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

Liquid crystallinity of newly synthesized glucose derivatives with mesogenic side chains

Bhavna Hirani; Hiroshi Kou-Shou; Junji Watanabe

Online publication date: 06 August 2010

To cite this Article Hirani, Bhavna , Kou-Shou, Hiroshi and Watanabe, Junji(1997) 'Liquid crystallinity of newly synthesized glucose derivatives with mesogenic side chains', Liquid Crystals, 23: 1, 59 — 67
To link to this Article: DOI: 10.1080/026782997208677
URL: http://dx.doi.org/10.1080/026782997208677

LIQUID CRYSTALS, 1997, VOL. 23, NO. 1, 59–67

Liquid crystallinity of newly synthesized glucose derivatives with mesogenic side chains

by BHAVNA HIRANI, HIROSHI KOU-SHOU AND JUNJI WATANABE*
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

(*Received 16 December 1996; accepted 1 February 1997*)

Synthesis of glucose derivatives by direct esterification of the five available sites on D-(+)-glucose with side chains containing a biphenyl mesogenic moiety, a pentyl spacer and an alkyl tail is reported for the first time. Liquid crystalline phase behaviour of these glucose derivatives was studied by optical microscopy, thermal and X-ray diffraction methods. A layered arrangement of the smectic A (SmA) type was commonly observed in the above materials. An increase in the length of the alkyl tail results in a change of the phase structure from smectic A_i (SmA_i), intercalated layer phase, to smectic A_s (SmA_s), segregated bilayer phase. From the transition temperature and enthalpy observations, the SmA_s phase has higher order than the SmA_i phase. Cholesteric and chiral smectic C phases were also observed in addition to the SmA for some of the glucose derivatives, demonstrating a potential for preparing chiral liquid crystals.

1. Introduction

The fact that glucose is inexpensive and available in abundance from renewable resources makes it understandable to study mesogens derived from it. Liquid crystallinity has long been known for alkylated derivatives of D-(+)-glucose [1–3]. The cyclic glucose core has five possible sites for substitution of an alkyl chain. Although the most straightforward alkoxy substitution is at C-1 or C-6, selective substitution [4–6] at any one or more of the hydroxyl groups of the glucose ring has also been studied. Cyclic saccharides monosubstituted at the anomeric carbon exhibit smectic mesophases [7, 8]. The SmA_d phase with a bilayered interdigitated structure has been suggested for some *n*-alkyl glucopyranosides substituted at the β-anomeric carbon [9, 10]. Recently, 4,4′-heptoxybiphenyl-(methyl 2-O-*n*-butyl-3,4-dideoxy-α-D-glucopyranoside) uronate [11] prepared from D-(+)-glucose as the starting material has been reported to exhibit a chiral smectic C phase on cooling from blue and cholesteric phases. The chiral liquid crystals have been also derived from the carbohydrates [12, 13].

The influence of the length of alkyl side chain on the phase behaviour of glucose derivatives has been explored by some researchers [14–16]. In the α- and β-anomers of penta-O-*n*-alkanoylglucopyranose exhibiting the discotic columnar mesophase, the longer homologues have a different molecular packing arrangement and the mesophase is no longer be monotropic [14, 16]. The chirality and asymmetry of the glucopyranose cores could be responsible for such complex behaviour. Columnar discotic mesophases have been reported in glucose derivatives etherified at anomeric carbon and esterified at other positions by alkyl side chains [15]. The possibility of complete substitution on glucose by rigid mesogenic side chains has not been explored to date.

The aim of this study was to synthesize and study glucose derivatives of the chiral core surrounded by rigid mesogenic biphenyl moieties. All the five available hydroxyl sites on glucose were esterified by the side chain substituent containing a flexible alkyl spacer, a biphenyl mesogenic moiety and a flexible alkyl tail. The chemical structure of the derivatives is shown below.

These were termed G-5-BP-*n*, where G denotes glucose, 5 the number of carbon atoms in alkyl spacer, BP the biphenyl group and *n* the number of carbon atoms in alkyl tail. The number of carbon atoms in the alkyl tail was varied from 1 to 8 to study the effect of chain length on the liquid crystallinity of these glucose derivatives.

2. Experimental

2.1. *Materials*

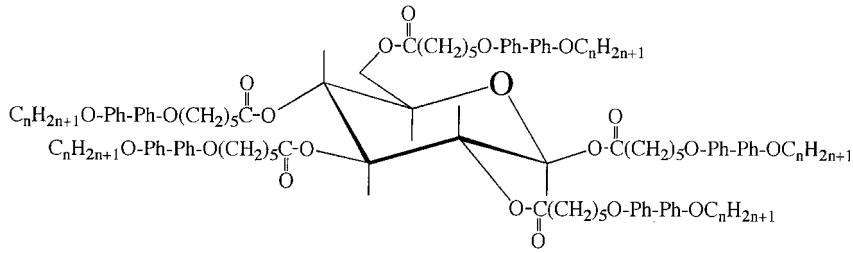
The G-5-BP-*n* compounds were synthesized according to the scheme. Each procedure is described in detail below.

2.1.1. *Synthesis of mesogenic side chain*

The mesogenic side chains were prepared from 4,4′-biphenol as the starting material. For the shorter alkyl

*Author for correspondence.

