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DSC studies on *p*-(*n*-alkyl)-*p*′-cyanobiphenyl (RCB's) and *p*-(*n*-alkoxy)-*p*′-cyanobiphenyl (ROCB's) liquid crystals

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Abstract

Solidification (supercooled nematic-to-solid or supercooled smectic-*A*-to-solid), melting (solid-to-nematic or solid-to-smectic-*A*), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transition temperatures ϑ_s, ϑ_m, ϑ_{AN}, and ϑ_c, respectively, and enthalpies ΔH_s, ΔH_m, ΔH_{AN}, and ΔH_c, respectively, have been determined by differential scanning calorimetry (DSC) for members of the *p*-(*n*-alkyl)-*p*′-cyanobiphenyl (RCB) and the *p*-(*n*-alkoxy)-*p*′-cyanobiphenyl (ROCB) homologous series of liquid crystals, where '*R*' is the number of carbon atoms in the *n*-alkyl or *n*-alkyloxy tails. The study shows that the transition of the less ordered nematic phase to the more ordered smectic-*A* phase, in liquid crystals that exhibit both phases (those with R=8 or 9), involves a transient phase of intermediate order. Broad or overlapping solidification exotherms indicate that two mesogenic aggregations supercool simultaneously. Finally, there is evidence for a transition between two solid forms that occurs at temperatures preceding ϑ_m or concurrent with it depending on '*R*' and the heating rate. This refutes an earlier view that during melting the solid form with the higher melting point solidifies. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Liquid crystals; Phase transitions; Transition temperatures; Transition enthalpies

1. Introduction

The low melting points, chemical and photochemical stability, and electro-optical properties [1,2] of the nematogenic homologous series *p*-(*n*-alkyl)-*p*′-cyanobiphenyls (RCB, Scheme 1, A) and *p*-(*n*-alkoxy)-*p*′-cyanobiphenyls (ROCB, Scheme 1, B); where *R* is the number of carbons in the *n*-alkyl or *n*-alkyloxy tails, make them suited for use as components for devices based on the twisted nematic or phase change effects and mixtures of them have been used in liquid crystal displays (LCD) [3].

From a thermodynamic point of view these liquid crystals are enantiotropic [4,5] with mesophases that are thermodynamically stable with respect to both the isotropic and crystalline phases, within the temperature range from the melting point, ϑ_m, to the clearing point temperature, ϑ_c.

Since the synthesis and characterization [1,6] of the RCB and ROCB series of liquid crystals several studies were carried out. BDH Chemicals [7] reported the electro-optical properties of these liquid crystals, their melting and clearing temperatures (obtained using a polarizing microscope), and their enthalpies of melting (using differential scanning calorimetry,

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A B

Scheme 1.

(DSC)). Coles and Strazielle [8] reported enthalpies of melting and mesophase-isotropic transitions for the RCB series. Several researchers [9–11] report the transition enthalpies for 8CB from DSC studies. Marynissen et al. [12] also report transition enthalpies for 8CB, 9CB, 10CB, and 11CB using an adiabatic scanning calorimeter. ΔH_{AN} was determined for 8OCB from DSC [13–15] and ac calorimeteric [15] measurements. The RCB and ROCB series of liquid crystals were also studied by Gray et al. [6]. Their observations of these systems under a polarizing microscope show that once melted, solidified, then reheated most of these liquid crystals start to melt at a temperature lower than the initial melting temperature but during the melting process the more stable solid form with the higher melting point forms.

Knowledge of the nematic-to-isotropic transition temperature and transition enthalpy of a pure liquid crystal and the infinite dilution activity coefficients of a dissolved solute in its nematic and isotropic phases allow an estimate of the effect of the solute on its nematic-to-isotropic transition temperature and on the creation of a region where the nematic and isotropic phases coexist [16]. Additives are intentionally added to modify the viscosity and electro-optical properties of liquid crystals used in LCD's. Accurate measurements of transition temperatures and enthalpies of liquid crystals are needed to assess the effect of these additives.

Electron paramagnetic resonance (EPR) [17,18] and differential scanning calorimetric (DSC) [18] studies on 6CB and the enantiotropic *n*-hexyl (6CBz) and *n*-heptyl (7CBz) members of *p*-cyanophenyl *p*-(*n*-alkyl)benzoate homologous series of liquid crystals indicate that they exhibit polymorphism in the solid state. Exotherms observed in the heating curves show that transformations between various solid forms occur before reaching the most stable form that, on further heating, melts at a reproducible melting point that is independent of the heating rate. Recent DSC [19] measurements on 2CBz, 3CBz, 4CBz, and 5CBz, the monotropic members of the RCBz series, give similar results. Exotherms appearing in heating curves prior to melting with onset temperatures that are dependent on the heating rate reflect solid–solid transformations that involve conformational changes at the molecular level.

In this study DSC measurements were carried out on members of the RCB and ROCB homologous series of liquid crystals. Heating and cooling cycles were carried out at different rates between temperatures above their clearing temperatures, ϑ_c, and -30°C using a Perkin–Elmer DSC-4 unit equipped with a Data acquisition and analysis station. The study revealed that for $R=8$ and $R=9$ members of the RCB and ROCB series a transient phase intermediate between the smectic-*A* and nematic phases appears. The study also revealed that the RCB and ROCB homologues exhibit polymorphism in the solid state but to a weaker extent relative to the corresponding members from the RCBz series [19]. These solid–solid modifications seem to involve conformational changes on heating. This transition between solid forms has been mistaken [6] for the formation of a solid with a higher melting point during the melting of another solid with a lower melting point.

