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Thermotropic and lyotropic liquid crystalline behaviour of 4-alkoxyphenyl β-D-glucopyranosides

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The liquid crystalline properties of a series of 4-alkoxyphenyl β-D-glucopyranosides (methoxy to decyloxy and dodecyloxy) were studied using polarized light microscopy and differential scanning calorimetry. The compounds with the shortest alkoxy substituents are not liquid crystalline. The butoxy derivative displays a monotropic smectic A phase and the higher homologues display enantiotropic smectic A phases. The lyotropic behaviour was studied as a function of concentration and temperature. Hexagonal, cubic and lamellar phases were observed for compounds with alkoxy chains longer than butoxy. The nonyloxy derivative forms long ribbons in dilute solution as revealed by electron microscopy.

1. Introduction

The liquid crystalline (LC) behaviour of amphiphilic carbohydrate derivatives has been an object of study for some time [1, 2]. This interest derives largely from the fact that carbohydrates can be substituted relatively easily with one or more alkyl chains; hence, the products constitute a potentially large class of mesogenic compounds [3–5]. The occurrence of LC behaviour and the phase transition temperatures are strongly dependent on the nature of the carbohydrate moiety (e.g. cyclic or acyclic form, mono- or oligosaccharide), the hydrophobic alkyl chain(s), the type of linkage between the two parts [e.g. (thio-)ether, ester or amide] and the presence of a rigid spacer unit [6–11]. In contrast, the *type* of mesophase formed is solely governed by the overall molecular shape [12], as is the case for lyotropic LC phases formed in surfactant/water systems [13]. Microphase separation is the driving force for LC formation in amphiphilic carbohydrate derivatives; rod-like molecules form smectic phases (SmA_d), while wedge-shaped molecules aggregate into discs and form columnar mesophases (Col_{hd}) [12, 14]. The SmA_d phase resembles the lamellar (L_α) phase formed in lyotropic systems [15]. The molecules are packed in bilayers, with the (interdigitated) alkyl chains inside and the sugar head groups on the outside forming an extensive hydrogen bonded network [16]. Water can easily penetrate between the layers resulting in the formation of lyotropic mesophases. Even amphiphiles with a head group carrying only two vicinal hydroxyl groups (e.g. 1,2-propanediol derivatives) display lyotropic mesophases [17]. Variation of the carbohydrate head group has been investigated intensively; in this paper we therefore restrict ourselves to the study of glucose derivatives.

The size of the hydrated head group of carbohydrate amphiphiles is relatively small compared with ionic surfactants, and repulsive Coulomb interactions are absent. Consequently, variation of the alkyl chain length in a homologous series has a large effect on the polymorphism of the lyotropic LC behaviour. There is increasing interest in the lyotropic phase behaviour of carbohydrate amphiphiles since several of these compounds are excellent non-ionic surfactants [18]. So far, most studies involve the lyotropic LC behaviour of a few single compounds or deal with the effects of structural changes on the thermotropic LC behaviour.

The incorporation of a rigid spacer unit (a phenyl ring) as a linking group between the carbohydrate and the alkyl chain stabilizes the mesophases of the compounds, as was reported by Baeyens-Volant and co-workers [19] for 4-alkylphenyl D-gluconamides. Tschierske *et al.* [20] reported a similar effect for the thermotropic LC

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behaviour of octyl, 4-octylphenyl, and *trans*-4-butylcyclohexyl β-D-glucopyranosides (β-GPs); the lyotropic mesophase formation was neglected. Jeffrey and co-workers [21] focused on the differences in the behaviour of α- and β-anomers of 4-alkylphenyl GPs. Only three different alkyl chain lengths of each anomer were studied, and little attention was paid to the lyotropic LC behaviour.

The present work is concerned with the thermotropic and lyotropic LC behaviour of a homologous series of 4-alkoxyphenyl β-GPs (alkoxy=methoxy to decyloxy and dodecyloxy). The compounds were prepared in a two-step synthetic procedure (see scheme 1). The mesomorphic behaviour was studied using polarized light microscopy and differential scanning calorimetry (DSC).

2. Results and discussion

2.1. *Synthesis*

4-Alkoxyphenyl β-GPs were synthesized in two steps from penta-*O*-acetyl β-D-glucose and the appropriate 4-alkoxyphenol as illustrated in the scheme. The glucosidic bond was formed in a Lewis acid-catalysed (boron trifluoride etherate) reaction at room temperature to give the β-product exclusively [22]. The acetylated 4-alkoxyphenyl β-GPs were purified by recrystallization from ethanol (yields: 62–85%) and deprotected quantitatively using trimethylamine in aqueous methanol [23]. The crude 4-alkoxyphenyl β-GPs (compounds **1**–**12**) were purified by crystallization from methanol/acetonitrile (1:2).

