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Discotic columnar liquid crystals in oligosaccharide derivatives III. Anomeric effects on the thermo-mesomorphic properties of cellobiose octa-alkanoates

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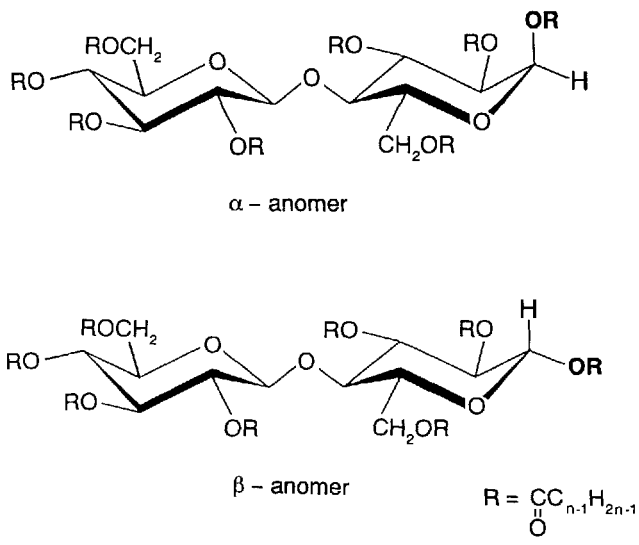
The α- and β-anomers of cellobiose octa-alkanoates with purities higher than about 95 per cent were prepared from β-cellobiose by two simple esterification methods. The carbon number *n* of the acyl substituents ranged from 7 to 10 in both anomers. Both α- and β-anomers exhibited two types of discotic columnar phases (D_{ho} and D_{ro}), depending on *n* and temperature, but their phase diagrams were appreciably different. Generally, the α-anomers formed more stable mesophases than the β-anomers. In the D_{ro} phase of the β-anomers, the column axis was tilted from the normal to the 'disks', while no such tilting was observed in the other phases.

1. Introduction

The derivatization of carbohydrates provides a vast source of thermotropic mesogens [1–3]. Those derivatives with one or a few alkyl substituents have an amphiphilic character with hydrogen-bonding ability and form, in most cases, layered [1–3], columnar [2, 3] or cubic [2] phases. The occurrence, type and stability of the mesophases are determined by the number, position, and stereochemical arrangement of the alkyl substituents and hydroxyl groups [3].

Fully substituted inositols [4–6] and cello-oligosaccharides [7–11], which apparently lack the hydrogen-bonding ability, are also known to function as discotic columnar mesogens. Molecular shape or configuration must play a key role in the structuring of these systems. In this regard, it is particularly interesting to study the effect of the stereochemical arrangement on the occurrence and stability of the mesophases of these compounds. Such a study on inositols has been reported by Kohne and Praefcke [6].

We have now examined fully alkanoated cellobiose, which has two stereoisomers at the anomeric carbon, i.e. the C-1 position at the reductive end unit—see the scheme. In previous papers [8, 9], we have dealt with mixtures of the α- and β-anomers of cellobiose octa-alkanoates with a β content of 50 to 80 per cent. In the present work, we have prepared nearly pure α- and β-anomers of the same compounds having various alkyl chain lengths, and studied the differences in their mesomorphic properties.



Cellobiose octaalkanoate

Scheme

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2. Experimental

2.1. *Materials*

β-Cellobiose (Nacalai Tesque, Inc.), trifluoroacetic anhydride (TFAA), alkanoic acids, and acid chlorides (Tokyo Kasei Kogyo Co., Ltd.) were used as received. ^{1}H NMR analysis showed that the β-cellobiose contained more than 97 per cent β-form. Chloroform and pyridine (Nacalai Tesque, Inc.) were distilled over calcium hydride prior to use.

2.2. *Synthesis of the α-anomers*

α-Cellobiose octa-alkanoates (the α-anomers) were synthesized by esterification of β-cellobiose according to the TFAA method [12, 13]: in a typical procedure, a mixture of alkanoic acid (0·187 mol, 8 eq. to the hydroxyl groups of cellobiose) and TFAA (14·7 g, 0·070 mol, 3 eq. to the hydroxyl groups) was activated at 100°C for 30 min; to this mixture, cellobiose (1·00 g, $2{\cdot}97 \times 10^{-3}$ mol) was added, allowing reaction to proceed at a *high* temperature of 100°C for about 6 h. After being cooled, the mixture was poured into a 10-fold excess of methanol with a small portion of water (< 1/10 part). The precipitate was filtered off and further purified by recrystallization more than three times from a tetrahydrofuran (THF)/MeOH mixture.

