REVIEWS

Carbohydrate-based liquid crystals

Madan Kumar Singh AND N. Jayaraman

Abstract | The carbohydrate based mesogens have gained an importance in the field of liquid crystals, primarily through the amphiphilic nature of many sugar derivatives. A constitutional requirement for the amphiphilic mesogen is that the molecule consists of distinct regions within the molecule that separately would have different responses to changes in thermal energies and/or solvations. Such molecules can be synthesized by linking one or more alkyl chains of appropriate length to both cyclic and acyclic sugars. A driving force for the mesophase formation in these molecules is the phase segregation, leading to aggregates, possessing distinct lyophilic and hydrophilic regions. In this review, we discuss the thermotropic behavior of the carbohydrate amphiphiles. We discuss the relationship between constitutions, configurations, functionalities of the sugar component and the length of the hydrophobic chains necessary to form the various types of thermotropic phases. The influence of the linking group between the hydrophilic sugar head groups and lyophilic alkyl chains on the transition temperatures and mesophase stabilities are also presented.

1. Introduction

Molecular aggregation and self-assembly of discrete structures, leading to supramolecular structures, are important for the functions of living system, for example, the formation of the nucleic acids helical structures, collagen, microtubules, ribosomes and multi-subunit enzymes. The study of molecules that self-assemble into supramolecular structures with desirable functionality and physical properties at the nano- and the mesoscopic scales is an exciting area of research.[1] Studies in the area of liquid crystals (LCs) exemplifies an exceptionally fine interplay of molecules, their self-assembly, formation of supramolecular and super-structures and the function that result from the ensembles. Non-covalent interactions, such as, van der Waals forces, dipolar interactions, charge transfer interactions and hydrogen bonding play a crucial role in the formation of molecular assemblies and the emerging functional properties in molecular systems that exhibit LC properties.[2] Liquid crystalline state is considered traditionally as an intermediate state between the solid and the liquid. In this intermediate state, the molecules exhibit the positional and the orientational order. Liquid crystals are dynamic, functional molecules and find applications in information storage, mass transport, sensing, catalysis, templates, and stimuli responsiveness, as well as, electro-optical displays.[3] The anisotropic fluid states of rigid polymers are used for processing of high strength fibers. Liquid crystals are also common in biological systems. An example is the lyotropic lamellar complexes of DNA and cationic lipids, which have potential for gene therapy.[4] Another major class of biological systems that show the liquid crystalline behavior are the glycolipids, embedded mostly in cell-wall components. Glycolipids are neutral in many instances, composed of a sugar head group, which forms as the hydrophilic portion, and an alkyl chain, which forms the lyophilic region of the self-organized glycolipid structures.[4]

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India
jayaraman@orgchem.iisc.ernet.in

Most amphiphiles, which contain sugars as the polar head groups, are found to exhibit smectic A (SmA) phase.[5] Thermotropic columnar mesophases with the hydrophilic groups located towards the interior of the columns have also been obtained by grafting several fatty-acid chains on to the polar head, leading to changes in the curvature and, hence, the packing of the molecules. Columnar mesophases have also been obtained by increasing the volume of the head group, relative to the aliphatic region. Thus, head groups containing more than one sugar moiety, but still possessing a single aliphatic chain, tend to form columnar phases in which the aliphatic chains are located towards the interior of the columns, with head groups at the exterior region. The addition of a solvent to glycolipids causes swelling of the head groups and results in the formation of lamellar, cubic and/or columnar phases, as a function of the induced curvature in the packing arrangements of the molecules. Consequently, a higher degree of liquid-crystalline diversity is found in the lyotropic phases, relative to the thermotropic phases.

Synthetic carbohydrates provide a wide range of well-defined constitutional and configurational isomers, even at the monosaccharides level, with which to study complex phase transitions associated with the liquid crystalline state. Sugars permit an unusual opportunity to study the effect of varying the chemical constitution or configuration of one portion of the amphiphile, while retaining other portion intact. A requirement for the amphiphilic mesogens is that the molecules consist of distinct hydrophilic and lyophilic components, interconnected covalently, without which it is not possible to achieve the mesogenic properties. Such molecules can be synthesized by linking one or more alkyl chains to cyclic or acyclic sugar derivatives. In this review, the thermotropic behavior of carbohydrate based amphiphiles will be discussed. The relationship between the constitution, configuration, the number and the length of the lyophilic chains necessary to form the various types of thermotropic phases will also be discussed.

2. Carbohydrate amphiphiles, with one sugar head group and one alkyl chain
a. Cyclic carbohydrates.

The observation of a double melting behavior of certain long chain alkyl glucopyranosides, e.g. hexadecyl β-D-glucopyranoside by Fischer and Helferich in 1911, was the first observation of the thermotropic liquid crystalline properties of amphiphilic carbohydrates.[6] Later on, the liquid crystalline properties of alkyl glucopyranosides were studied systematically.[7] The homologous series of both alkyl β-D-glucopyranosides (**1**) and alkyl α-D-glucopyranosides (**2**) exhibits the SmA phase. The SmA phase exhibits characteristic defect textures when observed using polarizing optical microscopy. The focal conic texture is characterized by hyperbolic and elliptical lines of optical discontinuity,[8] as shown in the Figure 1. These defects are diagnostic of the presence of a lamellar phase and the fan-like regions also indicate that the phase is SmA*. The SmA–isotropic (I) transition temperature increased with increasing alkyl chain length, for both the anomers and reached a plateau. In the case of the monosaccharides, this plateau is reached when alkyl chain length was ranging between C_{14} and C_{16}.

The introduction of a double bond in to the aliphatic chain decreased the melting point of the glycosides and the mesophase could be obtained at nearly ambient temperature.[9] The introduction of a double bond has an effect on the packing of alkyl chains, as well as, the hydrogen bonding interactions. The clearing temperatures of the α-glucosides are found to be more than the corresponding β-anomers. Also, the mesomorphic range of the α-anomers is more generally. The axial substituents increase the clearing temperatures only slightly, because of the rod-like shape of these molecules. In the liquid crystalline state, the molecules form an interdigitated bilayer structure, where the layer thickness to molecular length has a ratio of 1.4:1.

In the classical non-carbohydrate and non-amphiphilic thermotropic liquid crystals, it is common to identify a structure–property relationship *via* an investigation of the variation in the transition temperatures, as a function of the systematic changes in the molecular structures. Usually, it is found that the clearing and mesophase to mesophase transition temperatures are extremely sensitive to small structural changes. Such studies

Figure 1: The focal conic texture of SmA phase of octyl β-D-glucopyranosides.
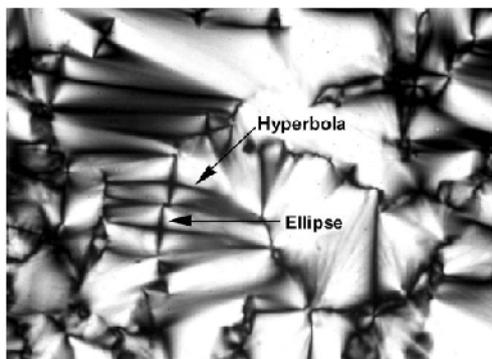
Figure 2: The substitution of the dodecyl chain on the liquid crystalline properties of the *O*-dodecyl-*α*, *β*-D-glucopyranoses and glucopyranosides.

Cr 80.4 SmA 143.4 I   Cr 92.5 SmA 167.2 I   Cr 127.5 SmA 141.8 I

Cr 77 SmA 151 I   Cr 94 SmA 163 I   Cr 109 SmA 140 I
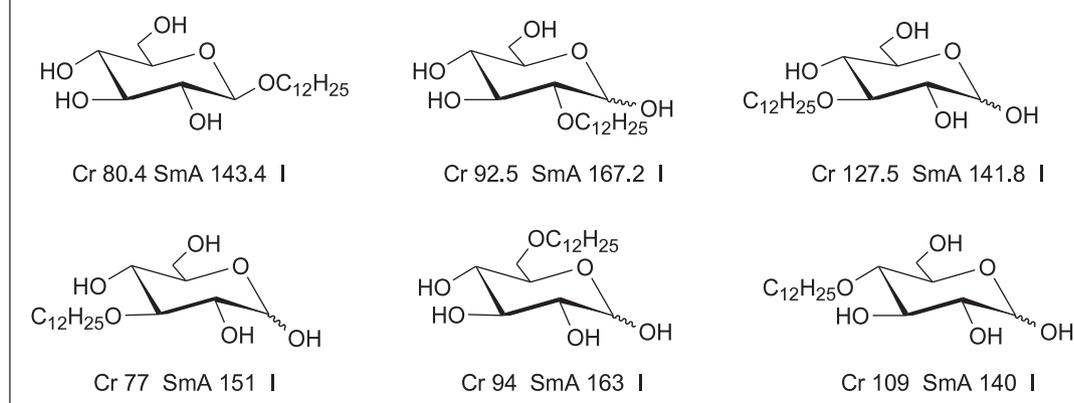
for amphiphilic systems, with respect to their thermotropic and/or their lyotropic behavior, are less. However, comparisons have been reported for the thermotropic properties of the *O*-alkyl-*α*, *β*-D-glucopyranoses.[10] The effect on the clearing point temperatures as the dodecyl chain was moved sequentially from one position to the next in substituted D-glucopyranose systems was demonstrated. As shown in Figure 2, the placement of the dodecyl chain was moved from the C-1 to C-6, whereas, the ratio of *α* to *β* anomer for this series of materials varied from one member to the next, except for the 1-*O*-substituted homologue, where either 100% *α*- or 100% *β*-anomer could be achieved. Nevertheless, even though the anomeric purity varied across the series, the clearing points ranged from 140 to 167.2 °C, with the C-2-substituted derivative, having the highest clearing temperature and the C-4-substituted compound, exhibiting the lowest clearing temperature. Interestingly, the mesophase exhibited by the homologues remained same, namely, the SmA phase. The fact that the mesophase type was lamellar suggested that the shapes of the molecules were rod-like, with the carbohydrate head group having a similar cross-sectional area to the aliphatic chain. As a consequence, the sequential movement of the chain did not encounter

a curvature in the system, which might have led to the formation of the cubic or the columnar phases.

In addition to linear long alkyl chain, carbocyclic and phenyl rings were also incorporated into the alkyl glucosides and the influence of the structural variations on mesophase stabilities were studied.[11] The cyclohexyl substituted derivatives, for example, derivative **3**, exhibited higher clearing temperatures, when compared with the linear alkyl derivatives. The mesophase stability also increased significantly by the introduction of an aromatic unit, for example, derivative **4**. As observed commonly for the non-amphiphilic calamitic mesogens, the clearing temperatures of the alkoxy substituted derivatives increased, in comparison to the alkyl derivatives. However, a significant reduction of the clearing temperature was observed when an additional methylene group was introduced between the glycosidic oxygen and the phenyl group.

The alkyl mannopyranosides (**5**) and alkyl galactopyranosides (**6**) exhibit SmA phase, however, with higher clearing temperatures, when compared to the alkyl glucopyranosides analogues.[12] The volume increase due to the axial hydroxyl groups in the above amphiphilic sugar might contribute to the increased clearing points. Thus, the sugar amphiphiles with axial hydroxyl groups, such as, galactose, exhibit higher clearing points than those sugars, such as, glucose, having only the equatorial

1

n = 8: Cr 67.1 SmA 106.4 I
n = 12: Cr 80.4 SmA 143.4 I
n = 16: Cr 110.0 SmA 145 I

2

n = 8: Cr 71.8 SmA 118.0 I
n = 12: Cr 77.0 SmA 151.0 I
n = 16: Cr 108.0 SmA 175.1 I
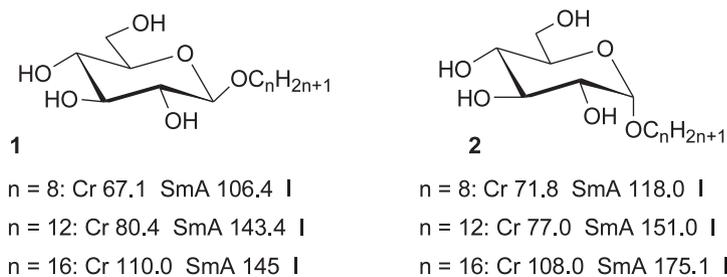
substituents. The homologous members of 6-*O*-alkyl-*α*-D-galactopyranoses (**7**), having two axial substituents, exhibit higher clearing points, than the corresponding alkyl *β*-D-galactopyranosides and alkyl glucopyranosides.[13]

The thermotropic behavior of alkyl *β*-fructopyranosides (**8–10**) have been studied and found to exhibit a novel mesophase, X, for the alkyl chain length C_6 to C_{18}.[14] In addition, the SmA phase was observed for the dodecyl derivative (**9**) and diminished for octadecyl derivative (**10**). The melting point was not affected much by the alkyl chain length, except for the C_{18} alkyl chain.

Studies on the liquid crystalline behavior of alkyl furanosides are less, in comparison to the pyranosides.[15] Figure 3 provides the phase transition temperatures of alkyl glycofuranosides, which is divided into two groups, based on the alkyl chain length. These alkyl glycosides also exhibit SmA phase and it is found that the clearing points of *β*-form of the alkyl furanosides are higher, in comparison to their *α*-anomers. This trend is reverse for the alkyl glycopyranosides and the order of the clearing temperatures is: *α*-pyranosides > *β*-pyranosides > *β*-furanosides > *α*-furanosides.

In order to develop the structure–property relationship, the effect of the linking group between the sugar moiety and the aliphatic chain has also been examined. The thermotropic behavior of alkyl 1-thio-D-glycopyranosides (**11–13**) was investigated and it was found that these compounds exhibited the SmA phase.[16] Both the melting point and the clearing points were higher, in comparison to the corresponding alkyl glycosides, which indicated that the thioether linking group was more efficient in the formation of the thermotropic phases. Whereas, the clearing points of the derivatives of *α*-D-glucose (**14**), *α*-D-mannose (**15**) were comparable, that of *α*-D-talose (**16**) was much lower. This difference was attributed to the presence of an intramolecular hydrogen bond between 2-OH and 4-OH, in the case of D-talopyranose. Single crystal X-ray analysis of the octyl 1-thio-*α*-D-talopyranoside and an MD simulation of D-talose in aqueous solution provided evidence on the hydrogen bonding properties. Due to the formation of an intramolecular hydrogen bond, the talose moieties were less capable of maintaining the hydrogen bond network. The crystal structure of heptyl-1-thio-*α*-D-glucopyranosides show that the carbohydrate moieties form hydrogen-bonded double layers.[17] The hydrocarbon chains extended from these layers and interdigitized with the alkyl chains of the next layer.

The liquid crystalline behavior of 6-alkyl-*α*-D-galactopyranoses (**17–19**), with the linking group thioether, ester and propylthioether, have been investigated.[18] The results indicated that the order of the efficiency of the linking group in favoring the liquid crystal formation was: S ≈ OCO > O > OC_3H_6S. This correlated well with the order of the polarizability of the linking unit.

