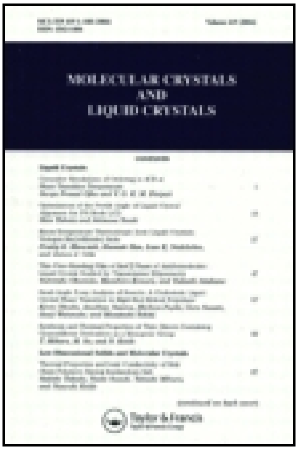

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Thermotropic Liquid Crystalline Glucose Derivatives with Mesogenic side Chains

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THERMOTROPIC LIQUID CRYSTALLINE GLUCOSE DERIVATIVES WITH MESOGENIC SIDE CHAINS

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Abstract Many glucose derivatives have been studied so far for their liquid crystalline behavior. Penta-O-n-alkanoylglucopyranoses have been reported to form discotic columnar mesophases. Thermotropic liquid crystals of glucose with mesogenic side chains, consisting of a mesogen, an alkyl spacer and a tail, form the subject of this study. The glucose derivatives were prepared by complete esterification of the hydroxyl groups of glucose with the mesogenic side chains. Their characterization was based on the analysis from cross polarizing microscopy, differential thermal calorimetery, wide-angle X-ray diffraction pattern and nuclear magnetic resonance (both ^{13}C and ^{1}H) spectra. Smectic and chiral nematic (cholesteric) phases have been observed in these macromolecules. The effect on the phase behavior of varying the tail length in the side chains of the molecule was studied. The structural arrangement of such molecules has been proposed based on the observations. These are reported here as the first such observations of liquid crystalline phases in completely substituted chiral glucose molecules with mesogenic side chains.

INTRODUCTION

The study of carbohydrate liquid crystals started in 1938 when some long-chain n-alkyl glucopyranosides were recognized as thermotropic liquid crystals.[1] Since then, many n-alkyl glucopyranosides have been studied for their liquid crystalline behavior. The earlier results that (i) an alkyl chain of at least seven carbon atoms was necessary for liquid crystalline formation, (ii) blocking of the hydrogen-bonding functional groups of the carbohydrate moiety inhibited liquid crystal formation, and (iii) that the presence of a polar or functional group (CN, OH, Cl) at the terminus of the alkyl chain inhibited liquid crystal formation,[2] do not seem to agree to our findings.

To our knowledge, till date, Smectic A, A_d and discotic mesophases have been observed in glucose derivatives. Smectic A phases have been reported[3] to be observed in n-alkyl substituted glycosides with the hydrocarbon chains forming an interdigitated structure in a tail-to-tail packing, and the carbohydrate moieties hydrogen-bonded in a head-to-head bilayered structure. The interdigitated bilayer structure seemed to suggest the presence of Smectic A_d phase.[4] The position of the alkyl substituent on the glucose moiety did not seem to effect the phase formation. Appearance of tilted or higher ordered phases has not been seen.[5,6]

Later it was considered that the anomeric effect of the ester substituents was significant.[7] A preferred axial position was preferable to an all-equatorial conformation because of the difficulty in obtaining stabilized gauche interactions between all of the ester groups. Decyl and dodecyl-β-glucopyranosides formed anisotropic phase with homeotropic and spherolytic texture that can be compared to discotic phases.[8]

Similarly, tetrakis(triacetylgalloyl) -β-D-glucopyranoside exhibited a mesophase that could be discotic.[7] The above derivatives of glycosides were formed from alkyloxy group at the anomeric center rather than acyloxy in order to reduce the influence of anomeric effect. It was concluded that a polar nucleus to hydrophobic side chains seems to form a disc like structure. Some additional mesophases were observed, but unidentified, after Smectic A phase when the rigid chiral core of glucopyranose was used for Schiff base derivatives.[9] They were claimed to be calamitic mesogens of monosaccharides. α- and β- anomers of penta-o-n-alkanoylglucopyranoses have been found to form chiral discotic columnar mesophases with no hexagonal columnar ordering. An interesting suggestion has been made on the twist in the columns of the α-anomers formed by the tilting of disk planes with respect to one another.[10] The anomeric effect of 1,5 pentacetyl α- and β-D-glucose has also been studied by ^{13}C-NMR analysis.[11]

In carbohydrates two or more crystal-to-crystal phase transitions have been observed before any liquid crystal phase formation,[12] but there is no structural information about the conformational or reorientational changes during these transitions.

