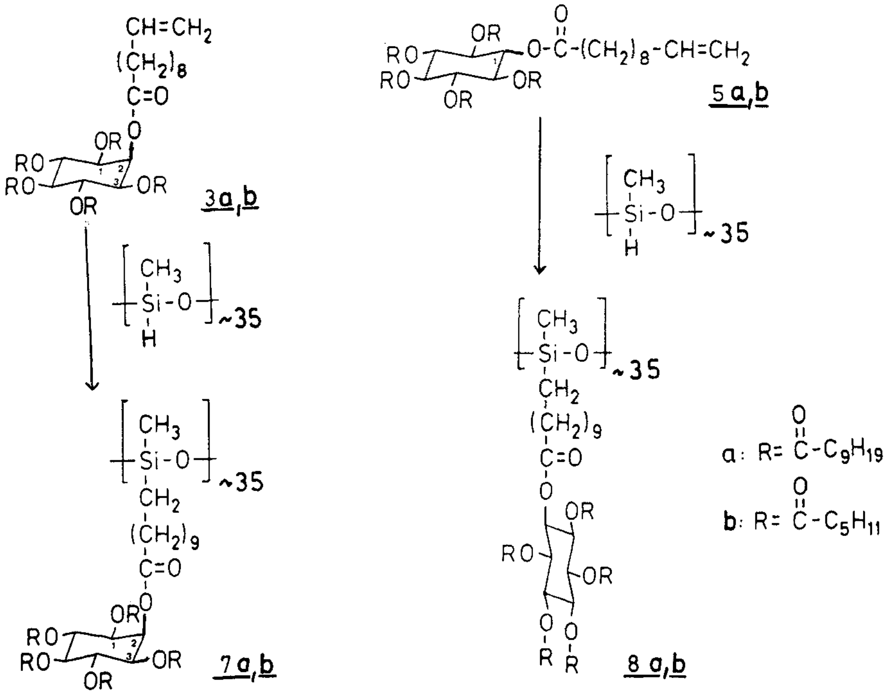


Table 2. Transition temperatures of the polymers **7** and **8**.

No.	*R*	Transition temperatures in °C						
7a	CO-C_9H_{19}	C_1	1	C_2	40	I		
7b	CO-C_5H_{11}	g	−30	I				
8a	CO-C_9H_{19}	C_1	51	C_2	71	D	176	I
8b	CO-C_5H_{11}	g	55	D	164	I		

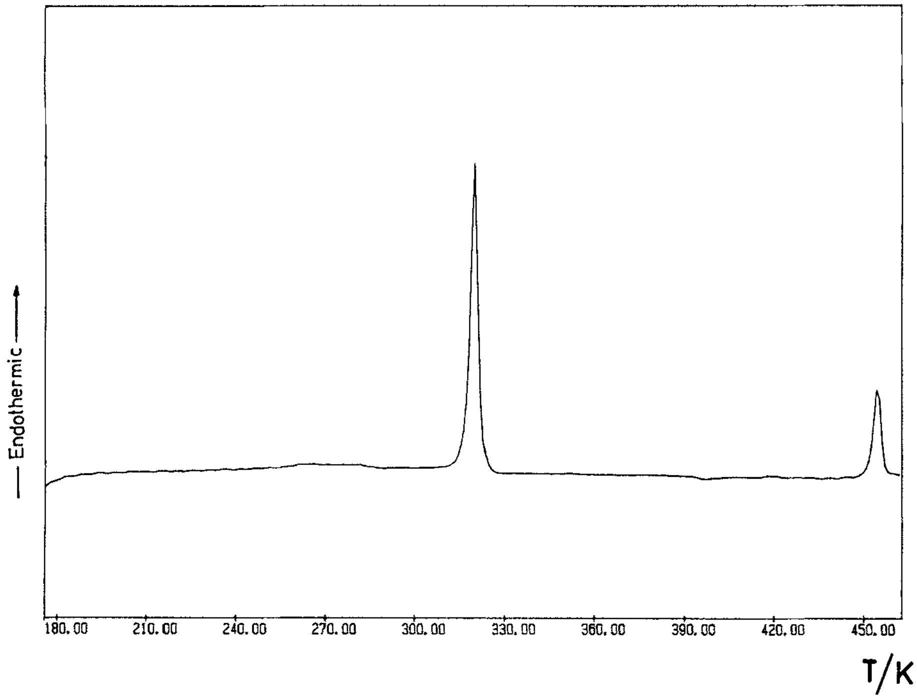


Figure 2. D.S.C. curve for the low molecular weight inositol derivative **5b** (heating rate 20 K/min).