2.3. *Synthesis of the β-anomers*

The β-anomers were synthesized by the acid chloride method [14, 15] at a *low* temperature. To a suspension of β-cellobiose (1·00 g) at − 20°C in chloroform (40 ml) and pyridine (7·39 g, 0·094 mol), the acid chloride (0·070 mol) was added dropwise: if the acid chloride crystallized out, the system was warmed until the solid acid chloride disappeared. After this, the reaction mixture was kept at a temperature of 0°C or lower for over 24 h; it was then poured into a 10-fold excess of methanol with a small portion of water to recover the product as a precipitate. Purification was performed in the same way as for the α-anomers.

2.4. *Measurements*

Nuclear magnetic resonance (NMR) measurements were carried out on $CDCl_3$ solutions at 25°C using a JEOL GSX-400 (400 MHz) spectrometer. Chemical shifts were calibrated with tetramethyl silane (TMS) as standard. The calorimetric behaviour was investigated with a Rigaku Denki DSC-8230 calorimeter, at a scanning rate of 10°C min^{-1}. Polarizing microscopic observations were made with a Nikon Optiphot-Pol microscope equipped with a Mettler FP-82 hot stage and FP-80 temperature controller. X-ray diffraction patterns were recorded with a flat-plate camera using a Rigaku Denki X-ray generator with Ni-filtered CuK_α radiation. The sample was placed between thin pieces of glass and its temperature regulated by the Mettler hot stage and controller.

3. Results and discussion

3.1. *Sample characterization*

Acetylation of glucose to obtain α- and β-glucose penta-acetates [16–19] is typically referred to for the stereoselective esterification of cellobiose. However, these methods are not always suitable for the esterification of cellobiose with a long chain fatty acid, because of the low yield and low stereoselectivity. Therefore, we examined some other approaches and found the relatively simple methods to synthesize the α- and β-anomers from β-cellobiose, as described in § 2. These anomers will be denoted α-CB-*n* and β-CB-*n* (or simply α-*n* and β-*n*), respectively, where *n* refers to the total number of carbon atoms in the acyl side chain. The ^{1}H NMR spectra for α-CB-8 and β-CB-8 are shown in figures 1 (*a*) and (*b*), respectively. All the signals for ring protons were assigned as given in the figures by coupling the ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY measurements and referring to results reported for glucose derivatives such as α- and β-glucose

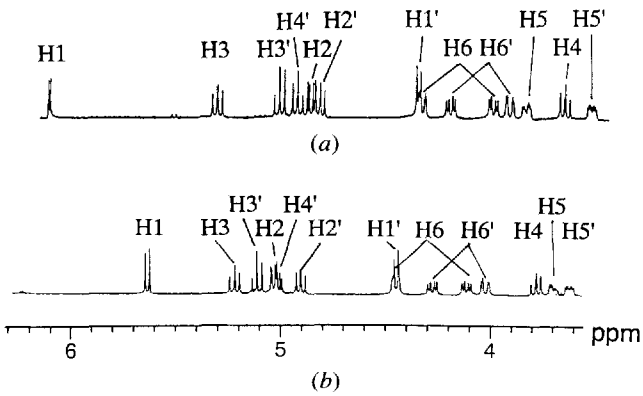
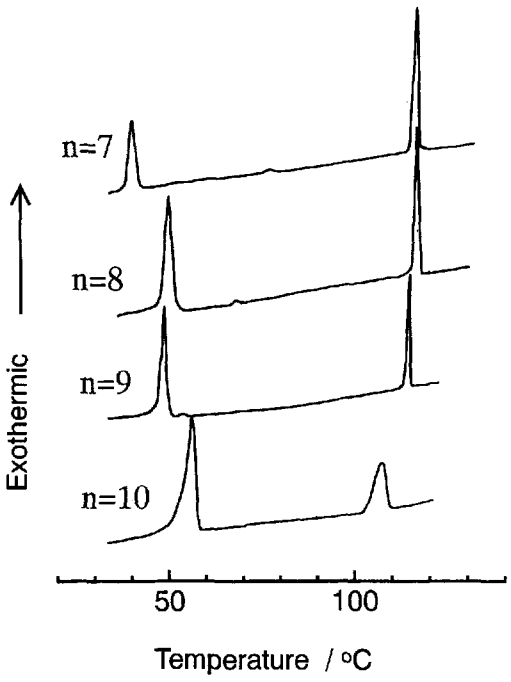


Figure 1. ^{1}H NMR spectra of cellobiose octa(decanoate)s: (*a*) α-anomer and (*b*) β-anomer.