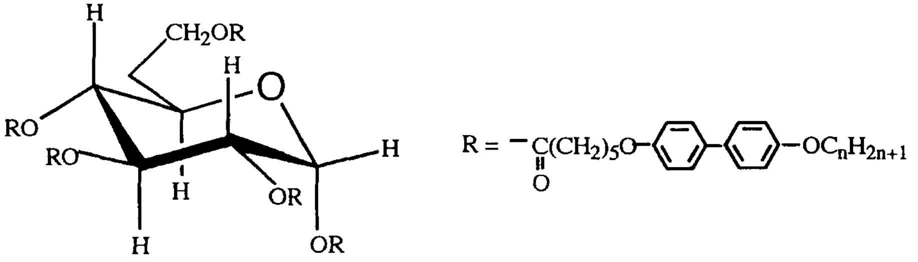
Given the above work it is surprising to note that glucose derivatives with mesogenic side chains have not been studied. Reported in this paper is the synthesis and characterization of first such compounds. The side chain contains a mesogen, an alkyl spacer and an alkyl tail. Figure 1 shows the structures of these glucose derivatives. The above components of the glucose derivative being incompatible with each other could lead to a possibly segregated structure. Such glucose derivatives can be synthesized in a very economical and simple way. Purity of the derivatives and the complete degree of substitution of side chains onto the glucose unit was assured from ^{13}C-, ^{1}H- and 2D-NMR analysis.

The effect of number of carbon atoms in the alkyl tail on the phase behavior is reported here. The longer alkyl tail length exhibits smectic phase in a bilayered arrangement. With a decrease in the length, chiral nematic phase appears followed by a smectic phase in a single layer arrangement with intercalated mesogenic side chains.

EXPERIMENTAL

Synthesis

Glucose derivatives were synthesized from α-D-glucose purchased from TCI Co. Ltd. The acid chlorides of mesogenic side chains were prepared by refluxing the side chain, with a terminal carboxylic group, with excess of thionyl chloride for about 4-5 hours. The synthesis of mesogenic side chains is given in the appendix. These were refluxed with the glucose unit in pyridine using 1,4-dioxane as solvent. The acid chloride side chain was in excess of 2 equivalents and pyridine was in excess of 10 equivalents of glucose. The reaction was carried out for about 100 hours at 80°C. The above conditions were determined by experimentation in order to obtain complete esterification at the five hydroxyl groups of glucose. On completion, the reaction mixture was poured into 5% acidified water and the residue was then purified in chloroform/water followed by column chromatography using alumina. Chemical structure of the glucose derivatives is shown in Figure 1. Purity of the derivatives was checked by thin layer chromatography and ^{13}C-NMR and ^{1}H-NMR analyses. The complete degree of substitution was confirmed from the detailed NMR analysis including two-dimensional NMR spectrum. A complete synthesis scheme for G-5-BP-4 is given in Figure 10.



G-5-BP-n **5-BP-n**

(glucose - C atoms in spacer - biphenyl - carbon atoms in tail)

where n = 4 or 1

FIGURE 1: Chemical structure of the glucose derivatives

Characterization

Cross-polarizing optical micrographs of pure samples were obtained on Olympus BH-2 attached to a Mettler hot stage. Thermal analysis was performed on a Perkin-Elmer differential scanning calorimeter. Wide-angle X-ray diffraction patterns were obtained on Rigaku R-axis machine using CuK$_{\alpha}$ radiation. JEOL GSX-500 NMR spectrometer was used for carbon, proton and two-dimensional analysis of the samples in CDCl$_3$

solvent at room temperature.

RESULTS AND DISCUSSION

Mesogenic side chains

The side chain, 5-BP-4, with four carbon atoms in the alkyl tail, showed a fan-shaped texture typical of a Smectic A phase on cooling from the isotropic melt at 10°C/min. This liquid crystalline phase was observed for a very short period of about 4°C before the crystalline phase was formed. The differential thermal analysis also exhibited a sharp transition peak at about 156°C on cooling and another at about 152°C. This phase was monotropic and homeotropic texture could be obtained with no birefringence.

On the other hand, the 5-BP-1 side chain with one carbon atom in the alkyl tail showed no signs of any mesophase region. The melting temperature was about 158°C.

This could imply that the length of the alkyl tail influences the order of the molecules in the material. A longer alkyl tail in the side chain favors a layered structural arrangement of the molecules.