2.2. *Thermotropic liquid crystalline behaviour*

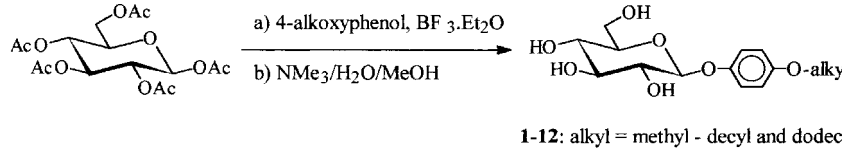
The 4-alkoxyphenyl β-GPs with an alkoxy chain longer than butoxy (**5**–**12**) form enantiotropic liquid crystals (compound **4** displays a monotropic mesophase) as was established by polarization microscopy and DSC. The phase transition temperatures and the corresponding enthalpies are given in table 1. The graphical presentation (figure 1) shows an odd–even effect in the melting points which becomes smaller with lengthening of the alkoxy chains, to reach an almost constant melting temperature of 100°C for **9**–**12**. The mesophase stability increases with increasing chain length; the clearing points rise from 140°C for **4** to 205°C for **12**. Based on their textures, the mesophases were characterized as smectic A and they are miscible with the SmA phase of nonyl 1-thio-β-D-glucopyranoside [23]. When a sample was cooled from the isotropic state, bâtonnets were formed at the transition from the isotropic to the liquid crystalline phase. Further cooling gave a focal-conic fan-like texture with large homeotropic areas (figure 2).

Compound **3** is not liquid crystalline, although the DSC cooling scan shows two exothermic peaks very close to each other. These peaks arise from crystallization followed by a crystal–crystal transition as was observed by light microscopy. Upon cooling of an uncovered droplet of **3** from the isotropic state, long, thin crystals were formed at 164°C, curling like whiskers. Further cooling induced a crystal–crystal transition at 153°C. Apparently, the propoxy group of **3** is too short to induce mesophase formation.

The melting, and particularly the clearing, temperatures of the 4-alkoxyphenyl β-GPs (compound **8**: m.p.=127°C, c.p.=204°C) are significantly higher than the transition temperatures of the alkyl β-GPs (octyl β-GP: m.p.=69°, c.p.=110°C) [20]; the rigid 1,4-phenylene moiety stabilizes the thermotropic mesophase. A comparison of the two homologous series [24] shows that introduction of the phenylene unit increases the melting points by about 20°C, and the clearing temperatures by 50–90°C.

In non-amphiphilic calamitic liquid crystals, it is generally observed that compounds with alkoxy-substituted phenyl rings have higher clearing temperatures than the alkyl-substituted analogues. This behaviour is not clear for the alkoxy- and alkyl-substituted aryl β-GPs. From a comparison between 4-heptyloxyphenyl β-GP (Cr 107 SmA 202 I) with 4-octylphenyl β-GP (Cr 108 SmA 192 I), Tschierske *et al.* [20] concluded that replacement of a methylene group by an oxygen atom stabilizes the LC phase. But, while **2** and **3** are not LC (and **4** forms a monotropic LC), Jeffrey and co-workers [21] reported enantiotropic SmA phases for propyl- and butyl-phenyl GP. The transition temperatures of heptylphenyl GP (m.p.=155°, c.p.=207°C) [21] are significantly higher than those of **6**, which contradicts Tschierske *et al.*'s [20] observation. A relevant general conclusion on the differences in behaviour of amphiphilic mesogens with alkyl- and alkoxy-substituted phenyl rings cannot be drawn on the basis of these data.

Replacement of a single (oxygen) atom linking group (odd) between two rigid units by O–CH_2 (even) has a stabilizing effect on the mesophases of calamitic



1-12: alkyl = methyl - decyl and dodecyl

Scheme 1. Synthesis of 4-alkoxyphenyl β-D-glucopyranosides (**1**–**12**).

Table 1. Thermotropic liquid crystalline behaviour of 4-alkoxyphenyl β-D-glucopyranosides **1–12**. Values in parentheses indicate crystal–crystal transitions.

Compound	m.p./°C	$\Delta H_{melting}$ kJ mol^{-1}	c.p./°C	$\Delta H_{clearing}$ kJ mol^{-1}
1	172·1–173·8	35·7	—	—
2	148·8–173·2	44·7	—	—
3	(129·9–131·5)	(16·8)	—	—
	155·4–159·4	21·1		
4	(121·7–123·2)	(17·5)	140·4–140·0	1·87
	150·5–151·9	26·5		
5	(101·0–103·5)	(22·1)	159·8–161·4	2·48
	109·2–112·4	3·2		
6	(90·1–93·4)	(15·6)	177·7–178·2	2·46
	131·0–134·4	21·0		
7	(83·9–88·3)	(12·4)	182·9–185·0	2·59
	90·2–96·0	6·5		
8	89·0–94·0	14·3	195·4–196·3	2·18
9	94·8–101·0	23·0	202·1–202·8	2·31
10	98·0–102·7	20·0	204·7–205·0	1·86
12	99·8–104·3	27·7	203·7–206·4	1·67