The amides linkage was incorporated between the carbohydrate moieties and the alkyl chain to study the effect of an additional site for the hydrogen bonding.[19] The homologous member of *N*-acyl-*β*-D-glucopyranosylamines (**20**) exhibited SmA mesophase for the alkyl chain length C_9 to C_{17}. Both the melting and the clearing points were high and a SmA phase was observed. A relatively small dependence on the chain length was observed. This observation is typical of many liquid crystalline carbohydrate homologous series and suggests that a minimum ratio of the hydrophobic to hydrophilic balance is necessary for the mesophase formation. The mesomorphic behavior of the homologous series of *N*-acyl-*β*-D-mannopyranosides (**21**) was different. Although the mannose derivatives exhibited SmA phase, both the melting and the clearing points were lower, in general, and the longer chain length was required for the mesophase formation. It seems that the high melting and clearing points of the amides are primarily due to a high degree of hydrogen bonding between the adjacent carbohydrate cores, with a minimum interdigitation of the aliphatic chain. Changing the position of the alkylamido group from C-1 in the *N*-acyl-*β*-D-glucopyranosylamines to C-2 in the corresponding 2-alkylamido-2-deoxy-*β*-D-glucopyranoses (**22**) resulted in an increased melting point and the disappearance of the thermotropic mesomorphism. Steric interactions and electrostatic repulsions between the carbonyl oxygen atom and the hydroxyl group at the anomeric centre probably caused a degree of rotation around the amide linkage, leading to a non-linear conformation of the alkyl chain and the carbohydrate core. Comparison of the transition temperatures of the dodecyl *β*-D-glucopyranoside (**1**) and *N*-dodecanoyl-*β*-D-glucosylamine (**20**) demonstrated clearly the effect of the additional hydrogen bonding and the reduced conformational freedom, attributable due to the


3

Cr 137 SmA 167 I

Cr 108 192 SmA 192 I

4
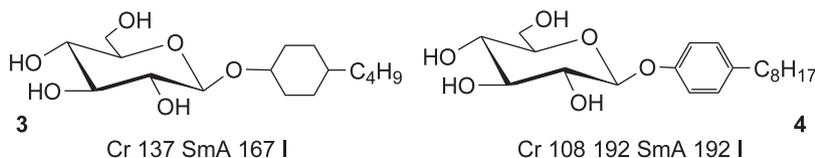
Figure 3: The transition temperatures for the alkyl glycofuranosides.

Octyl α-D-glucofuranoside
Cr 51.0 °C SmA 60.6 I

Octyl β-D-glucofuranoside
Cr 53.1 SmA 96.7 I

Octyl β-D-galactofuranoside
Cr 96.0 SmA 128.5 I

Octyl α-D-mannofuranoside
Cr 92.7 SmA 103.2 I

Decyl α-D-glucofuranoside
Cr 61.0 SmA 99.2 I

Decyl β-D-glucofuranoside
Cr 64.7 SmA 132.0 I

Decyl β-D-galactofuranoside
Cr 98.0 SmA 155.0 I

Decyl α-D-mannofuranoside
Cr 62.4 SmA 107.0 I
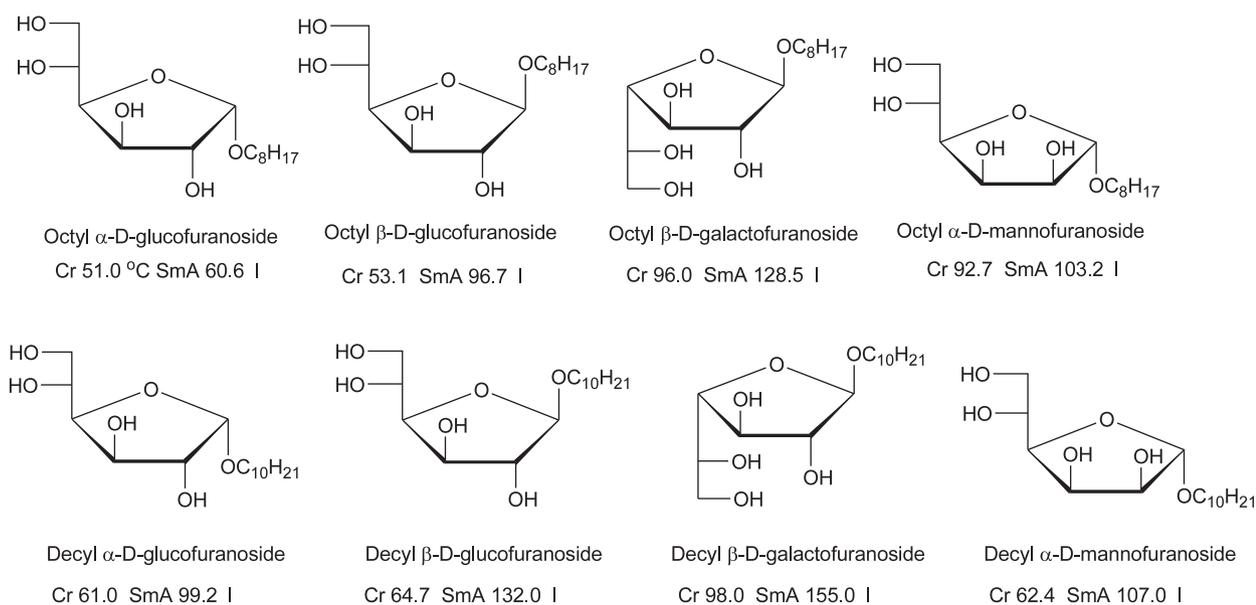
presence of the amide linkage. Both the melting and clearing points of the amide were significantly higher.[20] The sulphonamide derivatives **25** exhibited a higher clearing point than the amide derivatives, due to apparent differences in the polarities.

Liquid crystalline carbohydrates with a primary amino group situated in the hydrophilic part of the molecule have been studied.[21] The homologous series of alkyl 2-amino-2-deoxy-β-D-glucopyranosides **26** exhibited SmA phase. Although their melting points were higher, the clearing points were found to be lower, than the corresponding alkyl glucosides. The ω-hydroxy compounds with long alkyl chain **27** showed a smectic phase, with a low clearing point. When a terminal carboxyl group was introduced, the resulting amino acid

exhibited an internal salt formation and melted at a higher temperature. A particular feature of the liquid crystalline amino compounds is the ability to form salts with organic acids. For example, the hydrochloride **28** has a high polarity and with only one alkyl chain, a SmA phase, with a high clearing point, was observed.

Alkyl glucosides with amino linked alkyl chains **29** and **30** formed a mesophase.[22] The 2-deoxy compounds, such as, **31** exhibited a monotropic SmA phase. The 2-deoxy derivative **31** exhibited melting points, in the same range as that of **29** and **30**. However, rapid heating and cooling runs of the derivatives **29** and **30** led to clearing points of approximately 125 °C, which was ∼40–45 °C higher than the derivatives **31**. This observation illustrated

5
n = 8: Cr 55.0 SmA 133.9 I
n = 10: Cr 64.7 SmA 152.7 I
n = 12: Cr 74.2 SmA 161.7 I

6
n = 8: Cr 98.3 SmA 132.9 I
n = 10: Cr 93.5 SmA 157.3 I
n = 12: Cr 99.4 SmA 165.7 I

7
n = 8: Cr 113.0 SmA 169.0 I
n = 10: Cr 117.0 SmA 172.0 I
n = 12: Cr 119.0 SmA 171.0 I

8
Cr 128.5 X 131.0 I

9
Cr 128.6 X 131.6 SmA 132.7 I

10
Cr 114.5 X 128.2 I

11
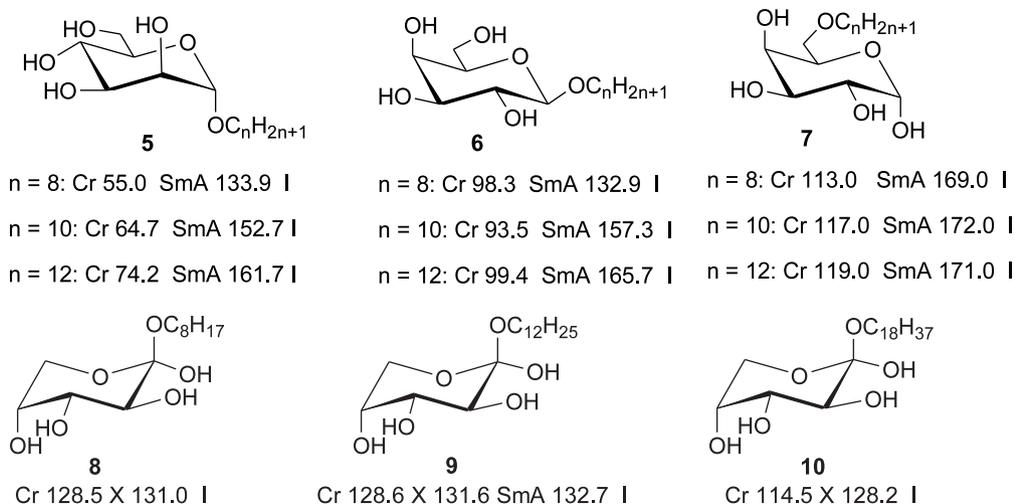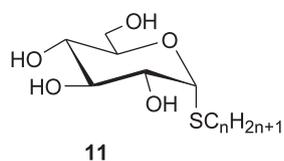
n = 6: Cr 99.0 SmA 116.4 I

n = 8: Cr 77.0 SmA 154 I

12
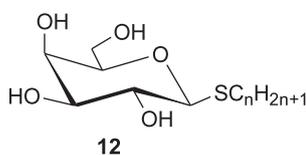
n = 6: Cr 87.1 SmA 90.9 I

n = 8: Cr 91.7 SmA 140.5 I

13
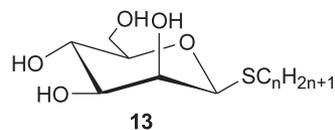
n = 6: Cr 115.3 SmA 125.4 I

n = 8: Cr 118.9 SmA 156.1 I

14

Cr 90.3 I 85.6 °C SmA

15

Cr 62.1 SmA 152.4 I

16

Cr 91.7 SmA 105.7 I

17
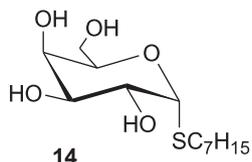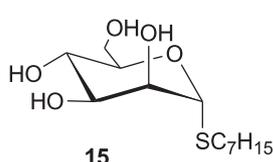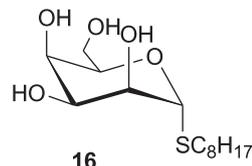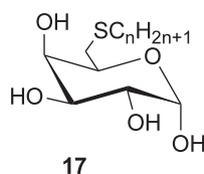
n = 8 : Cr 98 SmA 173 I

n = 10: Cr 104 SmA 191 I

n = 12: Cr 109 SmA 185 I

18
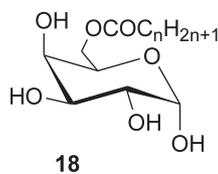
n = 8 : Cr 90 SmA 155 I

n = 10: Cr 115 SmA 181 I

n = 13: Cr 117 SmA 184 I

19
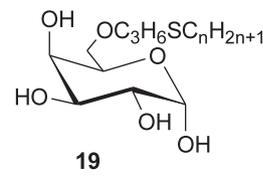
n = 8: Cr 95 SmA 156 I

n = 10: Cr 101 SmA 166 I

n = 12: Cr 99 SmA 165 I

20
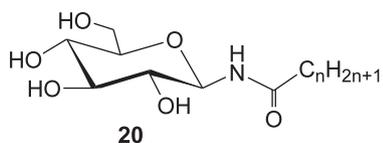
n = 8: Cr 183 I

n = 11: Cr 182 SmA 223 I

n = 17: Cr 170 SmA 220 I

21
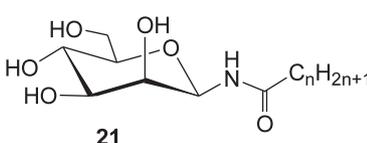
n = 9: Cr 194 I

n = 11: Cr 188 SmA 198 I

n = 17: Cr 180 SmA 216 I

22
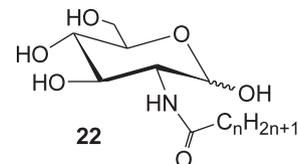
n = 9: Cr 214 I

n = 11: Cr 210 I

n = 17: Cr 197 I

23

Cr 119 SmA 164 I

24

Cr 134 SmA 197 I

25
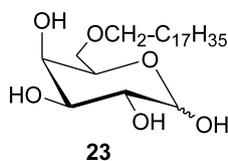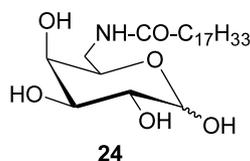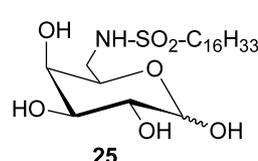
Cr 142 SmA 235 I

that the hydroxyl group at C-2 plays an important role in the stabilization of the mesophase.

To investigate the influence of the C-2 hydroxyl group on the mesophase formation of alkyl glycosides, the mesomorphic behavior of alkyl glycosides wherein 2-deoxy sugar constitutes the hydrophilic segment was studied.[23] Among the alkyl 2-deoxy-β-glucosides (C_n-2d-β-Glc) (**32**), compounds C_9 to C_{14} ($n = 9$ to 14) exhibited a monotropic SmA phase (Fig. 4). It is important to note that the melting and the isotropic to SmA transition temperatures do not seem to have a systematic variation with the alkyl chain lengths.

The corresponding α-anomers, namely, alkyl-2-deoxy-α-D-glucosides (C_n-2d-α-Glc) (**33**) were all non-mesomorphic.

The melting points of the α-anomers are slightly more than the corresponding β-anomers in alkyl glycosides generally. The crystal structures of alkyl D-glucosides revealed that the molecules formed bilayer structures.[24] The observation that the mesomorphism existed not only in short temperature ranges, but also, was dependent on the anomeric configuration could be accounted due to the absence of the hydroxyl group at C-2 in the alkyl 2-deoxy glucosides. These observations are in

Figure 4: The fan-shaped texture of the SmA phase obtained upon slow cooling of the isotropic liquid of C_{13}-2d-β-Glc (left) and binary mixture C_{12}-2d-α,β-Glc (1:1) (right).

contrast to the mesophase behavior of normal alkyl glycosides that show not only a non-distinction of the anomeric configurations, but also present the mesophase at wider temperature ranges.

The binary mixtures of alkyl-2-deoxy-α-D-glucosides and alkyl-2-deoxy-β-D-glucosides in equimolar ratio exhibited SmA phase, similar to that of the pure β-derivatives in the cooling cycle. The texture of SmA phase for C_{12}-2d-α,β-Glc (1:1) is shown in Figure 4. The crystal structure of the binary mixtures of octyl α-D-glucoside and octyl β-D-glucoside in equimolar ratio is known previously.[25] In the crystalline state, both α- and β- derivatives arrange in an alternate fashion. A similar possibility could be considered with the binary mixtures of the 2-deoxy glycosides. The thermal behavior of the binary mixture of C_{13}-2d-α-Glc and C_{13}-2d-β-Glc, as well as, C_{15}-2d-α-Glc and C_{15}-2d-β-Glc, in different molar ratios, from 10 mol% to 90 mol%, was also investigated. As the amount of the α-anomer increased in the pure β-anomer, the mesophase range increased and it reached a maximum at 50 mol %. Further increase in the

α-component reduced the mesophase range and above 80 mol %, the mesophase ceased to exist. For C_{15}-2d-Glc, where both α- and β-anomers were not liquid crystalline, 25 mol % of α-anomer induced a mesomorphism in the pure β-anomer. As the component of the α-anomer increased, the mesomorphic range increased, with a maximum at 50 mol %. At higher concentrations of the α-anomer, the mesomorphic range decreased. These results showed that both the α- and the β-anomers were able to induce the mesomorphism in the counterpart anomer equally. Importantly, the results suggested that not only the hydroxyl group of the sugar moiety, but also, the anomeric configuration played a significant role in the mesophase formation.