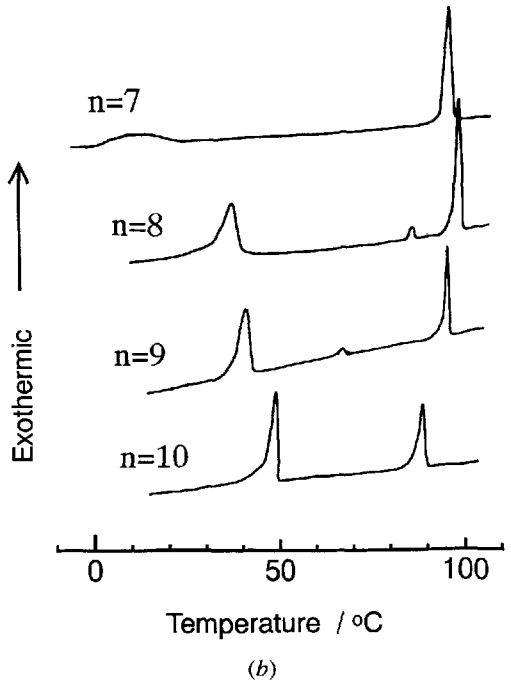
Table 1. Characterization of cellobiose octa-alkanoates.

Samples	MW	Elemental analysis/per cent found (calculated) C	H	α/β ratio
α-7	1239·57	66·1 (65·9)	9·57 (9·60)	95/5
α-8	1351·79	67·6 (67·5)	9·75 (9·99)	97/3
α-9	1464	69·3 (68·9)	10·3 (10·2)	97/3
α-10	1576·22	71·0 (70·1)	10·0 (10·6)	100/0
β-7	1239·57	66·5 (65·9)	9·52 (9·59)	7/93
β-8	1351·79	67·6 (67·5)	9·75 (9·99)	4/96
β-9	1464	69·5 (68·9)	10·0 (10·3)	0/100
β-10	1576·22	71·0 (70·1)	10·2 (10·6)	4/96

penta-alkanoate [20–22]. The signal for the anomeric proton appears at 6·26 ppm for the α-anomers, while it is observed at 5·55 ppm for the β-anomers. The anomeric content was thus determined from the relative intensities



(*a*)



(*b*)

Figure 2. DSC thermograms of (*a*) α- and (*b*) β-anomers of cellobiose octa-alkanoate recorded at a cooling rate of 10°C min^{-1}.

of these two characteristic signals. It is found that both the α- and β-anomers have a purity higher than 95 per cent (see table 1). As already noted, the β-anomers were prepared from β-cellobiose by using the low temperature acid chloride method. The anomerization reaction hardly occurred at the low temperatures applied (below or about 0°C). This is similar to the observation that α- and β-glucose penta-acetates can be quantitatively synthesized at 0°C with acetic anhydride starting with the α- and β-glucoses, respectively [19]. On the other hand, the α-anomer of high purity was obtained from β-cellobiose by the high-temperature TFAA method. This result compares interestingly with the results of Hudson *et al.* [23, 24], who showed that β-glucose penta-acetate can be perfectly converted to α-glucose penta-acetate at high temperatures in the presence of acetic anhydride and an acidic catalyst like zinc chloride or sulphuric acid. Although the reaction conditions are not exactly the same, their results suggest that in our system (with trifluoroacetic acid), the transformation from the β-anomer to the α-anomer proceeds after the esterification reaction.