GLUCOSE DERIVATIVE, G-5-BP-4

NMR analysis

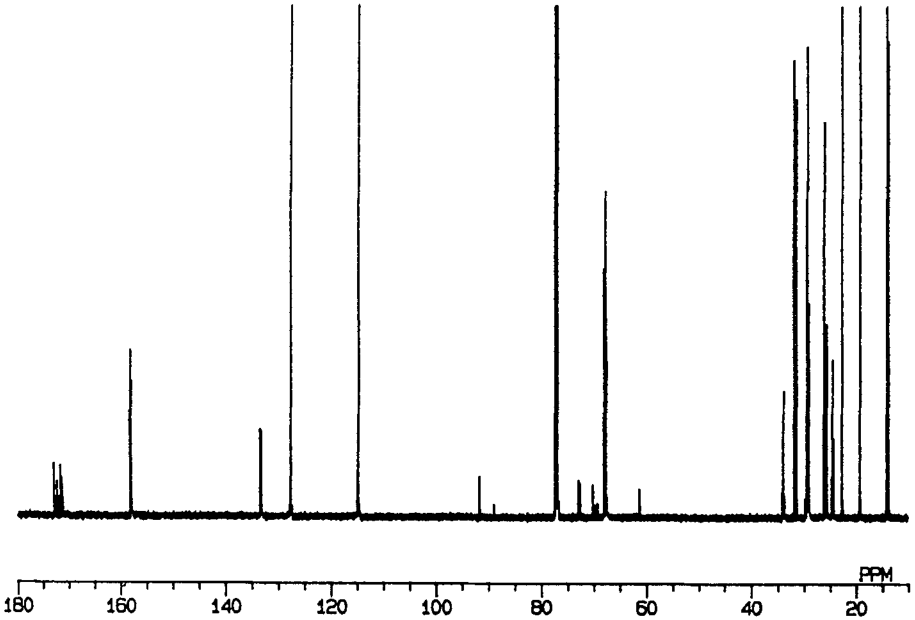


FIGURE 2: ^{13}C-NMR spectrum of the pure material, G-5-BP-4.

The chemical shifts of ^{13}C-NMR spectrum (Fig.2) were assigned based on the spectrum of the mesogenic side chains and the data from Van Doren[9], et al. and Hutchinson[11]. Results indicated the presence of a pure compound. The proton (^{1}H) NMR spectrum was used for measuring the ratio of peak intensities. Since the peak assignment of the protons of this large molecule could not be done easily, two-dimensional NMR measurement was performed. The peak intensity ratios verified the complete degree of substitution with five long mesogenic side chains substituted on one glucose monomeric unit.

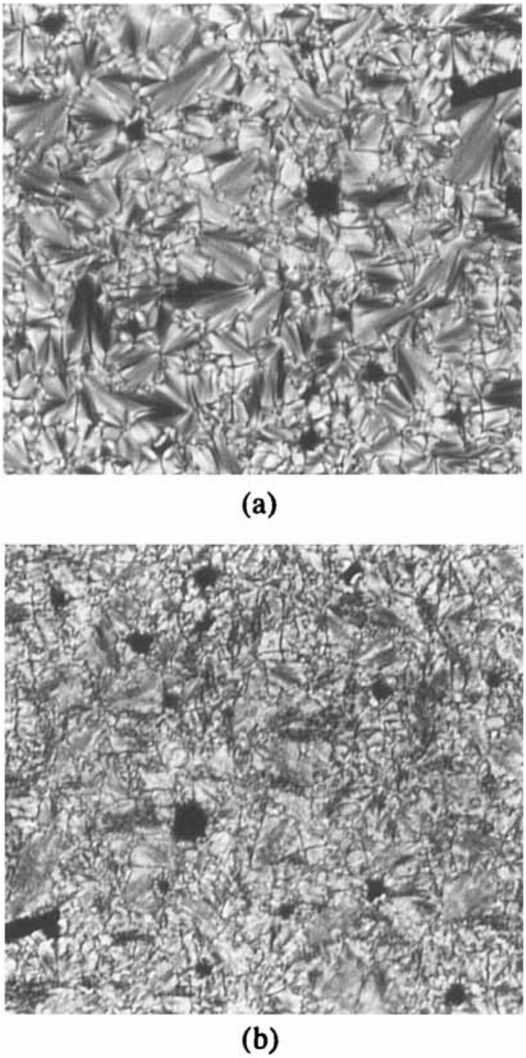


FIGURE 3: Cross polarizing microscope textures of G-5-BP-4. The fan-shaped (a) of S_A phase was seen at about 150°C and the transition bars (b) were observed for S_B phase from about 140 to 130°C.

Cross polarizing microscopy

On cooling from the isotropic melt, well-defined fan-shaped texture (Fig.3) of S_A phase, formed from batonnets, appeared at about 170°C. Homeotropic texture with no birefringence was observed. On further cooling, appearance of transition bars and the continuing fan-shaped texture (Fig.3) at about 140°C suggested the formation of S_B phase. The highly ordered S_B phase was also evident from the high viscosity of he material on the glass slide. Homeotropic texture could be observed in this phase too. Crystalline phase was observed at about 10°C below the S_B phase. This glucose derivative showed enantiotropic behavior.