2. Experimental

2.1. Materials

The members of the RCB and ROCB homologous series of liquid crystals were obtained from Merck Industrial Chemicals and used as supplied. Cyclohexane and octadecane from Fluka (both puriss grade) were used as supplied to calibrate the DSC unit.

2.2. Differential scanning calorimetry (DSC)

The thermal properties of the members of the RCB and ROCB series were studied using a Perkin–Elmer differential scanning calorimeter (DSC-4). Indium was used to calibrate the DSC unit for temperature and energy. In accordance with the procedure recommended by the Perkin–Elmer company when liquid nitrogen is used as coolant, high purity cyclohexane was used to calibrate the temperature axis. The onset of melting for cyclohexane was 6.84°C, which compares well with the literature value of 6.54°C. Additionally, since our measurements extended beyond the ambient temperature, octadecane was used to double check the temperature calibration by cyclohexane. Its onset of melting was at 28.38°C and the enthalpy of melting was 232.80 J/g, which also compared well with the respective literature values of 28.24°C and 241.4 J/g. All the calibration runs were carried out at a heating rate of 10°C/min and at which, according to the Perkin–Elmer users manual, $T_{\mathrm{true}}=T_{\mathrm{observerd}}$. The masses of the liquid crystal samples as well as compounds used for temperature and energy calibrations were between 4.30 and 7.70±0.01 mg.

Prior to the DSC runs each sample was heated to about 10°C above its reported [7] clearing point and held at that temperature for about 2–3 min to be sure of its complete transformation to the isotropic phase. A cooling curve was recorded at a rate of 10°C/min between this temperature and −30°C. Since earlier studies [18,19] showed that the solidification temperature of similar liquid crystals (the RCBz's) is rate dependent, more heating and cooling runs were carried out at a rate of 5°C/min. The appearance of an exothermic peak in the initial stages of the onset of melting in 7OCB, 8OCB, 9OCB, and 10OCB combined with earlier experience [18,19] (again with the RCBz's) that the temperatures at which such peaks appear are strongly dependent on the heating rate, led us to run these samples again at 2°C/min or lower.

3. Results and discussion

Solidification (supercooled nematic-to-solid or supercooled smectic-*A*-to-solid), melting (solid-to-nematic or solid-to-smectic-*A*), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transition temperatures, ϑ_{s}, ϑ_{m}, ϑ_{AN}, and ϑ_{c} respectively, and enthalpies, ΔH_{s}, ΔH_{m}, ΔH_{AN}, and ΔH_{c}, respectively, are given for members of the RCB and ROCB homologous series of liquid crystals in Tables 1 and 2, respectively. Wherever possible, results from earlier studies are incorporated within Tables 1 and 2. The values from this study in Tables 1 and 2 represent averages of a cooling run at 10°C/min (the rate used in the temperature calibration) and cooling and heating runs at 5 and occasionally at 2°C/min (see Tables 3 and 4). The transition temperature shifts for the heating and cooling runs at rates other than 10°C/min were generally in the expected opposite directions and were assumed self-canceling.

Fig. 1(A,B) gives the cooling curves for representative members of the RCB (7CB, 8CB, 9CB, and 10CB) and ROCB (7OCB, 8OCB, 9OCB, and 10OCB) homologous series of liquid crystals, respectively. The cooling curves of 6CB, 11CB, and 12CB are respectively similar to those for 7CB, 9CB, and 10CB. The cooling and heating curves for 5CB are somewhat more complex and are excluded from parts A of Figs. 1 and 2, respectively. The cooling curves for 5OCB and 6OCB are similar to those for 7OCB, while the cooling curves for 11OCB and 12OCB are similar to those for 9OCB and 10OCB, respectively.

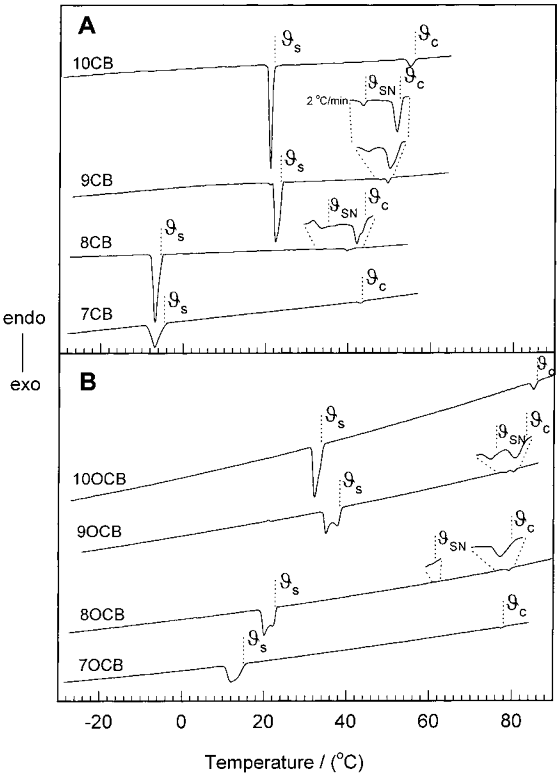

Fig. 1. DSC cooling curves for representative members of the (A) RCB and (B) ROCB series of liquid crystals at a rate of 5°C/min. The vertical dotted lines indicate the onset of the solidification (supercooled nematic-to-solid or supercooled smectic-*A*-to-solid), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transition temperatures ϑ_{s}, ϑ_{SN}, and ϑ_{c}, respectively. The magnification for the insets is five-times that of the original curves.