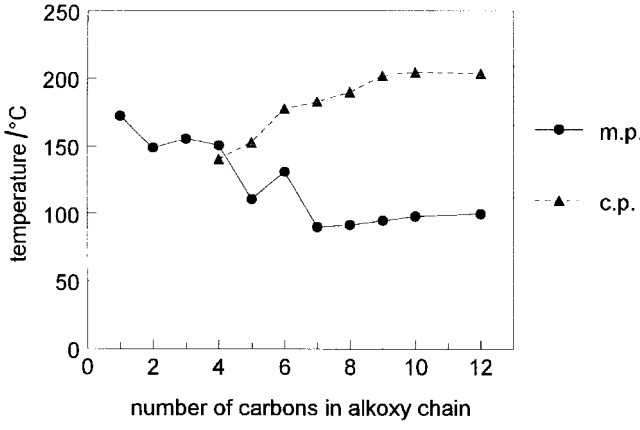


Figure 1. Phase transition temperatures of **1–12** plotted versus number of carbons in the alkoxy chain (● melting and ▲ clearing points in °C, measured by DSC).

mesogens. This effect is not observed for amphiphilic carbohydrate liquid crystals. Hexyloxybenzyl β-GP melts at 115°C and its c.p. is 127°C [20], and for octyloxybenzyl β-GP the m.p.=111·1°C and the c.p.=141·4°C. The mesophase ranges of alkoxybenzyl β-GPs (12 and 30°C) are small compared with 34 and 104°C for compounds **6** and **8**, respectively, with their much higher c.p.s. This contrasting behaviour of amphiphilic and calamitic LCs most likely has its origin in the different driving forces for mesophase formation, i.e. microphase separation versus anisotropic interactions [25].

2.3. *Lyotropic liquid crystalline behaviour*

Amphiphilic carbohydrate derivatives form not only thermotropic LC phases; a wealth of lyotropic mesophases are often formed in the presence of water. The type of mesophase formed is dependent on the temperature and the concentration and also on the relative sizes of the hydrophobic and hydrophilic parts of the molecules. The non-ionic hydrophilic carbohydrate head group is relatively small, therefore increasing the alkoxy chain length, as in the series **1–12**, will have a significant effect on the lyotropic behaviour. A straightforward, qualitative method for studying the lyotropic phase behaviour of **1–12** is the water penetration method [26, 27]. A minute amount of compound is heated to the isotropic phase on a microscope slide and covered with a cover slip. After the sample has cooled and solidified, water is added at the edge of the cover slip; due to capillary action, water is brought into contact with the sample. A concentration gradient, ranging from pure water to pure compound, appears immediately or upon heating in the heating stage.

Water can only penetrate into the crystals to form lyotropic mesophases above the Krafft temperature (T_{Krafft}), the discontinuity in the solubility versus temperature curve observed for surfactants [28, 29]. Generally, T_{Krafft} increases with increasing alkyl chain length. Krafft temperatures can be measured conveniently by monitoring the heat effect when a sample containing *c.* 5 wt. % of amphiphile in water is heated in the differential scanning calorimeter. The melting points of the anhydrous crystals **1–12** in water first decrease with increasing chain length, with a minimum for **6**, and then increase when the alkoxy chain is lengthened further (see table 2 and figure 3; no transition was observed for compound **1**). However, with the exception of **2** and **3**, the transition temperatures measured in the second heating scans show the normal behaviour [5, 30]. The

