

D-XYLOSE DERIVATIVE LIQUID CRYSTALS

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(Received February 21, 2000; in revised form July 15, 2000)

Abstract

We studied the phase transition temperatures of a series of amphiphilic *D*-xylopyranose and *D*-xylofuranose derivatives in which the lipophilic part is an alkyl chain $R(n-C_nH_{2n+1})$, regiospecifically linked to *D*-xylose, at different positions, by *Z* which is an atom or a functional group (O, S, O-(CH₂)₃-S). The alkyl chain was moved from the C-1 to the C-5 position in the xylose moiety, thereby allowing us to compare directly the phase transition temperatures of the individual materials. These compounds give thermotropic and/or lyotropic liquid crystals. In some cases, we also observed solid–solid phase transitions.

Keywords: amphiphile, DSC, *D*-xylose derivatives, lyotropy, thermotropy

Introduction

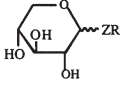
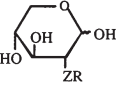
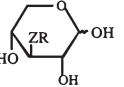
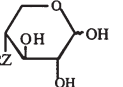
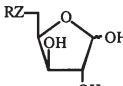
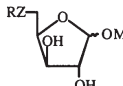
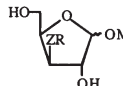
In 1983 Jeffrey and Bhattacharjee [1] showed that *n*-alkyl glucopyranosides exhibit thermotropic liquid crystalline properties. Subsequently, many studies were performed on liquid crystalline carbohydrates and related materials. The majority of the undertaken studies involved the investigation of substituted cyclic furanose and pyranose systems. However, no results have been reported involving *D*-xylose. Thus, this work is concerned with a systematic investigation of the effects of the linking group *Z*, alkyl chain length and its position, on liquid crystalline properties of *D*-xylose derivatives. For this purpose we have selected to study the mesomorphic behaviour of alkyl substituted *D*-xylose where the aliphatic chain is attached to the *D*-xylose moiety via either an ether or a thioether linkage.

Materials and methods

Synthesis

The *D*-xylose amphiphilic derivatives *x*-ZR-*D*-xylose (Table 1) in which *R* is an alkyl chain linked to the *D*-xylose moiety at the *x* position (C-1 to C-5) by $Z=O, S, O-(CH_2)_3-S$, were described previously [2, 3].

Table 1 Studied *D*-xylose derivatives, 1–7

<i>D</i> -xylopyranose				
	1	2	3	4
<i>D</i> -xylofuranose				
	5	6	7	
<i>ZR</i>	<i>n</i>			
<i>O</i> - <i>n</i> -C _n H _{2n+1}	a – 8	b – 12	c – 16	
<i>S</i> - <i>n</i> -C _n H _{2n+1}	a' – 8	b' – 12	c' – 16	d' – 18
<i>O</i> -(CH ₂) ₃ - <i>S</i> - <i>n</i> -C _n H _{2n+1}	a'' – 8	b'' – 12	c'' – 16	

General methods

Phase transition temperatures were determined by DSC using Mettler FP85 furnace and/or by thermal polarized light microscopy using Olympus BX50 polarizing transmitted light equipped with a Mettler FP82 microfurnace. Both Mettler apparatus were recorded to an FP90 central processor. For thermotropic liquid crystals, transition temperatures, noted M_p (solid→liquid crystal) and C_p (liquid crystal→isotropic liquid) are T_{onset} measured at different scanning rates by DSC. For lyotropic liquid crystals, transition temperatures, noted T_1 (liquid crystal apparition) and T_2 (liquid crystal disappearance) are determined by simply allowing crystals of the test material to dissolve in water, thereby creating a concentration gradient which supports mesophases formation. Since we observed close T_1 and T_2 values with both water and ethylene glycol, this was used when $T_1, T_2 > 90^\circ\text{C}$, to eliminate erroneous data due to water evaporation.

Results and discussion





Tables 2 and 3 give the phase transition temperatures corresponding to both thermotropic liquid crystals and lyotropic liquid crystals; in some cases phase transition temperatures solid–solid ($S_1 \rightarrow S_2$) were observed.