Table 1
Transition temperatures (ϑ in °C) and enthalpies (ΔH in kJ/mol) for the RCB liquid crystals. The subscripts s, m, AN and c refer, respectively, to solidification (nematic-to-solid or smectic-*A*-to-solid), melting (solid-to-nematic or solid-to-smectic-A), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transitions

Liquid crystal	ϑ_{ss}	ΔH_s	ϑ_m		ΔH_{mo}		ϑ_{AN}		ΔH_{AN}		ϑ_c		ΔH_c	
			Other studies	This study	Other studies	This study	Other studies	This study[f]	Other studies	This study[f]	Other studies	This study	Other studies	This study
5CB	−11.41	−3.81	24[a]	14.72	17.15[a]	15.95	–	–	–	–	35[a]	33.70	–	0.54
			22.5[b]		17.15[b]						35[b]		–	
			24[c]		13.39[c]						34.3[c]		0.33[c]	
6CB	6.08	−16.36	14.5[a]	13.34	24.27[a]	16.53	–	–	–	–	29[a]	28.02	–	0.50
			13.5[b]		24.27[b]						27[b]		–	
			14.4[c]		20.92[c]						30.1[c]		0.29[c]	
7CB	−6.27	−19.62	30[a]	29.81	25.94[a]	28.49	–	–	–	–	42.8[a]	42.37	–	0.75
			28.5[b]		25.94[b]						42[b]		–	
			30.3[c]		25.52[c]						42.6[c]		0.63[c]	
8CB	−6.31	−24.14	21.5[a]	19.74	22.18[a]	29.16	33.5[a]	33.09	–	0.08	40.5[a]	39.23	–	0.88
			21[b]		22.18[b]		32.5[b]		–		40[b]		–	
			21.5[c]		23.43[c]		33.7[c]		0.04[c]		40.2[c]		0.67[c]	
			24[d]		25.3[d]		34[d]		0.13[d]		42.6[d]		0.971[d]	
					25.3[d]				0.13[d]				0.879[d]	
									0.20[d]				0.70[d]	
			22[e]		25.7[e]		33.7		$\leq 4\times10^{-4}$[e]		40.8[e]		0.612[e]	
9CB	20.87	−32.93	42[a]	41.15	33.47[a]	37.57	48[a]	47.15	–	≈0.29[g]	49.5[a]	48.90	–	≈1.44[g]
			40.5[b]		33.47[b]		44.5[b]		–		47.5[b]		–	
			42.2[c]		30.96[c]		48.3[c]		0.25[c]		49.2[c]		1.00[c]	
			42.6[e]		34.5[e]		47.6[e]		$\leq 5\times10^{-3}$[e]		49.6[e]		1.00[c]	
10CB	21.15	−29.71	44[a]	47.72	23.73[a]	37.87	–	–	–	–	50.5[a]	54.63	–	3.05
			44.2[c]		33.47[c]						50.5[c]		2.68[c]	
			44.4[e]		36.0[e]						51.1[e]		2.83[e]	
11CB	21.49	−39.99	53[a]	52.07	–	46.82	57[a,i]	–	–	–	57.5[a]	56.08	–	4.18
			53.1[c]		38.07[c]		57.6[c,i]		–[h]		59.0[c]		3.39[c,h]	
			53.1[e]		43.2[e]						56.9[e]		3.8[e]	
12CB	26.95	−37.91	48[a]	45.71	55.23[a]	39.71	–	–	–	–	58.5[a]	58.33	–	4.77
			48.3[c]		33.47[c]						58.2[c]		4.06[c]	

[a] [7].
[b] [6].
[c] [8].
[d] [9–11].
[e] [12].
[f] 5CB, 6CB, and 7CB do not show a smectic-*A* phase, while 10CB, 11CB and 12CB do not show a nematic phase.
[g] See footnote to Table 3.
[h] Ref. [8] gives $\Delta H_{\text{S-N-I}}$ for $\Delta H_{\text{S-N}}+\Delta H_{\text{N-I}}$.
[i] This study and the work of Marynissen et al. [12] show that no nematic phase intervenes between the smectic-A and isotropic phase of 11CB. According to [12] BDH [7] have later confirmed that high purity 11CB does not show a nematic phase.