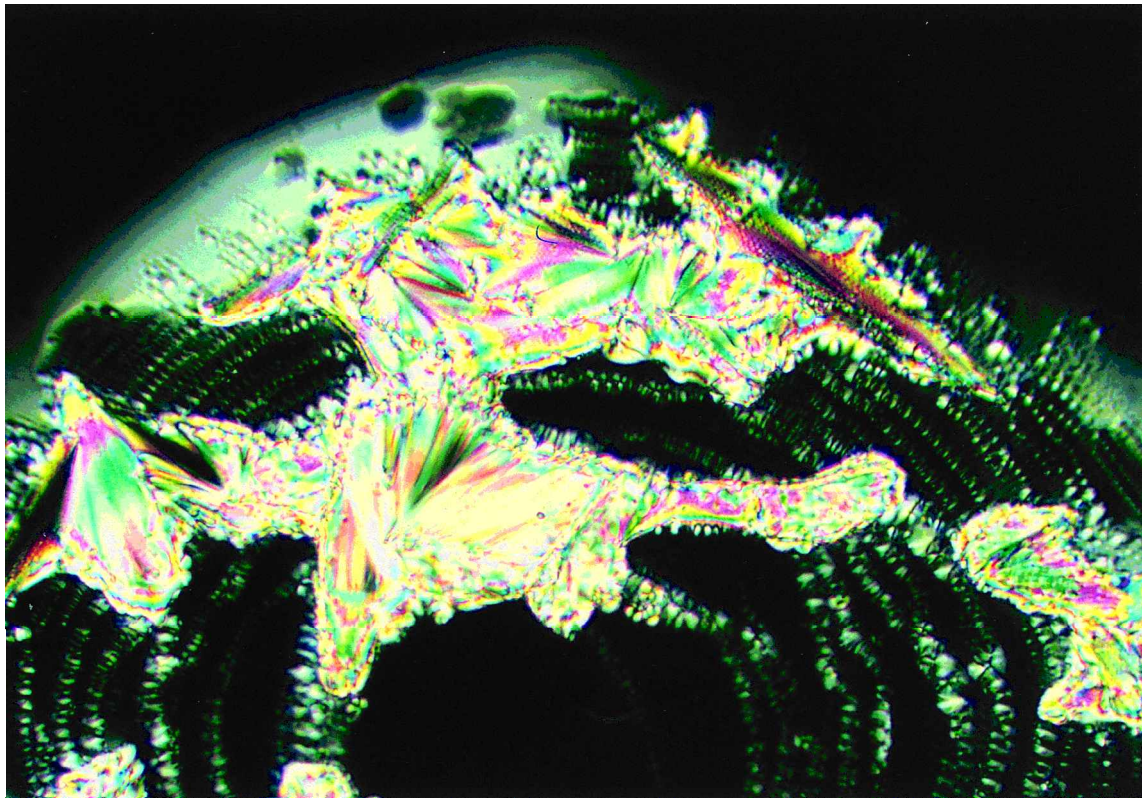


Figure 2. Bâtonnets formed at the isotropic to smectic A transition of compound **6** (178°C, uncovered droplet). Magnification 150×.

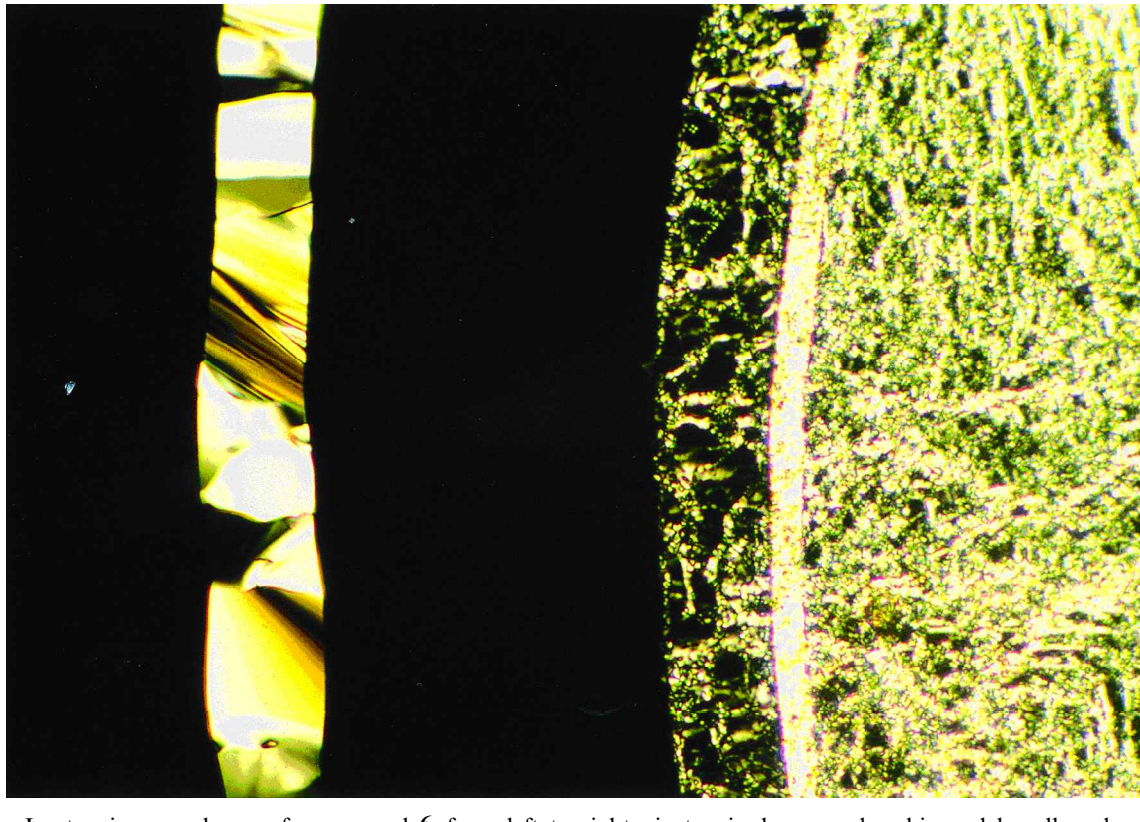


Figure 4. Lyotropic mesophases of compound **6**; from left to right—isotropic, hexagonal, cubic and lamellar phases. Contact preparation 72°C, magnification 150×.

Table 2. Lyotropic liquid crystalline behaviour.

Compound	Alkyl	T_{Krafft} [a]	H_I [b]	V_I [b]	L_α [b]
3	Propyl	60·3–63·6	—	—	—
4	Butyl	54·0–55·5	61–75	71–89	85–97
5	Pentyl	44·3–48·1[c]	37–76	53–95	40–97
6	Hexyl	31·1–35·0	38–82	44–95	42–95
7	Heptyl	40·7–43·2	—	36–80	51–95
8	Octyl	43·3–45·3[c]	—	40–95	54–95
9	Nonyl	49·5–52·8[c]	—	86–95	65–95
10	Decyl	53·7–57·1	—	—	53–95
12	Dodecyl	57·7–61·1	—	—	64–95

[a] Measured by DSC; melting point of the anhydrous crystal in water.
[b] Determined by polarization microscopy.
[c] Broad transition (three unresolved peaks).

