Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

6,6-Di-*C*-alkyl-d-galactopyranoses. A new group of liquid crystalline compounds forming columnar phases [1]

R. Miethchen[a]; M. Schwarze[a]; J. Holz[a]
[a] Department of Organic Chemistry, University of Rostock, Rostock, Germany

To cite this Article Miethchen, R. , Schwarze, M. and Holz, J.(1993) '6,6-Di-*C*-alkyl-d-galactopyranoses. A new group of liquid crystalline compounds forming columnar phases [1]', Liquid Crystals, 15: 2, 185 — 191
To link to this Article: DOI: 10.1080/02678299308031949
URL: http://dx.doi.org/10.1080/02678299308031949

LIQUID CRYSTALS, 1993, VOL. 15, NO. 2, 185–191

6,6-Di-*C*-alkyl-D-galactopyranoses

A new group of liquid crystalline compounds forming columnar phases [1]

by R. MIETHCHEN*, M. SCHWARZE and J. HOLZ

Department of Organic Chemistry, University of Rostock,
Buchbinderstraße 9, D 18051 Rostock, Germany

(Received 26 January 1993; accepted 24 March 1993)

The geminally *C*-branched 6,6-di-*C*-*n*-alkyl-D-galactopyranoses **3a–d** prepared in two steps from 1,2:3,4-di-*O*-isopropylidene-D-galacturonic acid methylester **1** and the even numbered C_8–C_{12}-alkylmagnesium bromides, represent a new group of 'double tailed' thermotropic mesogens forming columnar supramolecular structures based on hydrogen bridged (disc-like) multimers in accordance with the hypothesis of the Praefcke group. Furthermore, the thermal behaviour of the homologous 6-*O*-alkyl-D-galactopyranoses **4a–e** is discussed in connection with the revised model for the molecular arrangement in smectic A phases of 'single tailed' carbohydrates.

1. Introduction

It is well-known that 'single tailed' amphiphilic monosaccharides consisting of a hydrophilic head and one lipophilic chain form only smectic supramolecular structures in their liquid crystalline phases (see, for example, [2–9] and earlier papers cited therein). The formation of columnar phases necessitates more than one lipophilic *n*-alkyl chain at the hydrophilic moiety (see, for example [1, 10–12]). Praefcke *et al.* [13] first recognized that, for instance, 'double tailed' multiols like 1,2-*scyllo*-inosit-diethers [14] or *S,S*-dialkyl-dithioacetals of sugars [10] can form columnar mesophases based on hydrogen bridged multimers. This means that amphiphilic thermomesogens themselves need not necessarily have a disc-like shape, but may aggregate to form disc-like structures [14, 15]. Thiem *et al.* [11] recently described a further possibility of a supramolecular arrangement of 'double tailed' 1,6-di-*O*-*n*-alkyl-D-galactopyranoses inside a thermotropic columnar mesophase.