The binary mixtures of the α- and the β-anomers of alkyl-D-glucopyranosides were studied to describe the molecular packing and co-solubility in the crystalline state and the liquid crystalline phase.[26] A cubic phase could be induced in the binary mixture, with one component forming the columnar phase in its pure state and the other component forming the lamellar phase.[27]

26

n = 12: Cr 102.2 SmA 125.2 I

n = 14: Cr 90.2 SmA 125.0 I

27

n = 9: Cr 115.9 I

n = 14: Cr 122.3 I 103.5 SmA

28

Cr 129 SmA 199 I

29

n = 7 - 16

30

n = 7 - 16

31

n = 10: Cr 101.2 I 73.2 SmA

n = 12: Cr 102.6 I 89.7 SmA

n = 15: Cr 97.2 I 79.2 SmA
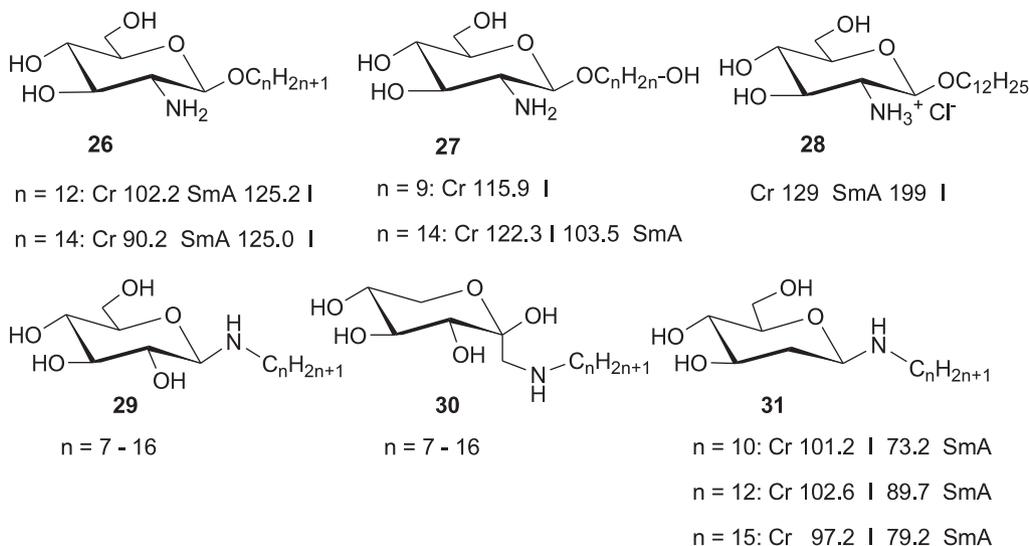
The stability of the induced cubic phase was temperature, as well as, concentration-dependent. The binary mixtures of the glycoglycerolipids with phospholipids have been studied to determine the glycolipid-phospholipid miscibility in solid and liquid crystalline states.[28]

b. Acyclic carbohydrate systems

The liquid crystalline behavior of acyclic carbohydrates, were investigated as a function of the alkyl chain lengths, the number of hydroxyl groups and the type of the linkage. The acyclic sugar derivatives also exhibit both thermotropic and lyotropic mesophases, i.e. they are amphotropic liquid crystals. The derivatives with one aliphatic chain and one sugar group exhibit a lamellar SmA phase, as a result of a microphase segregation. The systems with two aliphatic chain and one sugar group exhibit columnar phases.

Goodby and co-workers reported the effect on the clearing point of alkyl-substituted polyols with respect to increasing number of the hydroxyl groups.[29] It was found that the clearing point increased with increasing number of the hydroxyl group in the head group of the amphiphile. Compounds A–F in Figure 5 exhibited SmA phase. There is no appreciable effect of the structure or the sugar type with a given number of hydroxyl group on the clearing points, unlike in the case of the cyclic derivatives. The comparison between the erythritol and threitol derivatives showed that the nature of the stereochemistry at C-3 did not affect the clearing temperatures markedly.

The self-assembling properties could be affected by the sequential movement of the position of the alkyl chain in acyclic polyol systems.[30] As the dodecyl chain in x-dodecyl-D-xylitols moved towards the centre of the carbohydrate moiety, the clearing transition temperatures raised almost linearly, in relation to the position of the aliphatic chain (Figure 6). The melting points also increased as the chain moved towards the centre of the carbohydrate moiety. The placing of the dodecyl chain from the terminal position C-1 or C-5 to the inner positions C-2 or C-4 led to introducing a curvature into the system. At the same time, due to the steric hindrance interfering with the motion of the aliphatic chain, the internal flexibility reduced.

However, the induced curvature was not enough to form the columnar phases. For the 3-substituted xylitols, the head group was forked, yet no columnar phase was found. The mesophase (SmA) phase to isotropic transition temperature was considerably higher than other isomers.

The thermotropic properties of glucitols (**34–37**), galactitols (**38, 39**), mannitols (**40–42**), xylitols (**43, 44**), erythritols (**45, 46**) and threitols (**47, 48**) have been studied, as a function of placing the alkyl chain at different carbons of the sugar.[31] Generally, a thermotropic phase appeared when the alkyl chain was hexyl to octyl and the phase transition temperature increases with increasing alkyl chain length. However, for 3-O-alkyl galactitols, 2-O-alkyl-mannitols and 2-O-n-alkyl-erythritols, the thermotropic phase was observed only with dodecyl derivatives and the 1-O-alkylerythritol did not exhibit liquid crystalline behaviour at all. Placing the alkyl chain at a particular carbon of the sugar strongly affected the phase transition temperatures, in the order: 6-O-alkyl- ≫ 3-O-alkyl-galactitols; 1-O-alkyl- ≈ 6-O-alkyl- > 4-O-alkyl-glucitols; 1-O-alkyl- > 3-O-alkyl- ≫ 2-O-alkyl-mannitols. These results indicated that for hexitols, compounds with the alkyl chain at the terminal carbon (C-1 or C-6) have the highest phase transition temperatures. In contrast, for xylitol, erythritol and threitol series, the alkyl chain at the terminal carbons exhibited the lowest phase transition temperatures. Comparing 2-O-alkyl-mannitols (having 5 hydroxyl groups) to the corresponding 2-O-alkyl-mannitol monoacetal (3 hydroxyl groups), and comparing the xylitol derivatives (4 hydroxyl groups) to the corresponding erythritol and threitol (3 hydroxyl groups) derivatives, it appeared that both the crystal-liquid crystal transition temperature and the mesophase range raised with increased number of OH groups. It was also observed that 3-O-dodecyl galactitol (5 OH groups) exhibited lower melting point and mesophase range than 1-O-dodecyl and 2-O-dodecyl-threitol (3 OH groups). Thus, it is difficult to explain the phase transition temperatures only as a consequence of both the alkyl chain position and the number of the hydroxyl groups. The configurations on each polyol substrate exert a strong influence.

32

C_n-2d-β-Glc, n = 8-18

n = 9: Cr 91.9 I 83.9 SmA 72.1 Cr
n = 10: Cr 97.7 I 88.1 SmA 86.5 Cr
n = 11: Cr 99.2 I 93.8 SmA 86.5 Cr
n = 12: Cr 103.7 I 99.5 SmA 97.6 Cr
n = 13: Cr 104.0 I 98.9 SmA 91.4 Cr
n = 14: Cr 106.1 I 97.2 SmA 92.4 Cr

33

C_n-2d-α-Glc, n = 8-18

n = 9: Cr 104.3 I
n = 10: Cr 111.4 I
n = 11: Cr 109.0 I
n = 12: Cr 110.4 I
n = 13: Cr 113.2 I
n = 14: Cr 113.6 I
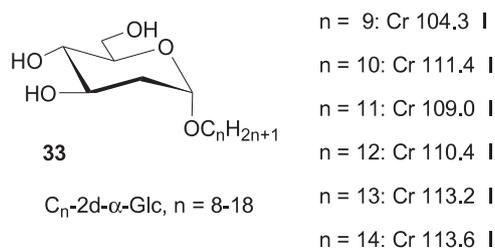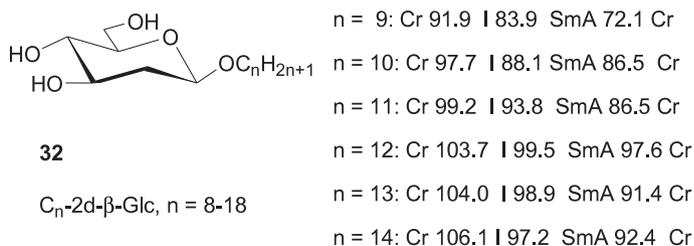
Figure 5: Structures of the acyclic sugar derivatives and their phase transition temperatures.

|					
A	**B**	**C**	**D**	**E**	**F**
Cr 48 ⎮ 32 SmX	Cr 58.2 SmA 71.0 ⎮	Cr 68.5 SmA 73.9 ⎮	Cr 49.5 SmA 114.7 ⎮	Cr 142.0 SmA 168.7 ⎮	Cr 111.2 SmA 167.0 ⎮
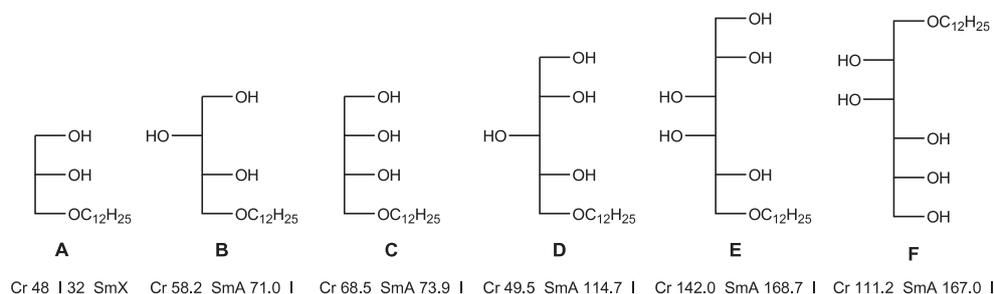
Figure 6: Effect on transition temperatures caused by the sequential movement of the position of a dodecyl chain in the acyclic x-O-dodecyl-(D or L)-xylitols.

Cr 49.5 SmA 111.1 ⎮	Cr 69.1 SmA 120.3 ⎮	Cr 101.3 SmA 137.3 ⎮	Cr 67.8 SmA 123.7 ⎮
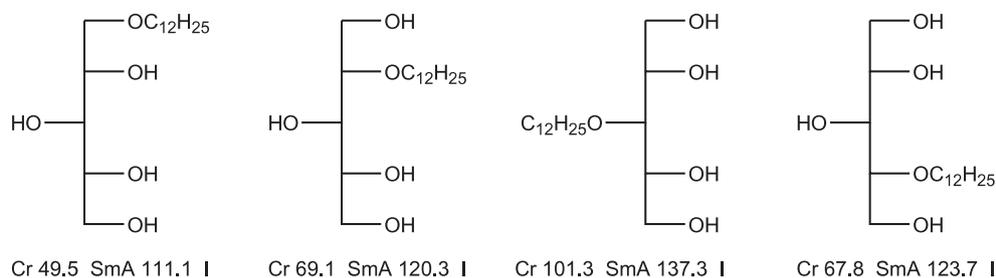
The mesomorphic behavior of 6-O-alkyl-D-galactitols (**38**) was compared with those of the 6-O-alkyl-α-D-galactopyranoses (**7**).[32] Both the homologous series exhibited a SmA phase. The melting point of galacitols was more than the corresponding galactose derivatives. The even members of the acyclic systems were found to have higher melting points and exhibited strong odd–even effect in the clearing points. The higher clearing points were related to the hydrogen bonding patterns. It is not clear, however, why the odd-even effect is so strong for the galacitols. The galacitols appeared to decompose more readily at higher temperatures, than the galactopyranoses. The cyclic derivatives exhibit mesomorphism at lower alkyl chain lengths than the acyclic derivatives.

Similar to cyclic sugars, the effects of the linking group between the sugar moiety and the aliphatic chain were investigated for the acyclic sugars also.[33] The mesomorphic behavior of the alkyl substituted xylitols, where the aliphatic chain was attached to the xylitol moiety *via* ether, ester and thioether linkage, were studied. The liquid crystalline behavior of 1-O-alkyl-D,L-xylitols (**43**), 1-S-alkyl-1-thio-D,L-xylitols (**49**) and 1-O-acyl- D,L-xylitols (**50**) were investigated. It is interesting to note that the thioethers exhibit higher clearing points, in

34	**35**	**36**	**37**
n = 6: Cr 75.6 SmA 81.0 ⎮	n = 6: Cr < -8.9 SmA 2.1 ⎮	n = 8: Cr < RT SmA 61.8 ⎮	n = 6: Cr 50.6 SmA 98.8 ⎮
n = 8: Cr 80.5 SmA 131.8 ⎮	n = 8: Cr < -10.0 SmA 54.0 ⎮	n = 10: Cr 33.0 SmA 136.2 ⎮	n = 8: Cr 72.6 SmA 135.3 ⎮
n = 10: Cr 82.4 SmA 160.6 ⎮	n = 10: Cr 56.9 SmA 144.3 ⎮	n = 12: Cr 64.7 SmA 164.2 ⎮	n = 10: Cr 78.8 SmA 147.7 ⎮
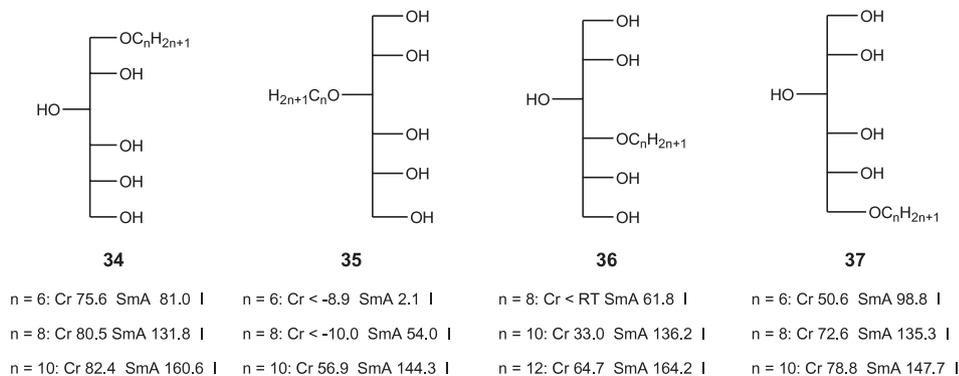
comparison to the esters, which are, in turn, higher than the corresponding ethers.

Amides have also been used as linking groups, as the amide groups can induce further sites for hydrogen bonding. The liquid crystalline properties of alkyl gluconamide **51** were studied extensively.[34] This work was one of the earliest to demonstrate that microsegregation could be used as a model to support not only the lyotropic, but also the thermotropic mesophase formation. The gluconamides have a tendency to decompose, and it is interesting to note that the decomposition is more rapid in the materials that exhibit liquid crystal phases. A comparison of the thermal behavior of octyl gluconamide with octyl gluconate **52** indicated that both were having similar phase sequences and transition temperatures.[35] In the liquid crystal systems, a progression from an ester linkage to a hydrogen bonding amide linkage would produce

differences in the transition temperatures and the phase type. In the case of **51** and **52**, however, the inter- and intra-molecular hydrogen bonding by the amide group is only a small fraction of the total hydrogen bonding in the system. Thus, the derivatives **51** and **52** become almost iso-structural and consequently have similar phase behavior.

c. Disaccharide head groups.