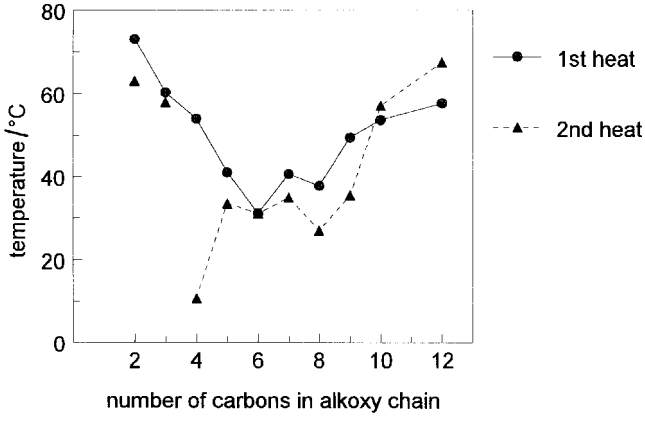


Figure 3. Krafft temperatures of compounds **3**–**12** in 5 wt.% mixtures in water as measured by DSC (● first and ▲ second heating scans).

higher melting points of the anhydrous crystals of **2**–**5** in water most likely arise from different crystal packings compared with the longer chain analogues. This is reflected by the enthalpies of melting, which are significantly higher for the short chain compounds than for the higher homologues (table 1). Upon cooling in the presence of water, compounds **4** and **5** apparently crystallize as their hydrates; these hydrates melt at a lower temperature than the anhydrous crystals. This most likely does not occur for compounds **2** and **3** since these do not form lyotropic mesophases in water.

Apparently, the hydrophobic moieties of **2** and **3** are too small to induce surface-active behaviour. Compounds **4**–**12** form several mesophases in the presence of water when heated above T_{Krafft}. The temperature ranges of the different phases formed are listed in table 2. Indeed, the shape of the hydrated molecules changes substantially as a function of alkyl chain length (from conical to cylindrical) [31, 32]. This is reflected by the hexagonal phases formed by compounds **4**–**6**, whereas compounds **10**–**12** form only lamellar phases. Compounds **4**–**9** also form a cubic phase [33]; a viscous isotropic band is formed between the hexagonal (**4**–**6**) or isotropic (**7**–**9**) and lamellar phases. Figure 4 shows the mesophases formed by **6** in a contact preparation. Compounds **7** and **8** form a cubic phase immediately after the crystalline hydrate has melted; in the contact preparation of compound **9**, the cubic phase was formed at 86°. Compounds **10** and **12** form only lamellar phases. At the interface between the lamellar phase and isotropic solution of compounds **9**–**12**, myelin structures are formed at ambient temperature, which is indicative of vesicle formation in the dilute solutions [34, 35]. We tried to visualize the vesicles using electron microscopy, and chose to perform the experiments with compound **9**, because it has a lower T_{Krafft} than compounds **10** and **12**; the latter have not yet been examined. To our surprise, a 5 wt.% solution of **9** in water does not contain vesicles but long ribbons (figure 5) [36]. The ribbons, consisting of 3–5 segments, each having a width of *c.* 8 nm, are several hundreds of micrometers long and most of the ribbons are twisted irregularly. The solution has a gel-like character and the aggregates are also visible in the light microscope as long threads. Tubular aggregates, which are used for the crystallization of membrane proteins, are generally formed from complex chiral amphiphilic molecules [37]. The driving forces for the formation of ribbons, and their aggregation to tubules are not well understood [38–40]. Various *N*-alkyl aldonamides are also known to form helical thread-like structures in water; the hydrogen bonds formed by the hydroxyl groups of the sugar moiety and the amide groups stabilize the aggregates and determine the morphology [18, 36, 41, 42]. Compound **9** has only four hydroxyl groups, and most probably π–π interactions between the phenyl groups play a dominant role in the aggregation behaviour, since alkyl β-GPs do not display this special behaviour. A more extensive electron