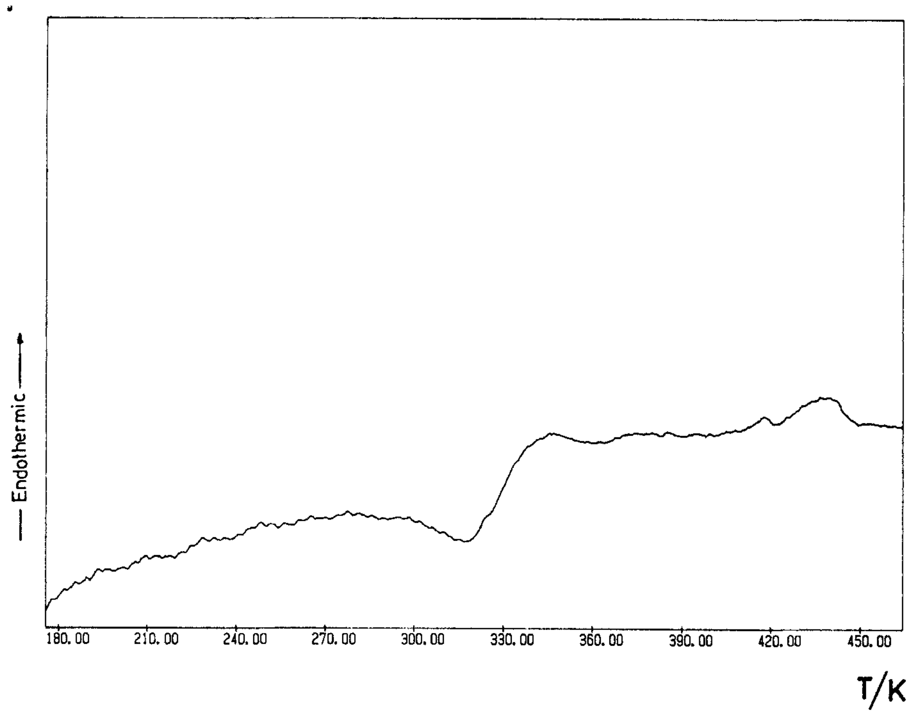


Figure 3. D.S.C. curve of the polymer **8b** (heating rate 20 K/min, heating after cooling from the isotropic melt).

The attachment of the non-discotic *myo*-inositol derivatives **3a** and **3b** to a polymer backbone does not lead to liquid–crystalline polymers **7a** and **7b** this means that in this case the attachment to the polymer did not increase the tendency for liquid-crystalline phase formation. In contrast to this, and as expected, the attachment of the discotic *scyllo*-inositol derivatives **5a** and **5b** to the polysiloxane lead to discotic liquid–crystalline polymers **8a** and **8b**. If the spacers have a similar length as the lateral substituents the monomeric and polymeric compounds show the same phase behaviour and the transition temperatures differ only slightly (see **3a** and **7a**, **5a** and **8a**). In contrast to this, if the spacer is longer than the lateral substituents the phase behaviour of the monomeric and polymeric compounds is not the same. For example the low molecular weight inositol derivative **5b** is a crystalline compound at room temperature (see table 1 and figure 2). At room temperature the polymer **8b** is in a glassy state and does not crystallize (see table 2 and figure 3).

As for the *myo*-inositol derivatives the phase behaviour of the *scyllo*-inositol derivatives were not drastically influenced by attachment to the polymer. The temperature range of the discotic phase is comparable. The phase widths of the polymers are even slightly smaller. A preliminary miscibility experiment showed that the polymer **8a** and *n*-hexaoctanoyloxybenzene (HOB) belong to the same type of mesophase. In the literature the mesophase of HOB is described as D_t [22]. None the less detailed X-ray studies of polymers **8a** and **8b** are in progress.