The glycolipids with a single alkyl chain and disaccharides, such as, maltose, lactose and cellobiose, are relatively small.[36] The α- and β-anomers of dodecyl and tetradecyl maltoside (**53, 54**) and both anomers of tetradecyl lactosides (**55, 56**) exhibited bilayer SmA phase. On the other hand, dodecyl α-gentiobiosides (**57**) exhibited a cubic phase. The position of both the alkyl chain and the linkage between the sugar units led to a non-linear molecular structure. The molecules,
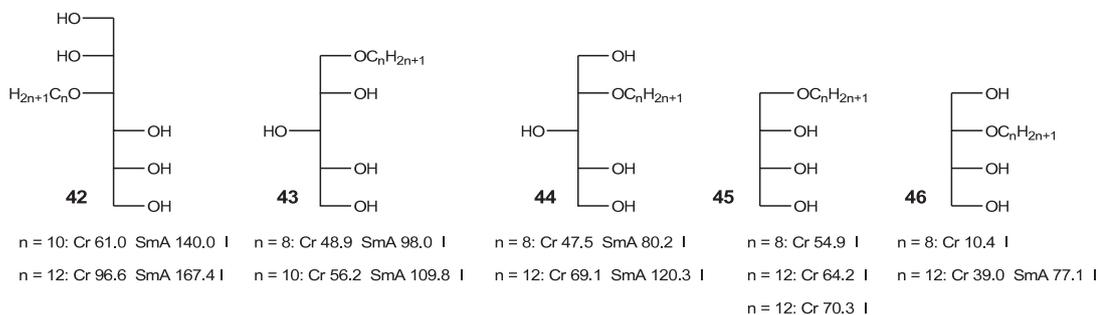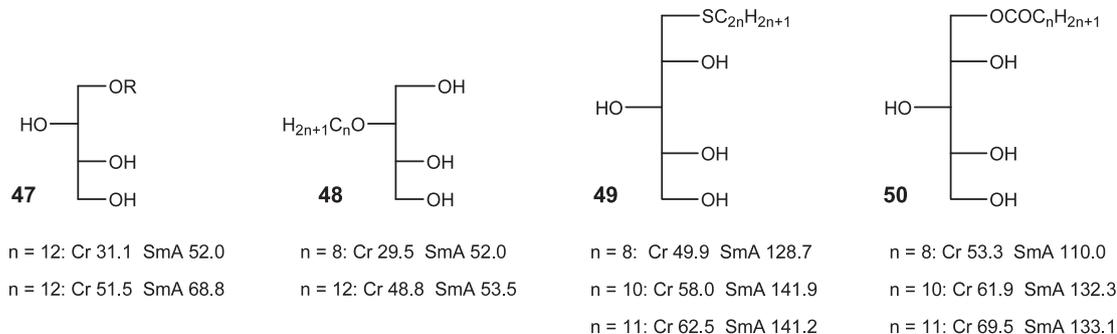
thus, self-organize to provide a cubic phase, with a curvature of the molecular packing.

The clearing points of the disaccharide derivatives were much more in comparison to the monosaccharide derivatives. This could be attributed to the increased hydrogen bonding in the polar sugar region. The optimal hydrophilic-hydrophobic balance and, therefore, a higher clearing temperature is reached in the case of monosaccharide head groups with alkyl chain length between C_{12}–C_{14}. On the other hand, the optimal balance between the hydrophilic and hydrophobic moieties is reached at even longer chain lengths in the case of the disaccharide polar groups. The introduction of an un-saturation in the alkyl chain of the disaccharide derivatives (58) lowered the clearing point, although less as compared to the monosaccharide derivatives. It seemed that the effects of the structural changes in the aliphatic chain on the clearing temperatures were stronger in the case of monosaccharide derivatives than in the case of disaccharide derivatives. This hypothesis was supported further by the observation that when a thioether moiety was introduced as linking group between the alkyl chain and sugar moiety for maltobiosides, the clearing point was nearly the same as that of the oxygen analogue. The dodecyl thiomaltobioside (59) exhibited nearly the same clearing point as that of the oxygen-linked maltobioside (60). This behavior is in contrast to the monosaccharide derivatives, where the introduction of the thio-group raised the clearing point drastically, as discussed previously. The clearing point was also influenced by the type of glycoside linkage (α vs. β). The disaccharides sugar amphiphiles with a β-glycosidic bond displayed a higher clearing temperature and, hence, a more stable SmA phase, than the corresponding α-anomer 53. The difference of the mesophase stability was less for the 1–6 interglycosidic (61, 62) disaccharide

amphiphiles than those linked by 1–4 linkage (53, 54). The increased stability of the β-glycoside derivatives might be due to their more rod-like structure. This effect was not so strong in the case of compounds with a 1-6-linked disaccharide unit, as the sugar moiety would be angular, thereby causing the molecule to be banana-shaped. While this difference in stability between the two anomers was chain-length independent in case of a 1-6-linked head group, it was strongly dependent on the chain length in case of 1-4-linked disaccharide amphiphiles. When the α-1-4 linked maltoside (60) was replaced by β-1-4-linked cellobioside (63), the clearing point increased due to the stiffer and more rod-like structure of the cellobioside head groups. When β-1-4-linked glucopyranosyl residue of the cellobiosides 64 was replaced by a β-1-4-linked galactopyranosyl residue, the stability of the SmA phase was not affected and the clearing point of the resulting lactoside (65) was almost the same. Therefore, the configuration at C-4 of the sugar moiety seemed to have no influence on the stability of the SmA phase, in the case of 1-4-linked disaccharide amphiphiles. The octadecyl α- and β-lactoside (65) exhibited a monotropic cubic phase, similar to the octadecyl α-cellobioside (64). So far, only few sugar derivatives are known to show a thermotropic cubic phase. The occurrence of the thermotropic cubic phase for lactoside and cellobioside is unexpected and difficult to explain. The rod-like molecules are known to display SmA phase. On the other hand, when an imbalance between hydrophobic and hydrophilic moieties increased, a cubic phase might be observed, instead of a SmA phase. The difference between the alkyl glycosides with 1-6 and 1-4-linked disaccharide head group is the occurrence of the cubic phases in the former case. While the α-melibioside (62) exhibited a cubic phase, the α-isomaltoside did not. This difference in the mesogenic behavior could be

51

n = 7: Cr 150.4 SmA 156.4 I
n = 8: Cr 158.2 SmA 159.1 I
n = 12: Cr 155.0 SmA 189.0 I

52

Cr 160.1 I 160.0 SmA I

53

n = 12 Cr 82.0 SmA 205.0 I
n = 14 Cr 102.5 SmA 231.0 I

54

n = 12 Cr 80.0 SmA 244.0 I
n = 14 Cr 86.0 SmA 264.0 I

55

Cr 173.0 SmA > 249.0 I

56

Cr 183.0 SmA 246.0 I
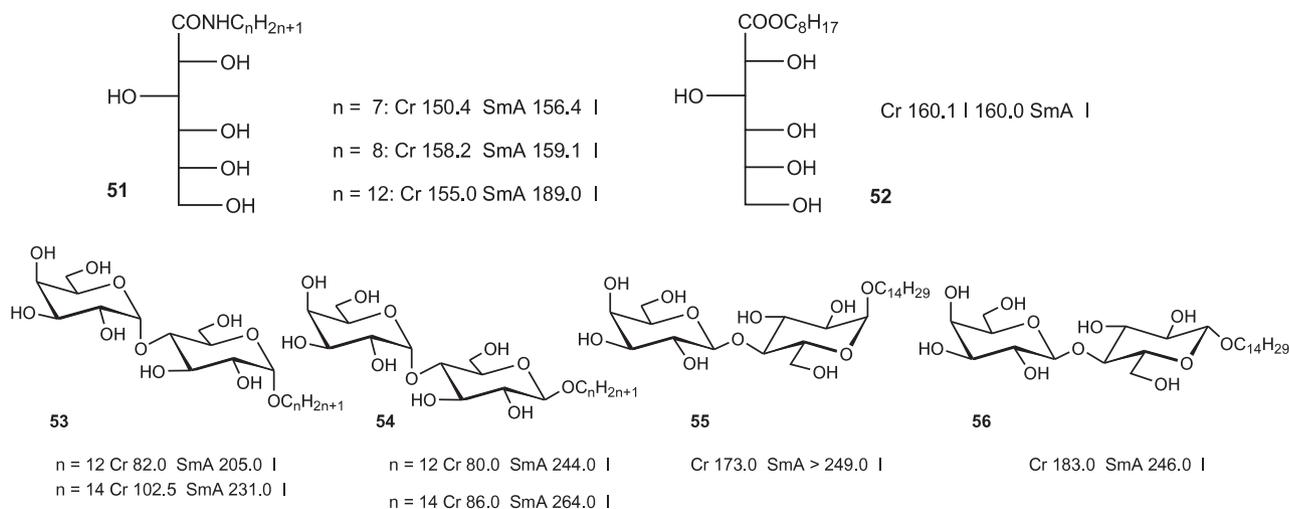
attributed to the changed configuration at C-4 of the sugar residue at the non-reducing end.

As in the case of x-O-dodecyl-α,β-D-glucopyranoses and x-dodecyl-D-xylitols, a dodecyl aliphatic chain was sequentially moved from one position to the next for the mono-O-(2-hydroxydodecyl)-sucrose family of derivatives, and the liquid crystaline behavior were examined.[37] Sucrose itself provides a unique opportunity to prepare and study the combination of a pyranose and a furanose ring system. Comparisons have been made on furanose and pyranose based glycolipids. The clearing points of the α- and β-anomers showed an inverted relationship with respect to the ring type of the sugar moiety. The transition temperatures and the phase types are shown in the Figure 7. When the dodecyl chain is attached to C-3, C-4 and C-6 of the pyranose ring or C-6 of the furanose ring, the shape of the molecular structure is rod-like and the derivatives exhibit SmA phase. When the dodecyl chain attached to C-2 of the pyranose ring or C-3 of the furanose ring, the molecular structures become T-shaped, with the cross-sectional area of the head group being larger than that of the aliphatic chain. Consequently, these molecules have wedge-like structures and exhibit cubic and columnar phases, respectively. The compounds where the dodecyl chain is at C-6 of either the pyranose (**d**) or the furanose (**g**), the mesophase to isotropic transition temperature is high. Compounds (**a**) and (**f**) have much lower clearing point temperatures, when compared to other members of the series. The change-over from one type of phase to another, i.e. lamellar to columnar, also involves a large change in the clearing temperatures. The columnar and cubic phases tend to occur at much lower temperatures, $\sim 50\,°C$, relative to the lamellar phase.

The columnar or cubic phases could be stabilized in disaccharide derivatives by changing the alkyl chain length. Molinier and co-workers described the effect of the aliphatic chain length on the mesomorphic properties of mono-substituted sucrose fatty acid esters.[38] The octyl derivatives of mono-1' (**66**), mono-6 (**67**) and mono-6' (**68**) saturated fatty acid sucrose esters exhibited columnar phases. The longer alkyl chain derivatives, from decyl to octadecyl exhibited SmA phase. The head group size relative to the over-all molecular length is much greater for the smaller alkyl chain derivatives and when the molecules pack together, a curved structural arrangement forms, leading to the formation of the columnar phase. Thus, for derivatives with a larger cross-sectional area of the head group relative to the aliphatic chain, then as the chain length is increased, the lamellar phases become more stable, as a result of the reduction in the curvature in the packing of the molecules. However, for systems that have a larger cross-sectional area, the longer the aliphatic chain(s), the more stable the columnar and cubic phases become.

3. Carbohydrate amphiphiles, with two sugar groups and an alkyl chain

The mesomorphic behavior of the glycolipids where the head group is composed of two sugar moieties attached to a single aliphatic chain is relatively less known.[39] Compounds of the type **69** generally exhibit columnar/cubic phases due to the larger cross-sectional area of sugar head groups, relative to the aliphatic chains. The thermal behavior of the bivalent glycolipids can be influenced by a linker group between the alkyl chain and glycerol moiety, the chain length and the type of the alkyl chain.[40] An un-saturation in the hydrophobic part of the

57

Cr 75.0 Cub 162.0 I

58

Tg ? SmA 267.0 I

59

n = 12: Cr 135.7 SmA 246.2 I

n = 13: Cr 139.4 SmA 260.0 I

60

n = 12: Cr 120.0 SmA 245 I

n = 18: Cr 106.0 SmA 274.0 I

61

n = 12: Cr 155.0 SmA 171.0 I 137.0 Cub

n = 18: Cr 152.0 SmA 262.0 I

62

n = 12: Cr 90.5 Cub 151.0 SmA 160.5 I

n = 18: Cr 129.8 SmA 252.0 I
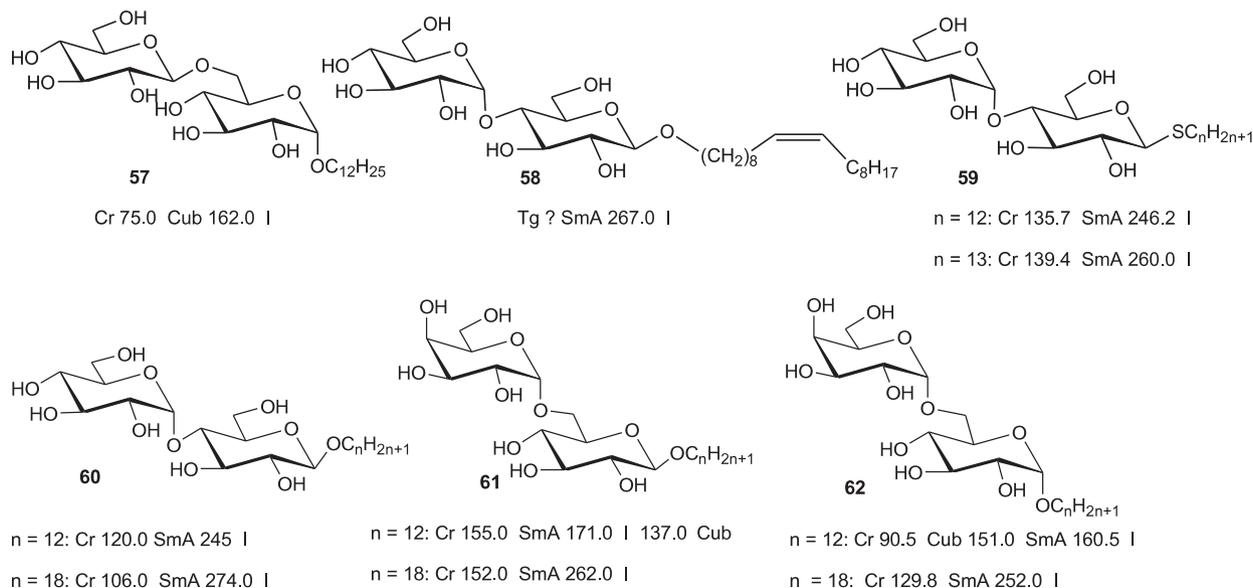
Figure 7: Molecular structures of various mono-*O*-(2-hydroxydodecyl) sucroses and their phase transition temperatures.
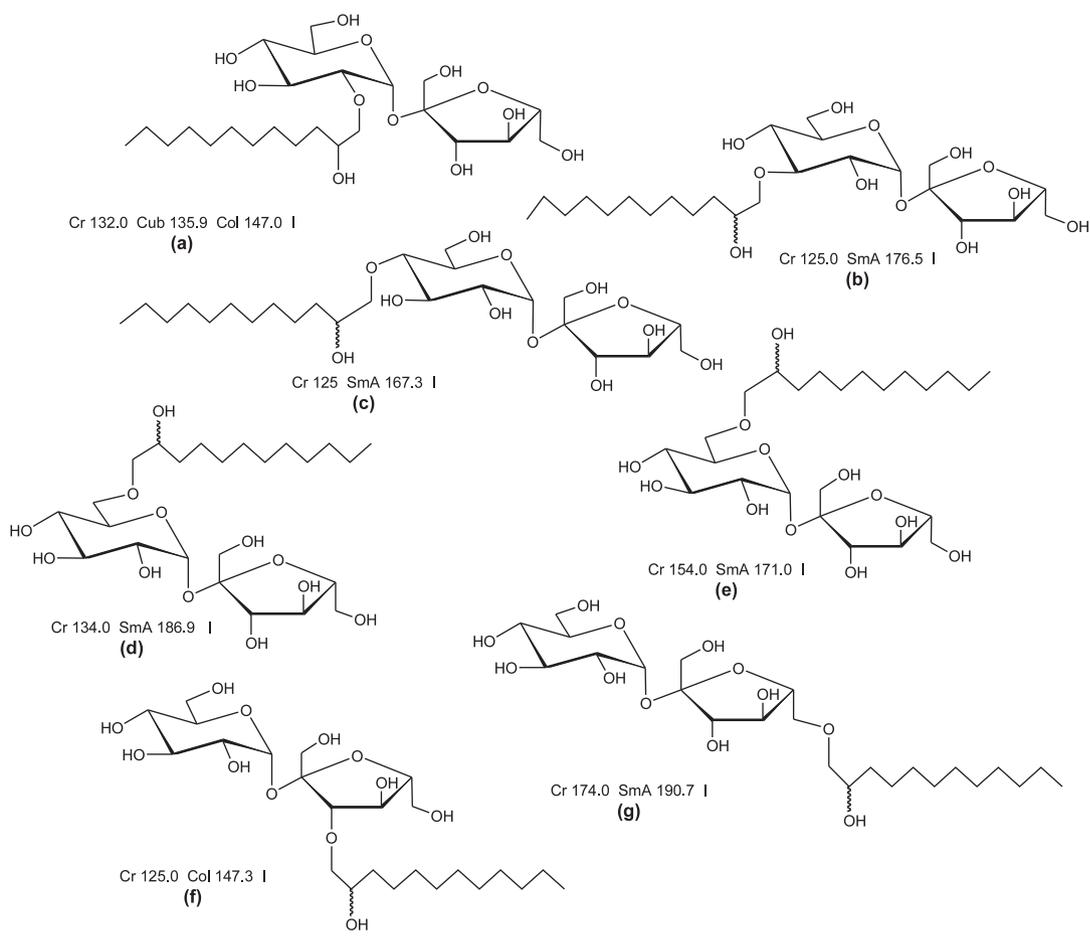
molecule (**70**) leads to liquid crystallinity even at ambient temperatures, due to a disturbed packing of chain. Compared to the ester linked derivative **70**, the amide linked derivative **71** exhibited unusual melting behavior, due to a more complex hydrogen bonding network. The mesomorphic behavior of a homologous series of bivalent glycolipids, constituted with 1, 3-*bis-O*-(*β*-D-glucopyranosyl)-2-*O*-alkyl glycerol, bearing two sugar head groups and one alkyl chain on a glycerol backbone (**72**) was investigated recently.[41] The compounds with alkyl chain length from C_6–C_{16} exhibited SmA phase, in contrast to the compounds **69–71**, that showed columnar and cubic phases. The observed