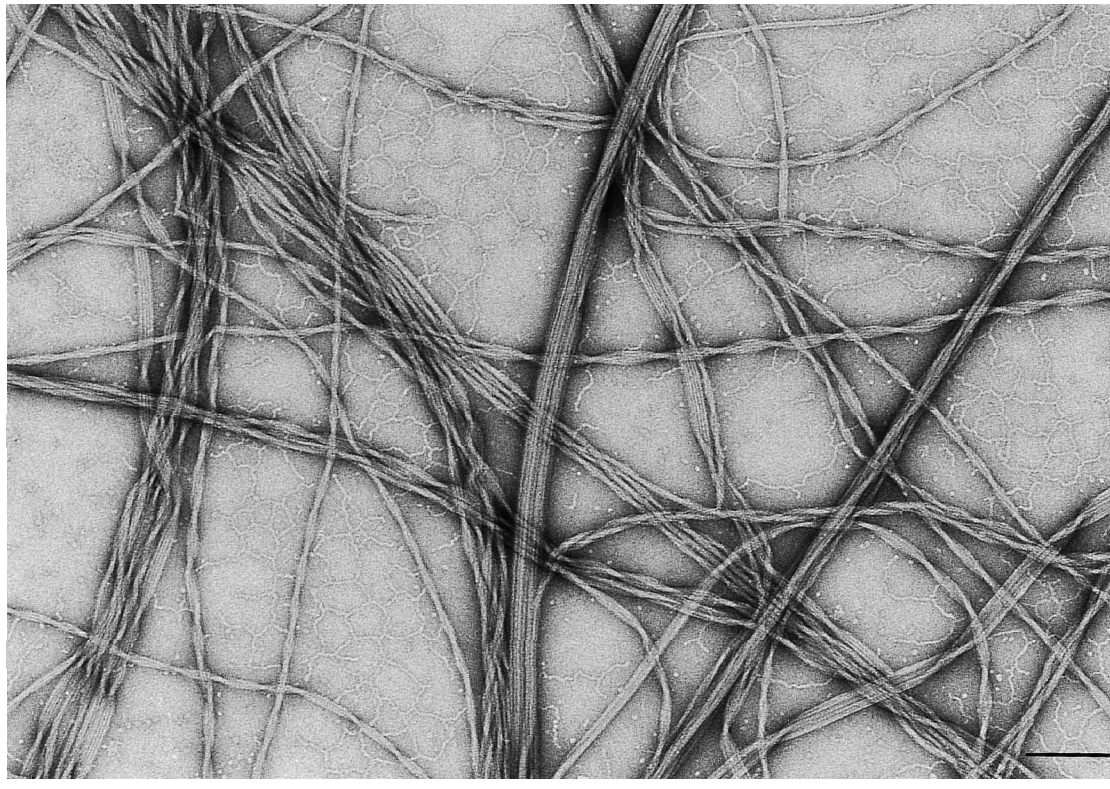


Figure 5. Ribbons formed by **9** in water (electron micrograph, negative staining; the bar represents 200 nm).

microscopic study of the aggregates of compound **9** and other long-chain 4-alkoxyphenyl β-GPs is needed to obtain further insight into their fascinating supramolecular behaviour.

3. Experimental

3.1. *General*

Thermomicroscopy was performed with a Mettler FP 800 system; the hot stage was mounted on a Nikon microscope. Quantitative thermal analyses were performed using a Perkin Elmer PC Series DSC 7. The values reported are those from the first heating scans. For the measurements of the Krafft temperatures, DSC pans were filled with 3 mg of anhydrous compound and 50 μl of water. Electron microscopy was performed using a Philips 201 electron microscope operating at 80 kV. A dispersion of 5 wt. % of **9** in water was sonicated with an ultrasonic horn at 60°C and negatively-stained on carbon-coated Formvar grids according to the two-droplet method with a PTA solution [43]. All reagents and solvents were purchased from any one of the large chemical suppliers and were used without further purification. Elemental analyses indicated at least 99% purity. The structures of the products were confirmed by NMR spectroscopy. NMR spectra were recorded on a 300 MHz Varian VTR-300 spectrometer. Chemical shifts are related to $CHCl_3$ (^1H δ 7·24 ppm, ^{13}C: 77·5) or CD_3OD (^1H: δ 3·35 ppm, ^{13}C: 49·0).

3.2. *4-Alkoxyphenyl β-D-glucopyranosides* [22]

3·9 g (10 mmol) of penta-*O*-acetyl β-D-glucose and 10 mmol of 4-alkoxyphenol were dissolved in 20 ml of anhydrous CH_2Cl_2; $BF_3{\cdot}Et_2O$ (1·25 ml, 10 mmol) was then added. The reaction mixture was stirred at room temperature for 24 h and then poured into 40 ml of 5% aqueous $NaHCO_3$. The organic layer was separated, washed with aqueous $NaHCO_3$ and subsequently with water, dried over Na_2SO_4 and concentrated. The crude products were crystallized from ethanol (yields: 62–85%). The acetylated 4-alkoxyphenyl β-GPs were deprotected quantitatively with trimethylamine in aqueous methanol [23]. This reagent was prepared by mixing a 45 wt. % solution of NMe_3 in water with 4 volumes of methanol. After stirring at room temperature for 24 h, the solvent was evaporated and the remaining syrup was crystallized from methanol/acetonitrile (1:2). The melting points of the acetylated 4-alkoxyphenyl β-GPs are given in table 3, and the elemental analyses of the protected and deprotected products are given in table 4.

As a typical example the ^1H and ^{13}C NMR spectra of hexyloxyphenyl β-D-glucopyranoside are given: δ ^1H 0·92 (t, 3H, H-6′); 1·35 (m, 6H, H-3′/5′); 1·37 (m, 2H,

Table 3. Melting points of 4-alkoxyphenyl 2,3,4,6-tetra-*O*-acetyl β-D-glucopyranosides. Values in parentheses indicate crystal–crystal transitions.