3. Experimental part

3.1. *1,3,4,5,6-Penta-0-alkanoyl-*myo*-inositol 2a and b*

2a. The preparation and characterization of this compound was published earlier in two detailed procedures [8].

2b. The synthesis of this compound followed the same procedure as for **2a** [8] using dioxane as a solvent ([8], note 11) starting from 5·40 g (30 mmol) *myo*-inositol (**1**) and 20·6 g (150 mmol) hexanoyl chloride. The crude product was purified by successive recrystallization from petroleum ether (b.p. 30–70°C) and ethanol ($\approx 1:1$), yielding 5·21 g (26 per cent) colourless crystals with the melting point 80–84°C.

I.R.: $\nu = 1751\,\mathrm{cm}^{-1}$ (C=O).

^{1}H-N.M.R.: δ (p.p.m.) = 5·62 (dd, $J \approx 10 + 10$ Hz; 2 H, 4-H and 6-H), 5·20 (*t*, $J \approx 10$ Hz; 1 H, 5-H), 5·04 (dd, $J \approx 10 + 2{\cdot}5$ Hz; 2 H, 1-H and 3-H), 4·28 (dt, wide, $J \approx 2{\cdot}5 + 2{\cdot}5$ Hz; 1 H, 2-H), 2·33, 2·88 (2 dt, $J \approx 16 + 7{\cdot}5$ Hz; 4 H, 2 CO–CH_2 of C-1 and C-3), 2·20 (*t*, $J \approx 7{\cdot}5$ Hz; 6 H, 3 CO–CH_2), 1·62–1·47 (m; 10 H, 5 CO–CH_2–CH_2), 1·35–1·18 (m; 20 H, 10 CH_2), 0·91–0·84 (m; 15 H, 5 CH_3). ^{13}C-N.M.R. (off-resonance, 20 MHz): δ (p.p.m.) = 172·48 (s; 5 C, 5 CO), 70·75, 69·34, 68·74 (3 d; 6 C, C-1 to C-6).

M.S. (280°C): m/e (per cent) = 670 (M^+, 0·5), 652 (M^+–H_2O, 6), 555 (2), 322 (5), 224 (54), 126 (30), 99 (100), 71 (66), 55 (12).

$C_{36}H_{62}O_{11}$ (670·9) Calculated C 64·45 H 9·32, Found C 64·55 H 9·03.

3.2. *2-0-(10-Undecenoyl)-1,3,4,5,6-penta-0-alkanoyl-*myo*-inositol 3a and b*

3a. The synthesis from the corresponding penta-ester **2a** has been published elsewhere [8].

3b. The same procedure as for **3a** was used here starting from 1·34 g (2 mmol) penta-ester **2b** and 0·51 g (2·5 mmol) 10-undecenoyl chloride. The crude product was purified by repeated flash chromatography (silica, 230–240 mesh) with (1) petroleum ether (30–70°C)/ethyl acetate (20 : 1) and (2) *n*-hexane/ethyl acetate (5 : 1) as eluents, yielding 0·89 g (53 per cent) light yellow oil.

I.R.: ν = 1754 cm^{-1} (C=O).