Differential Scanning Calorimetery

The thermal heating and cooling curves (Fig.4) obtained at a rate of 10°C/min. showed three marked transition peaks at temperatures corresponding to that observed on polarizing microscope. The respective enthalpies and transition temperatures are listed in Table 1. The presence of two smectic phases was confirmed from the above measurements. The transition enthalpy of isotropic to S_A phase transition was much higher than that of S_A to S_B phase or S_B to crystal transition.

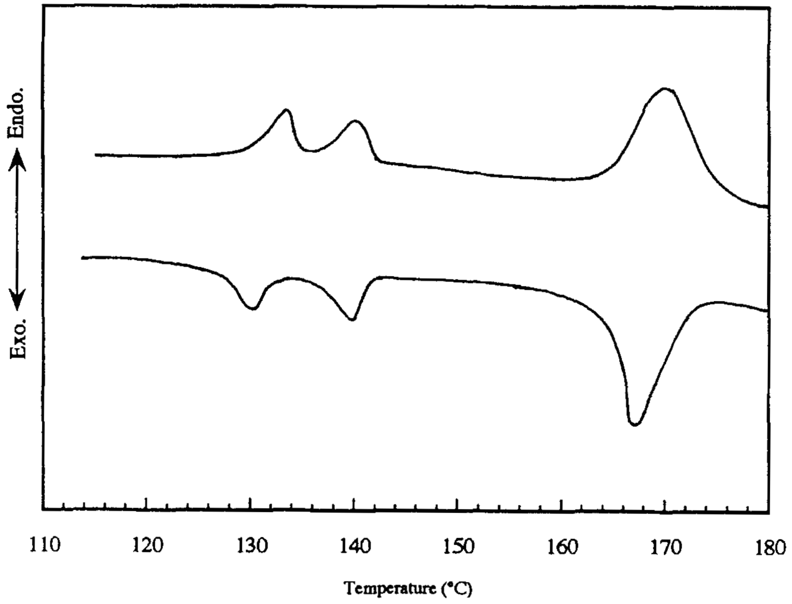


FIGURE 4: The DSC thermogram of G-5-BP-4 obtained at a rate of 10°C/min.

Wide-angle X-ray diffraction

The Smectic A phase was identified from sharp inner ring reflections and a diffuse outer ring (Fig.5) obtained on cooling from the isotropic melt at 10°C/min. The inner ring corresponds to an observed layer spacing of about 50Å (measurement error of ±0.5 Å). Theoretically, the extended all-trans conformation of this glucose derivative has a calculated length of about 51 Å. This implies that the thermodynamically stable structural arrangement is a fully bilayered one with no tail-to-tail interaction of the mesogenic side chains.

TABLE 1: Transition temperatures and transition enthalpies of G-5-BP-4 determined from optical microscopy and DSC curves on heating at 10°C/min. The value in parenthesis was obtained on the cooling cycle. The temperature values are reported with a possible error of ±0.5°C.

Phase	K		S_B		S_A		I
Transition temperature (°C)		137 (130)		140 (140)		170 (167)	
Transition enthalpy (kJ mol^{-1})		9.61 (13.84)		10.16 (13.67)		57.85 (46.90)	

In the S_B phase region, the outer ring became sharp (Fig.5) and the intermolecular spacing was about 4.4 Å. The intermolecular interaction is higher in the S_B phase. Observed layer spacing was the same suggesting that the molecules are oriented perpendicular to the layer as seen in smectic B phase. The transition to crystalline phase was clearly observed at about 130°C from the multiple sharp reflections.

On the basis of the above observations, a bilayered structure, shown in Figure 6 can be proposed for G-5-BP-4 with complete segregation in the three incompatible components of the molecule, namely, glucose moiety, aliphatic spacer and the biphenyl mesogen.

Similar structural arrangement has been proposed for cyclic tetrameric molecules[13] containing three distinct parts - a biphenyl aromatic core, a paraffin chain and a central siloxane group. Their mutual incompatibility results in three different sub-layers superposed in a partially bilayered smectic A structure.

GLUCOSE DERIVATIVE, G-5-BP-1

NMR analysis

Similar results as before were obtained for the pure sample.