3.2. *Thermotropic phase behaviour and mesophase structure*

As shown in figure 2, all the samples in both the α- and β-anomeric series give two *distinct* DSC peaks, which correspond to the melting temperature T_m and the isotropization temperature T_i. Between these temperatures there was observed a thermotropic mesophase. For samples with an acyl length $n = 7$ through 9, another *small* transition peak was observed between the two large peaks. The transition temperatures determined in the cooling mode are listed in table 2, and plotted against n in figure 3 (*a*) and (*b*) for the α- and β-anomers, respectively. The results reveal the existence of two mesophases, the higher temperature and lower temperature mesophases. The lower temperature mesophase is formed by those esters

Table 2. Phase transition temperautres and enthalpies (in parentheses), (ΔH/kJ mol^{-1}) for cellobiose octa-alkanoates; Cr = crystal; I = isotropic.

Samples	Cr		D_{ro}		D_{ho}		I
α-7	•	33 (18·58)	•	70 (0·377)	•	109 (25·49)	•
α-8	•	44 (30·01)	•	62 (0·548)	•	111 (29·13)	•
α-9	•	43 (41·02)	•	48 (0·243)	•	109 (24·65)	•
α-10	•	52 (43·99)		—	•	104 (22·43)	•
β-7	•	4 (19·13)	•	—		91 (12·14)	•
β-8	•	36 (19·88)	•	82 (1·306)	•	96 (11·09)	•
β-9	•	38 (28·04)	•	66 (3·470)	•	94 (14·40)	•
β-10	•	49 (36·46)		—	•	89 (14·82)	•

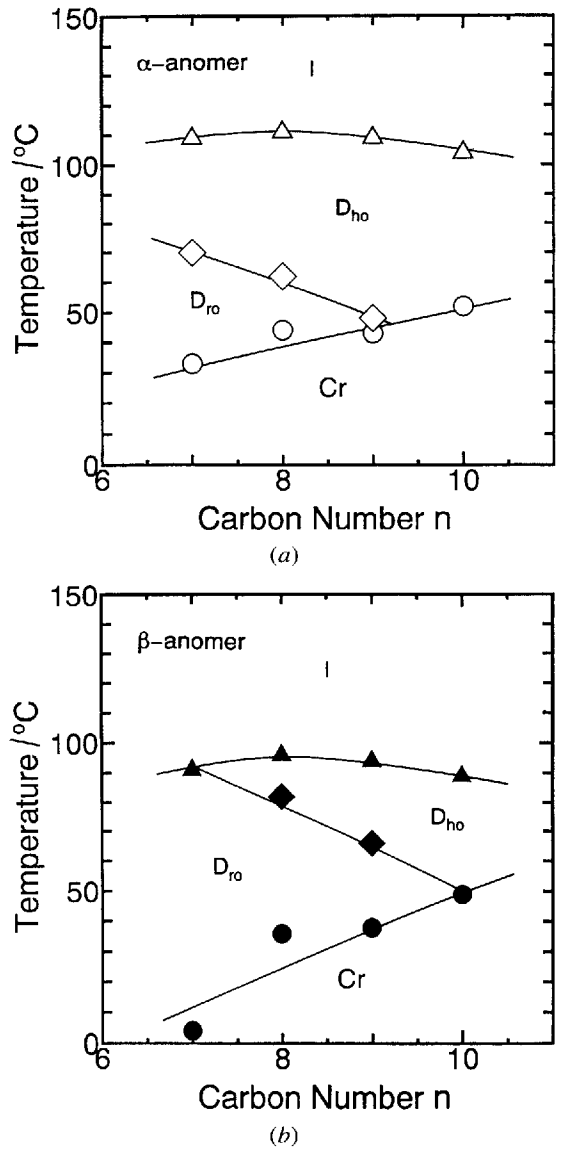


Figure 3. Variation of transition temperatures with n (total carbon number of the acyl group). The data are based on the DSC cooling thermograms: Cr = crystal; I = isotropic liquid.

with a side chain $n = 9$ or shorter in both series of anomers, but its temperature span is wider in the β-system than in the α-system.

3.2.1. *Higher temperature mesophase*

To examine the phase structures, we have analysed the X-ray diffraction patterns. Figure 4 (*a*) shows the X-ray pattern observed for the higher temperature phase of α-CB-10 oriented by shearing [9]. In the equatorial direction in a small angle region, three distinct reflections are observed, and their spacings, 20·9 Å, 12·1 Å and 10·47 Å, are in the ratios of $1:1/\sqrt{3}:1/2$, showing that there is a packing into a hexagonal lattice. In the meridional direction, a reflection is observed at a wide angle. This reflection has a spacing of 5·4 Å and can be assigned to a (0 0 1) reflection, showing that the cellobiose moieties are periodically stacked to form a column. These overall structural features are the same as those observed for the α/β mixtures in the previous papers [8, 9]. Thus, the higher temperature mesophase can be assigned as a hexagonally ordered columnar phase (D_{ho}). The structure of the D_{ho} phase is schematically illustrated in figure 5.