Alkyl group	m.p./°C	$\Delta H_{melting}$ kJ mol^{-1}
Methyl	(93·2–95·5)	(5·5)
	100·6–102·3	19·2
Ethyl	110·1–111·4	36·1
Propyl	109·3–115·7	25·3
Butyl	113·3–114·7	30·3
Pentyl	114·7–115·8	34·4
Hexyl	101·6–102·9	30·9
Heptyl	107·1–108·4	39·7
Octyl	98·8–100·0	32·8
Nonyl	(66·2–67·3)	(7·7)
	97·2–101·6	28·5
Decyl	88·0–89·3	1·8
Dodecyl	99·3–101·1	67·2

H-2′); 3·4 (m, 2H, sugar); 3·7 (m, 1H, H-6); 3·9 (m, 3H, sugar); 4·77 (d, 1H, J_{1-2}=7·7 Hz); 6·82, 7·04 (2×d, 4H, arom.). δ ^{13}C: 14·3 (t, C-6′); 23·6, 26·8, 30·4, 32·7 (4×d, C-2′/5′); 62·5 (t, C-1); 69·5 (t, C-6′); 71·4, 74·9, 77·9, 78·0 (4×d, C-2/5); 103·4 (d, C1); 116·2, 119·2 (2×d, arom. CH); 153·1, 156·0 (2×s, arom. CO).

4. Conclusions

A study of the liquid crystalline behaviour of a homologous series of alkoxyphenyl β-D-glucopyranosides has shown that compounds **4**–**12** display thermotropic SmA phases; as a result of the rigid phenyl moiety, the mesophase stability is enhanced compared with alkyl β-D-glucopyranosides. In lyotropic systems, compounds **4**–**12** form several mesophases depending on the length of the alkoxy chain, similar to those of other homologous series of carbohydrate amphiphiles. The aggregation behaviour of compound **9** is remarkable; ribbons are formed in dilute solution and most probably the phenyl ring plays a crucial role in the formation of the aggregates.

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References

[1] Fischer, E., and Helferich, B., 1911, *Liebigs Ann.*, **383,** 68.
[2] Jeffrey, G. A., 1984, *Mol. Cryst. liq. Cryst.*, **110,** 211.
[3] Jeffrey, G. A., and Wingert, L. M., 1992, *Liq. Cryst.*, **12,** 179.
[4] Prade, H., Mietchen, R., and Vill, V., 1995, *J. prakt. Chem.*, **337,** 427.
[5] Mietchen, R., and Peters, D., 1987, *Wiss. Z. Wilhelm-Pieck-Universität Rostock*, **36,** 55.
[6] Mietchen, R., Holz, J., and Prade, H., 1993, *Colloid Polym. Sci.*, **271,** 404.
[7] Goodby, J. W., Marcus, M. A., Chin, E., Finn, P. L., and Pfannemüller, B., 1988, *Liq. Cryst.*, **3,** 1569.
[8] Dahlhoff, W. V., Radkowski, K., Riehl, K., and Zugenmaier, P., 1995, *Z. Naturforsch.*, **50b,** 1079.
[9] Dahlhoff, W. V., Riehl, K., and Zugenmaier, P., 1993, *Liebigs Ann.*, 1079.
[10] Jeffrey, G. A., and Bhattacharjee, S., 1983, *Carbohydr. Res.*, **115,** 53.
[11] Marcus, M. A., 1986, *Mol. Cryst. liq. Cryst. Lett.*, **3,** 85.
[12] van Doren, H. A., and Terpstra, K. R., 1995, *J. mater. Chem.*, **5,** 2153.
[13] Charvolin, J., and Seddon, J. F., 1994, *Micelles, Membranes, Microemulsions, and Monolayers*, edited by W. M. Gelbart, A. Ben-Shaul and D. Roux (Springer), Chap. 4.
[14] Mietchen, R., Schwarze, M., and Holz, J., 1993, *Liq. Cryst.*, **15,** 185.
[15] Marcus, M. A., and Finn, P. L., 1985, *Mol. Cryst. liq. Cryst. Lett.*, **2,** 159.
[16] van Doren, H. A., and Wingert, L. M., 1991, *Mol. Cryst. liq. Cryst.*, **198,** 381.

Table 4. Elemental analytical data.