fan-shaped texture of SmA phase for $C_8(Glc)_2$ and $C_{14}(Glc)_2$ is shown in Figure 8.

The amphiphiles did not show transition to a crystalline phase upon cooling to room temperature and the mesophase texture persisted in a glassy state. It was presumed that the presence of two glucose units in the molecule could lead to stronger hydrogen bonding interactions and probably hindered free movement of the molecule with respect to each other. In this scenario, the formation of a glassy state becomes easier than a highly ordered crystalline state. The SmA to isotropic transition temperature increased with increasing alkyl chain length.

63

Cr 151.7 SmA 283.5 I

64

Cr 130.0 SmA 263.0 I 127.4 Cub

65

a: Cr 181.4 SmA 260.2 I 178.0 Cub
b: Cr 183.0 SmA 284.0 I 181.5 Cub
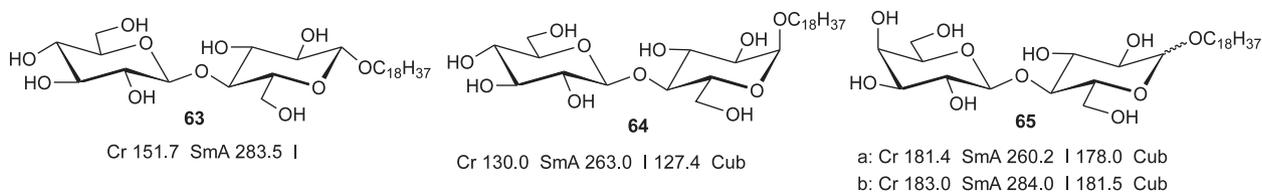
Figure 8: The fan-shaped texture of SmA phase obtained upon slow cooling of isotropic liquid for $C_8(Glc)_2$ at 80 °C (left panel) and $C_{14}(Glc)_2$ at 188 °C (right panel).
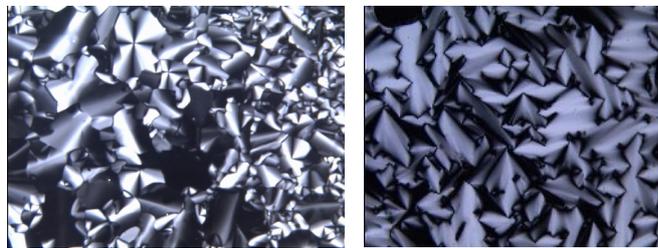
The mesophase was also characterized by X-ray diffraction method. The XRD patterns consisted of a strong sharp reflection in the low angle region and a diffuse scattering in the wide angle region (Figure 9). The low angle diffraction peak is attributed to the layer ordering of the molecules in the mesophase. The spacing d corresponding to this reflection measured at 25 °C was noticed to be only slightly higher than the d values measured at high temperature in the mesophase, indicating that the molecular ordering is nearly the same as that in the LC phase at the ambient temperature. These results confirm the DSC results, wherein a broad and weak thermal signature attributable to the mesophase to glassy state transition was observed during cooling.

4. Carbohydrate amphiphiles with one sugar moiety and two alkyl chains

The compounds having one sugar head group and two alkyl chains exhibit columnar/cubic phases due their wedged-shaped structure. The mesogenic properties of 1,2-di-*O*-stearoyl-3-*O*-(*β*-D-glucopyranosyl)-sn-glycerol (**73**) were reported by Mannock and co-workers and it exhibited a columnar phase.[42] The introduction of an unsaturation in the alkyl chain (**74**) lowered the clearing temperature of the columnar phase and its effect on the melting point was much stronger than that of the clearing point.[43] The effect of the configuration of the hydroxyl groups in

(**75**) has less effect on the mesophase stability. However, when the monosaccharides were replaced by disaccharides (**76**), the clearing points raised significantly, due to the increased hydrogen bonding. The interglycosidic linkage (*α*-1-4 or *β*-1-4) did not influence significantly the stability of columnar mesophase. If the position of the linkage between the two sugar moieties in the disaccharide was changed from 1→4 (**76**), to 1→6 (**77**), a complex polymorphism was found. Derivative **77**, with a *β*-1-6 linked disaccharides, displayed a SmA phase up to 82°C, followed by a broad cubic phase, which transformed at 149°C into a columnar mesophase and cleared at 200°C. With increasing temperature the molecule adopted a wedge-like shape, due to an increased motion of the aliphatic chains, and thus at 149°C, a columnar phase was found. In the temperature range between 82 and 149°C, a cubic phase formed. The methyl branching of the alkyl chains (e.g. **78**) lowered both the melting and the clearing points. The methyl branching disturbed the interaction in the hydrophobic region and therefore destabilized the mesophase, even while increasing the mesophase range. In this respect, the methyl branching exhibits the same effect on the mesogenic properties as that of the introduction of double bonds into the alkyl chains. Since these branched compounds are much more stable, e.g. they cannot be degraded by oxidation, they might be interesting for future applications, in


66

n = 6: soft solid-col 90 I

n = 10: Tg 46.2 SmA 186.8 I

n = 16: Cr 48.5 SmA 210 I

67

n = 6: soft solid-col 95.6 I

n = 10: Cr 65.8 SmA 179.5 I

n = 16 :Cr 39.3 SmA 212 I

68

n = 6: soft solid-col 105.0 I

n = 10:Cr-SmA 204.5 I

n = 16: Cr-SmA 211.0 I
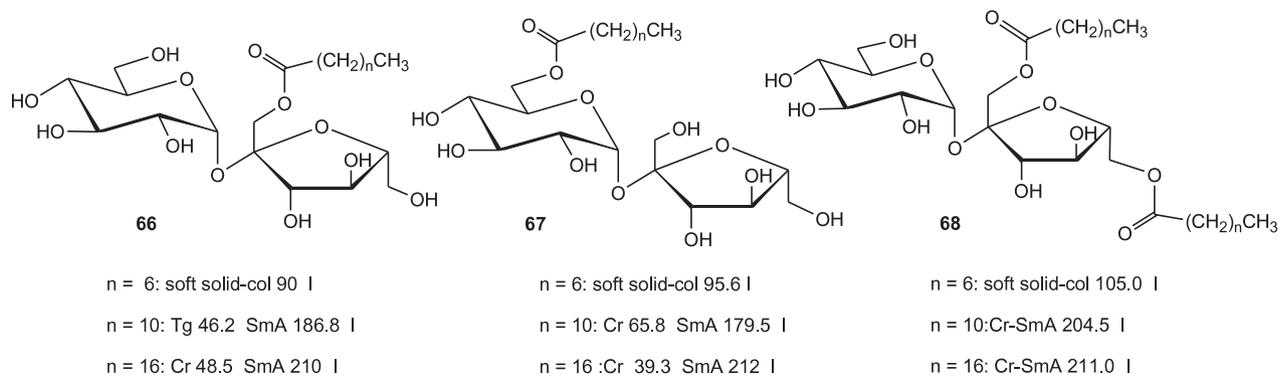
Figure 9: X-ray diffraction of (a) $C_{10}(Glc)_2$; (b) $C_{12}(Glc)_2$ and (c) $C_{14}(Glc)_2$ in SmA phase.
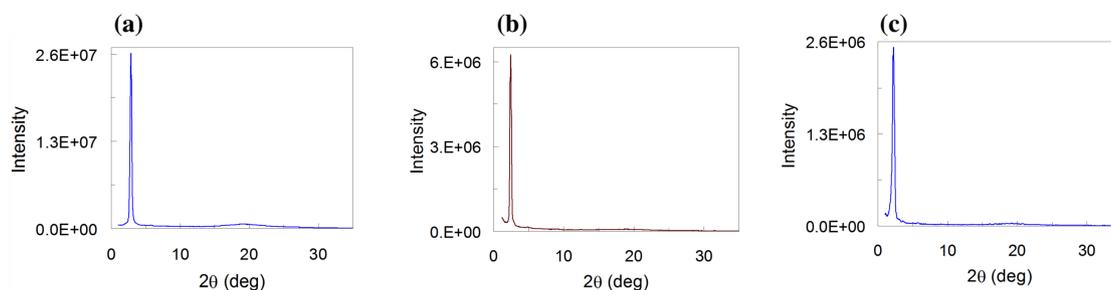
drug carriers and the development of cubic phases derived nano-porous materials, since they could substitute un-saturated lipids, while maintaining favorable transition temperatures.

The liquid crystalline properties of commercially available stearoyl (**79**), palmitoyl (**80**), oleoyl (**81**) and nervonyl (**82**) galactocerebrosides derived from bovine brain have been reported by Goodby *et al.*[44] All these glycolipids exhibited hexagonal columnar phases, over wide temperature ranges. The glycosides were found to have high clearing temperatures. Interestingly, the stearoyl and oleoyl members of the series showed almost identical clearing points, indicating that the un-saturation in at least one of the terminal aliphatic chains did not affect markedly the self organizing properties of the derivatives. Where the two chains are only slightly different in length, ± 2 carbon atoms, e.g., for the palmitoyl derivative, higher clearing points were realized, whereas when the chains have considerably different lengths (asymmetrical) then the melting points were much lower.

Similar to the naturally occurring cerebrosides, the synthetic D, L-dihydro analogues (**83** and **84**) were also found to exhibit columnar mesophases.[44] However, the melting points were much lower than those of the naturally occurring glycolipids. Moreover, there was virtually no change in the isotropization temperature with respect to the change in the sugar unit (i.e. galactose *vs* glucose), again demonstrating that the polar head group did not affect the mesomorphic properties greatly.

The liquid crystal properties of synthetic cerebroside mimics (**85**) have also been investigated and the results were compared with natural and synthetic cerebrosides.[44b] The mimics were, however, non-mesogenic when one or two short aliphatic chains constituted the hydrophobic region of the glycolipid. Similarly, when the alkyl chains were of similar lengths, mesomorphism was again suppressed. For derivatives with long aliphatic

69

n = 12: Cr 120.0 Col 173.3 I
n = 16: Cr 110.0 Col 126.0 Cub 175.0 I

70

Cr 20 Col 72.0 Cub 156.0 SmA 217 I

71

glass-Col 65 Cub 134 I

72

$C_n(Glc)_2$, n = 6-12, 14, 16

n = 8: Tg 18.0 SmA 95.6 I 88.7 SmA 8.7 Tg
n = 9: Tg 63.1 SmA 132.9 I 129.1 SmA 56.0 Tg
n = 10: Tg 38.2 SmA 153.0 I 150.1 SmA 28.2 Tg
n = 11: Tg 62.0 SmA 179.3 I 176.1 SmA 52.3 Tg
n = 12: Tg 55.8 SmA 174.5 I 162.3 SmA 46.6 Tg
n = 14: Tg 59.7 SmA 206.6 I 195.6 SmA 51.5 Tg
n = 16: Tg 55.9 SmA 239.5 I 227.6 SmA 43.1 Tg
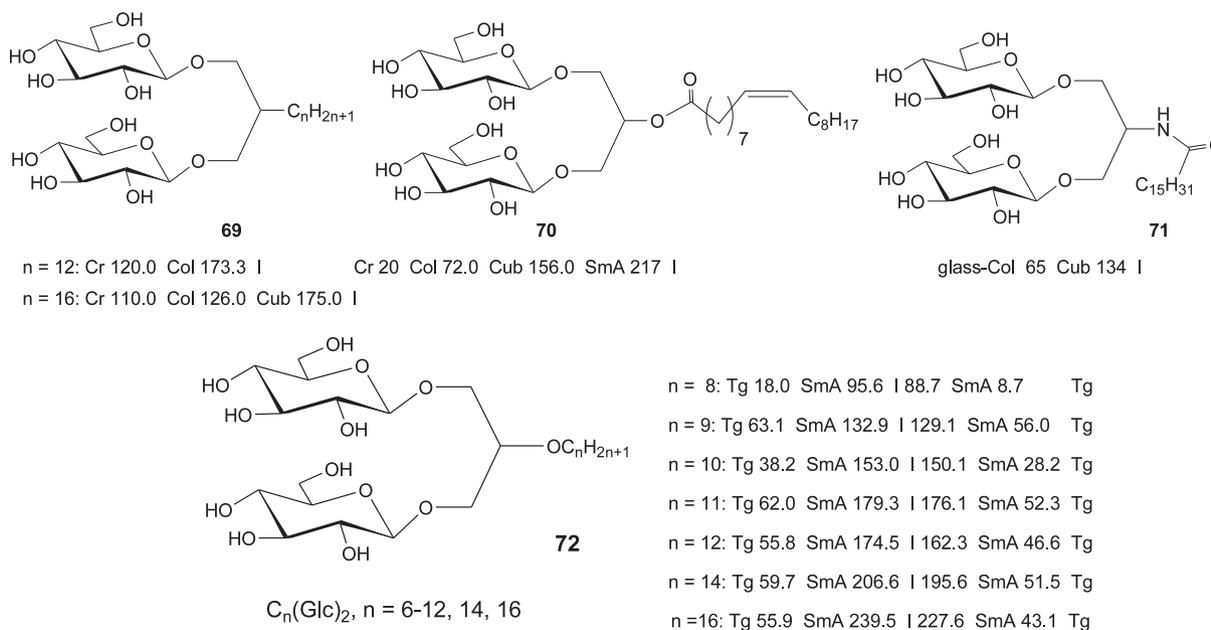
chains attached to the amide unit, e.g. C_{16}, the transition temperature to the solid state was reduced and the clearing point was raised, leading to the stabilization of the mesophase. Overall, the clearing points were considerably lower than those found for the natural and synthetic cerebrosides.