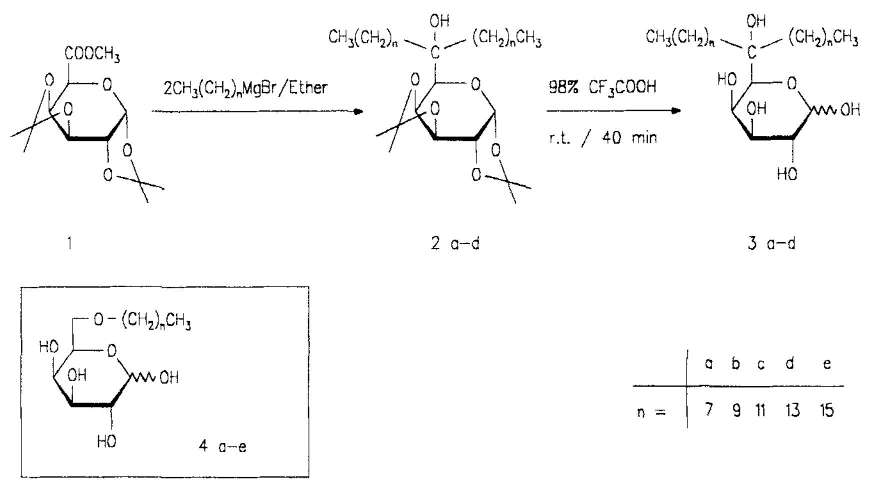
2. Discussion and results

We have prepared the amphiphilic 6,6-di-*C*-*n*-alkyl-D-galactopyranoses **3a–d** that are geminally branched by alkyl chains at a *C*-atom of a cyclic monosaccharide derivative to prove the hypothesis of Praefcke *et al.* [14, 15], that geminally branched amphiphiles should be able to associate by hydrogen bonding forming disc-like units, which then aggregate to give columnar supramolecular structures. Secondly, the homologous 6-*O*-alkyl-D-galactopyranoses **4a–e** were synthesized to obtain further information in connection with the revised model for the molecular arrangement in smectic A phases of 'single tailed' carbohydrates [5, 16].

The two step synthesis of **3a–d** is shown in scheme 1. It is to be noted that the tertiary hydroxyl function in the 6-position of **2a–d** and **3a–d** show a relatively high tendency to

---

* Author for correspondence.



	a	b	c	d	e
n =	7	9	11	13	15

Scheme 1. Synthesis of the homologous 6,6-di-*C*-*n*-alkyl-α/β-D-galactopyranoses **3a–d**; structural formulae of the 6-*O*-*n*-alkyl-α/β-D-galactopyranoses **4a–e**.

dehydration when catalysed by acids. Therefore, the hydrolysis steps must be carried out carefully (see procedures). To prepare the 6-*O*-alkyl ethers of the D-galactopyranoses **4a–e** in two steps from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, we used the *O*-alkylation procedure of Cabaret *et al.* [17], followed by acid catalysed deketalization in aqueous acetic acid (80 per cent) with the addition of some drops concentrated sulphuric acid (see scheme 1). The competitive ether cleavage is suppressed under these conditions. Derivatives **4a** [17] and **4c** [18] were known already.

The thermotropic properties of **3a–d** and **4a–e** were studied by polarizing microscopy. Both homologous series of D-galactopyranose amphiphiles show enantiotropic behaviour and form wide mesophase ranges with differences of about 40–50 K between the melting and clearing points. Moreover, the observed clearing points are in the range about 165°C, showing relatively high stabilities of the liquid crystalline phases (see figure 1).

A comparison of the thermal data for the 6-*O*-alkyl-D-galactopyranoses **4a–e** with those of the 6-*O*-alkyl-D-glucopyranoses [7] described by us earlier shows similarities in the clearing temperatures (nearly 165°C), but the melting points are different. The 6-*O*-alkyl-D-glucopyranoses melt about 10–25 K below the D-galactose derivatives. Such a result is to be expected in accordance with the proposed model for the molecular arrangement in smectic A phases consisting of 'single tailed' carbohydrates [5, 16], if the attractive component of the hydrogen bonds is predominantly reduced at the melting point. The sugar moiety of the derivatives having an identical alkyl chain length is the same except for the steric arrangement of the OH-group at the 4-position. This sole structural difference between the corresponding D-glucose and D-galactose derivatives only affects the melting point, and not the clearing point. The clearing points of the mesogens within each homologous series are not significantly different. However an influence of hydrogen bonding seems still to be present at the clearing point because of the significant differences amongst 2-*O*-, 3-*O*-, 4-*O*- and 6-*O*-alkyl-D-glucopyranoses, which have the same alkyl chain. The mesophases of both 'single tailed' monosaccharide series were identified as smectic A in type by microscopic