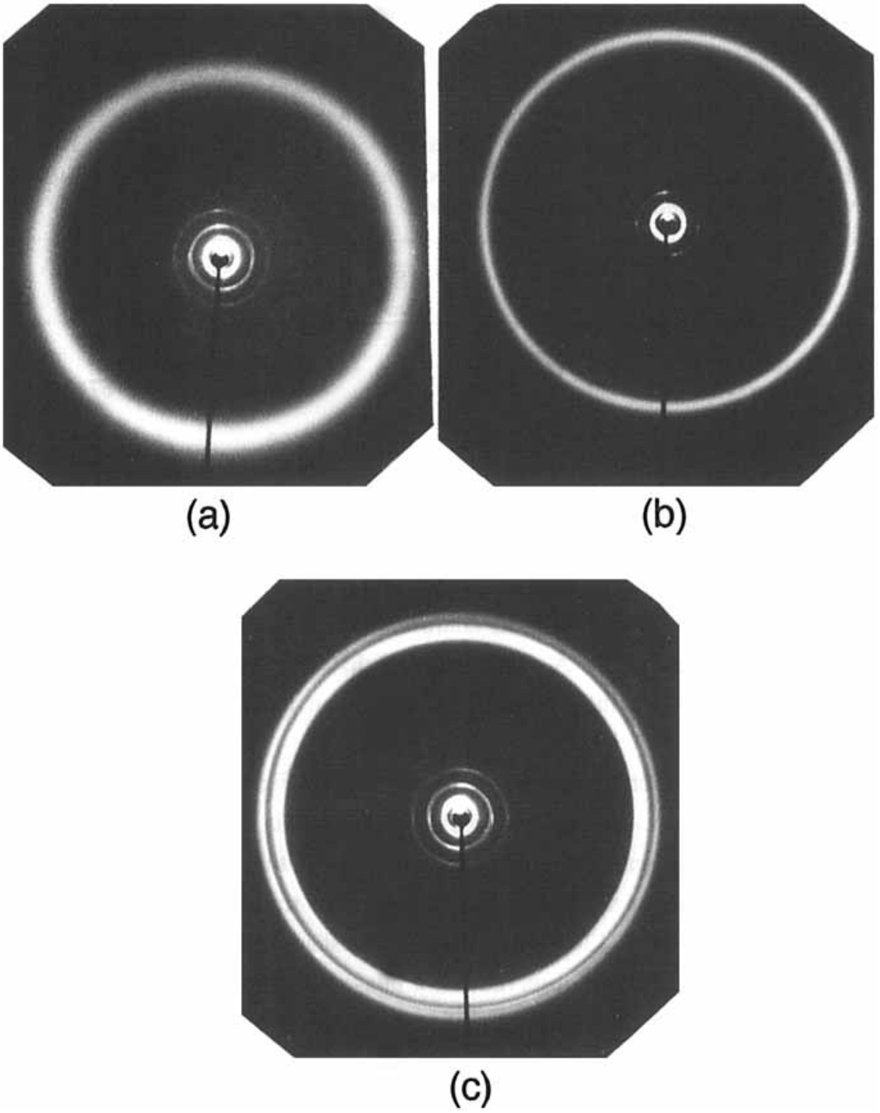


FIGURE 5: Wide-angle X-ray diffraction pattern of G-5-BP-4 at (a) 150°C, (b) 135°C and (c) 125°C obtained on cooling from the isotropic melt at 10°C/min. The transition from S_A to S_B phase was observed with the appearance of sharp outer ring in (b).

Cross polarizing microscopy

Enantiotropic behavior was observed on observation under cross polarizing microscope with the formation of nematic and smectic mesophases. The nematic phase obtained on cooling from the isotropic melt at about 136°C was marked by the schlieren and oliy-

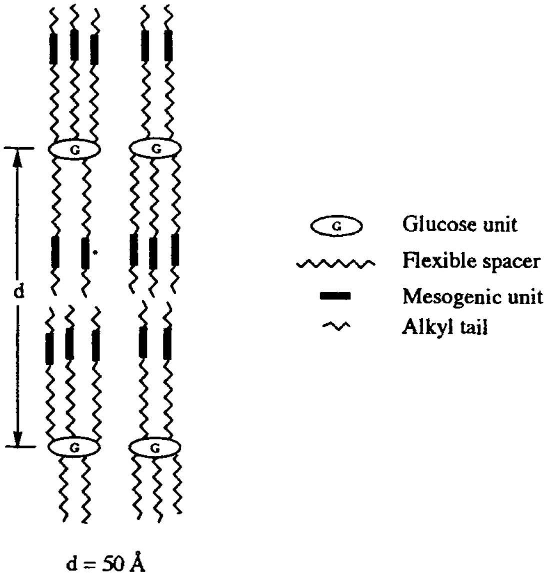


FIGURE 6: The segregated bilayered structural arrangement of G-5-BP-4.

streaked textures (Fig.7). In some parts of the sample, molecules stood perpendicular to the glass slide and exhibited the helical pitch lines typical of a cholesteric phase with a fingerprint texture. Since the material under observation is chiral in nature, it can be said to exhibit a chiral nematic mesophase.