All the other specimens of both α- and β-types showed similar X-ray patterns for the higher temperature phase. The spacings of the equatorial and meridional reflections are listed in table 3, where we find the expected trend that the spacing, d_{100}, between neighbouring columns increases with increasingly acyl length n in both series, while the distance, d_{001}, between the discotic cellobiose cores in a column remains almost constant. By comparing the α- and β-anomers, however, we find that the d_{100}

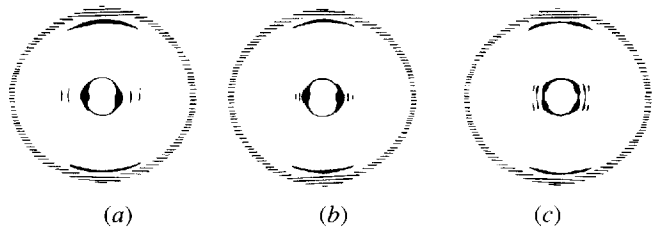


Figure 4. Schematic illustration of the X-ray diffraction patterns observed for oriented samples: (*a*) D_{ho} phase of α-anomers, (*b*) D_{ro} phase of α-anomers and (*c*) D_{ro} phase of β-anomers.

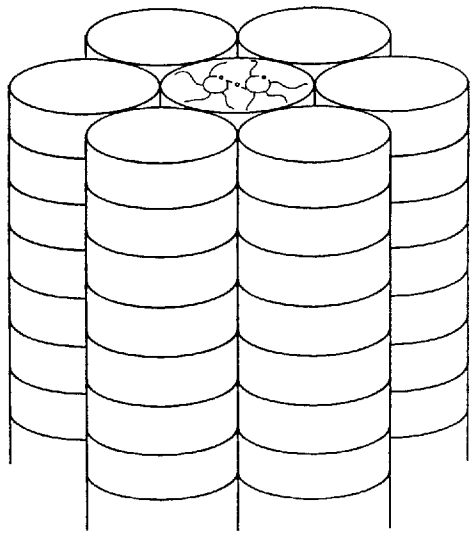


Figure 5. Schematic representation of the two-dimensional hexagonal packing of columns in the D_{ho} phase.

spacing is somewhat larger for the β-anomer than for the corresponding α-anomer, while the d_{001} spacing is shorter in the former than in the latter. This result seems to be consistent with the configurations of the two anomers: in the β-anomers, all the substituent groups take up an equatorial configuration, while in the α-anomers, the anomeric group is axial and this will lead to a smaller value of d_{100} and a larger value of d_{001} than in the β-anomers.

Table 3. X-ray data for D_{ho} phases (d/Å).

α-7, 100°C	α-8, 80°C	α-9, 100°C	α-10, 70°C
18·08 (100)	18·85 (100)	19·88 (100)	20·92 (100)
10·90 (110)	11·05 (110)	11·41 (110)	11·88 (110)
9·05 (200)	—	—	10·40 (200)
5·52 (001)	5·47 (001)	5·44 (001)	5·48 (001)
β-7	β-8, 92°C	β-9, 95°C	β-10, 80°C
No D_{ho} phase	18·98 (100)	20·17 (100)	21·05 (100)
	11·10 (110)	11·42 (110)	11·92 (110)
	—	10·20 (200)	10·42 (200)
	5·42 (001)	5·39 (001)	5·43 (001)

Table 4. X-ray data for D_{ro} phases (d/Å).