^{1}H-N.M.R.: δ (p.p.m.) = 5·81 (ddt, $J \approx$ 17 + 10 + 7 Hz; 1 H, CH$_2$=C*H*–CH$_2$), 5·59 (*t*, $J \approx$ 2·5 Hz; 1 H, 2-H), 5·51 (dd, $J \approx$ 10·5 + 10 Hz; 2 H, 4-H and 6-H), 5·20 (*t*, $J \approx$ 10 Hz; 1 H, 5-H), 5·10 (dd, $J \approx$ 10 + 2·5 Hz; 2 H, 1-H and 3-H), 4·99 (ddt, $J \approx$ 17 + 2 + 2 Hz; 1 H, H$_{\text{trans}}$–CH=CH–), 4·92 (ddt, $J \approx$ 10 + 2 + 2 Hz; 1 H, H$_{\text{cis}}$–CH=CH–), 2·44 (t, $J \approx$ 7·5 Hz; 2 H, CO–CH$_2$ of C-2), 2·27–2·12 (m; 10 H, 5 CO–CH$_2$), 2·04 (m, centre; 2 H, C*H*$_2$–CH=CH$_2$), 1·66 (tt, $J \approx$ 7·5 + 7·5 Hz, 2 H, CO–CH$_2$–C*H*$_2$ of C-2), 1·59–1·47 (m; 10 H, 5 CO–CH$_2$–C*H*$_2$), 1·41–1·18 (m; 20 H, 10 CH$_2$), 0·90–0·83 (m; 15 H, 5 CH$_3$). ^{13}C-N.M.R. (off-resonance, 270 MHz): δ (p.p.m.) = 172·53, 172·35, 172·32, 172·16 (4 s; 6 C, 6 CO), 139·13 (d; 1 C, *C*H=CH$_2$), 114·12 (t; 1 C, CH=*C*H$_2$), 70·56 (d; 1 C, C-5), 69·20, 68·50 (2 d; 4 C, C-1 C-3, C-4 and C-6), 68·00 (d, 1 C, C-2). MS (room temperature) = m/e (per cent): 836 (M$^+$, 1·5), 720 (M$^+$–C$_6$H$_{12}$O$_2$, 23), 653 (5), 622 (4), 555 (11), 224 (17), 205 (32), 166 (27), 99 (100). C$_{47}$H$_{80}$O$_{12}$ (837·1) Calculated: C 67·43, H 9·63. Found: C 67·44, H 9·64.

3.3. *2-0-Methylsulphonyl-1,3,4,5,6-penta-0-alkanoyl-*myo*-inositol **4a** and **b***

4a. To a stirred solution of 7·61 g (8 mmol) penta-ester **2a** in 40 ml dry pyridine 8 ml freshly distilled methanesulphonylchloride was added dropwise at 0°C. After addition was complete the mixture was stirred at room temperature for 20 hours. The brown solution was poured into water, acidified with 2 N hydrochloric acid and extracted three times with diethylether. The combined organic phases were washed three times with a saturated aqueous solution of sodium chloride and dried over magnesium sulphate. After filtration and evaporation of the solvent the residue (8·17 g light yellow crystals) was purified by recrystallization from a 1 :1 mixture of methanol and ethanol yielding 7·66 g (93 per cent) of colourless crystals melting at 60–63°C. I.R.: ν = 1754 cm^{-1} (C=O), 1365 cm^{-1} (S=O). ^{1}H-N.M.R.: δ (p.p.m.) = 5·51 $J \approx$ 10·5 + 10·5 Hz; 2 H, 4-H and 6-H), 5·22 (t, $J \approx$ 2·7 Hz; 1 H, 2-H), 5·21 (t, $J \approx$ 10·5 Hz; 1 H, 5-H), 5·10 (dd, $J \approx$ 10·5 + 2·7 Hz; 2 H, 1-H and 3-H), 3·15 (s; 3 H, CH$_3$–SO$_2$), 2·33, 2·27 (2 dt, $J \approx$ 16 + 8 Hz; 4 H, 2 CO–C*H*$_2$ of C-1 and C-3), 2·20 (t, $J \approx$ 7·5 Hz; 6 H, 3 CO–CH$_2$), 1·62–1·47 (m; 10 H, 5 CO–CH$_2$–C*H*$_2$), 1·33–1·17 (m; 60 H, 30 CH$_2$), 0·88 (t, $J \approx$ 7 Hz; 15 H, CH$_3$). ^{13}C-N.M.R. (off-resonance, 20 MHz): δ (p.p.m.) = 172·31, 172·22 (2 s; 5 C, 5 CO), 76·31 (d; 1 C, C-2), 70·44 (d; 1 C, C-5), 68·89, 68·21 (2 d; 4 C, C-1, C-3, C-4 and C-6), 39·01 (q; 1 C, CH$_3$–SO$_2$). – MS (260°C): m/e (per cent) = 1028 (M$^+$, 1), 917 (4), 876 (4); 858 (2), 722 (7), 704 (20), 550 (10), 280 (10), 232 (16), 155 (100), 126 (7), 109 (7), 98 (12), 85 (30), 71 (50), 57 (40). C$_{57}$H$_{104}$O$_{13}$S (1029·5).