The transition from nematic to smectic liquid crystalline phase was observed from the fan-shaped texture that appeared on cooling to about 125°C. The homeotropic texture with no birefringence was characteristic of a Smectic A phase. Transition from S_A phase to the crystalline phase was marked by a change in texture with the disappearance of fan-like shape.

Differential Scanning Calorimetery

The heating and cooling curves (Fig.8) obtained at a rate of 10°C/min. indicated three sharp peaks. Two mesophases were expected from these transition peaks. The transition temperatures were in agreement with that observed on cross polarizing microscope, thus suggesting the presence of chiral nematic and smectic liquid crystalline phases. The transition temperatures and respective enthalpies are listed in Table 2. As expected, the transition enthalpy of isotropic to nematic phase is lower than the smectic to crystal transition.

A small peak was observed on cooling from the isotropic melt at about 100°C which was apparently a crystal-to-crystal transition. The peak at about 111°C on the

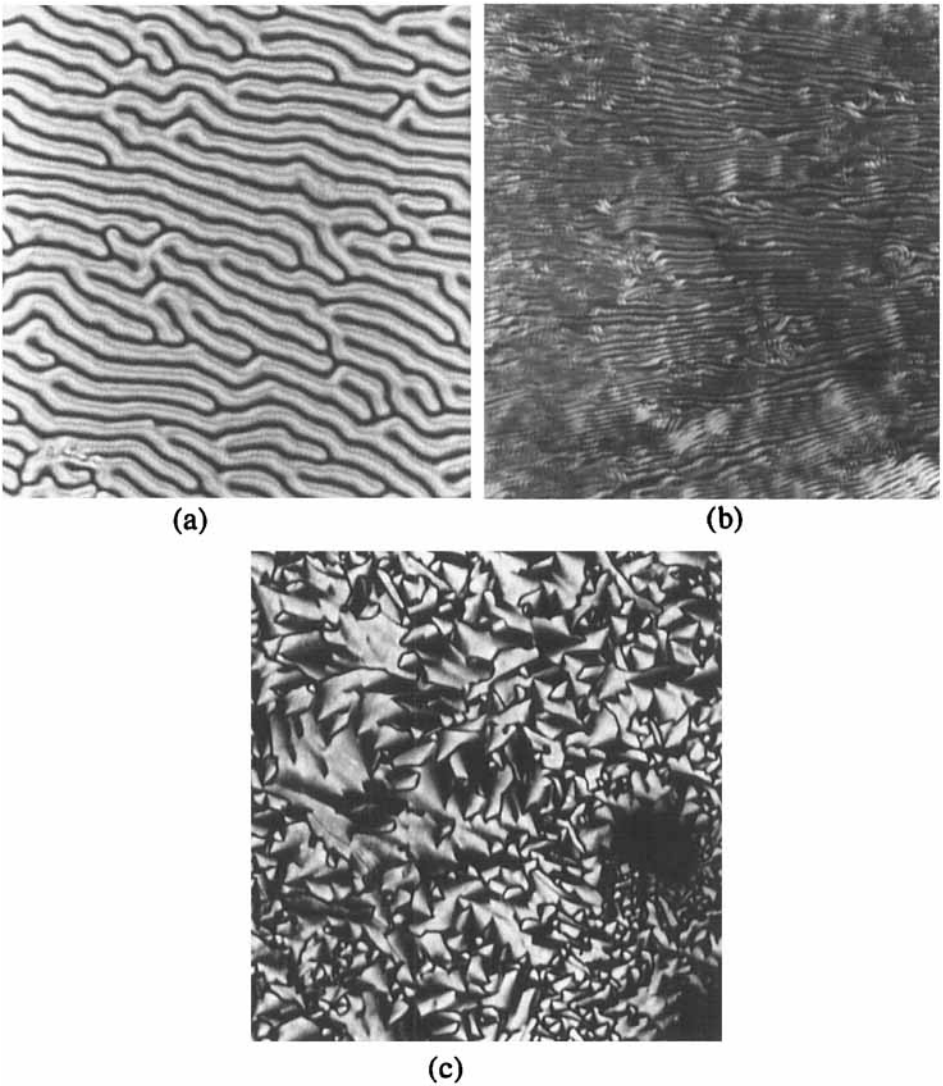


FIGURE 7: Cross polarizing microscopic textures of G-5-BP-1. The oily-streaked texture (a) of chiral nematic phase and the fingerprint texture (b) of cholesteric phase are shown. The transition to smectic A phase on cooling to about 125°C was marked by the fan-like appearance shown in (c).

heating curve disappeared completely if the sample was heated from about 100°C instead of room temperature. It is shown by the dashed line on heating curve in Figure 8. This could be due to the presence of a metastable crystalline phase.