Thermotropic liquid crystals

All the studied compounds gave thermotropic liquid crystals (smectic A) except the 3-*Z*-alkyl-*D*-xylopyranose derivatives (type 3 compounds) and some compounds with short alkyl chain (**1b**, **6b**, **6a'**, **6b'**). Moreover, we observed that phase transition temperatures grow either by increasing alkyl chain length (the discrepancy observed




with compound **1b** can be explained by its α configuration) or by changing the Z junction in the order O-(CH₂)₃-S<O<S (Table 3; **5a''**, **5a**, **5a'**); similar effects are observed with a large range of 1-Z-alkyl-DL-xylitol derivatives [4].

Table 2 Phase transition temperature (°C) and enthalpies (kJ mol⁻¹) of *x*-Z-alkyl-D-xylopyranose

Product	ZR	α/β	$S_1 \rightarrow S_2$ (ΔH)	Thermotropy		
				M_p	ΔH	C_p
	OC ₈ H ₁₇	1a	β	67.1	23.84	99.8
	OC ₁₂ H ₂₅	1b	α	65.1 ^a	38.85	
	OC ₈ H ₁₇	2a	1:1	62.8 (7.45)	73.0	27.52
	OC ₁₂ H ₂₅	2b	1:1	52.5 (9.59)	76.4	16.05
	OC ₈ H ₁₇	3a	β	93.6 ^a	30.46	
	OC ₁₂ H ₂₅	3b	β	100.9 ^a	35.39	
	OC ₁₆ H ₃₃	3c	β	102.8 ^a	36.16	
	SC ₈ H ₁₇	3a'	7:3	71.8 ^a	17.30	
	OC ₈ H ₁₇	4a	α	83.5	25.05	118.0
	OC ₁₂ H ₂₅	4b	α	95.5	38.25	124.0

^ano thermotropic liquid crystals

Table 3 Phase transition temperature (°C) and enthalpies (kJ mol⁻¹) of *x*-Z-alkyl-D-xylofuranose

Product	ZR	α/β	$S_1 \rightarrow S_2$ (ΔH)	Thermotropy		
				M_p	ΔH	
	OC ₈ H ₁₇	5a	1:1	28.8 (5.91)	64.4	24.12
	OC ₁₂ H ₂₅	5b	2:3		69.8	34.10
	SC ₈ H ₁₇	5a'	1:1	29.2 (8.99)	104.0	25.14
	SC ₁₂ H ₂₅	5b'	1:1	47.5 (4.03)	92.6	17.04
	SC ₁₆ H ₃₃	5c'	1:1		98.2	43.82
	O(CH ₂) ₃ SC ₈ H ₁₇	5a''	3:2		<10	
	O(CH ₂) ₃ SC ₁₆ H ₃₃	5c''	1:1		67.2	58.33
	OC ₁₂ H ₂₅	6b	2:3		10.8 ^a	31.05
	SC ₈ H ₁₇	6a'	β		<10 ^a	
	SC ₁₂ H ₂₅	6b'	β		39.5 ^a	15.03
	SC ₁₈ H ₃₇	6d'	β		53.8	8.21
	OC ₁₂ H ₂₅	7b	β		<10	

^ano thermotropic liquid crystals

We also observed that xylofuranose derivatives (type 5) have higher melting point temperatures (M_p) than corresponding methyl xylofuranosides (type 6 and 7). This suggests that M_p values increase in parallel to the OH group number. However,