0267–8292/97 $12·00



G-5-BP-n
(n = 1-4, 8)

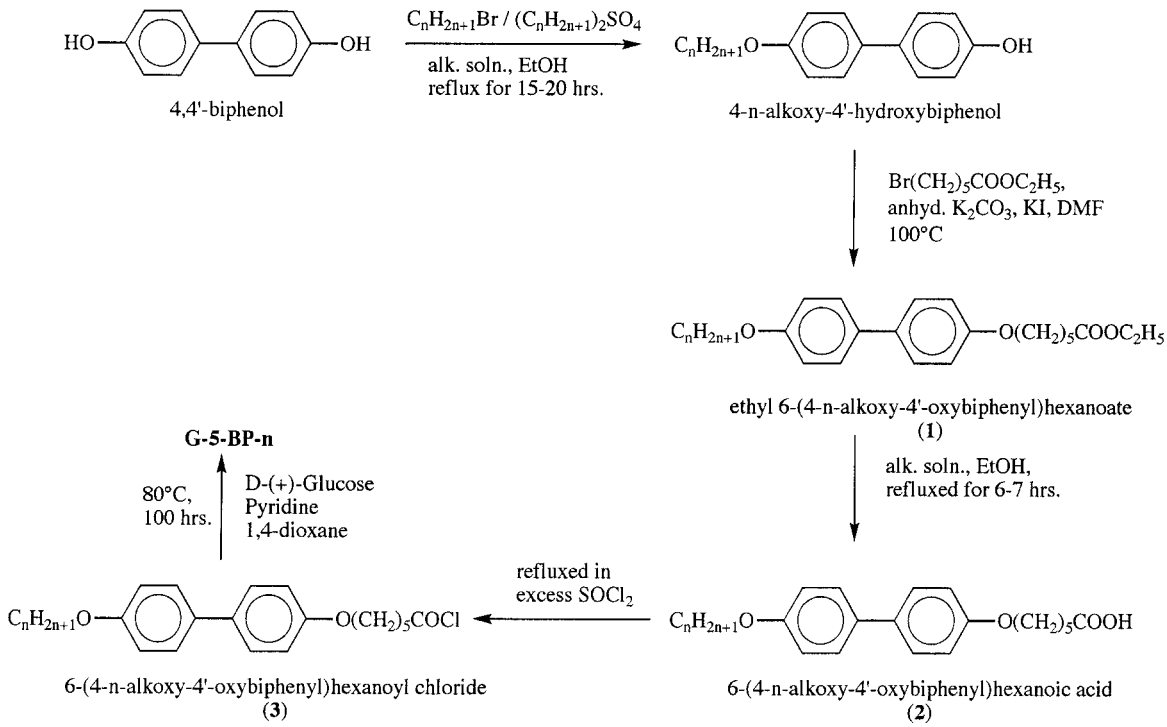
tail chains ($n=1$–3) the respective alkyl sulphates were used in aqueous alkaline solution at room temperature for about 24 h to get the 4-*n*-alkoxy-4′-hydroxybiphenyl. For the longer alkyl tail chains ($n=4, 8$), 4,4′-biphenol in an alkaline solution with ethanol as solvent was treated with the appropriate bromoalkane at about 80–90°C to give 4-*n*-alkoxy-4′-hydroxybiphenyl. It was recovered from the mixture containing the unreacted biphenol and then recrystallized from ethanol. Further purification by column chromatography using silica gel was required.

The pure compound was treated with 6-bromohexanoic acid ethyl ester in a molar ratio of 1:1·5 at about 100°C using anhydrous potassium carbonate, potassium iodide as indicator and DMF as solvent. The resulting ethyl 6-(4-*n*-alkoxy-4′-oxybiphenyl) hexanoate (**1**) was purified and recrystallized from ethanol.

The ester end group was then hydrolysed to the acid using aqueous sodium hydroxide and ethanol at about 100°C, neutralized in acidic solution, recrystallized from acetone and dried completely to get the pure 6-(4-*n*-alkoxy-4′-oxybiphenyl) hexanoic acid (**2**). The thermodynamic phase behaviour of the side chain compounds is given in table 2. The hexanoic acid was then reacted to hexanoic acid chloride (**3**) by heating at reflux with a four times excess of thionyl chloride for 2–3 h. Completely dried acid chloride was obtained by adding hexane and applying vacuum distillation to remove any gases.

2.1.2. *Esterification of glucose with mesogenic side chain*

The acid chloride (side chain) (**3**) was dissolved in anhydrous 1,4-dioxane and stirred thoroughly. Completely dried D-(+)-glucose ($M_w=180$), purchased from Tokyo Kasei Chemical, was added to the mixture



Scheme Synthesis scheme for the mesogenic side chain substituents and their glucose derivatives.

such that the side chain composition was in a two equivalent excess. A slightly higher equivalence of pyridine was added to this mixture both as base and catalyst. The esterification reaction was carried out at about 80°C with constant stirring for about 50 h.

The reaction mixture was then poured into a slightly acidified excess of water and stirred thoroughly before filtration. The residue was dissolved in chloroform and shaken with water in a separating funnel. The required glucose derivative material dissolved in chloroform and the pyridium salt and partially substituted glucose derivatives remained suspended in water. The chloroform was evaporated and the material recovered by recrystallization from a chloroform (solvent)/methanol (non-solvent) mixture.

The remaining impurity of the acid component (of unreacted side chain) (**2**) was removed by alumina gel column separation, using chloroform as solvent, and further recrystallized from a chloroform/methanol mixture. The final yield was about 30 per cent because of a considerable loss of end product during the isolation of the pure material.