α-7, 65°C	α-8, 60°C	α-9, 50°C
17·93 (100)	18·85 (100)	19·83 (100)
15·31 (200)	15·79 (200)	16·45 (200)
11·74 (020)	12·43 (020)	13·28 (020)
5·44 (001)	5·45 (001)	5·44 (001)
β-7, 60°C	β-8, 70°C	β-9, 60°C
18·06 (100)	18·98 (100)	20·10 (100)
15·40 (200)	16·18 (200)	16·83 (200)
12·08 (020)	—	13·48 (020)
5·41 (001)	5·37 (001)	5·39 (001)

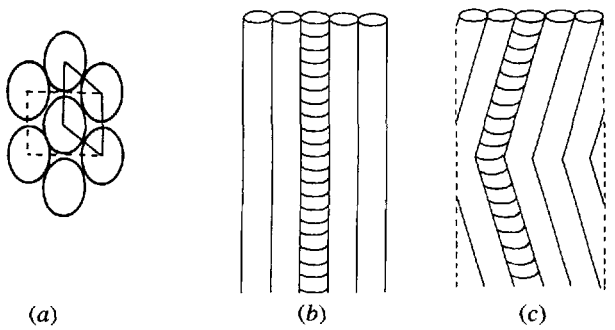


Figure 6. Schematic representations of the two dimensional rectangular packing of columns in the D_{ro} phase: (*a*) cross-section, (*b*) columns built up by the disks of the α-anomer and (*c*) of the β-anomer.

From the viewpoint of the shapes of discotic molecules, pyranose derivatives of an all-equatorial type are expected to form more stable mesophases than those with axial groups. Actually, fully substituted derivatives of *scyllo*-inositol, which are all-equatorial types of compound, form discotic mesophases, while the corresponding derivatives of *myo*-inositol, which has an axial group, form no mesophase [6]. Thus we had expected that the β-CB-*n* would form more stable mesophases than the α-counterparts. However, the facts show the reverse to be true: the T_is of the α-anomers are about 20°C higher than those of the β-equivalents (see figure 3), and the transition enthalpies for the α-anomers are about twice as large as those for the corresponding β-anomers (see table 2). This seems to indicate that the α-configuration produces a significant energetic effect favouring the columnar structuring of the alkanoates, but we are unable to give an interpretation of this at this time.

3.2.2. *Lower temperature mesophase*

In figures 4 (*b*) and (*c*) are shown the X-ray diffraction patterns observed for the oriented lower temperature mesophases. The spacings obtained from these patterns are listed in table 3, which immediately shows that the mesophases of the two anomers have the same structural features; the equatorial reflections can be assigned to a rectangular lattice, and the outer reflection with a spacing of around 5·4 Å indicates a regular packing of the cellobiose cores along the column. The overall features thus correspond to those observed for the lower temperature mesophase in the mixed system of α- and β-anomers [9], leading to the conclusion that the lower temperature mesophase of both α- and β-anomers can be assigned as a D_{ro} phase.

However, there are some differences between the D_{ro} phases of the α- and β-anomers. First, the spacings of the reflections are different (see table 4); the spacings of the equatorial reflection are somewhat larger for the β-anomers than for the α-anomers, while the reverse is true for the spacing of the meridional reflection. This trend is similar to that encountered with the higher temperature (D_{ho}) phase and can be interpreted similarly (see above). The most significant difference can be seen in the X-ray patterns of oriented samples. As found in figure 4 (*c*) for β-CB-8, the structural change from D_{ho} to D_{ro} is followed by a splitting of the reflections on both the equatorial and meditorial lines; the splitting angle observed from the lines is about 20°. In α-CB-8, however, the geometric profile is not changed at all before and after the transition (see figure 4 (*b*)). We thus conclude that the columns in the D_{ro} phase of the β-anomers are constructed by a tilted association of the cellobiose cores, while in the D_{ro} phase of the α-anomers, the cores are packed into a column with their