The RCB and ROCB homologues with $R\leq 7$ do not show a smectic-*A* phase [6–8] and the homologues with $R\geq 10$ do not show a nematic phase. These finding agree with earlier studies [6,8,12] and refute earlier reports [7,8] of a narrow nematic phase for 11CB. Homologues with $R\leq 7$ have low ΔH_c values (averaging 0.56 kJ/mol) that reflect isotropic-to-nematic transitions while homologues with $R\geq 10$ have much higher ΔH_c values (averaging 4.00 kJ/mol) that reflect isotropic-to-smectic-*A* transitions. The homologues with the $R=8$ and $R=9$ values show nematic and smectic-*A* phases. The transitions between these phases are less straightforward than the previously reported [6–8,12] separated isotropic-

Table 2
Transition temperatures (ϑ in °C) and enthalpies (ΔH in kJ/mol) for the ROCB liquid crystals. The subscripts s, m, AN and c refer, respectively, to solidification (nematic-to-solid or smectic-*A*-to-solid), melting (solid-to-nematic or solid-to-smectic-*A*), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transitions

Liquid Crystal	ϑ_s	ΔH_s	ϑ_m		ΔH_m		ϑ_{AN}		ΔH_{AN}		ϑ_c		ΔH_c	
			Other studies	This study	Other studies	This study	Other studies	This study[d]	Other studies	This study[d]	Other studies	This study	Other studies	This study
5OCB	19.17	−18.16	48[a] 48[b]	47.28	28.87[a] 28.87[b]	29.58	–	–	–	–	68[a] 67.5[b]	67.56	–	0.42
6OCB	33.77	−26.57	57[a] 58[b]	56.91	29.71[a] 29.71[b]	34.18	–	–	–	–	75.5[a] 76.5[b]	76.02	–	0.63
7OCB	13.92	−22.72	54[a] 53.5[b]	50.56	28.87[a] 28.87[b]	28.07	–	–	–	–	74[a] 75[b]	76.23	–	0.54
8OCB	21.73	−25.10	54.5[a] 54.5[b]	52.86	24.69[a] 24.69[b]	29.79	67[a] 67[b] 67.1[c]	66.65	– – 0.06[c] 0.032[c] 0.026[c]	0.04	80[a] 80[b] 80.2[c]	79.43	–	0.88
9OCB	36.46	−31.97	64[a]	62.46	39.33[a]	35.48	77.5[a]	80.02	–	≈0.38[e]	80[a]	79.97	–	≈0.92[e]
10OCB	33.63	−33.89	59.5[a]	57.57	–	36.07	–	–	–	–	84[a]	83.98	–	3.31
11OCB	44.96	−46.94	71.5[a]	68.62	–	44.73	–		–		87.5[a]	86.64	–	4.10
12OCB	48.14	−41.51	70[a]	67.47	51.04[a]	43.18	–	–	–	–	90[a]	88.48	–	4.77

[a] [7].

[b] [6].

[c] [15,13,14].

[d] 5OCB, 6OCB, and 7OCB do not show a smectic-*A* phase, while 10OCB, 11OCB and 12OCB do not show a nematic phase.

[e] See footnote to Table 4.

to-nematic and nematic-to-smectic-*A* transitions. With the exception of the solidification temperature, which increases as the cooling rate decreases (see Tables 3 and 4), the temperatures of all the transitions in cooling and heating cycles are practically independent of the cooling and heating rates, respectively.

As Tables 1 and 2 show this is the first study to report solidification temperatures, ϑ_s, and enthalpies, ΔH_s, for these liquid crystals. Except for 5CB where the reported ϑ_m is higher than ours by about 10°C, the ϑ_m values in this study are in acceptable agreement with those from earlier studies [6–15]. The enthalpies of melting, ΔH_m, obtained in this study are more or less comparable to earlier studies [6–15] which occasionally do not agree amongst themselves. The clearing transition temperatures (Tables 1 and 2), ϑ_c, in this study are in good agreement with previous studies [6–15]. Table 1 shows that the ΔH_c values from this study for members of the RCB series of liquid crystals are generally in good agreement with results from earlier studies [8–12]. To our knowledge this is also the first time that the clearing transition enthalpies, ΔH_c, are reported individually for the ROCB liquid crystals. Table 2 shows that the ΔH_c values for 5OCB, 6OCB, 7OCB, and 8OCB are within the range of 0.4–1.3 kJ/mol reported by Gray et al [6].

The ΔH_c values given in Table 1 for 8CB, 9CB, 10CB, and 11CB are from this study, other DSC studies [8–11], and from the adiabatic calorimetric measurements [12]. In addition, several ΔH_c values are reported [9–11] for 8CB from DSC measurements. For 8CB the ΔH_c values of Marynissen et al. [12] and Coles and Strazielle [8] agree while our higher ΔH_c value agrees with those of Hulme et al. [9–11] and Liebert and Daniels [9–11]. For 9CB, 10CB, and 11CB the ΔH_c values obtained by Marynissen et al. [12] are intermediate between our higher values and those of Coles and Strazielle [8]. For 8CB the ΔH_c values obtained by Marynissen et al. [12] and Coles and Strazielle [8] are, respectively, lower than our value by 29 and 24%. For 9CB the ΔH_c values obtained by Marynissen et al. [12] and Coles and

Table 3
Transition temperatures (ϑ in °C) and enthalpies (ΔH in kJ/mol) from curves for the RCB liquid crystals using different cooling and heating rates. The subscripts s, m, AN and c refer, respectively, to solidification (nematic-to-solid or smectic-*A*-to-solid), melting (solid-to-nematic or solid-to-smectic-*A*), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transitions