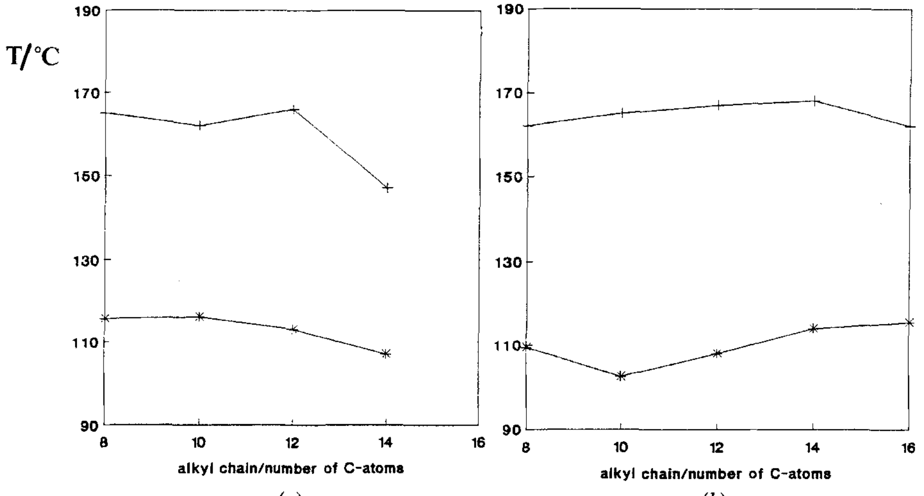


Figure 1. The thermal behaviour of the homologous 6,6-di-*C*-alkyl-α/β-D-galactopyranoses **3a–d**, (*a*) and 6-*O*-alkyl-α/β-D-galactopyranoses, **4e–e** (*b*) studied by polarizing microscopy. *--*--*--* = melting point; — + — + — + = clearing point.

studies of their textures and by miscibility tests (contact method) with the 6-*O*-alkyl-D-glucopyranoses and other known smectic reference substances described in [19].

The mesophases of the geminally 'double tailed' D-galactopyranoses **3a–d** show, as expected, a supramolecular structure, but of a different type to that of **4a–e**. The higher viscosities of these liquid crystalline phases compared with the smectic ones gave the first indication of another phase type. As expected the compounds **3a–d** are not miscible in a contact preparation with any one of **4a–e**. Furthermore, miscibility studies (contact method) of **3a–d** with selected smectic amphiphiles such as octyl-β-D-glucopyranoside of *S*-octyl-β-D-thioglucopyranoside (both of S_A type and not miscible with **3a–d**) confirm the changed type of mesophase. Finally, the miscibility of the 6,6-di-*C*-*n*-octyl-α/β-D-galactopyranose **3a** with *S*,*S*-di-octyl-D-arabino-dithioacetal (hexagonal-columnar type [10]) leads to the conclusion that a columnar phase type is formed. Figure 2 shows the texture of the 6,6-di-*C*-octyl-α/β-D-galactopyranose **3a** and the texture of the contact preparation of **3a** with *S*,*S*-di-octyl-D-arabino-dithioacetal.

3. Experimental

Column chromatograpy and TLC were carried out by use of Silicagel 60 (63–200 μm) and TLC aluminium foil Silicagel 60 F_{254} (Merck), respectively. ^1H and ^{13}C NMR spectroscopic data were determined with a Bruker AC-250 NMR instrument. The mesomorphic properties were studied by polarizing microscopy using a Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90.

4.1. *Preparation of 6,6-di-C-alkyl-1,2 : 3,4-di-O-isopropylidene-α-D-galactopyranoses* (**2a–d**)

1·16 g (4 mmol) of 1,2 : 3,4-di-*O*-isopropylidene-D-galacturonic acid methylester **1**, (prepared from 1,2 : 3,4-di-*O*-isopropylidene-D-galacturonic acid [20] and diazomethane in ether), dissolved in 10 ml of absolute ether was added dropwise to a Grignard solution prepared from 10 mmol of the corresponding *n*-alkyl bromide and magnesium in 10 ml of absolute ether (stirring at room temperature). After that, the mixture was