The liquid crystalline properties of glycolipids bearing one furanosyl head group have been reported.[45] The compounds in the series 86–92 were found to exhibit columnar mesophases. It is interesting to note that only the glycolipid 90, bearing two linear saturated chains, exhibited a defined melting point, in addition to the clearing point. All other glycosides with two methyl branched aliphatic moieties exhibited no detectable melting points. Thus, the glycolipids are liquid crystals at room temperature and can be cooled down to −50°C, without the on-set of the recrystallisation. On cooling, the derivative 91, which possessed mixed linear and branched chains, was found to have a glass transition temperature below −25°C.

The liquid crystalline properties of disubstituted sucrose esters, such as, 93 and 94, were reported and these derivatives exhibited SmA phase.[46] Both the melting and clearing points of $6, 6'$ diesters (93) was found to be more than the corresponding $1', 6'$ (94) diesters. A strong temperature dependence of the layer spacing was also observed in the smectic phase, from the XRD studies. The molecules were interdigitated at higher temperatures and the extent of interdigitation reduced with temperature.

5. Carbohydrate amphiphiles, with one sugar unit and three alkyl chains

The mesomorphic behavior of pentaerythritol derivatives with (i) one sugar head group and three alkyl chains; (ii) two sugar head groups and two alkyl chains and (iii) three sugar head groups and one alkyl chain were studied.[47] Compounds with three alkyl chains and one carbohydrate unit (95) have wedge-like shape and the sugar units are at

the apices of the wedges. These compounds exhibit cubic and columnar phases with inverted structures. A hexagonal columnar phase was proposed, with individual molecules disordered up and down the column axis. In the columnar phase, the molecules were expected to adopt a relatively flat conformation to enable them to self-organize into a cylindrical columnar arrangement. However, at higher temperatures, the homologous series of these compounds exhibited cubic mesophases and it was found that the cubic mesophase was a micellar cubic phase. Compounds with one alkyl chain and three sugar units (96) exhibited the cubic phase and the structures of the cubic phases were essentially the inverse of those found for the compounds with three alkyl chains and one carbohydrate unit. For compounds with two alkyl chains and two sugar units (97), the cross-sectional area of the head groups were similar to those of the aliphatic chains. Thus, when the molecules pack together they formed lamellar SmA phase.

6. Bola-amphiphiles

The self-organizing properties of archaeal glycolipids have been studied.[48] These molecules are characterized by having two polar heads, linked together by two C_{40} polyisoprenoid chains, which are thought to span the membrane and therefore determine the thickness of the lipid layer. For example, compound 98 is a bola-amphiphile, derived from *Methanospirillum hungatei*, which is a methanogen species of bacteria.[49] The LC properties of the mimics of archaeal lipids 99–101 have also been reported. These compounds exhibited distorted hexagonal columnar phases. The clearing point temperatures for 99–101 did not vary much, as a function of a change in the configurations. The mesophase of each compound was found to supercool quite substantially to temperatures well below 0 °C. Two models were postulated for the structures of the columnar

73   Cr 94.0 Col 153.0 I

74   Cr 20.0 Col 132.0 I

75   Cr-Col 136.8 I

76   Cr-Col 238.6 I
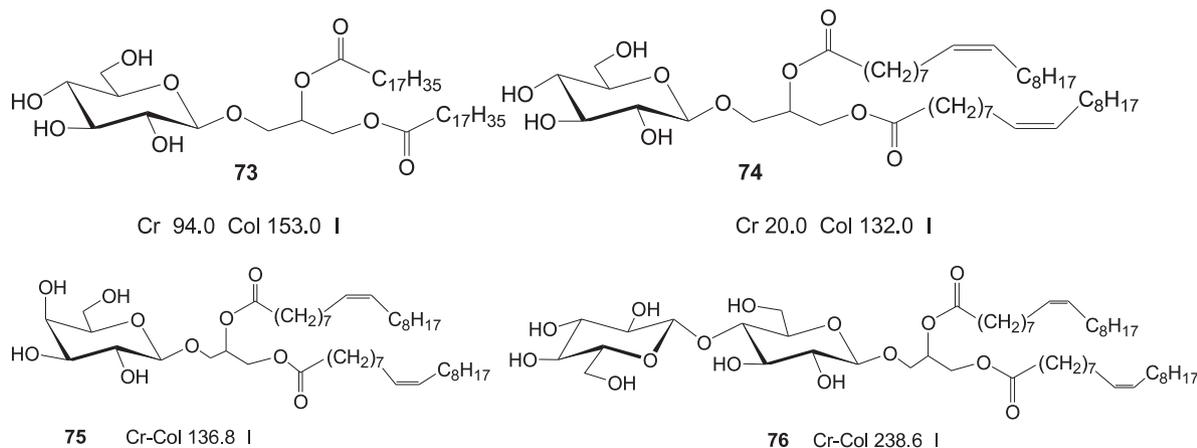
phase. In one model, the aliphatic chains were at the exterior and the sugar moieties formed the interior of the columns, and in the second model the aliphatic chains were at the interior and the sugar moieties at the exterior. However, it was found that the controlled addition of water to the neat phase showed that the thermotropic columnar phase was not continuously miscible with water. This apparent lack of miscibility with water indicated that the aliphatic chains must be located towards the exterior of the columnar structure. The results of XRD were also in agreement with the model, where the alkyl chains located towards the exterior of the columnar structure. The LC behavior of the un-symmetric bola-amphiphiles **102–104**, which are also the mimics of naturally occurring archaeal lipids, have been investigated to study the effects of bridging groups on the self-organizing and self-assembling properties. All three of these compounds **102–104** are characterized by having a disaccharide and monosaccharide head groups. Interestingly, although all of them exhibited thermotropic columnar phases, compounds **102** and **103** were also found to be cubic.

Although amphiphilic sugars possess an abundance of chiral centers, their liquid crystalline phases are generally smectic or columnar and/or cubic phases. The absence of macroscopic chirality in the amphiphilic sugars and glycolipids is attributed to the presence of a strong hydrogen bonding network. Molecular features that affect the hydrogen bonding network can lead to the formation of chiral mesophases in sugar-based bola-amphiphiles. A series of rigid aromatic core containing bolaamphiphiles (**105**) were synthesized and studied for their LC behavior.[50]

Except the lower homologue **Azo-bis 5**, the higher homologues exhibited a chiral SmC phase. **Azo-bis 5** exhibited a focal-conic texture, characteristic of a SmA phase, whereas, **Azo-bis 8** exhibited a liquid crystalline behavior at 137°C and concentric circular rings and finger-print type texture characteristic of chiral phases started to appear, close to the isotropization at 215 °C. On cooling from the isotropic state, formation of bâtonnets was observed first, followed by the formation of spiral arrangements. The striated
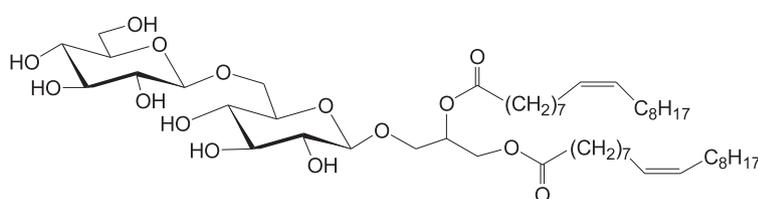
77 Cr-SmA 82.0 Cub 149.0 Col 200 I
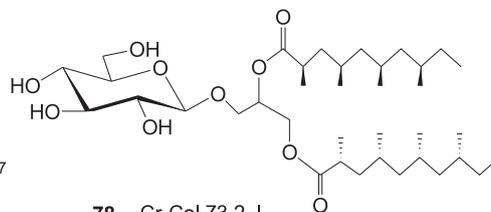
78 Cr-Col 73.2 I
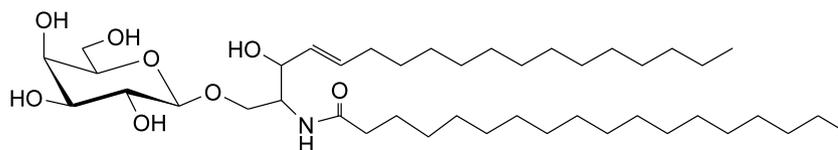
Cr 91.2 Col 178.5 I   **79**
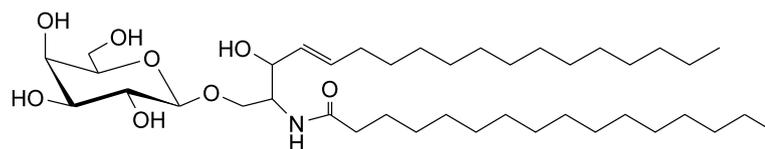
Cr 146.6 Col 185.7 I   **80**
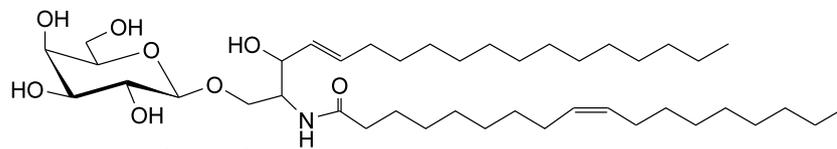
Cr 128.3 Col 176.5 I   **81**
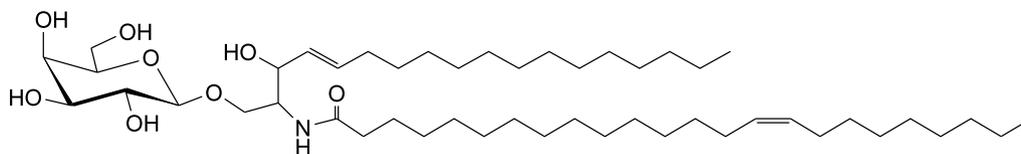
Cr 138.4 Col 186.6 I   **82**
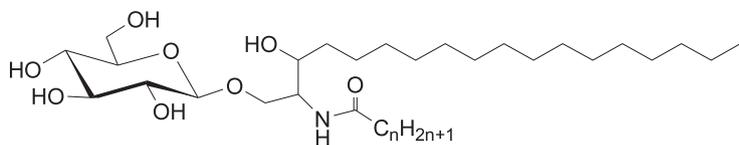
n = 15: Cr 94.7 Col 184.5 I

n = 17: Cr 108.1Col 191.1 I

n = 15: Cr 95.6 Col 193.1 I

83
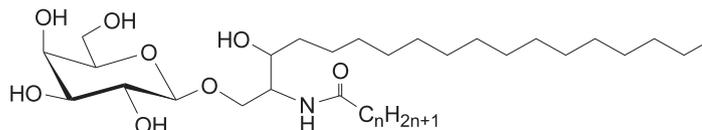
84

n = 15: Cr 95.3 Col 185.5 I

n = 17: Cr 91.3 Col 193.2 I

n = 15: Cr 102.1 Col 193.0 I

n = 12: m = 11: Cr 136.4 I

n = 12: m = 17: Cr 115.8 Col 132.7 I

n = 6: m = 5: Cr 115.9 I
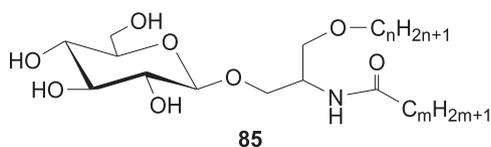
n = 6: m = 17: Cr 119.8 I

85

n = 16: m = 5: Cr 94.7 I

n = 16: m = 11: Cr 137.5 I 132.5 Col

n = 16: m = 17: Cr 134.0 Col 154.7 I
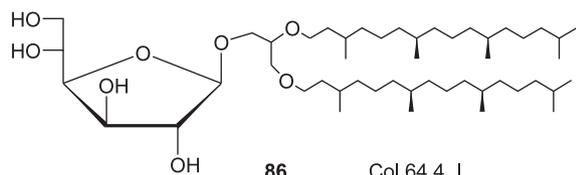
86   Col 64.4 I
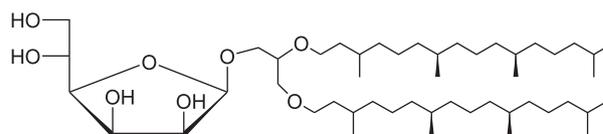
87   Col 53.9 I
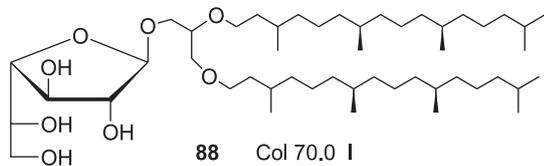
88   Col 70.0 I
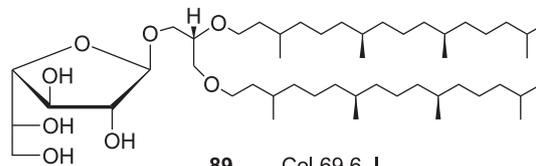
89   Col 69.6 I
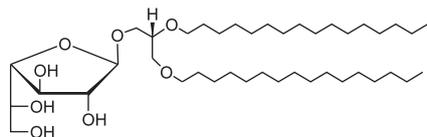
90   Col 75.4 Col 124.8 I
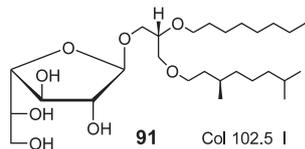
**91**   Col 102.5 I
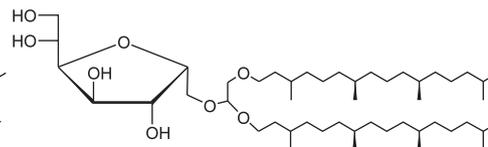
92   Col 68.5 I
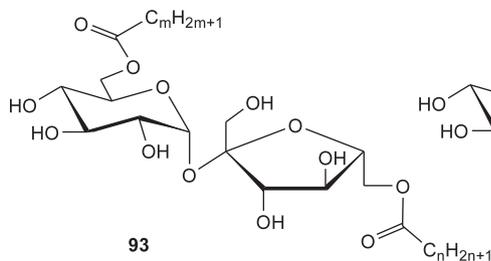
93

m = 10: n = 14, Cr 84.7 SmA 167.8 I

m = 17: n = 17, Cr 109.8 SmA 164.3 I
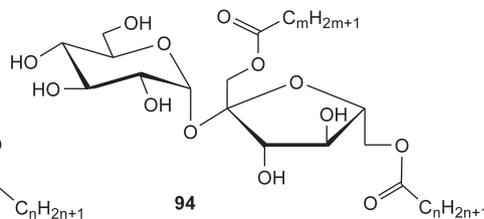
94

m =10: n= 14: Cr 42.1 SmA 120.0 I

m =10: n= 10: Cr 30.0 SmA 115.9 I

95
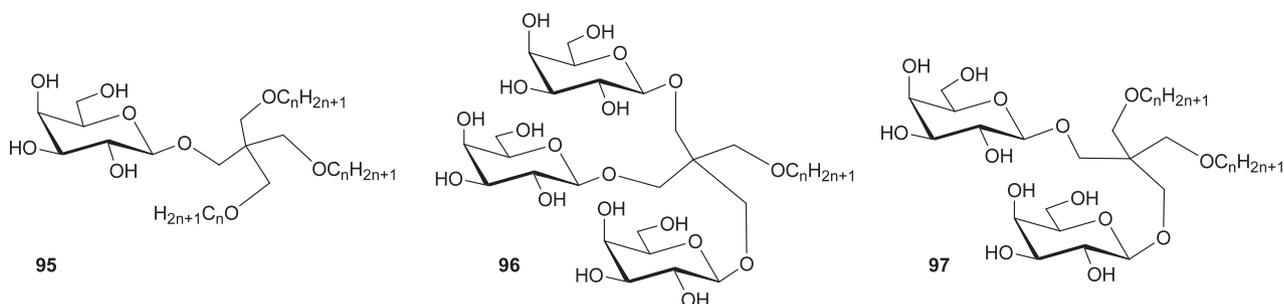
n = 7: Cr 44.0 Col 72.1 Cub 82.3 I

n = 9: Cr 36.0 Col 59.4 Cub 76.2 I

n = 11: Cr 30.0 Col 38.3 Cub 43.4 I

96

n = 12: Cr 91.6 Cub 204 I

n = 16: Cr 150.0 Cub >200 I(dec).