The purity of the final product was checked by thin layer chromatography and NMR analysis using ^{13}C, ^{1}H and 2-D measurements. The peak assignment and the chemical shifts from ^{13}C and ^{1}H NMR of G-5-BP-4, for instance, are given in table 1. These are based on the assignment given in previous papers for similar compounds

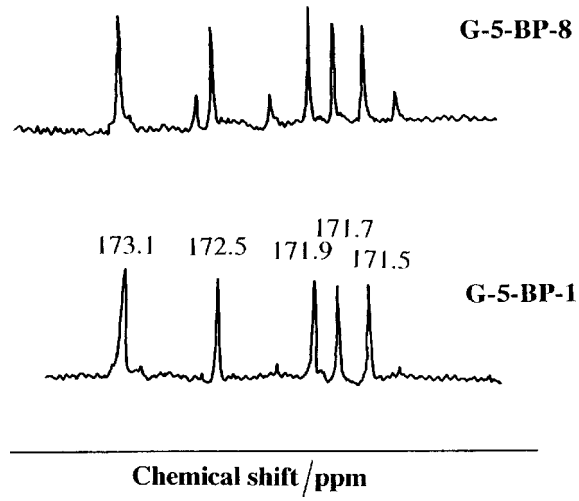


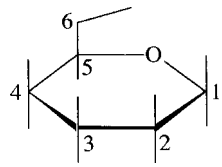
Figure 1. The carbonyl peaks of the ^{13}C NMR spectra expanded in the 170–175 ppm region of G-5-BP-1 and G-5-BP-8.

[6, 7, 17, 18]. An estimation of the perfect substitution on glucose was made from the peak integration intensity ratios of the carbonyl peaks in the ^{13}C NMR spectra expanded in the 170–175 ppm region shown in figure 1.

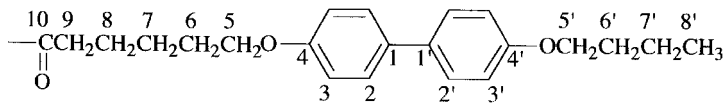
2.2. *Characterization*

The textures were observed through an Olympus BH-2 cross-polarizing microscope attached to a Mettler

Table 1. The ^{13}C and ^{1}H NMR chemical shifts (in ppm) for the G-5-BP-4 glucose derivative in $CDCl_3$ with internal TMS.



C atom	C-1	C-2	C-3	C-4	C-5	C-6
ppm	91·72	70·13	72·89	68·07	72·58	61·32
H atom	H-1	H-2	H-3	H-4	H-5	H-6
ppm	5·7	5·2	5·5	5·3	4·3	3·9



C atom	C-1,1′	C-2,2′	C-3,3′	C-4,4′	C-5,5′	C-6	C-6′	C-7	C-7′	C-8	C-8′	C-9	C-10
ppm	133·2	127·6	114·6	158·2	67·5	29·2	31·8	26·0	19·3	24·5	14·1	33·8	[a]
H atom		H-2,2′	H-3,3′		H-5,5′	H-6	H-6′	H-7	H-7′	H-8	H-8′	H-9	
ppm		7·4	6·9		3·9			1·2–1·8			0·8	2·3	

[a] Chemical shift of C-10 was observed as 5 peaks of 171·52, 171·73, 171·88, 172·50 and 173·10 ppm.

FP-80 hot stage. A Perkin–Elmer differential scanning calorimeter (DSC-II) was used for the thermal analysis. Wide-angle X-ray diffraction patterns were obtained on Rigaku–Denki X-ray generator with Ni-filtered CuK_α radiation. A Jeol GSX-500 NMR spectrometer was used for analysis of the chemical shifts and peak integration ratios using $CDCl_3$ as solvent at room temperature. The spontaneous polarization measurement for the chiral smectic C phase was performed using 1920A multifunction synthesizer, 4005 high speed power amplifier, PM332 Philips oscilloscope and Mettler FP-80 as temperature controller.

3. Results and discussion

3.1. *Average degree of substitution*

From the ^{13}C NMR spectra of the glucose derivatives, the carbonyl peak region (170–175 ppm) is expanded and shown in figure 1. A highly substituted glucose derivative has five carbonyl carbon peaks at 171·5, 171·7, 171·9, 172·5 and 173·1 ppm. In a mixture of fully and partially-substituted glucose derivatives, there are not only five but many peaks in the carbonyl carbon region of the ^{13}C NMR spectra. These peaks originate from the existence of magnetically different side chain groups in the fully and partially substituted glucopyranose rings. From figure 1 it can be concluded that the compounds G-5-BP-1, -2, -3 and -4 are fully substituted. In contrast, G-5-BP-8 exhibits not only five but many other peaks and thus the average degree of substitution can be estimated to be about 4·5 by measuring the integrated peak intensity of the carbonyl carbon peaks. The long side chains of G-5-BP-8 may not offer enough space for a reaction to result in a fully substituted glucose derivative. From ^1H NMR measurement, all the derivatives are mixtures of β- and α-anomers with a relatively higher β-content of around 70–80 per cent [14, 19].

3.2. *Phase behaviour*

3.2.1. *Side chain materials*

The thermal characteristics of the side chain substituents with varying *n* are listed in table 2. The ethyl 6-(4-*n*-alkoxy-4′-oxybiphenyl)hexanoates, (**1**), do not exhibit a liquid crystalline phase whereas the corresponding hexanoic acids, (**2**), could be expected to form a layered structure in the mesophase because of formation of dimers due to intermolecular hydrogen bonding between the acid end groups. However, only the butoxy side chain compound of (**2**) showed a monotropic SmA phase with the formation of batonnets resulting in a focal-conic, fan-shaped texture on cooling from the isotropic melt at 10°C min^{-1}. This mesophase range was about 3–4°C. The above side chain behaviour has also been reported by Imrie, *et al.* [20]. The other side chain materials showed only one transition, T_m, from the isotropic to crystal state.

Table 2. Thermal characteristics of the side chain compounds 5-BP-*n* for $n=1$–4, 8. The temperatures were recorded from DSC and polarizing optical microscopy at a heating rate 10°C min^{-1}.