Liquid crystal	Scan rate/ (°C/min)	Cycle	Type of transitions							
			Solidification		Melting		Smectic-to-nematic		Clearing	
			ϑ_s	ΔH_s	ϑ_m	ΔH_m	ϑ_{AN}	ΔH_{AN}	ϑ_c	ΔH_c
5CB	10	Cooling	−11.41	−3.81	–	–	–	–	33.83	−0.54
	5	Heating	–	–	14.72	15.94			33.56	0.54
	5	Cooling	−8.54	−3.77	–	–			34.51	−0.50
6CB	10	Cooling	3.20	−15.98	–	–	–	–	28.00	−0.59
	5	Heating	–	–	13.64	16.53			28.07	0.46
	5	Cooling	5.25	−16.69	–	–			28.18	−0.59
7CB	10	Cooling	−7.04	−19.46	–	–	–	–	41.43	−0.84
	5	Heating	–	–	29.81	28.49			42.62	0.67
	5	Cooling	−5.50	−19.79	–	–			43.05	−0.79
8CB	10	Cooling	−7.11	−24.02	–	–	32.89	0.13	39.33	−0.92
	5	Heating	–	–	19.74	29.16	29.07	0.04	39.07	0.84
	5	Cooling	−6.31	−24.23	–	–	33.09	0.04	39.39	−0.92
9CB	10	Cooling	18.38	−34.31	–	–	46.85	≈−0.17[a]	48.76	≈−1.34[a]
	5	Heating	–	–	41.15	37.20	46.97	≈0.21[a]	48.98	≈1.34[a]
	5	Cooling	23.36	−35.27	–	–	47.15	≈−0.25[a]	48.97	≈ −1.38[a]
	2	Heating	–	–	42.56	37.95	48.43	≈0.29 [a]	50.40	≈1.42[a]
	2	Cooling	21.67	−29.20	–	–	48.98	≈−0.25[a]	50.87	≈ −1.46[a]
10CB	10	Cooling	21.13	−29.92	–	–	–	–	54.45	−3.10
	5	Heating	–	–	47.72	37.87			54.29	3.05
	5	Cooling	21.18	−29.50	–	–			55.16	−3.05
11CB	10	Cooling	21.32	−40.58	–	–	–	–	55.38	−4.18
	5	Heating	–	–	52.07	46.82			56.40	4.10
	5	Cooling	21.66	−37.40	–	–			56.46	−4.23
12CB	10	Cooling	26.43	−37.87	–		–	–	58.15	−4.81
	5	Heating	–	–	45.71	39.71			58.20	4.85
	5	Cooling	27.46	−37.95	–	–			58.63	−4.64

[a] These values are approximate because the isotropic-to-nematic (or nematic-to-isotropic) transition and the nematic-to-smectic-*A* (or smectic-*A*-to-nematic) transition overlap and are, as explained in the text for 8CB, interrupted by a phase intermediate in order between the nematic phase and the smectic-*A* phase. For 9CB the results at the rate of 2°C/min are the most dependable as the contribution of overlap in them is least and their average is the one reported in Table 1.

Strazielle [8] are also, respectively, lower than our value by 17 and 31%. These very large differences might, at first sight, be attributed to the smallness of the ΔH_c values themselves and to variations in the purity of the samples as evidenced by variations in their ϑ_c values. The differences between our ΔH_c values for 5CB, 6CB, and 7CB and those of Coles and Strazielle [8] are attributable to these reasons and/or our use of the more sophisticated Perkin–Elmer DSC-4 unit which is equipped with a data acquisition and analysis station. On the other hand our ΔH_c values for 10CB and 11CB are in good agreement with those of Marynissen et al. [12] which on average are lower by about 8%. This agreement is very good if one keeps in mind that, while precise, the absolute accuracy of the ac calorimetric technique for determining the heat capacity *Cp* is no better than 5% and usually worse and is not reliable for measuring or even detecting latent heats with any accuracy [15]. We attribute the large differences between our ΔH_c results for 8CB and 9CB and those of Marynissen et al. [12] and Coles and Strazielle [8] to an overlap/proximity of another transition with/to the nematic-to-isotropic transitions. As shown in Fig. 1A, and explained in greater detail later

Table 4
Transition temperatures (ϑ in °C) and enthalpies (ΔH in kJ/mol) from curves for the ROCB liquid crystals using different cooling and heating rates. The subscripts s, m, AN and c refer, respectively, to solidification (nematic-to-solid or smectic-*A*-to-solid), melting (solid-to-nematic or solid-to-smectic-*A*), smectic-*A*-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transitions