97

n = 12, Cr 53.3 SmA 203.1 I

n = 14, Cr 46.9 SmA 202.2 I

n = 16, Cr 41.7 SmA 202.2 I

98

99

Col 115.2 I

100   Col 117.6 I

101   Col 118.4 I
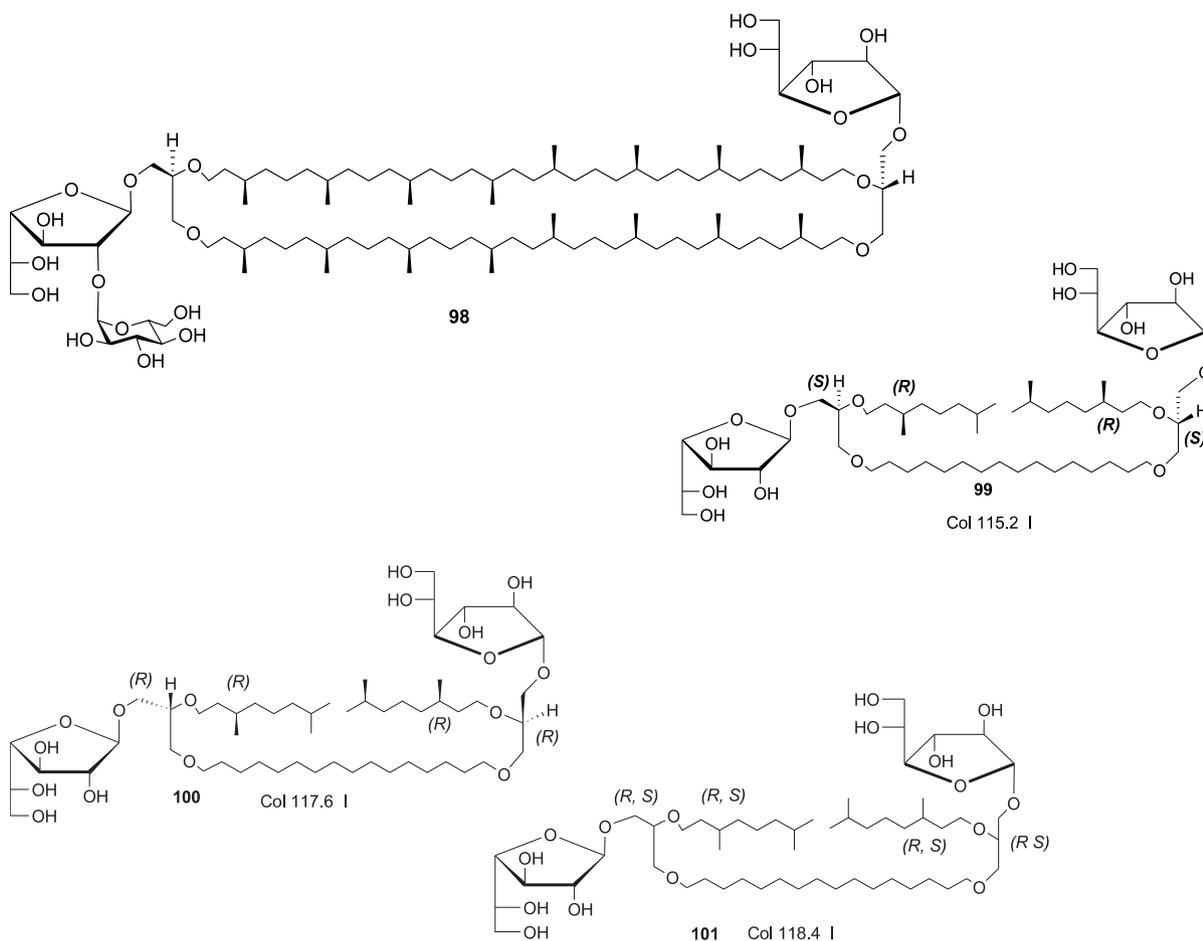
textures with stripes characteristic of SmC* phase formed slowly (Fig. 10). Similarly, **Azo-bis 7**, **Azo-bis 10** and **Azo-bis 12** exhibited chiral smectic phases in the heating and cooling cycles. The striated textures with stripes characteristic of SmC* phase observed at high temperatures remained up to room temperature. The texture of the solidified crystalline phase, as observed under polarizing optical microscopy, was identical to that observed for the SmC* phase, suggesting that the two phases possess sufficiently similar lattice parameters. Thus, the SmC* structure was well maintained in the

crystal and no significant reorientation or formation of grain boundaries took place on crystallization.

The mesophase was also characterized by X-ray diffraction methods. The sharp lower angle peak accompanied by a diffuse peak at higher angles is characteristic of a smectic phase in which the molecules are stacked in to layers with short-range liquid-like positional order within the layers.

In the SmC* phase, the application of an electric field with a triangular waveform resulted in a current peak, the area under which is a direct measure of the spontaneous polarization. The polarization
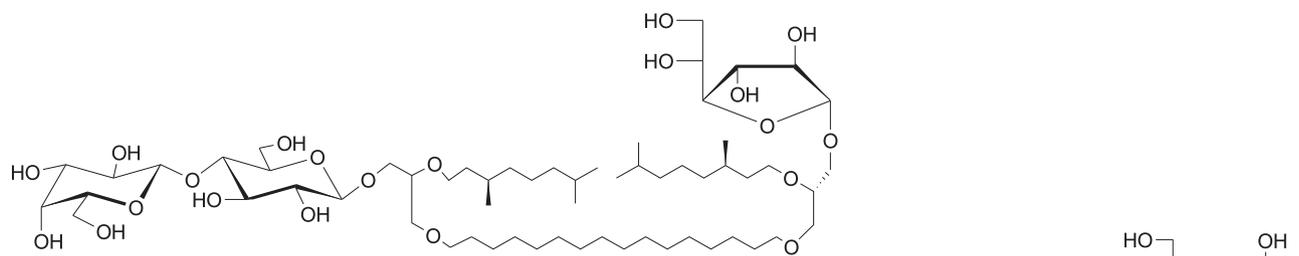
102   Cub 70 Col 195.5 I
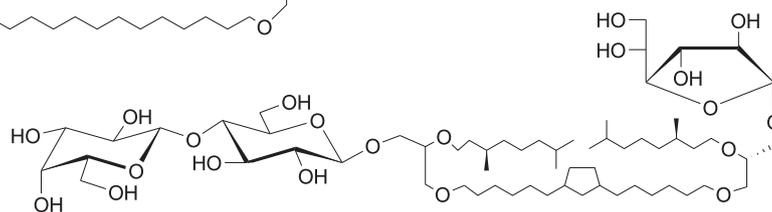
Cub 70 Col 181 I   **103**   cis:trans = 4:1
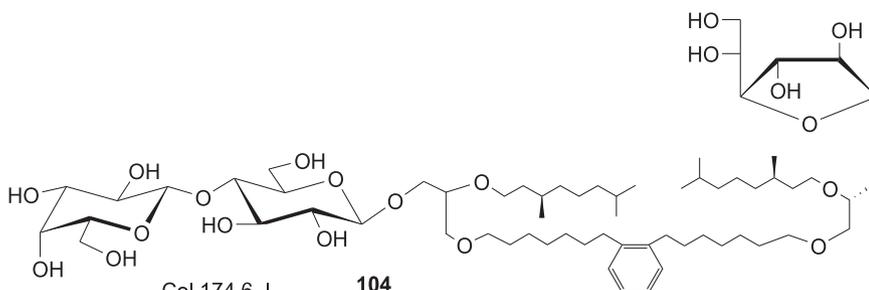
Col 174.6 I   **104**
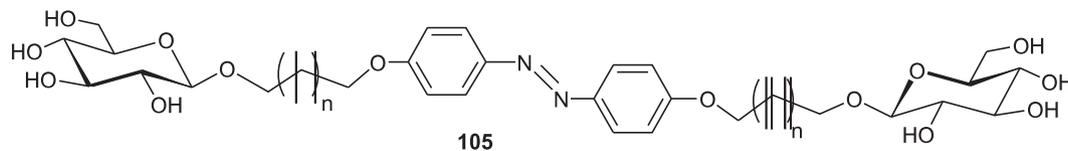
105

n = 3 (Azo-bis 5): Cr 220 SmA 241 dec.   n = 6 (Azo-bis 8): Cr1 124 Cr2 173 SmC* 205 I

n = 5 (Azo-bis 7): Cr 140 SmC* 217 I   n = 8 (Azo-bis 10): Cr1 133 Cr2 167 SmC* 217 I

                                               n = 10 (Azo-bis 12): Cr 118 SmC* 218 I
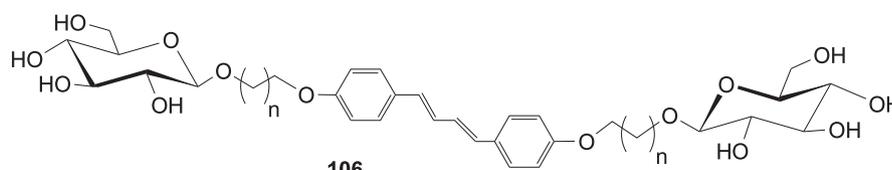
106

n = 1 (C$_2$GB): Cr 201 SmA* 261 I 260 SmA 212 SmC* 150 Plastic

n = 2 (C$_3$GB): Cr$_1$ 97 Cr$_2$ 140 Cr$_3$ 189 SmA* 268 I 266 SmA* 229 SmC* 194 Cr

n = 3 (C$_4$GB): Cr$_1$ 187 Cr$_2$ 198 SmA* 258 I 257 SmA* 222 SmC* 198 Cr

n = 4 (C$_5$GB): Cr$_1$ 167 Cr$_2$ 183 SmC* 259 I 257 SmC* 199 Cr

n = 6 (C$_7$GB): Cr$_1$ 168 Cr$_2$ 191 SmC* 262 I 261 SmC* 203 Cr

n = 7 (C$_8$GB): Cr$_1$ 145 Cr$_2$ 173 Cr$_3$ 194 SmC* 265 I 258 SmC* 166 Cr

n = 9 (C$_{10}$GB): Cr$_1$ 164.3 Cr$_2$ 203 SmC* 260 I 255 SmC* 205 Cr

n = 11 (C$_{12}$GB): Cr$_1$ 109 Cr$_2$ 203 SmC* 256 I 251 SmC* 206 Cr

value was determined to be 850 nCcm^{-2}(at 155 °C), a value much higher than that normally obtained for the SmC* phase. This was attributed to the appreciable hindrance to the rotation of the molecule caused by the strong hydrogen bonding interactions.

The replacement of the azobenzene core in bolaamphiphile by moieties with enhanced ability to form aggregates could result in the formation of a highly stabilized SmC* phase. The mesophase behavior of a homologous series of symmetrical bolaamphiphiles possessing a 1,4-diphenylbutadiene core and glucopyranoside head groups linked together by oligomethylene spacers (106) was also studied.[51] The molecules in the series 106 exhibited the SmC* phase, and the stability of SmC* phase increased with increase in the length of the oligomethylene spacers.

The bolaamphiphiles with shorter oligomethylene spacers underwent a crystal to SmA*phase transition characterized by their typical focal-conic texture. Cooling the isotropic phase of these derivatives, resulted initially in the formation of the SmA*, which on subsequent cooling transformed to the SmC*, i.e., tilted lamellar phase. For example, on cooling the isotropic phase of C2GB, transition to the SmA* phase was observed by the formation of *bâtonnets* at 260 °C, which coalesced to form focal-conic domains. At 212 °C, a change in the texture with appearance of stripes across the fans was observed which indicated a transition to the SmC* phase. For the derivatives with ⩾C5 oligomethylene spacers, the SmC* phase was observed in the heating cycle also. Thus, the compounds melted to yield a striated fan-shaped texture, indicating the formation of the SmC*phase. Upon cooling, an isotropic to SmC*phase transition was observed for the derivatives with pentamethylene spacers. The evidence for the SmC* phase was observed even in the lower homologue studied, where the sugar head groups are separated from the butadiene core by only two methylene units, although in the cooling phase only. This suggests that the butadiene core is capable of inducing macroscopic chirality more effectively than azobenzene-cored bola-amphiphiles 105.

7. Conclusion

Ever since the first report of the double melting behavior of alkyl glycosides nearly a century ago, sustained investigations of the LC properties of alkyl glycosides and glycolipids have uncovered many finer details, in relation to their constitutions and configurations. The studies on the LC behavior of glycolipids assume even greater significance, as a result of the importance of the glycolipids in many biological functions and cell-membrane functions. Most alkyl glycosides and glycolipids are neutral and non-ionic. Whereas the thermal behavior of the glycolipids have been studied largely, leading to the identification of the varying phase behavior, depending on the constitutions and configurations of the sugar moiety, studies on the lyotropic behavior lags behind. Studies on the lyotropic behavior bear significance, as a result of the direct relevance to the functions of the cell-membrane systems. The transformation of the chirality present in the sugars to the chiral mesophases has been difficult, due to overwhelming control of the molecular organization through hydrogen-bonding. However, recent studies show that efforts to off-set the hydrogen bonding can permit the formation of chiral mesophases from alkyl glycosides and glycolipids. It is also seen that off-set of the hydrogen bonding through reduction in the hydrogen bonding sites alone is not sufficient, rather, additional interactions, such as aromatic stacking interactions, are beneficial in order to bring-out the chiral mesophases in alkyl glycosides and glycolipids. Having a detailed knowledge on the LC behavior, it is worthwhile to encompass the LC behavior of glycolipids, having more than a monosaccharide unit and one or two alkyl groups. Amphiphilic glycolipids are emerging prominent, for example, in drug delivery systems. Thus, studies of the inherent properties of the glycolipids will not only have fundamental importance in the area of liquid crystals, but also, in the emerging technologies that rely on the self-assembly and self-organization processes.