5-BP-*n*	Melting point of the side chain ester (**1**)/°C	Melting point of the side chain acid (**2**)/°C
5-BP-1	100	158
5-BP-2	96	167
5-BP-3	98	158
5-BP-4	101	160[a]
5-BP-8	102	153

[a] Shows a monotropic SmA phase at 157–153°C on cooling from the isotropic melt.

3.2.2. *G-5-BP*-n

It was observed that the glucose derivative with a methoxy terminal group (G-5-BP-1) exhibited a cholesteric (Ch) mesophase followed by a smectic A (SmA) phase on lowering the temperature from the isotropic melt (see table 3). Under the optical polarizing microscope, a fingerprint polydomain texture, shown in figure 2, was observed for the cholesteric phase in the temperature region of 128–140°C, on both cooling and heating. From the fine striation lines in the fingerprint texture, the pitch of the helical structure could be estimated to be larger than a few μm. A strong dependence of the helical pitch on temperature was observed in this phase, the details of which will be reported elsewhere. The SmA phase below 128°C was identified by the homogeneous fan-shaped texture, the homeotropic texture without birefringence, and the inner layer reflection with a broad outer halo on the wide-angle X-ray diffraction pattern. The above mesophases were enantiotropic in nature.

An increase in the number of carbon atoms in the terminal alkyl group from one to three (methoxy to propyloxy, i.e. G-5-BP-2 to G-5-BP-3), resulted in the formation of an enantiotropic SmA phase (see table 3). This phase was stable over a large temperature range. The typical fan-shaped homogeneous texture of the SmA phase and the layered X-ray diffraction pattern support the above finding.

A further increase in the length of the terminal alkyl chain to four (butoxy) carbon atoms (derivative G-5-BP-4), resulted in the formation of a smectic B (SmB) phase in the lower temperature region of 131°C to 140°C, in addition to the SmA phase in the higher temperature region of 140°C to 170°C (see table 3). Both these phases form fan-shaped textures shown in figure 3.

Table 3. The transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) (in italics) for the glucose derivatives G-5-BP-*n* with $n=1$–4 and 8 observed by DSC. The values obtained on the cooling cycle at a rate of 10°C min^{-1} are given in parentheses.

Compound	Transitional data						
G-5-BP-1	Cr	116(105) *23·3 (21·0)*	SmA	128(125) *9·4 (8·4)*	N*	140(136) *5·7 (5·9)*	I
G-5-BP-2	Cr	131(124) *15·5 (16·1)*	SmA	153(148) *21·5 (22·5)*			I
G-5-BP-3	Cr	137(132) *34·1 (35·7)*	SmA	147(141) *29·3 (27·9)*			I
G-5-BP-4	Cr	131(130) *9·6 (13·8)*	SmB	140(140) *10·2 (13·7)*	SmA	170(167) *47·9 (46·9)*	I
G-5-BP-8	Cr	137(130) *39·6 (38·6)*	SmC*	154(157) *~3·0*	SmA	173(167) *53·7 (53·7)*	I

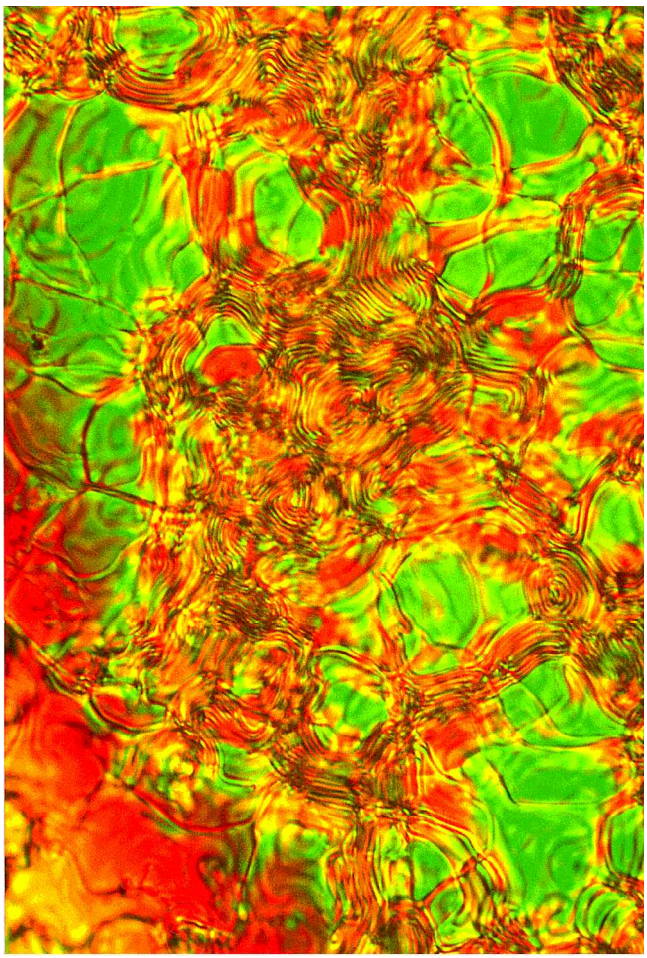


Figure 2. Fine striation lines in the fingerprint texture of G-5-BP-1 at about 136°C under the polarizing microscope.