Calculated: C 66·50 H 10·18, Found: C 66·23 H 10·00.

4b. Starting from 2·68 g (4 mmol) penta-ester **2b** the same procedure as for **4a** was used. The crude product (2·94 g light yellow solid) was purified by repeated flash chromatography (silica, 230–400 mesh) with petroleum ether (30–70°C)/ethyl acetate 1) 40 : 1 and 2) 60 : 1 mixtures as eluents, yielding 1·78 g (60 per cent) light yellow crystals melting at 48–49°C.

I.R.: ν = 1754 cm^{-1} (C=O), 1365 cm^{-1} (S=O). ^{1}H-N.M.R.: δ (p.p.m.) = 5·51 (dd, $J \approx$ 10·5 + 10·5 Hz; 2 H, 4-H and 6-H), 5·21 (t, $J \approx$ 2·7 Hz; 1 H, 2-H), 5·20 (t, $J \approx$ 10·5 Hz; 1 H, 5-H), 5·09 (dd, $J \approx$ 10·5 + 2·7 Hz; 2 H, 1-H and 3-H), 3·15 (s; 3 H, CH$_3$SO$_2$), 2·32, 2·16 (2 dt, $J \approx$ 16 and 8 Hz; 4 H, 2 CO–CH$_2$ of C-1 and C-3), 2·20 (t, $J \approx$ 7·5 Hz; 6 H, 3 CO–CH_2), 1·62–1·47 (m; 10 H, 5 CO–CH_2–CH_2), 1·33–1·17 (m; 20 H, 10 CH_2), 0·85 (t, $J \approx$ 7 Hz; 15 H, 5 CH_3). ^{13}C–N.M.R. (off-resonance, 20 MHz): δ (p.p.m.) = 172·33, 172·23 (2 s; 5 C, 5 CO), 76·30 (d; 1 C, C-2), 70·49 (d; 1 C, C-5), 68·90, 68·23 (2 d; 4 C, C-1, C-3, C-4 and C-6), 39·03 (q; 1 C, CH_3SO_2). M.S. (280°C): m/e (per cent) = 748 (M^+, 0·4), 652 (0·8), 633 (6), 535 (1·5), 437 (1), 322 (4), 302 (3), 224 (14), 99 (100), 71 (75). $C_{37}H_{64}O_{13}S$ (749·0). Calculated: C 59·34, H 8·61. Found: C 59·63, H 8·49.

3.4. *1-0-(10-Undecenoyl)-2,3,4,5,6-penta-0-alkanoyl-*scyllo*-inositol* ***5a*** *and* ***b***

Compounds **5a**, **b** were synthesized by making use of the caesium effect [23] and by modification of a known procedure [24]. Both compounds **5a** and **b** are not pure. As a result of a side reaction in the caesium ion assisited substitution of the mesylates **3a**, **b** the corresponding hexa-0-alkanoyl-*scyllo*-inositols **6a** [8] or **6b** [8] are also formed. Integration of their ^{1}H N.M.R. spectra show that these mixtures contain about 60 per cent of the unsaturated compound **5** and of about 40 per cent of the saturated compound **6**. For this reason the number of hydrogens are not given in the ^{1}H–N.M.R. spectra of **5a** and **b** reported here. Because of the similar molecular weights for **5a** and **6a** an elemental analysis was performed for **5a** only.