Liquid crystal	Scan rate/ (°C/min)	Cycle	Type of transitions							
			Solidification		Melting		Smectic-to-nematic		Clearing	
			ϑ_s	ΔH_s	ϑ_m	ΔH_m	ϑ_{AN}	ΔH_{AN}	ϑ_c	ΔH_c
5OCB	10	Cooling	18.77	−18.12	–	–	–	–	67.55	−0.46
	5	Heating	–	–	47.28	29.58			67.43	0.42
	5	Cooling	19.56	−18.16	–	–			67.69	−0.38
6OCB	10	Cooling	33.38	−26.53	–	–	–	–	76.01	−0.63
	5	Heating	–	–	56.91	34.18			75.75	0.59
	5	Cooling	34.16	−26.61	–	–			76.30	−0.63
7OCB	10	Cooling	12.77	−22.55	–	–	–	–	75.74	−0.63
	5	Heating	–	–	50.56	28.07			75.98	0.50
	5	Cooling	15.06	−22.84	–	–			76.96	−0.50
8OCB	10	Cooling	21.31	−25.06	–	–	66.24	0.04	79.40	−0.96
	5	Heating	–	–	52.86	29.79	66.65	0.04	79.10	0.84
	5	Cooling	22.15	−25.10	–	–	66.30	0.04	79.79	−0.88
9OCB	10	Cooling	34.40	−31.63	–	–	77.77	≈−0.25[a]	79.93	≈−0.84[a]
	5	Heating	–	–	62.46	35.48	78.21	≈0.33[a]	79.83	≈0.88[a]
	5	Cooling	38.52	−32.30	–	–	77.70	≈ −0.38[a]	80.31	≈−0.92[a]
10OCB	10	Cooling	33.70	−33.89	–	–	–	–	83.90	−3.35
	5	Heating	–	–	57.57	36.07			83.81	3.26
	5	Cooling	33.56	−33.89	–	–			84.24	−3.31
11OCB	10	Cooling	44.60	−47.15	–	–	–	–	85.69	−4.23
	5	Heating	–	–	68.62	44.73			86.94	4.02
	5	Cooling	45.32	−46.69	–	–			87.29	−4.10
12OCB	10	Cooling	47.97	−42.13	–		–	–	87.21	−4.73
	5	Heating	–	–	67.47	43.18			89.04	4.77
	5	Cooling	48.30	−40.84	–	–			89.20	−4.77

[a] These values are approximate because the isotropic-to-nematic (or nematic-to-isotropic) transition and the nematic-to-smectic-*A* (or smectic-*A*-to-nematic) transition overlap and are, as explained in the text for 8CB, interrupted by a phase intermediate in order between the nematic phase and the smectic-*A* phase. The results at the rate of 5°C/min are the most dependable as the contribution of overlap in them is least and their average is the one reported in Table 2.

on, the nematic-to-isotropic transitions in 8CB and 9CB overlap with a transient phase of order intermediate between the semectic-*A* and nematic phases. The existence of such an 'embedded' transient phase is clearly deducible from a comparison of the clearing exotherms (Fig. 1A) or endotherms (Fig. 2A) for 8CB and 9CB which are broad and unsymmetric with those where R>9 or R<8, which are much narrower and more symmetric. We suspect that these embedded transient phases are behind our higher ΔH_c values for 8CB and 9CB since once the nematic phase disappears in the higher 10CB and 11CB homologues our ΔH_c values become much closer to those obtained by Marynissen et al. [12] and the agreement is good considering the accuracy of the adiabatic calorimetric technique for latent heats [15]. In the case of the melting transitions which have large ΔH_m values and sharp endotherms (see Fig. 2) our values for 8CB, 9CB, 10CB, and 11CB are in good agreement with those of Marynissen et al. [12].

At this juncture we address the remarks made by Marynissen et al. [12] on the ability of the adiabatic scanning calorimetric technique to separate 'true' latent heats from pretransitional heat effects. Such claim was initially based on the extremely low ΔH_{AN} value obtained by them [12] for 8CB relative to values from earlier DSC studies [8–11]. According to Marynissen et al. [12] the higher ΔH_{AN} values for 8CB are

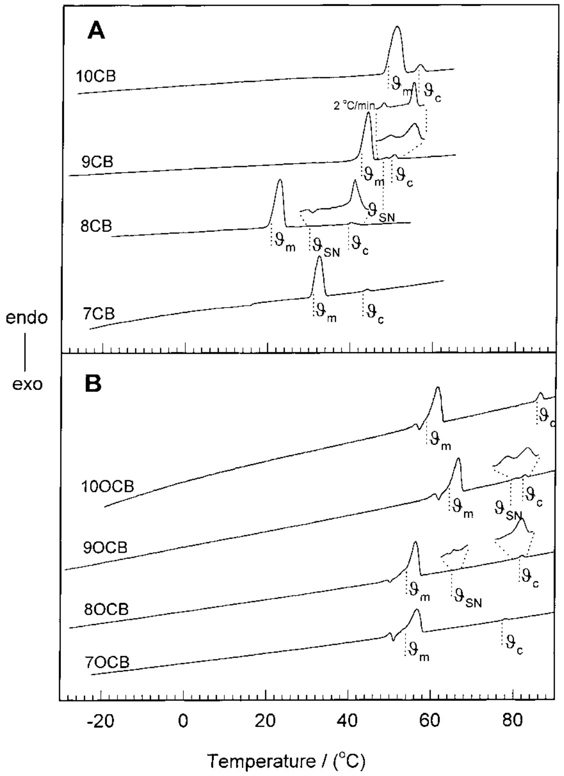

Fig. 2. DSC heating curves for representative members of the (A) RCB and (B) ROCB series of liquid crystals at a rate of 5°C/min. The vertical dotted lines indicate the onset of the melting (solid-to-nematic or solid-to-smectic-*A*), smectic-A-to-nematic, and clearing (nematic-to-isotropic or smectic-*A*-to-isotropic) transition temperatures ϑ_m, ϑ_{SN}, and ϑ_c, respectively. The magnification for the insets is five-times that of the original curves.