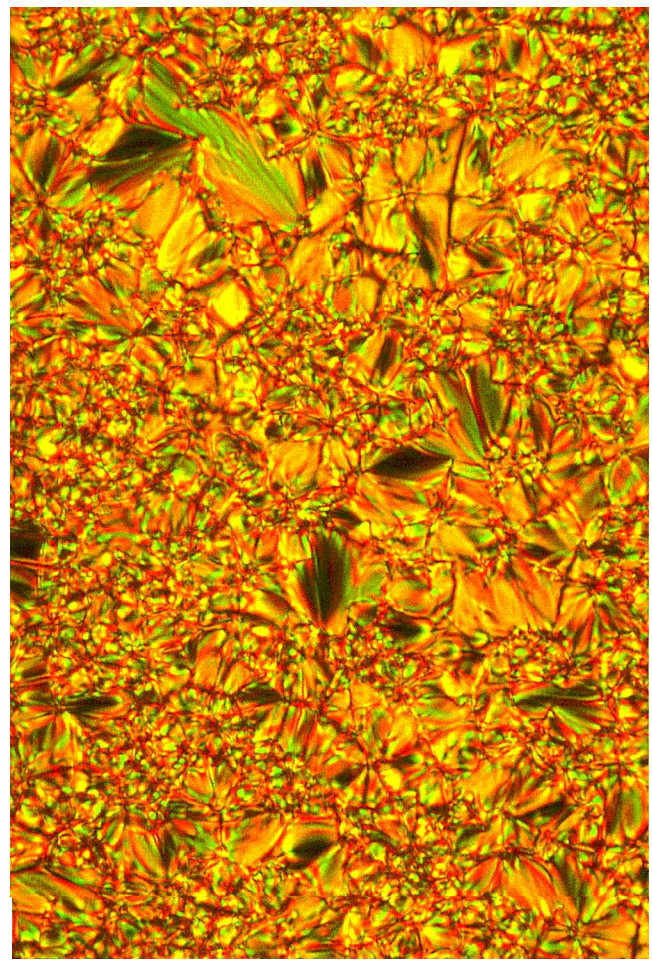


Figure 3. Focal-conic fan-shaped texture of the SmA phase of G-5-BP-4 observed under the polarizing microscope at about 150°C.

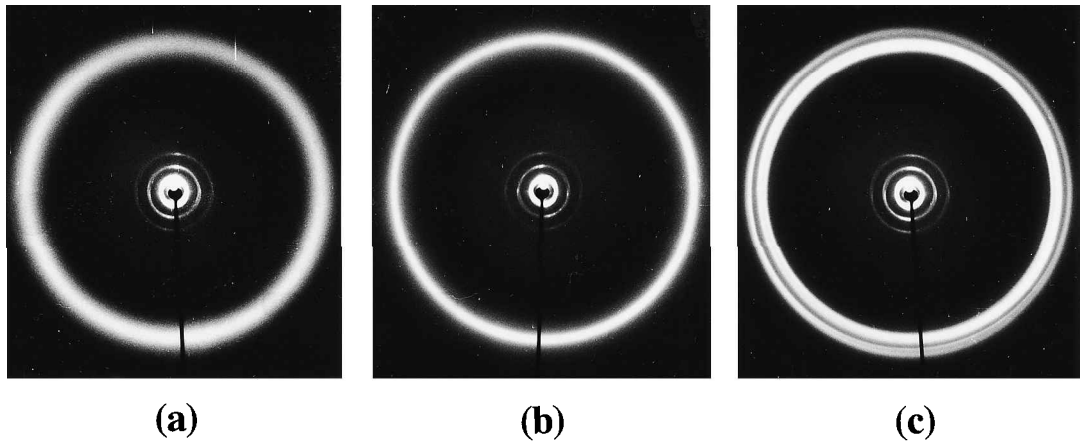


Figure 4. Wide angle X-ray diffraction pattern of G-5-BP-4. (*a*) Layer reflection of the SmA phase with a diffuse outer ring observed at 150°C, (*b*) sharpening of the diffuse outer ring at 135°C indicating a SmB phase, and (*c*) crystal phase at 120°C.

The SmB phase was identified from the transition bars superimposed on the fan-shaped texture of the SmA phase on cooling. The homeotropic texture without birefringence could be seen on shear alignment of the molecules parallel to the glass surface. Also, the wide-angle X-ray diffraction pattern (see figure 4 (*b*)) at the SmB temperature shows a sharpening in the outer diffuse ring of the SmA phase (see figure 4 (*a*)). Both the above phases, SmA and SmB were enantiotropic in nature.

Increasing the length of the terminal chain to octyloxy ($n=8$) resulted in a glucose derivative, G-5-BP-8 that showed an enantiotropic SmA phase with a well-defined fan-shaped texture in the temperature region of 154°C to 173°C. On cooling from the SmA phase, dechiralization lines appear in the fan-shaped texture at about 154°C (see figure 5). The lower temperature phase was thus identified as the chiral smectic C (SmC*) phase. From the X-ray diffraction measurement, an approximately 2 per cent decrease in the layer spacing of the first (52·5 Å to 51·7 Å), second (26·3 Å to 25·9 Å) and third (17·6 Å to 17·2 Å) reflections was observed on cooling from the SmA phase (at 160°C) to the SmC* phase (at 145°C). This decrease corresponds to a tilt angle of about 10°. Further, we observed the switching current due to spontaneous polarization on reversal of the applied electric field. The spontaneous polarization was evaluated to be 50 nC cm^{-2} for the SmC* phase at 145°C.