Alkyl group	2,3,4,6-Tetra-*O*-acetyl alkoxyphenyl β-D-glucopyranosides					Alkoxyphenyl β-D-glucopyranosides				
		Calculated		Found			Calculated		Found	
	Formula	%C	%H	%C	%H	Formula	%C	%H	%C	%H
Propyl	$C_{23}H_{30}O_{11}$	57·26	6·27	57·17	6·29	$C_{15}H_{22}O_7$	57·32	7·05	56·82	6·97
Butyl	$C_{24}H_{32}O_{11}$	58·06	6·50	57·97	6·52	$C_{16}H_{24}O_7$	58·53	7·37	58·51	7·35
Pentyl	$C_{25}H_{34}O_{11}$	58·82	6·71	58·70	6·72	$C_{17}H_{26}O_7$	59·64	7·65	59·34	7·87
Hexyl	$C_{26}H_{36}O_{11}$	59·53	6·92	59·55	6·94	$C_{18}H_{28}O_7$	60·66	7·92	60·55	7·91
Heptyl	$C_{27}H_{38}O_{11}$	60·21	7·11	60·07	7·06	$C_{19}H_{30}O_7$	61·60	8·16	61·21	8·06
Octyl	$C_{28}H_{40}O_{11}$	60·86	7·30	60·78	7·24	$C_{20}H_{32}O_7$	62·48	8·39	62·25	8·32
Nonyl	$C_{29}H_{42}O_{11}$	61·47	7·47	61·39	7·56	$C_{21}H_{34}O_7$	63·30	8·60	63·06	8·67
Decyl	$C_{30}H_{44}O_{11}$	62·05	7·64	61·96	7·48	$C_{22}H_{36}O_7$	64·05	8·80	63·50	8·76
Dodecyl	$C_{32}H_{48}O_{11}$	63·14	7·95	62·90	7·93	$C_{24}H_{40}O_7$	65·43	9·15	64·91	9·14

[17] van Doren, H. A., and van der Geest, R., 1990, *Recl. Trav. Chim. Pays-Bas*, **109,** 197.
[18] Pfannemüller, B., 1988, *Starch*, **40,** 476.
[19] Loos, M., Baeyens-Volant, D., David, C., Sigaud, G., and Achard, M. F., 1990, *J. Colloid Interface Sci.*, **138,** 128.
[20] Tschierske, C., Lunow, A., and Zaschke, H., 1990, *Liq. Cryst.*, **8,** 885.
[21] Wingert, L. M., Jeffrey, G. A., Jahangir, and Baker, D. C., 1993, *Liq. Cryst.*, **13,** 467.
[22] Smits, E., Engberts, J. B. F. N., Kellogg, R. M., and van Doren, H. A., 1996, *J. chem. Soc., Perkin Trans. I*, 2873.
[23] van Doren, H. A., van der Geest, R., Kellogg, R. M., and Wynberg, H., 1989, *Carbohydr. Res.*, **194,** 71.
[24] Vill, V., Böcker, T., Thiem, J., and Fischer, F., 1989, *Liq. Cryst.*, **6,** 349.
[25] Laughlin, R. G., 1994, *The Aqueous Phase Behavior of Surfactants*, edited by R. H. Ottewil and R. L. Rowell (London: Academic Press), Chaps 8, 9 and 11.
[26] van Doren, H. A., and Wingert, L. M., 1994, *Recl. Trav. Chim. Pays-Bas*, **113,** 260.
[27] van Doren, H. A., and Wingert, L. M., 1991, *Liq. Cryst.*, **9,** 41.
[28] Krafft, F., 1899, *Ber. Deutsche Chem. Ges.*, **32,** 1596.
[29] Shinoda, K., Yamaguchi, N., and Carlsson, A., 1989, *J. phys. Chem.*, **93,** 7316.
[30] Galema, S. A., 1992, PhD thesis, University of Groningen, The Netherlands.
[31] Hall, C., Tiddy, G. J. T., and Pfannemüller, B., 1991, *Liq. Cryst.*, **9,** 527.
[32] Borisch, K., Diele, S., Göring, P., and Tschierske, C., 1996, *J. chem. Soc. chem. Commun.*, 237.
[33] Sakya, P., Seddon, J. M., and Templer, R. H., 1994, *J. Phys. II. Fr.*, **4,** 1311.
[34] van Doren, H. A., Galema, S. A., and Engberts, J. B. F. N., 1995, *Langmuir*, **11,** 687.
[35] van Hall, D. A., Bouwstra, J. A., van Rensen, A., Jeremiasse, E., de Vringer, T., and Junginger, H. E., 1996, *J. Colloid Interface Sci.*, **178,** 263.
[36] Fuhrhop, J. H., and Helfrich, W., 1993, *Chem. Rev.*, **93,** 1565.
[37] Yamada, N., Koyama, E., Kaneko, M., Seki, H., Ohtsu, H., and Furuse, T., 1995, *Chem. Lett.*, 387.
[38] Fuhrhop, J. H., Svenson, S., Boettcher, C., Rössler, E., and Vieth, H. M., 1990, *J. Am. chem. Soc.*, **112,** 4307.
[39] Svenson, S., Kirste, B., and Fuhrhop, J. H., 1994, *J. Am. chem. Soc.*, **116,** 11969.
[40] Frankel, D. A., and O'Brien, D. F., 1994, *J. Am. chem. Soc.*, **116,** 10057.
[41] Fuhrhop, J. H., and Boettcher, C., 1990, *J. Am. chem. Soc.*, **112,** 1768.
[42] Hafkamp, R. J. H., 1996, PhD thesis, University of Nijmegen, The Netherlands.
[43] Haschemeyer, R. H., and Meyers, R. J., 1972, *Principles and Techniques of Electron Microscopy*, edited by M. A. Hayat (New York: Van Nostrand Reinhold), Vol. 2, Chap. 3.