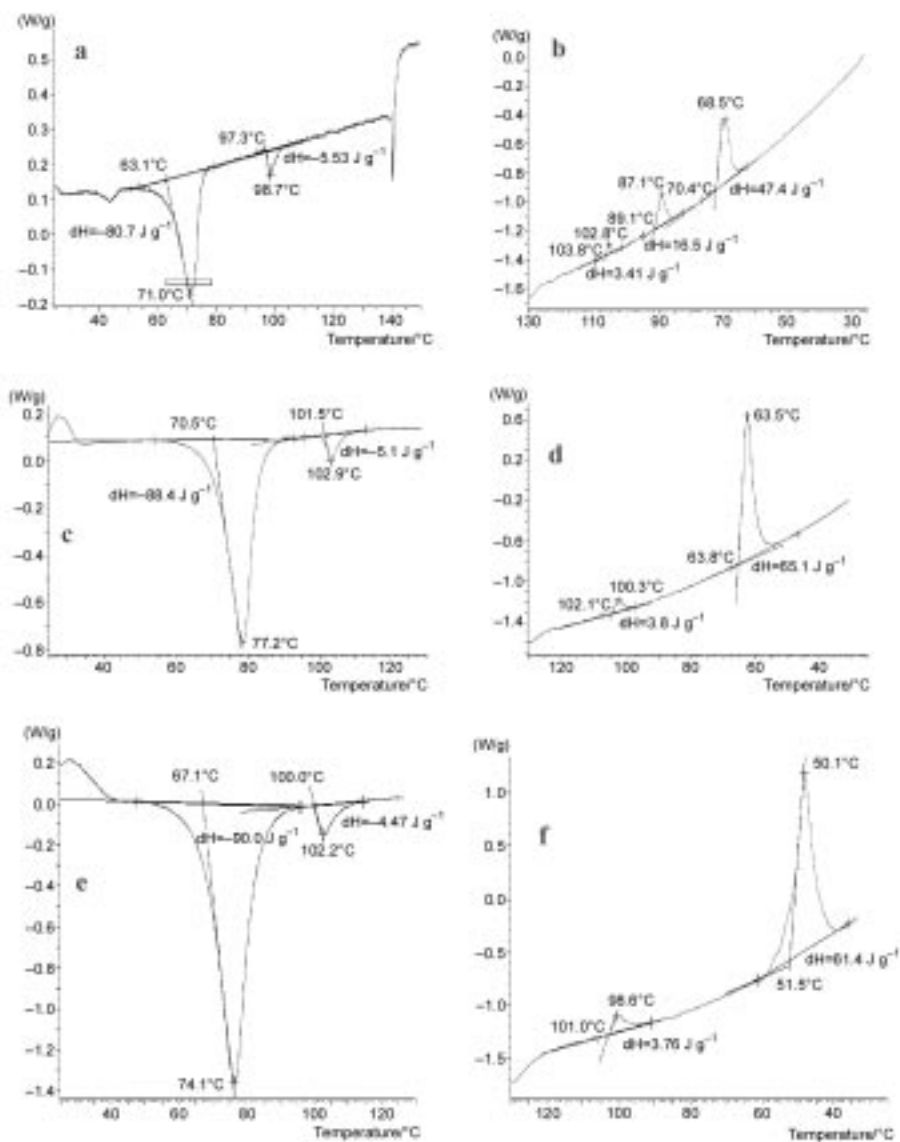


Fig. 1 DSC curves of the octyl β -*D*-xylopyranoside (**1a**) at different heating and cooling rates. a – $2.0^{\circ}\text{C min}^{-1}$, 6.40 mg; b – cooling rate $2.0^{\circ}\text{C min}^{-1}$, 11.80 mg; c – $5.0^{\circ}\text{C min}^{-1}$, 10.60 mg; d – cooling rate $5.0^{\circ}\text{C min}^{-1}$, 10.60 mg; e – $10.0^{\circ}\text{C min}^{-1}$, 9.50 mg; f – cooling rate $10.0^{\circ}\text{C min}^{-1}$, 9.50 mg;

this number is not the preponderant factor to obtain liquid crystals since methyl 3-O-dodecyl- β -D-xylofuranoside (**7b**) gives thermotropic liquid crystal but not the corresponding xylofuranose derivative **6b**. In contrast the ZR group position in the D-xylose ring affects strongly the phase transition temperatures. Thus by changing the ZR position from C-1 to C-5, clearance temperatures (C_p) increase in the order $T_{C-2} \approx T_{C-5} < T_{C-1} < T_{C-4}$, whereas when ZR is at C-3 (type **3** compounds), any derivative showed thermotropic liquid crystals. This structural effect should be examined in relation to both the OH group relative orientation and the α or β xylose configuration.