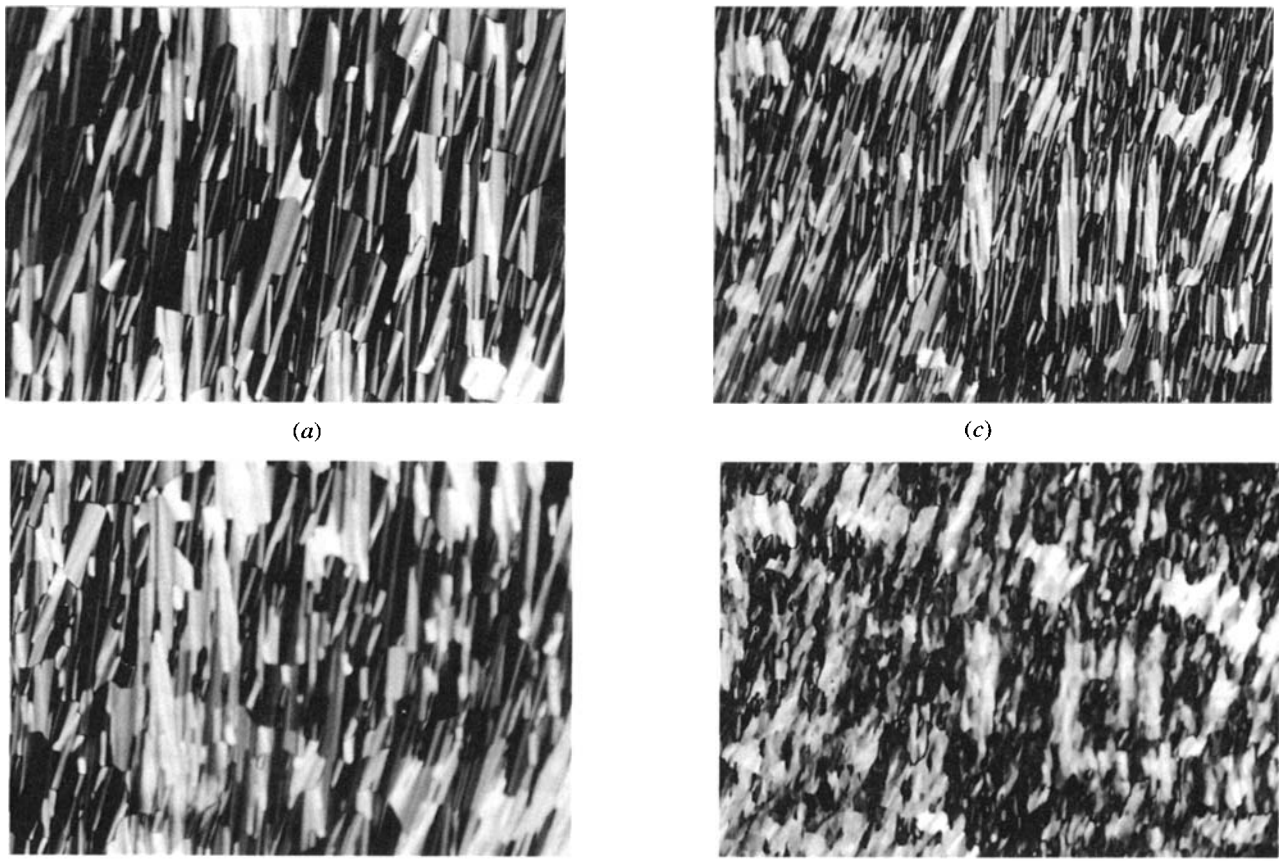
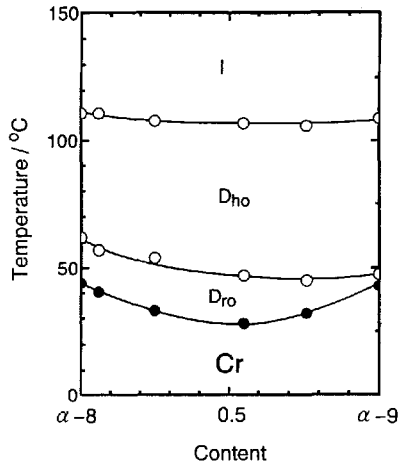


Figure 7. Optical textures of oriented samples: (*a*) α-CB-8 at 80°C, (*b*) α-CB-8 at 60°C, (*c*) β-CB-8 at 80°C, and (*d*) β-CB-8 at 50°C.

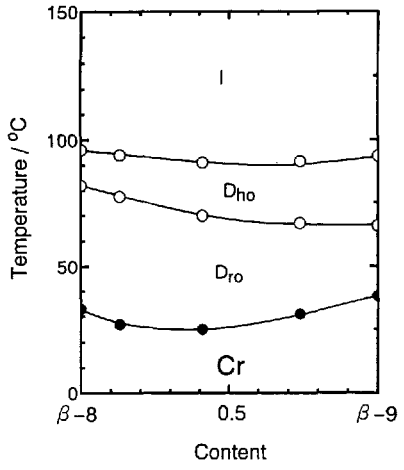
planes perpendicular to the column axis, as in the D_{ho} phases (see figure 6). Such a difference in the association of the cores is also reflected in the microscopic textures of the phases. As can be seen in figure 7, the texture of the β-anomers changes from a fan-shaped type to a broken fan-shaped type when the phase changes from D_{ho} to D_{ro}, while no such change is observed for the α-anomers.