Wide-angle X-ray diffraction

No layer reflection was observed on cooling at 10°C/min. from the isotropic melt till

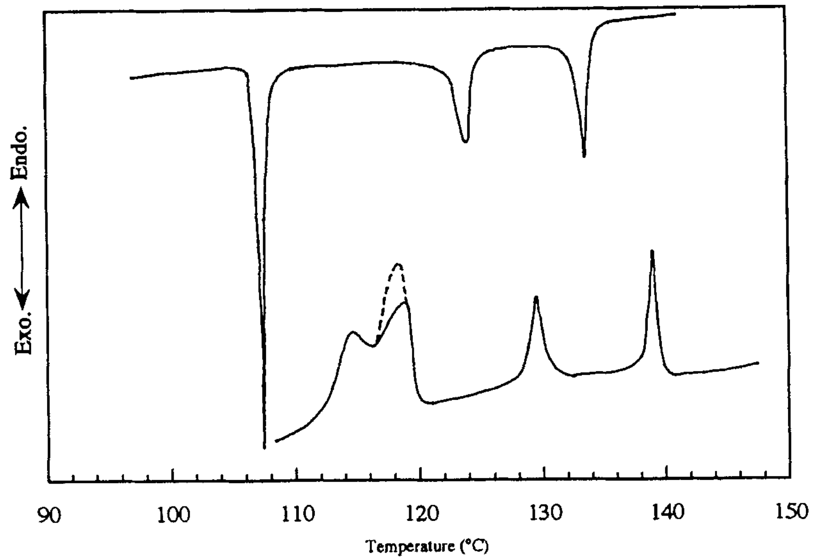


FIGURE 8: The DSC thermogram of G-5-BP-1 obtained at a rate of 10°C/min. The dashed line shows heating from about 100°C instead of RT.

TABLE 2: Transition temperatures and transition enthalpies of G-5-BP-1 determined from optical microscopy and DSC curves on heating at 10°C/min. The value in parenthesis was obtained on the cooling cycle. The temperature values are reported with a possible error of ±0.5°C.

Phase	K		S_A		N*		I
Transition temperature (°C)		116 (105)		128 (125)		140 (136)	
Transition enthalpy (kJ mol^{-1})		23.32 (17.05)		9.36 (8.44)		5.68 (5.85)	

about 125°C. The presence of a nematic phase formed from the isotropic was confirmed.

The inner layer reflection in the smectic region along with the broad outer reflection observed at 125°C suggested the presence of S_A phase. The observed layer spacing was about 22 Å. It corresponds to about half the calculated length of the molecule in a fully extended trans form. Thus, it can lead to the conclusion that single layer structure, with a possible arrangement shown in Figure 9, exists at equilibrium in the liquid crystalline phase. The mesogenic side chains arrange themselves in an intercalated structure. The crystalline phase appeared with the multiple reflections on the X-ray pattern taken at about 105°C.

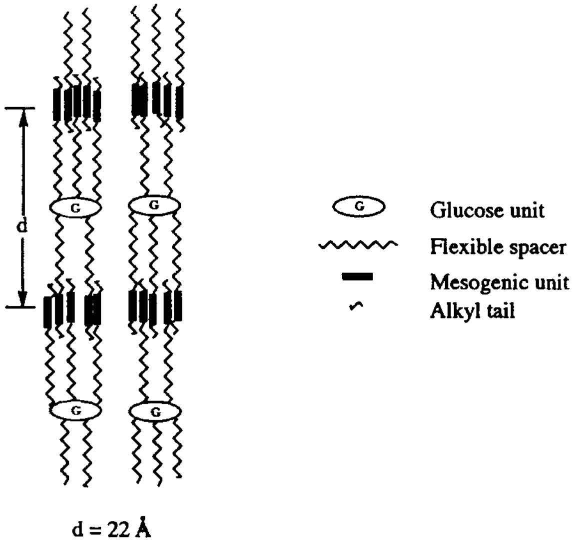


FIGURE 9: The intercalated single layered structural arrangement of G-5-BP-4

Comparing the two liquid crystalline glucose derivatives reported above, we found that the length of alkyl tail of the side chain plays a significant role in the phase behavior of the material. Mesophase with positional order (smectic) is preferred over the nematic phase when the alkyl tail contains four carbon atoms. The shorter alkyl tail with just one carbon atom forms the helical structure of a cholesteric phase and then arranges into a layered structure at lower temperatures.