Table 4 M_p , C_p temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) of the octyl β -D-xylopyranoside (**1a**) measured at different scanning rates

Scanning rate/ $^{\circ}\text{C min}^{-1}$	Heating				Cooling			
	M_p	ΔH	C_p	ΔH	M_p	ΔH	C_p	ΔH
2	64.8	25.25	96.9	1.39	70.6	12.40	103.8	1.07
5	70.2	23.32	100.9	1.22	63.8	16.97	101.9	0.92
10	67.1	23.84	99.8	1.23	50.6	15.82	100.4	1.05
20	72.8	16.37	101.2	0.69	50.5	–	99.7	0.79

Table 4 reports the scanning rate influence on the thermotropic phase transitions temperatures for the octyl β -D-xylopyranoside (**1a**). Both slow and fast heating or cooling rates have some inconvenience. Slow rate ($<2^{\circ}\text{C min}^{-1}$) gives well-separated peaks, but they have a large base, little height and a bad baseline. These inconveniences disappear by increasing the heating or cooling rate from 2 to $10^{\circ}\text{C min}^{-1}$ (Fig. 1). In contrast, the diagram analysis is fastidious by heating or cooling at $20^{\circ}\text{C min}^{-1}$ as shown in Fig. 2 (bad baseline and overlapped peaks). Moreover, we

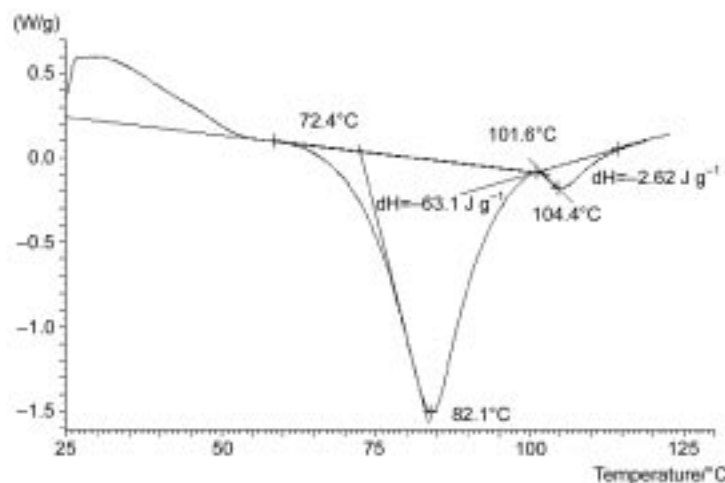


Fig. 2 DSC curve of the octyl β -D-xylopyranoside (**1a**) at $20^{\circ}\text{C min}^{-1}$ heating rate, sample mass 7.40 mg

can observe that the cooling rate strongly affects the melting point temperatures while the heating rate has no significant effect.

Lytotropic liquid crystals

All the studied compounds show lyotropic liquid crystal properties except **6b** (Table 3). It must be noted that the observations were made at atmospheric pressure between slide and cover slide with unknown water concentrations, thus we always observed lamellar lyotropic liquid crystals.

The alkyl chain length and *Z* linkage have the same influence on phase transition temperatures as it is observed in thermotropic transitions. It is impossible to compare the *ZR* position influence on isotropization temperatures (T_2) since precise T_2 values higher than 96°C are not available due to the experimental method (no sealed cells). Nevertheless, we observe that lyotropic phase appearance temperatures (T_1) increase, for $ZR=O-n-C_8H_{17}$, in the order $T_{C-2} < T_{C-3} < T_{C-4} \approx T_{C-5} \approx T_{C-1}$.

Conclusions

This preliminary study of *x-Z*-alkyl-*D*-xylose derivatives shows that there are potentialities in the field of liquid crystals. The influence of structural parameters examined so far suggests that this compound range should be further extended and molecular simulation studies should be developed with view to rationalize the liquid crystalline properties. We also anticipate that more interesting results will be obtained on lyotropic mesophases at controlled water concentrations (in high pressure cells).

References

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