The transition temperatures and enthalpies of the above materials observed from the DSC study are listed in table 3, and the phase diagram is shown in figure 6. As can be seen in figure 6, the most stable liquid crystalline phase observed in a wide temperature region is the SmA phase. The presence of other mesophases, like cholesteric, SmB and SmC* was seen in the methoxy ($n=1$), butoxy ($n=4$) and octyloxy ($n=8$) derivatives,

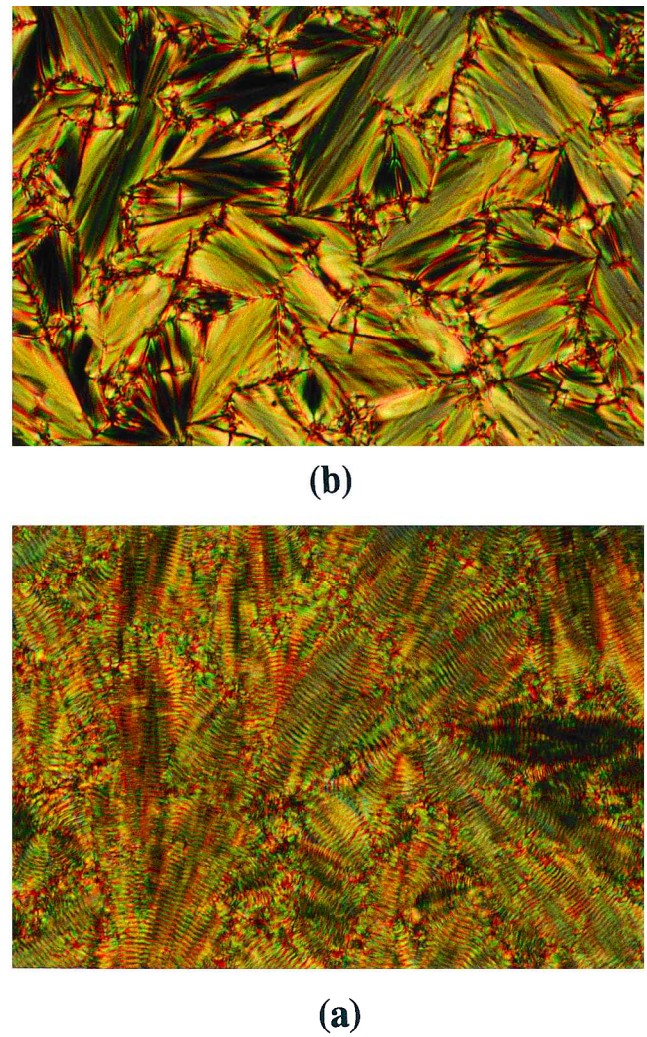


Figure 5. (*a*) Dechiralization lines in the SmC* phase of G-5-BP-8 (at 145°C) seen on cooling from (*b*) the SmA phase with the fan-shaped texture (at 160°C).

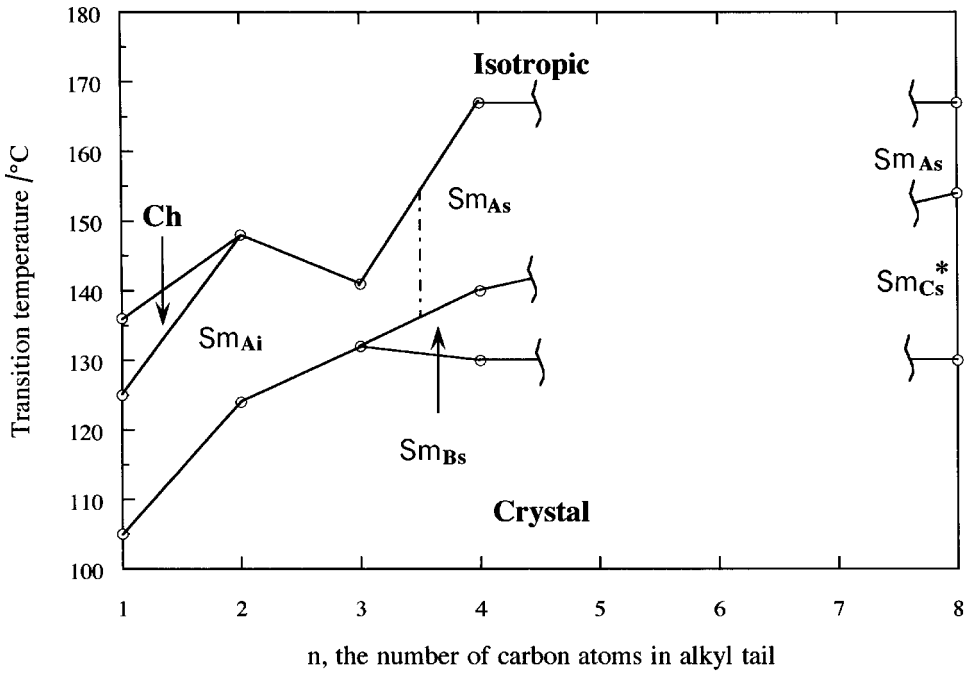


Figure 6. Phase diagram of the glucose derivatives, G-5-BP-*n* drawn from temperatures recorded by DSC on cooling at a rate of 10°C min^{-1}.

respectively. This could point to the conclusion that a layered arrangement is preferred in glucose units with mesogenic biphenyl moieties attached by a flexible alkyl spacer.

The degree of order in the liquid crystalline phase becomes higher with increasing *n*. For instance, the higher ordered SmB phase was observed for the derivative with $n=4$. A very long terminal group in the side chain substituent introduces a tilted layered structure, as seen for G-5-BP-8. Also, no liquid crystalline phase could be seen for the derivative with $n=0$, i.e. the presence of an alkyl tail is important for the mesophase formation in such materials.

It was also interesting to note that the side chain compound (**2**) with a butoxy terminal end was liquid crystalline in nature and the others were not, but when esterified to the chiral glucose unit all the alkoxy side chains induce liquid crystallinity in the derivatives. It suggests that the crystalline side chains are forced to form a layered liquid crystal when one end of the side chains is bonded to the cyclic glucose unit. This kind of phenomenon has been observed in many side chain polymers.