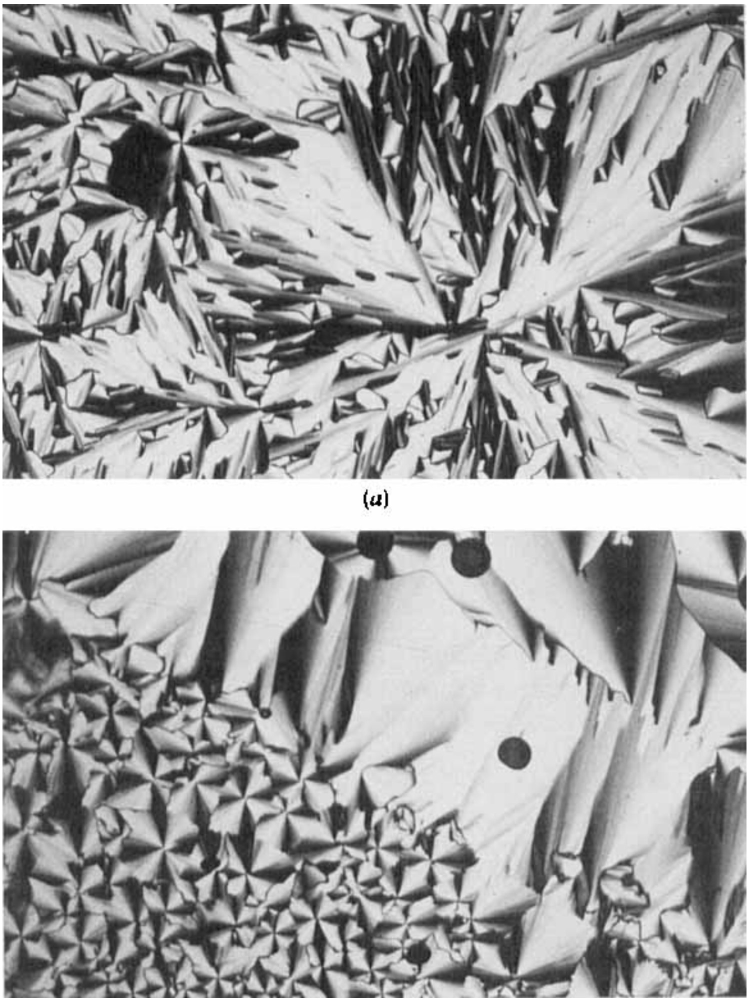


Figure 2. Textures: (*a*) of 6,6-di-C-octyl-α/β-D-galactopyranose **3a** and (*b*) of the contact zone for **3a** (smaller domains) with *S*,*S*-di-*n*-octyl-D-arabino-dithioacetal (larger domains). The photographs were taken using a 24 × 36 mm camera (enlargement = 25 ×); photoautomat WILD MPS 51, crossed polarizers, Leitz Laborlux 12 Pol polarizing microscope equipped with a Mettler FP 82 hot stage.

heated for 1 hour on a water bath and then hydrolysed by pouring onto 10 g of broken ice. The precipitate was dissolved by adding minimal amounts of diluted hydrochloric acid. The ether phase was separated and the aqueous phase shaken twice with 10–15 ml of ether. The extractions must be carried out quickly, because the compounds are acid labile. The combined ether phases were washed with 5–10 ml of saturated aqueous sodium hydrogensulphate solution and 5 ml of water and dried with magnesium sulphate. The residue obtained after evaporation of the solvent was purified by column chromatography (eluent: ethyl acetate/toluene 1 : 7 v/v); R_F(**2a–d**) = 0·52. The compounds **2a–d** crystallize as wax-like solids during cooling in a refrigerator; yields and analytical data are in table 1.

Table 1. Yields, melting and clearing points, elemental analysis results and ^{1}H and ^{13}C NMR data for the compounds **2a–d** and **3a–d**.