5a. A mixture of 3·09 g (3 mmol) mesylate **4a**, 0·83 g (4·5 mmol) 10-undecenoic acid and 1·47 g (4.5 mmol) caesium carbonate [23, 24] in 38 ml freshly distilled and dried dimethylformamide was stirred under argon for 72 hours at 80°C. Then 0·83 g (4·5 mmol) 10-undecenoic acid and 1·47 g (4·5 mmol) caesium carbonate was again added to the reaction mixture and stirring was continued at 80°C for another 18 hours. The reaction mixture was poured into 200 ml water and extracted three times with diethyl ether. The combined organic phases were washed three times with a saturated aqueous solution of sodium chloride and dried over magnesium sulphate. After filtration and evaporation of the solvent the residue was purified by column chromatography (silica, 0·2–0·3 mm) with petroleum ether (30–70°C)/ethyl acetate (10 : 1) as eluent. After repeated recrystallizations (3 times) from a mixture of ethanol with acetone ($\approx$ 1 : 1) 0·61 g (18 per cent) colourless crystals were obtained. M.p. (C → D_{ho}): 82·6–83·2°C, cl.p. (D_{ho} → I): 186–187°C. I.R.: ν = 1758 cm^{-1} (C=O). –^{1}H–N.M.R.: δ (p.p.m.) = 5·79 (ddt, $J \approx$ 17 + 10 + 7 Hz; CH_2=CH–), 5·25 (s; 1-H to 6-H), 4·98 (ddt, $J \approx$ 17 + 2 + 2 Hz; H_{trans}–CH=CH–). 4·92 (ddt, $J \approx$ 10 + 2 + 2 Hz; H_{cis}–CH=CH–), 2·19 (t, $J \approx$ 7·5 Hz; CO–CH_2), 2·03 (m, centre; CH_2–CH=CH_2), 1·50 (tt, $J \approx$ 7·5 + 7·5 Hz; CO–CH_2–CH_2), 1·32–1·19 (m; CH_2), 0·88 (t, $J \approx$ 7·5 Hz; CH_3). ^{13}C–N.M.R. (off-resonance, 270 MHz): δ (p.p.m.) = 172·14 (s; CO), 139·08 (d; CH=CH_2), 114·17 (t; CH=CH$_2$), 69·76 (q; C-1 to C-6), 33·95, 33·76, 31·85, 29·40 29·27, 29·13, 28·89, 24·81, 22·65 (9 t; CH_2), 14·07 (q; CH_3). M.S. (280°C): m/e (per cent) = 1116 (M^+, 1), 1104 (M^+ of **6a**, 0·5), 944 (M^+–$C_{10}H_{20}O_2$, 6), 792 (6), 780 (20), 626 (10), 280 (32), 166 (6), 156 (100). $C_{67}H_{120}O_{12}$ (1117·7) Calculated: C 72·00, H 10·82, Found: C 72·06, H 10·81.

5b. The synthesis of this compound followed the method described for **5a** starting from 3·62 g (4·85 mmol) of the mesylate **4b**. The crude product (4·35 g light yellow oil) was purified by repeated flash chromatography (silica, 230–400 mesh) with petroleum ether (30–70°C)/ethyl acetate 1) 30 : 1 and 2) 40 : 1 mixtures as eluents followed by recrystallization from ethanol, yielding 0·51 g (13 per cent) colourless crystals. M.p. (C → D_{ho}): 30–40°C, cl.p. D_{ho} → I): 176–179°C. I.R.: ν = 1756 cm^{-1} (C=O). ^{1}H–N.M.R.: δ (p.p.m.) = 5·80 (ddt, $J \approx$ 17 + 10 + 7 Hz, CH_2=CH–CH_2), 5·27 (s; 1-H to 6-H), 5·00 (ddt, $J \approx 17 + 2 + 2$ Hz; H_{trans}-CH=CH-), 4·94 (ddt, $J \approx 10 + 2 + 2$ Hz; H_{cis}-CH=CH-), 2·20 (t, $J \approx 7{\cdot}5$ Hz; CO-CH_2), 2·03 (m, centre; CH_2-CH=CH_2), 1·52 (tt, $J \approx 7{\cdot}5 + 7{\cdot}5$ Hz; CO-CH_2-CH_2), 1·35-1·18 (m; CH_2), 0·89 (t, $J \approx 7$ Hz, CH_3). ^{13}C-N.M.R. (off-resonance, 270 MHz): δ (p.p.m.) = 172·11 (s; CO) 139·08 (d; CH=CH_2), 114·15 (t; CH=CH_2), 69·76 (d; C-1 to C-6), 33·90, 33·78, 31·21, 29·26, 29·18, 29·10, 29·07, 28·88, 24·79, 24·45, 22·25 (11 t; CH_2), 13·82 (q; CH_3). M.S. (200°C): m/e (per cent) = (M^+, $C_{47}H_{80}O_{12}$, 0·2), 720 (M^+-$C_6H_{12}O_2$, 3), 653 (1·5), 555 (5), 457 (2·5), 322 (5), 224 (18), 166 (25), 99 (100), 71 (100).