3.3. *Miscibility studies*

A miscibility test provides a criterion of thermodynamic similarity of mesophases. Representative results of miscibility tests are shown in figures 8 and 9. Figures 8 (*a*) and (*b*) show the diagrams of state for mixtures of α-CB-8 and α-CB-9, and of β-CB-8 and β-CB-9, respectively. All three transition temperatures in both figures 8 (*a*) and (*b*) fall on smooth curves over the whole region of composition. Thus the miscibility between the same types of anomers is perfectly attained in the D_{ro} phase as well as in the D_{ho} phase. On the other hand, figure 9 shows the diagrams of state for three mixtures of the α- and β-anomers with the same acyl length. The transition behaviours appear different in some aspects from those observed in figure 8. Both the T_i and T_m of the mixtures form a gently changing curve over the whole range of composition, but the D_{ho} to D_{ro} transition temperatures T_{hr} of the pure anomers steeply drop on mixing a small amount of the other component. As a result, for α-CB-9 and β-CB-9 system, the D_{ro} phase disappears for intermediate mixing ratios (see figure 9 (*b*)). The system of α-CB-7 and β-CB-7 in figure 9 (*a*) also shows a steep drop of T_{hr}, but the D_{ro} phase can be observed over the whole range of composition, showing that the α- and β-anomers are essentially miscible in the D_{ro} phase too. We thus conclude that the D_{ro} phase, as well as the D_{ho} phase formed by the α and β-anomers are of the same type in a thermodynamic sense, although the thermal stability of the D_{ro} phase is remarkably decreased by mixing two anomers of different types.

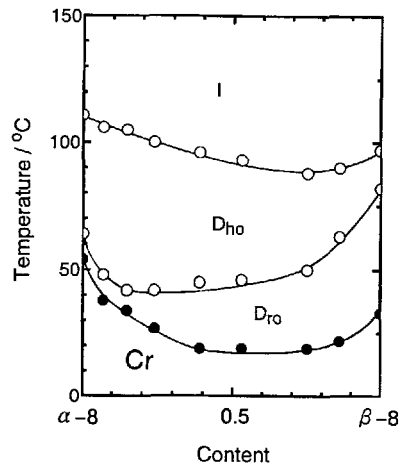


(a)



(b)

Figure 8. Diagrams of state for mixtures of the same types of anomer with different acyl lengths: (*a*) α-CB-8 plus α-CB-9 and, (*b*) β-CB-8 plus β-CB-9; Cr = crystal; I = isotropic liquid.



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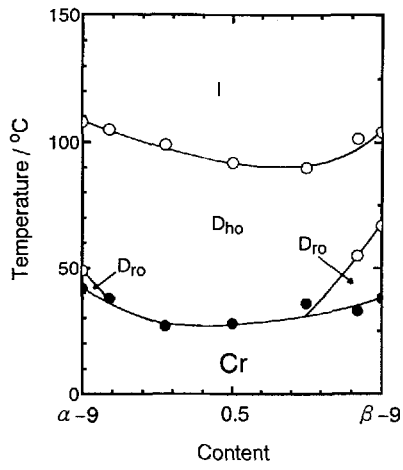

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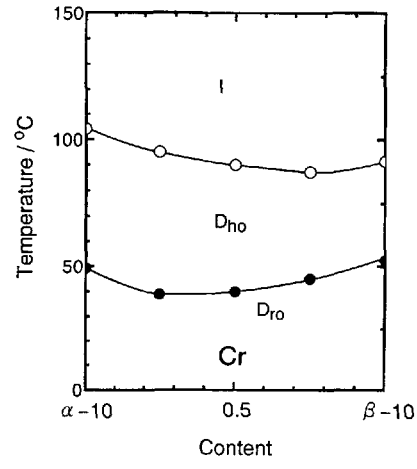

(c)

Figure 9. Diagrams of state for mixtures of different types of anomer with the same acyl length: (*a*) α-CB-8 plus β-CB-8, (*b*) α-CB-9 plus β-CB-9, and (*c*) α-CB-10 plus β-CB-10; Cr = crystal; I = isotropic liquid.

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