Compound	Melting point (Clearing point)/°C	Formula (mol wt) C/H analysis: calculated/found	Yield/ per cent	^{1}H NMR†/^{13}C NMR‡ TMS δ/ppm J/Hz
2a	32 (-)	$C_{28}H_{52}O_6$ (484·7) C = 69·4/69·8 H = 10·8/10·4	72	^{1}H NMR (CDCl$_3$)†: 5·62 (d, 1 H, $J_{1\cdot 2}$ ~5, H-1), 4·55 (dd, 1 H, $J_{2\cdot 3}$ ~2·5, H-3), 4·45 (dd, 1 H, $J_{3\cdot 4}$ ~8, H-4), 4·27 (dd, 1 H, H-2), 3·53 (d, 1 H, $J_{4\cdot 5}$ ~1·8, H-5), 3·47 (s, 1 H, tert.OH), 1·52/1·53 (s§), 12 H, CH$_3$-ketals), 1·24 (m, (CH$_2$)$_n$), 0·83 (t, 6 H, CH$_3$-Alkyl)
2b	30 (-)	$C_{32}H_{60}O_6$ (540·8) C = 71·1/71·0 H = 11·2/11·1	75	
2c	32 (-)	$C_{36}H_{68}O_6$ (596·9) C = 72·4/72·1 H = 11·5/11·9	82	^{13}C NMR (CDCl$_3$)‡: 110·0 (tert.C-ketal), 108·3 (tert.C-ketal), 97·0 (C-1), 77·2 (C-6, 72·2 (C-3), 71·2 (C-4) 70·2 (C-2), 67·7 (C-5), 25·8, 25·7, 24·8, 22·6 (4 CH$_3$-ketal), 22·6–36·2 ((CH$_2$)$_n$), 14·0, 14·0 (CH$_3$-Alkyl)
2d	39 (-)	$C_{40}H_{76}O_6$ (653·0) C = 73·6/73·5 H = 11·7/11·8	79	
3a	115–116 (164–166)	$C_{22}H_{44}O_6$ (404·6) C = 65·3/65·3 H = 11·0/10·8	92	^{1}H NMR (DMSO-d$_6$/D$_2$O)†: 3·5–5·2 (5 H, H-1, H-2, H-3, H-4, H-5) 3·42 (OH), 1·21 (m, (CH$_2$)$_n$), 0·83 (CH$_3$-Alkyl)
3b	115–117 (162)	$C_{26}H_{52}O_6$ (460·7) C = 67·8/67·6 H = 11·4/11·7	83	^{13}C NMR (DMSO-d$_6$)‡ *α-Anomer*: 92·4 (C-1), 75·9 (C-6), 73·6 (C-3), 69·6 (C-4), 69·3 (C-2), 68·6 (C-5), 20·3–31·3 ((CH$_2$)$_n$), 13·9, 13·9 (CH$_3$-Alkyl)
3c	112–114 (165–167)	$C_{30}H_{60}O_6$ (516·8) C = 69·7/69·8 H = 11·7/12·0	79	*β-Anomer*: 97·8 (C-1), 75·7 (C-6), 74·4 (C-3), 69·9 (C-4), 72·0 (C-2), 69·2 (C-5), 20·3–31·3 ((CH$_2$)$_n$), 13·9, 13·9 (CH$_3$-Alkyl)
3d	106–108 (146–148)	$C_{34}H_{68}O_6$ (572·9) C = 71·3/71·2 H = 12·0/12·1	95	

† Deviation within the homologous series $\Delta\delta = \pm 0{\cdot}01$ ppm.

‡ Deviation within the homologous series $\Delta\delta = \pm 0{\cdot}05$ ppm.

§ Overlapped singlets from four methyl groups of both isopropylidene ketal functions.

4.2. *Preparation of 6,6-di-C-alkyl-α/β-*D*-galactopyranoses* (3a–d)

A solution of 2 mmol of the corresponding 6,6-di-*C*-alkyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2a–d**) in 4–5 ml of 98 per cent aqueous trifluoroacetic acid was stirred at room temperature for 40 min. The 6,6-di-*C*-alkyl-*α*/*β*-D-galactopyranoses **3a–d** produced were isolated by co-evaporation of the solvent with toluene and ethanol, respectively. The residue crystallized upon standing and could be recrystallized from ethanol in the case of **3b–d**. The octyl derivative **3a** was purified by column chromatography (eluent: ethanol/chloroform 1:5 v/v); R_F(**3a–d**) = 0·5. Yields and analytical data are in table 1.

Table 2. Yields, melting and clearing points for the compounds **4a–e**.

Compound†	**4a**	**4b**	**4c**	**4d**	**4e**
Yield per cent	40	44	45	40	43
Melting point °C	109–110	101–104	107–109	113–115	114–117
Clearing point °C	162	165	167	168	162

† The deviations of the measured values from the elemental analyses were less than ±0·5 per cent compared with the calculated values for compounds **4a–e**.

4.3. *Preparation of 6-O-alkyl-α/β-D-galactopyranoses* (**4a–e**)

(*a*) *O*-Alkylation (analogously to [17]) 0·52 g (20 mmol) of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose [21] and 22 mmol of the corresponding *n*-alkyl bromide dissolved in 100 ml of DMF were treated successively with 1·6 g (40 mmol) of sodium hydride in small portions with stirring at 0°C. After warming to room temperature the solution was stirred to complete the reaction for about 4 hours (TLC control, dichloromethane/acetone = 95:5). The excess of sodium hydride was decomposed by careful addition of about 5 ml of methanol, followed by 10 ml of water. After evaporation of the solvents, the residue was shaken with 150 ml of dichloromethane and the CH_2Cl_2-phase washed with water (3 × 50 ml). The dried organic phase was evaporated and the syrupy residue used without further purification for the deketalization reaction.