References
1. (a) P. G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, Clarendon Press: Oxford, 1994; (b) J.-M. Lehn, *Supramolecular Chemistry*, VCH: Weinheim, 1995; (c) H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem., Int. Ed. Engl.* 1988, 27, 113; (d) G. M. Whitesides, B. Grzybowski, *Science* 2002, 295, 2418; (e) T. Kato, *Science* 2002, 295, 2414; (f) J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *J. Mater. Chem.* 2003, 13, 2661.
2. (a) J. W. Goodby, I. M. Saez, S. J. Cowling, V. Görtz, Mi. Draper, A. W. Hall, S. Sia, G. Cosquer, S.-E. Lee, E. P. Raynes, *Angew. Chem. Int. Ed.* 2008, 47, 2754; (b) C. M. Paleos, D. Tsiourvas, *Angew. Chem. Int. Ed.* 1995, 34, 1696; (c) C. M. Paleos, D. Tsiourvas, *Curr. Opinion Colloid Interface Sci.* 2001, 6, 257; (d) T. Kato, N. Mizoshita, K.Kishimoto, *Angew. Chem. Int. Ed.* 2006, 45, 38; (f) C. Tschierske, *Chem. Soc. Rev.* 2007, 36, 1930.

3. *Liquid Crystals-Application and Uses*, Ed. B. Bahadur, World Scientific: Singapore, 1990.

4. G. H. Brown, J. J. Wolken, *Liquid Crystals and Biological Structures*, Academic Press: New York, 1979.

5. (a) J. W. Goodby, V. Görtz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegnu, P. Boullanger, D. Lafont, Y. Queneau, S. Chamberte, J. Fitremannf *Chem. Soc. Rev.* 2007, 36, 1971; (b) H. A. van Doren, E. Smits, J. M. Pestman, J. B. F. N. Engberts, R. M. Kellogg, *Chem. Soc. Rev.* 2000, 29, 183; (c) H. Prade, R. Miethchen, *J. Prakt. Chem.* 1995, 337, 427; (d) V. Vill, R. Hashim, *Curr. Opin. Colloid Interface Sci.* 2002, 7, 395; (e) R. Miethchen, M. Hein, *Carbohydr. Res.* 2000, 327, 169.

6. E. Fischer, B. Helferich, *Liebigs Ann. Chem.* 1911, 383, 68.

7. (a) P. Q. Pfeffer, *J. Org. Chem.* 1976, 41, 2925; (b) J. W. Goodby, *Mol. Cryst. Liq. Cryst.* 1984, 110, 205; (c) G. A. Jeffrey, *Acc. Chem. Res.* 1986, 19, 168.

8. (a) G. Friedel, *C. R. Acad. Sci.* 1923, 67, 273; (b) D. Demus, L. Richter, *Textures of Liquid Crystals*, Verlag Chemie, Weinheim: New York, 1978; (c) G. W. Gray, J. W. Goodby, *Smectic Liquid Crystals, Textures and Structures*, Leonard Hill: Glasgow, 1984.

9. V. Vill, H.M. von Minden, M. H. J. Koch, U. Seydel, K. Brandenburg, *Chem. Phys. Lipids* 2000, 104, 75.

10. (a) J. W. Goodby, *Mol. Cryst. Liq. Cryst.* 1984, 110, 205; (b) H. Prade, R. Miethchen, V. Vill, *J. Prakt. Chem.*, 1995, 337, 427; (c) E. Barrall, B. Grant, M. Oxsen, E. T. Samulski, P. C. Moews, J. R. Knox, R. R. Gaskill, J. L. Haberfeld, *Org. Coat. Plast. Chem.* 1979, 40, 67; (d) R. Miethchen, J. Holz, H. Prade, A. Lipték, *Tetrahedron* 1992, 48, 3061; (e) V. Vill, T. Böcker, J. Thiem, F. Fischer, *Liq. Cryst.* 1989, 6, 349; (f) J. W. Goodby, *Liq. Cryst.* 2006, 33, 1229.

11. (a) C. Tschierske, A. Lunow, H. Zaschke, *Liq. Cryst.* 1990, 6, 885; (b) D. F. Ewing, M. Glew, J. W. Goodby, J. A. Haley, S. M. Kelly, B. U. Komanschek, P. Letellier, G. Mackenzie, G. H. Mehl, *J. Mater. Chem.* 1998, 8, 871; (c) E. Smits, J. B. F. N. Engberts, R. M. Kellogg, H. A. van Doren, *Liq. Cryst.* 1997, 23, 481; (d) H. Muller, C. Tschierske, *J. Chem. Soc. Chem. Commun.* 1995, 645; (e) D. Blunk, K. Praefcke, G. Legler, *Liq. Cryst.* 1995, 18, 149.

12. (a) V. Vill, T. Böcker, J. Thiem, F. Fischer, *Liq. Cryst.* 1989, 6, 349; (b) P. Sakya, J. M. S Seddon, V. Vill, *Liq. Cryst.* 1997, 23, 409.

13. B. P. Gode, G. Goethals, J. W. Goodby, J. A. Haley, S. M. Kelly, G. H. Mehl, G. Ronco, P. Villa, *Liq. Cryst.* 1998, 24, 283.

14. V. Ferrières, T. Benvegnu, M. Lefeuvre, D. Plusquellec, G. Mackenzie, M. J. Watson, J. A. Haley, J. W. Goodby, R. Pindak, M. K. Durbin, *J. Chem. Soc., Perkin Trans. 2*, 1999, 951.

15. J. W. Goodby, J. A. Haley, G. Mackenzie, M. J. Watson, V. Ferrières, D. Plusquellec, *J. Mater. Chem.* 1995, 5, 2209.

16. (a) H. A. van Doren, R. van der Guest, *Carbohydr. Res.* 1989, 194, 71; (b) S. A. Galema, J. B. F. N. Engberts, H. A. van Doren, *Carbohydr. Res.* 1997, 303, 423.

17. D. C. Carter, J. R. Ruble, G. A. Jeffrey, *Carbohydr. Res.* 1982, 102, 59.

18. P. Bault, P. Gode, G. Goethals, J. W. Goodby, J. A. Haley, S. M. Kelly, G. H. Mehl, P. Villa, *Liq. Cryst.* 1999, 26, 985.

19. D. F. Ewing, J. W. Goodby, J. A. Haley, S. M. Kelley, P. Letellier, G. Mackenzie, *Liq. Cryst.* 1997, 23, 759.

20. U. Jeschke, C. Vogel, V. Vill, H. Fischer, *J. Mater. Chem.* 1995, 5, 2073.

21. P. Stangier, V. Vill, S. Rohde, U. Jeschke, J. Thiem, *Liq. Cryst.* 1994, 17, 589.

22. H. A. van Doren, R. van der Guest, C. F. D. Ruijter, R. M. Kellogg, H. Wynberg, *Liq. Cryst.* 1990, 8, 109.

23. M. K. Singh, N. Jayaramana, D. S. S. Rao, S. K. Prasad, *Chem. Phys. Lipids* 2008, 155, 90.

24. (a) P. C. Moews, J. R. Knox, *J. Am. Chem. Soc.* 1976, 98, 6628; (b) G. A. Geffrey, Y. Yeon, *Carbohydr. Res.* 1987, 169, 1; (c) H. van Koningsveld, J. C. Jansen, J. J. Straathoff, *Acta.*

Cryst. 1988, C44, 1054; (d) V. Adasch, B. Hoffmann, W. Milius, G. Platz, G. Voss, *Carbohydr. Res.* 1998, 314, 177; (e) B. Hoffmann, W. Milius, G. Voss, M. Wunschel, S. van Smaalen, S. Diele, G. Platz, *Carbohydr. Res.* 2000, 323, 192.

25. G. A. Jeffrey, Y. Yeon, *Carbohydr. Res.* 1992, 237, 45.

26. D. L. Dorset, *Carbohydr. Res.* 1990, 206, 193.

27. (a) H. M. von Minden, G. Milkereit, V. Vill, *Chem. Phys. Lipids* 2002, 120, 45. (b) Y. Feng, Z.-W. Yu, P. J. Quinn, *Chem. Phys. Lipids* 2003, 126, 141.

28. R. D. Koynova, H. L. Kuttenreich, B. G. Tenchov, H.-J. Hinz, *Biochemistry* 1988, 27, 4612.

29. J. W. Goodby, M. J. Watson, G. Mackenzie, S. M. Kelly, S. Bachir, P. Bault, P. Godé, G. Goethals, P. Martin, G. Ronco, P. Villa, *Liq. Cryst.* 1998, 25, 139.

30. J. W. Goodby, J. A. Haley, M. J. Watson, G. Mackenzie, S. M. Kelly, P. Letellier, P. Godé, G. Goethals, G. Ronco, B. Harmouch, P. Martin, P. Villa, *Liq. Cryst.*, 1997, 22, 497.

31. P. Bault, S. Bachir, L. Spychala, P. Godé, G. Goethals, P. Martin, G. Ronco, P. Villa, *Carbohydr. Polym.* 1998, 37, 299.

32. P. Bault, P. Gode, G. Goethals, J. W. Goodby, J. A. Haley, S. M. Kelly, G. H. Mehl, G. Ronco, P. Villa, *Liq. Cryst.* 1998, 25, 31.

33. (a) J. W. Goodby, J. A. Haley, M. J. Watson, G. Mackenzie, S. M. Kelly, P. Letellier, O. Douillet, P. Godé, G. Goethals, G. Ronco, P. Villa, *Liq. Cryst.* 1997, 22, 367; (b) W. V. Dahlhoff, *Z. Naturforsch.* 1989, 44b, 1105.

34. B. Pfannemüller, W. Welte, E. Chin, J. W. Goodby, *Liq. Cryst.* 1986, 1, 357.

35. S. Bhattacharjee, G. A. Jeffrey, J. W. Goodby, *Mol. Cryst. Liq. Cryst.* 1985, 131, 245.

36. (a) V. Vill, T. Böcker, J. Thiem, F. Fischer, *Liq. Cryst.* 1989, 6, 349; (b) Y. D. Ma, A. Takada, M. Sugiura, A. Fukuda, T. Miyamoto, J. Watanabe, *Bull. Chem. Jpn.* 1994, 67, 346; (c) H.M. von Minden, K. Brandenburg, U. Seydel, M.H.J. Koch, V. Garamus, R. Willumeit, V. Vill, *Chem. Phys. Lipids* 2000, 106, 157.

37. Y. Queneau, J. Gagnaire, J. J. West, G. Mackenzie, J. W. Goodby, *J. Mater. Chem.* 2001, 11, 2839.

38. V. Molinier, P. J. H. Kouwer, J. Fitremann, A. Bouchu, G. Mackenzie, Y. Queneau, J. W. Goodby, *Chem.-Eur. J.* 2006, 12, 3547.

39. S. Fischer, H. Fischer, S. Diele, G. Pelzl, K. Jankowski, R. R. Schmidt, V. Vill, *Liq. Cryst.* 1994, 17, 855.

40. (a) G. Milkereit, V.M. Garamus, K. Veermans, R. Willumeit, V. Vill, *Chem. Phys. Lipids* 2004, 131, 51; (b) G. E. Milkereit, S. S. H. Gerber, K. Jankowski, A. Terjung, R. R. Schmidt, V. Vill, *J. Thermal Anal. Calorimetry* 2005, 82, 471.

41. N. Jayaraman, M. K. Singh, D. S. S. Rao, S. K. Prasad, *J. Mater. Chem.* 2007, 17, 2228.

42. D. A. Mannock, R. N. A. H Lewis, R. N McElhaney, *Chem. Phys. Lipids* 1987, 43, 113.

43. (a) H. M. von Minden, M. Morr, G. Milkereit, E. Heinz, V. Vill, *Chem. Phys. Lipids* 2002, 114, 55; (b) G. Milkereit, K. Brandenburg, S. Gerber, M. H. J. Koch, M. Morrd, J. Andö, U. Seydel, V. Vill, *Chem. Phys. Lipids* 2005, 135, 15.

44. (a) J. W. Goodby, *Liq. Cryst.* 1998, 24, 25; (b) F. Dumoulin, D. Lafont, P. Boullanger, G. Mackenzie, G. Mehl, J. W. Goodby, *J. Am. Chem. Soc.* 2002, 124, 13737.

45. (a) R. Auzély-Velty, T. Benvegnu, G. Mackenzie, J. A. Haley, J. W. Goodby, D. Plusquellec, *Carbohydr. Res.* 1998, 314, 65; (b) G. Lecollinet, R. Auzély-Velty, M. Danel, T. Benvegnu, G. Mackenzie, J. W. Goodby, D. Plusquellec, *J. Org. Chem.* 1999, 64, 3139; (c) R. Auzély-Velty, T. Benvegnu, D. Plusquellec, G. Mackenzie, J. A. Haley, J. W. Goodby, *Angew. Chem., Int. Ed.* 1998, 37, 2511.

46. (a) V. Molinier, P. H. J. Kouwer, Y. Queneau, J. Fitremann, G. Mackenzie, J. W. Goodby, *Chem. Commun.* 2003, 2860; (b) V. Molinier, P. H. J. Kouwer, J. Fitremann, A. Bouchu, G. Mackenzie, Y. Queneau, J. W. Goodby, *Chem.-Eur. J.* 2007, 13, 1763.

47. (a) F. Dumoulin, D. Lafont, T.-L. Huynh, P. Boullanger, G.

Mackenzie, J. W. Goodby, *Chem.-Eur. J.* 2007, 13, 5585; (b) K. Praefcke, P. Psaras, A. Eckert, *Liq. Cryst.* 1993, 13, 551.

48. G. Lecollinet, A. Gulik, G. Mackenzie, J. W. Goodby, T. Benvegnu, D. Plusquellec, *Chem.-Eur. J.* 2002, 8, 585.
49. G. Ferrante, I. Ekiel, G. D. Sprott, *Biochim. Biophys. Acta* 1987, 921, 281.
50. S. Abraham, S. Paul, G. Narayan, S. K. Prasad, D. S. S. Rao, N. Jayaraman S. Das, *Adv. Funct. Mater.* 2005, 15, 1579.
51. S. Das, G. Narayan, S. Abraham, N. Jayaraman, M. K. Singh, S. K. Prasad, D. S. S. Rao, *Adv. Funct. Mater.* 2008, 18, 1632.

M. K. Singh was born in Ratanpura (district, Mau), Uttar Pradesh, India, in 1974. He received his B.Sc. (1994) and M.Sc. (1996) degrees from the Purvanchal University, Jaunpur, India. He awarded his Ph.D. degree (2003) in inorganic chemistry under the supervision of Professor B. Singh from Department of Chemistry, Banaras Hindu University, Varanasi, India. His doctoral work was focused on the synthesis and characterization of metal containing liquid crystals (metallomesogens). Then he joined Professor N. Jayaraman, Department of Organic Chemistry, Indian Institute of Science, Bangalore, India, in 2005, where he worked on synthesis and studies of carbohydrate based liquid crystals. He was awarded a Research Associate Fellowship by Council of Scientific and Industrial Research in 2006 for three years. Currently, he is working as a postdoctoral fellow with Dr. Y. Queneau at Laboratoire de Chimie Organique, INSA-Lyon, France. He has published ten peer-reviewed articles in international journals.

Narayanaswamy Jayaraman received BSc (1984, University of Madras), MSc (1988, Annamalai University), and PhD (1994) from the Indian Institute of Technology, Kanpur, under the supervision of Professor S. Ranganathan. He was a postdoctoral fellow in the research group of Professor Sir J. F. Stoddart at the University of Birmingham, UK, and at the University of California, Los Angeles, USA. He joined the Department of Organic Chemistry, Indian Institute of Science, Bangalore, in 1999. His research interests are mainly in the areas of carbohydrate chemistry, carbohydrate-based liquid crystals and dendrimer chemistry.