The isotropization temperature of the glucose derivative decreases from 170°C to 140°C with a decrease in the length of the mesogenic side chain.

The bilayered structure in the longer side chain compound has a tail-to-tail arrangement with segregation in the alkyl tail ends. This could be due to a strong sense of segregation in the three incompatible components of the glucose derivative. On the other hand, the shorter side chain material arranges itself in an intercalated single layered structure. This could mean that the length of the alkyl tail affects the order and arrangement of the molecules in the liquid crystalline phase. Further study on the phase behavior by varying the length of spacer and tail is continuing. It is being extended to cellubiose and cellulose derivatives.

CONCLUSION

Two glucose derivatives were synthesized with mesogenic side chains of varying tail length. The glucose unit was completely esterified by the five long side chains. Phase behavior was analyzed and the first such appearance of chiral nematic mesophase in the derivative with shorter alkyl tail is reported. Layer spacing in the longer alkyl tail derivative suggests a bilayered arrangement in a segregated form while the shorter tail molecules arrange themselves in an intercalated single layer. A tail-to-tail end interaction possibly leads to the above findings. More work needs to be done in order to study the effect of varying length of the alkyl tail on the phase behavior of these glucose derivatives.

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APPENDIX

Synthesis of mesogenic side chain, G-5-BP-4

4,4'-biphenol was used as the starting material. Alkaline treatment with bromobutane in ethanol at about 100°C resulted in 4-butoxy-4'-hydroxybiphenol which was treated with acidic and alkaline solutions for purification and later recrystallized in ethanol. Further purification was done by column chromatography using silica gel. The pure compound was reacted with 6-bromohexanoic acid ethyl ester in a molar ration of 1:1.5 at about

100°C using anhydrous potassium carbonate, KI as indicator, and DMF as solvent. It was purified and then recrystallized in ethanol. The melting point of the pure compound was about 101°C.

The ester end group was hydrolyzed to carboxylic group using aqueous sodium hydroxide and ethanol at about 120°C and then neutralized in acidic solution. The product was recrystallized in acetone. It's clearing temperature was about 160°C and the phase behavior is reported in the results.

Synthesis of mesogenic side chain, G-5-BP-1

The above method was used for preparation but the starting material here was 4-methoxy-4'-hydroxybiphenol. The melting point of the resulting pure material was about 158°C.

Figure 10 shows a pictorial representation of the complete synthesis procedure for the glucose derivative (G-5-BP-4) with the longer alkyl tail length.

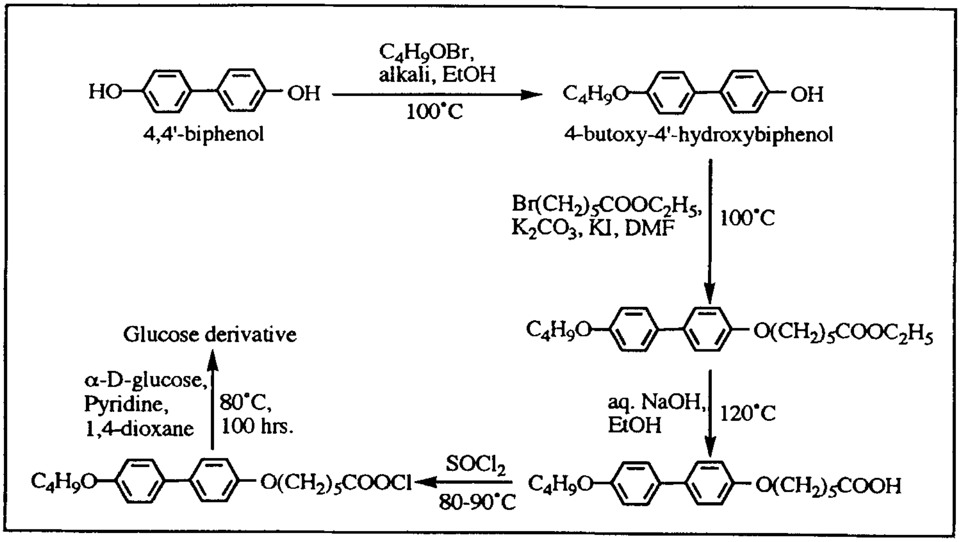

FIGURE 10: Pictorial representation of the synthesis of glucose derivatives.

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