(*b*) Deketalization. A solution of 15 mmol of the corresponding 6-*O*-alkyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (crude product) in 100 ml of acetic acid was heated to 90°C with stirring. After that, 20 ml of water and 0·1 ml of concentrated sulphuric acid were added and the mixture stirred for 5–8 hours at 90–100°C. Before the cooled solution was evaporated, 0·15 g of sodium hydrogencarbonate was added to neutralize the small amount of sulphuric acid in the solution. The residue was co-distilled several times with toluene/ethanol (5:1 v/v) and then crystallized from ethanol (see table 2).

The authors thank Professor Dr K. Praefcke and D. Blunk (TU Berlin) for discussions, for a preview of a manuscript [22] and for being able to take photographs of the liquid crystal textures. Furthermore, we would like to thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

[1] Miethchen, R., Holz, J., and Prade, H., 1993, *Colloid Polym. Sci.*, **271** (in the press).

[2] Jeffrey, G. A., 1986, *Accts Chem. Res.*, **19**, 168; Jeffrey, G. A., and Wingert, L. M., 1992, *Liq. Crystals*, **12**, 179.

[3] Goodby, J. W., Marcus, M. A., Chin, E., Finn, P. L., and Pfannemüller, B., 1988, *Liq. Crystals*, **3**, 1569.

[4] Vill, V., Böcker, T., Thiem, J., and Fischer, F., 1989, *Liq. Crystals*, **6**, 349.

[5] van Doren, H. A., and Wingert, L. M., 1991, *Molec. Crystals liq. Crystals*, **198**, 381.

[6] Praefcke, K., Kohne, B., Psaras, P., and Hempel, J., 1991, *J. Carbohydr. Chem.*, **10**, 523.

[7] Miethchen, R., Holz, J., Prade, H., and Liptak, A., 1992, *Tetrahedron*, **48**, 3061.

[8] Dahlhoff, W. V., 1992, *Justus Liebigs Annln Chem.*, 109.

[9] Praefcke, K., Kohne, B., Diehle, S., Pelzl, G., and Kjaer, A., 1992, *Liq. Crystals*, **11**, 1.

[10] Praefcke, K., Levelut, A.-M., Kohne, B., and Eckert, A., 1989, *Liq. Crystals*, **6**, 263.

[11] Vill, V., Sauerbrei, B., Fischer, H., and Thiem, J., 1992, *Liq. Crystals*, **11**, 949.

[12] VOGEL, C., JESCHKE, U., VILL, V., and FISCHER, H., 1992, *Justus Liebigs Annln Chem.*, 1171.

[13] ECKERT, A., KOHNE, B., and PRAEFCKE, K., 1988, *Z. Naturf* (*b*), **43,** 878.

[14] PRAEFCKE, K., MARQUARDT, P., KOHNE, B., and STEPHAN, W., 1991, *J. Carbohydr. Chem.*, **10,** 539.

[15] MARQUARDT, P., PRAEFCKE, K., KOHNE, B., and STEPHAN, W., 1991, *Chem. Ber.*, **124,** 2265; PRAEFCKE, K., MARQUARDT, P., KOHNE, B., STEPHAN, W., LEVELUT, A.-M., and WACHTEL, E., 1991, *Molec. Crystals liq. Crystals*, **203,** 149.

[16] JEFFREY, G. A., 1990, *Molec. Crystals liq. Crystals*, **185,** 209.

[17] CABARET, D., KAZANDJAN, R., and WAKSELMAN, M., 1986, *Carbohydr. Res.*, **146,** 464.

[18] HAVLINOVA, B., KOSIK, M., KOVAC, P., and BLAZEJ, A., 1978, *Tenside, Surfactants, Detergents*, **15,** 72.

[19] THIEM, J., VILL, V., MIETHCHEN, R., and PETERS, D., 1991, *J. prakt. Chem.*, **333,** 173.

[20] VOGEL, C., BOYE, H., and KRISTEN, H., 1990, *J. prakt. Chem.*, **332,** 28.

[21] RAYMOND, A. L., and SCHROEDER, E. F., 1948, *J. Am. Chem. Soc.*, **70,** 2785.

[22] PRAEFCKE, K., and BLUNK, D., 1993, *Liq. Crystals*, **14,** 1181.