due to the inclusion of the pretransitional enthalpy effect with a 'true' latent heat of transition. In our view the combination of an intrinsically low ΔH_{AN} value and a missed 'embedded' transient phase of order intermediate between the smectic-*A* and nematic phases is likely to be the cause for the different ΔH_{AN} values for 8CB. It seems that even though heat dissipation effects in the adiabatic scanning calorimetric measurements are kept to an extremely negligible minimum, the extreme slowness (0.6 mK/h) in heating, and the smallness of the ΔH values (the sum of ΔH's for the transition from the nematic phase to the intervening transient phase and the transition from the transient phase to the smectic-*A* phase in the cases of 8CB and 9CB) measured lead to missing the transition across the above mentioned intervening phase and/or relatively high errors in the measured adiabatic calorimetric ΔH values [12,15]. In Table 1 of their paper Marynissen et al. [12] contrast their 'true' latent heat values with the ΔH values (pretransitional heats plus 'true' latent heats) of Coles and Strazielle [8] for the different phase transitions exhibited by 8CB, 9CB, 10CB, and 11CB. These results are also incorporated within Table 1 in this paper. It is noteworthy that in only three out of 10 phase transitions in that table are the values of Marynissen et al. [12] lower than those of Coles and Strazielle [8]. These are the ΔH_{AN} values for 8CB and 9CB, for which we find a transient phase intermediate between the smectic-*A* and nematic phases, and the ΔH_c (ΔH_{NI}) value for 8CB which, excluding the ΔH_{AN} values, is the smallest ΔH value in the table. We find it difficult to accept how the ΔH_c (ΔH_{NI}) value for 9CB and the ΔH_c (ΔH_{AI}) values for 10CB and 11CB obtained by Coles and Strazielle [8] can in the same instance include pretransitional heats and be in 'reasonable agreement' with the higher values obtained by Marynissen et al. [12]. In any case, if the results of Marynissen et al. [12] accurately measure true latent heats then it is expected, as Table 1 shows, that our ΔH_c values for 8CB, 9CB, 10CB, and 11CB should be higher. A rationalization for our much higher ΔH_c values for 8CB and 9CB has already been given.

The enlargement of the appropriate section of the curves for 8CB in Fig. 1A shows two overlapping transitions between 36 and 42°C and a very small exotherm at about 33°C. If the exotherm whose onset temperature is 41°C is associated with an isotropic-to-nematic transition then the exotherm that overlaps with it and has a minimum at 38.6°C and an onset temperature of 39.4°C is a phase of intermediate order between that of the nematic phase and the smectic-*A* phase which we refer to as the 'more ordered nematic' phase. The size of the exotherm for this 'more ordered nematic' intermediate phase shows that it predominates. This intermediate phase is in line with the view that the nematic-to-smectic-*A* transition involves the displacement of the molecules along their long molecular axes [20]. The exotherm at 33°C is, therefore, for the transition from this 'more ordered nematic' phase to the smectic-*A* phase. In 9CB a single but broad isotropic-to-nematic transition exotherm is obtained indicating a predominance of the above mentioned 'more ordered nematic' form. Comparison of the ΔH_c values for 8CB (0.88 kJ/mol) and 9CB (ca. 1.46 kJ/mol) confirms that the 'more ordered nematic' phase predominates in the isotropic-to-nematic transition of 9CB. At rates of 10°C/min and 5°C/min, the 'more ordered nematic'-to-smectic-*A* transition exotherm overlaps slightly with the isotropic-to-nematic exotherm. This overlap is removed at cooling or heating rates of 2°C/min or lower (see enlargements in Fig. 1A and Fig. 2A).

As Fig. 1(B) shows the curves for 8OCB and 9OCB are, except for showing two overlapping solidification exotherms, somewhat similar to those for 8CB and 9CB, respectively. The two overalpping solidification exotherms reflect either two separate supercooled aggregates or a solid–solid transition during solidification. Two even sharper exothermic peaks observed in the curve for 11OCB puts it within the 8OCB and 9OCB category.

Fig. 2(A,B) gives the heating curves for representative members of the RCB and ROCB series. Comparison of the curves for the same liquid crystals in Figs. 1 and 2 shows that the transitions among the liquid (nematic, smectic-*A*, and isotropic) phases occur at identical temperatures in both the heating and cooling cycles irrespective of the heating or cooling rates. For each of the liquid crystals studied, the increase in their entropy on melting, ΔS_m, is generally larger than the decrease in entropy upon solidification. This and the occasional observation of endotherms during the cooling of the supercooled mesogenic phases of the liquid crystals and exotherms during the heating of the solid phases of these systems indicates that the solid phase preceding melting is more ordered than that formed from the supercooled mesogen. To examine the heating curves for the RCB and ROCB liquid crystals more closely expansions of representative members of them, with R=5, 6, 7, and 10, are given in Fig. 3.