3.3. *Structural arrangement*

Cyclophosphazenes and cyclosiloxanes, with biphenyl mesogens and alkyl-tailed side chains, are comparable with these glucose derivatives as examples of induced layered mesophases. Partially bilayered smectic A_d (SmA_d) structure has been suggested for tetrameric cyclosiloxanes [21, 22] with the siloxane ring aligned parallel to the layer direction and the side chains perpendicular to the layer. This is believed to be the result of intermolecular segregation of the constituent parts of the molecules. For cyclophosphazenes, the smectic C (SmC) phase has been observed and a nonplanar arrangement structure between the cyclic ring and the side chains is proposed [23, 24].

In an attempt to clarify the structural arrangement in the smectic layer phase, the layer spacings of the SmA phase were calculated from the wide angle X-ray diffraction patterns. These are plotted against *n* in figure 7. The observed layer spacing of the order of 20 Å in the shorter alkyl chains, i.e. $n=1$–3, was about half the theoretically calculated value for the fully extended *trans*-form of the derivative with side chains extending on both sides of glucose. An increase in the length of the alkyl tail (n 4) resulted in a layer spacing of the order of 50 Å, i.e. about the same as the fully extended *trans*-conformation of the derivative.

The observations suggest an intercalated layered structure (SmA_i) for the glucose derivatives with short terminal alkyl chains and a segregated bilayered structure (SmA_s) for the longer terminal alkyl tail derivatives. These structures are illustrated in figure 8. The five side chains extend on both sides of the chiral glucose unit. The longer tail chain forces a separation of the molecular units into segregated components to result in a tail-to-tail bilayered arrangement.

From the WAXS patterns of unoriented samples it was observed that there are three sharp layer reflections in the SmA_s phases of G-5-BP-4 and G-5-BP-8 while

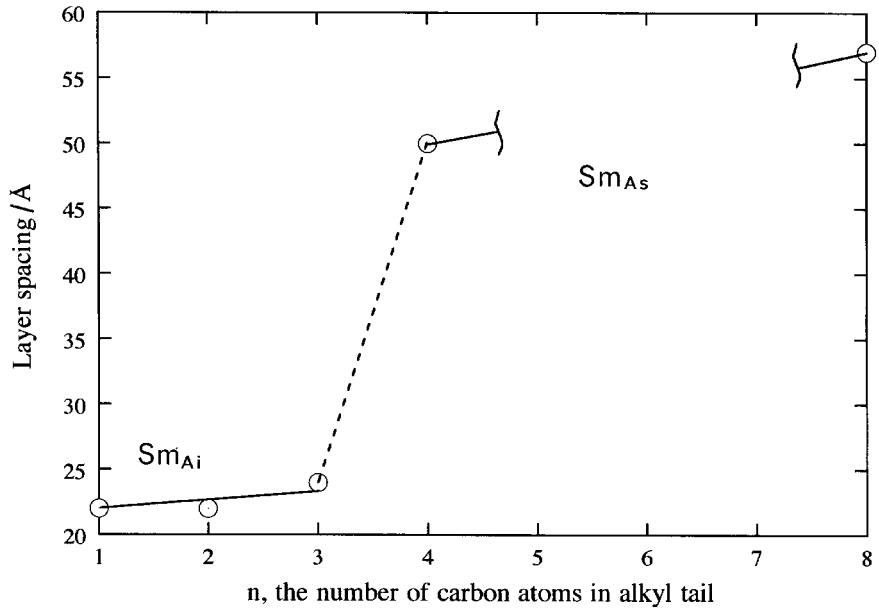


Figure 7. Layer spacing against n, the length of terminal alkyl group of the mesogenic side chain substituents in the SmA phases of G-5-BP-n.

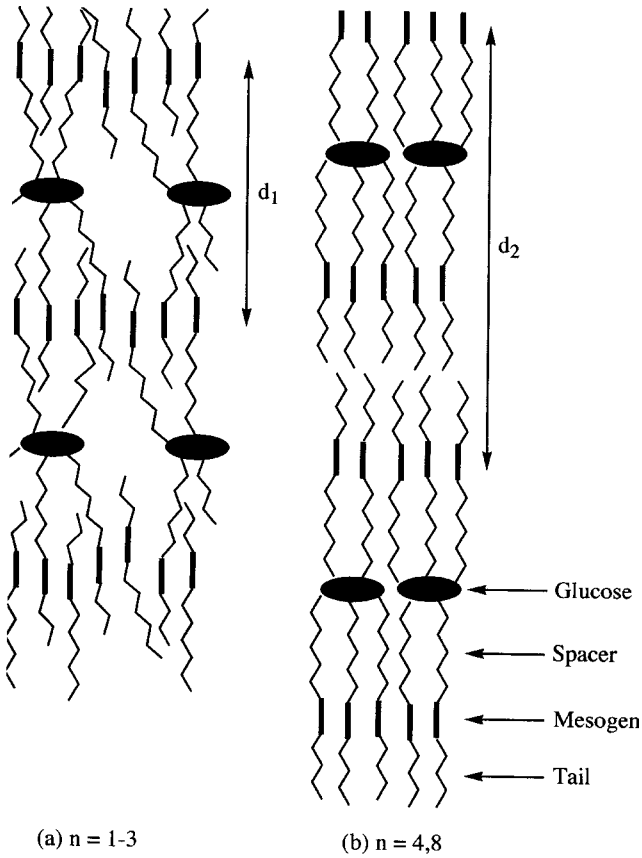


Figure 8. Structural arrangement of the glucose derivatives in the SmA phase proposed on the basis of X-ray pattern analysis. (*a*) Intercalated SmA; structure of the materials for $n=1$–3, and (*b*) bilayered segregated SmA_s arrangement of the compounds for n=4 and 8.

there is only one weak layer reflection in the SmA_i phase of G-5-BP-1, -2 and -3. This implies that there is higher order in the longer alkyl tail derivatives than the shorter tail homologues.