3.5. *Synthesis of the polymers **7a, b** and **8a, b***

0·39 mmol of the inositol derivatives **3** 0·68 mmol of the inositol derivatives **5** and 0·38 mmol polymethylhydrogensiloxane (degree of polymerization ≈35, from Merck) related to Si-H were dissolved in 4 ml dry toluene (distilled over $LiAlH_4$). The solution was degassed with a stream of dry nitrogen for 10 min. 20 μg of a catalyst derived from H_2PtCl_6 (from Wacker Chemie, Burghausen) in a solution of dry toluene was added. The sealed reaction vessel was kept at 80°C until the Si-H I.R. absorption at 2140 cm^{-1} had totally disappeared (reaction time was of the order of 3-5 days). The polymer was isolated by preparative G.P.C. using Sephadex LH 20 (Roth) and THF (distilled over potassium) as eluent.

Yields: **7a**. 76 per cent, **7b**. 71 per cent.

For the polymers **8a** + **8b** the yields are of the order of 60-70 per cent. There exist no correct data, because the starting materials were mixtures of the compounds **5** and **6** and the composition of these mixtures are not known exactly. For example **8b**:

I.R. ν = 1760 cm^{-1} (C=O), 1260 cm^{-1} (Si-CH_3, Si-CH_2), 1100-1000 cm^{-1} (Si-O-Si).

^{1}H-N.M.R. ($CDCl_3$): δ (p.p.m.) = 5·5-5·3 (s, 6 H, 1-H to 6-H), 2·2 (t, 12 H, 6 CO-CH_2), 1·5 (s†, 12 H, 6 CO-CH_2-CH_2), 1·2 (s†, 34 H, 17 CH_2), 0·85 (t, 15 H, 5 CH_3), 0·45 (s†, 2 H, Si-CH_2), 0·0 (s†, 4 H, Si-CH_3).

3.6. *Characterization methods*

Low molecular weight compounds

The detection of the melting and clearing points were carried out with a Leitz Laborlux 12 Pol polarizing microscope equipped with a Mettler FP 82 hot stage and using a Perkin Elmer D.S.C.-2c differential scanning calorimeter at a scan rate of 20 K/min. The I.R.-spectra were taken in $CHCl_3$ with a Beckmann I.R. 9 spectrometer. The ^{1}H- and ^{13}C-N.M.R. spectra (δ values in p.p.m.) were measured in $CDCl_3$ with a Bruker WM 400 and a Bruker AM 270, respectively, or a Varian CFT 20 instrument. A Varian MAT 711 was used for the mass spectra. Elemental analysis was performed on a Hewlett-Packard 185 instrument.

Polymer compounds

For the I.R.-spectra ($CHCl_3$ or KBr) a Perkin Elmer Grating Infrared Spectrometer 457 and for the ^{1}H-N.M.R.-spectra (δ values in p.p.m., $CDCl_3$) a 400 MHz instrument from Bruker (Aspect 3000) was used. The thermal behaviour was investigated using a Perkin Elmer D.S.C.-2c differential scanning calorimeter at a scan rate of 20 K/min. The peak maxima were taken as transition temperatures. Optical

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† No structure of these signals is detectable due to the large linewidth which is typical for polymers; the half width is about 20 Hz.

investigations were carried out with a Leitz POL-BK polarizing microscope equipped with a Mettler FP 5 hot stage.

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