Fig. 3(A,B) for the heating runs of representative members of the RCB and ROCB series, respectively, shows that the exotherms preceding melting or concurrent with it are less prominent in the RCB series. This is attributable to the weaker intermolecular forces between their molecules relative to the intermolecular forces between the ROCB molecules as exhibited by their lower melting and solidification temperatures. From previous experience with the RCBz series of liquid crystals [18,19] and biaxially oriented poly(ethylene)terephthalate (PET) [21] this exotherm reflects heat release as a fraction of the solid in an unstable form reverts to the more stable form. The absence of this exotherm in the curve for 6CB indicates that the unstable solid modification is very negligible in amount if nonexistent. Evidence for this is found in the proximity of the ΔH_m and ΔH_s values and the ϑ_m and ϑ_s values for 6CB (see Table 1).

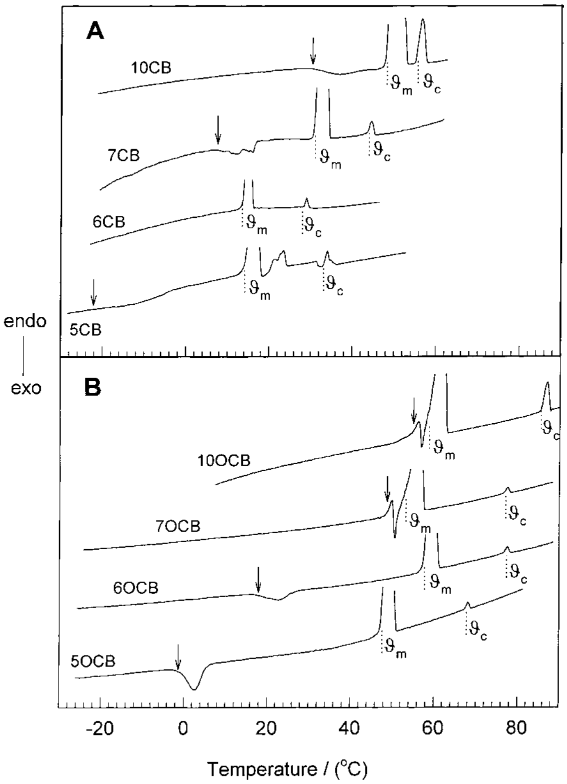

Fig. 3. Expanded DSC heating curves for some members of the (A) RCB and (B) ROCB series of liquid crystals. The arrows indicate the onsets of exotherms preceding or concurrent with melting. (The expansion factor is five).

Fig. 3(A,B) also reflects the observed trend of movement of the above mentioned exotherm in the direction of the endotherm for melting as R increases. This hints that the exotherm concurrent with the melting endotherm represents a transformation for a fraction of the solid from a less stable form to a more stable solid form. This is contrary to the view [6] that a melted fraction of the solid re-solidifies to form the

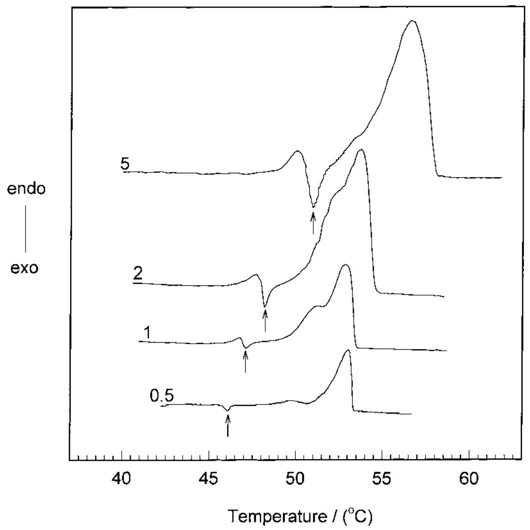

Fig. 4. DSC heating curves for 7OCB at different heating rates. The heating rates in °C/min are shown on the curves. The arrows illustrate the shift of the position of the exotherm on the temperature axis as the heating rate varies.

more stable solid that melts at a higher temperature. That this exotherm is due to a solid–solid transformation is confirmed by its displacement [18] away from the melting temperature, as the heating rate is decreased (see Fig. 4).

4. Conclusions

DSC heating and cooling curves over temperatures between −30°C and $\vartheta > \vartheta_m$ were used to determine transition temperatures and the enthalpies of transition between the different phases of members of the RCB and ROCB (from R=5 to R=12) series of liquid crystals. Whenever this study overlapped with earlier studies the data obtained were in good agreement. Such agreement established the reliability of data reported in this study for the first time. For liquid crystals exhibiting nematic and smectic-A phases (R=8 and 9) the study reveals that a transient mesogenic liquid phase intermediate in order between nematic and smectic-A phases may explain the deviation of our ΔH_c values for 8CB and 9CB from those of earlier studies. Observation of a broad solidification exotherm or two overlapping solidification exothermic peaks for these liquid crystals reveals that two mesogenic aggregations supercooled on cooling. The characteristics of an exotherm observed on heating at temperature below ϑ_m or concurrent with it reveal the existence of a transition between two solid forms, that is more prominent among the ROCB liquid crystals as a result of their stronger intermolecular interactions. This finding refutes the view [6] that during melting the solid form of the liquid crystals with the higher melting point solidifies.

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