The above structural arrangement very much explains the thermal transition behaviour shown in figure 6. The transition temperature from isotropic to the SmA_s phase of the bilayered glucose derivatives ($n=4$ and 8) is about 20°C higher than the intercalated ones ($n=1$–3). The isotropization enthalpies given in table 3 are also significantly higher in the G-5-BP-4 and -8 materials; the isotropization enthalpies of the SmA_i phase are in a range of $20\sim30\,kJ\,mol^{-1}$ while those of the SmA_s phase are around $50\,kJ\,mol^{-1}$. Both the thermal as well as the X-ray observations indicate that the tail-to-tail segregated bilayered smectic phase, SmA_s has a higher ordered structure as compared to the intercalated phase, SmA_i. This may be reasonable for such liquid crystalline materials with mesogenic side chains.

4. Conclusions

The thermotropic liquid crystallinity of derivatives of glucose with mesogenic side chains was studied. The mesogenic side chains consisted of a biphenyl mesogen, a pentyl spacer and terminal alkyl tail. The effect of varying the length of alkyl tail of the side chain substituent on the phase behaviour of glucose derivatives has been demonstrated. On increasing the number of carbon atoms in the tail from three to four, a change was observed in the layered structure from intercalated to segregated bilayer of the smectic A (SmA) phase. This implies that the longer alkyl tail of the substituent forces a separation of molecules into bilayers where one layer

consists of a glucose moiety and the side chains fully extended on both sides of the glucose moiety.

Glucose derivatives with short alkyl tail substituents ($n=1$) exhibit the cholesteric mesophase. A chiral smectic C (SmC*) phase was observed with a spontaneous polarization on application of an electric field for the longer alkyl tail ($n=8$) derivative. These demonstrate a potential for preparing chiral liquid crystals from glucose.

B. H. thanks the Ministry of Education (Monbusho) of Japan for the scholarship that gave her the chance to carry out research in Professor Watanabe's laboratory.

References

[1] Jeffrey, G. A., 1984, *Mol. Cryst. liq. Cryst.*, **110,** 221.
[2] Jeffrey, G. A., 1986, *Acc. Chem. Res.*, **19,** 169.
[3] Vill, V., Prade, H., and Miethchen, R., 1995, *J. Prakt. Chem.*, **337,** 427.
[4] Vill, V., Thiem, J., Fischer, H., and Sauerbrei, B., 1992, *Liq. Cryst.*, **11,** 949.
[5] Jeffrey, G. A., and Wingert, L. M., 1992, *Liq. Cryst.*, **12,** 179.
[6] Vill, V., Tunger, H., and Paul, M., 1995, *J. Mater. Chem.*, **5,** 2283.
[7] Hutchinson, C. R., 1874, *J. org. Chem.*, **39,** 1854.
[8] Vill, V., Thiem, J., Fischer, F., and Böcker, T., 1989, *Liq. Cryst.*, **6,** 349.
[9] Goodby, J. W., 1984, *Mol. Cryst. liq. Cryst.*, **110,** 205.
[10] van Doren, H. A., van der Geest, R., Kellogg, R. M., and Wynberg, H., 1989, *Carbohydrate Res.*, **194,** 71.
[11] Ho, W. H., Navailles, L., Destrade, C., Nguyen, H. T., Wong, N. C., and Isaert, N., 1995, *Tetrahedron*, **51,** 7373.
[12] Vill, V., Tunger, H-W., Stegemeyer, H., and Diekmann, K., 1994, *Tetrahedron: Asymmetry*, **5,** 2443.
[13] Vill, V., and Tunger, H-W., 1995, *Liebigs Ann.*, 1055.
[14] Morris, N. L., Zimmermann, R. G., Jameson, G. B., Dalziel, A. W., Reuss, P. M., and Weiss, R. G., 1988, *J. Am. chem. Soc.*, **110,** 2177.
[15] Vill, V., and Thiem, J., 1991, *Liq. Cryst.*, **9,** 451.
[16] Weiss, R. G., Zimmermann, R. G., Jameson, G. B., and Demailly, G., 1985, *Mol. Cryst. liq. Cryst. Lett.*, **1,** 183.
[17] Kamide, K., Okajima, K., and Kowsaka, K., 1988, *Polym. J.*, **20,** 827.
[18] Kamide, K., Okajima, K., and Kowsaka, K., 1988, *Polym. J.*, **20,** 1091.
[19] Takada, A., Ide, N., Fukuda, T., Miyamoto, T., Yamagata, K., and Watanabe, J., 1995, *Liq. Cryst.*, **19,** 441.
[20] Imrie, C. T., and Stewart, D., 1996, *Liq. Cryst.*, **20,** 619.
[21] Spes, P., Riepl, G., Haberle, N., Haas, W., Andrejewski, D., and Kreuzer, F. H., 1991, *Mol. Cryst. liq. Cryst.*, **199,** 345.
[22] Guillon, D., Skoulios, A., Ibn-Elhaj, M., Coles, H. J., Hodge, P., and Newton, J., 1995, *Liq. Cryst.*, **19,** 373.
[23] Moriya, K., Mizusaki, H., Kato, M., Yano, S., and Kajiwara, M., 1995, *Liq. Cryst.*, **18,** 795.
[24] Moriya, K., Nakagawa, S., Yano, S., and Kajiwara, M., 1995, *Liq. Cryst.*, **18,** 919.