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A DSC STUDY OF A NEW SERIES OF LIQUID CRYSTALS— 2-(4-ALKOXYBENZENE)-6-SUBSTITUTED BENTHIAZOLES

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ABSTRACT

The DSC measurement of a series of 2-(4-alkoxybenzene)-6-substituted benthiazoles, newly prepared compounds, was carried out in a nitrogen atmosphere. The results showed that with a few exceptions, these compounds are liquid crystal materials which is in good agreement with results obtained by other techniques. The transition temperatures, and the enthalpy and entropy changes of the compounds were obtained, and the results are discussed. The effects of the scanning rates on the supercooling and thermal history of the samples were also investigated.

INTRODUCTION

Because of the existence of multi-mesophases, liquid crystalline materials possess a variety of unique and attractive physicochemical properties. Many investigators have found differential scanning calorimetry to be particularly suitable for the detection and study of the mesomorphic state [1].

In this study, the thermal properties of a series of 2-(4-alkoxybenzene)-6-substituted benthiazoles, a new group of liquid crystalline compounds, were determined by DSC. Their transition temperatures, and enthalpy and entropy changes from one phase to another were measured or calculated. The effects of some factors, such as heating and cooling runs, scanning rates and treatment of samples on the experimental results were observed and briefly discussed. Some significant conclusions were obtained.

MATERIALS AND METHODS

Materials

All the compounds used in our experiments were newly synthesised and kindly provided by the Department of Chemistry, Suzhou University. The purity, composition and molecular structure were checked by elementary analysis, thin layer chromatography and IR spectrophotometry.

Apparatus and Method

The instrument employed for this study was a Delta series Differential Scanning Calorimeter DSC-7, Perkin–Elmer Corp., with a 3700 data station [2]. The sample mass used ranged from 3 to 5 mg, and aluminium pans were used for samples and reference material. All runs were carried out in pure dry nitrogen atmosphere with a flow rate of 20 ml min^{-1}. The scanning rate for both heating and cooling runs was $5\,^{\circ}\text{C min}^{-1}$, unless otherwise specified. The calibration of both temperature and energy was performed before starting the measurements using high purity samples, such as In, Zn, Sn and Pb, provided by Perkin–Elmer Corp. as standards.

RESULTS AND DISCUSSIONS

The transition temperatures and enthalpy changes measured are listed in Table 1. The mesophase identification was based on the value of each transition enthalpy change, together with corresponding optical evidence [3,4]. For this purpose, an Orthoplan-Pol model polarizing microscope, Leitz Corp., was used for observing the structural features and the texture of the samples. As all the transition processes can be safely supposed to follow a path consisting of successive equilibrium states when the samples are heated at a constant, preferably linear rate, the transition entropy changes can be calculated by direct application of the relation $\Delta S = \Delta H/T$. The results are shown in Table 1.

The results show quite clearly that the compounds studied mostly exhibit nematic mesophases [5]. This may be atributed to the fact that the terminal groups in the molecule of the samples are all benzoate esters. On the other hand, with an increase in the length of the alkyl chains, which favours smectic properties, the compounds have a greater or lesser tendency to exhibit smectic mesophases [6], e.g. samples 7 and 8. Although the reason for this phenomenon is not quite clear, the molecular geometry must be important: when the total length of both alkyl chains at the ends is long enough, in other words, the length-to-breadth ratio of the molecules reaches a certain value, the molecule has a more linear rod shape with a more regular orientation and better order [7]. The same argument may explain the fact that compound 1 only exhibits a monotropic nemastic mesophase. Compounds 9 and 10, with a substituting halogen atom, only exhibit a smectic mesophase. This result can probably be interpreted in terms of intermolecular forces: the substituting halogen atom makes the attractive forces between the molecules stronger. However, in contrast, the presence of

TABLE 1

Transition thermodynamic parameters for the series 2-(4-alkoxybenzene)-6-substituted benthiazoles

No.	Molecular formula	Crystal–nematic (C–N)			Smectic–nematic (S–N)			Nematic–isotropic (N–I)		
		T (°C) Heating (Cooling)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	T (°C) Heating (Cooling)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	T (°C) Heating (Cooling)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
1	C_4H_9OPh–CNS–$PhOCH_3$ [a]	T_m = 124.6 (101.3)	27.9	75	–	–	–	– (121.5)	0.67	1.7
2	$C_6H_{13}OPh$–CNS–$PhOCH_3$	95.70 (79.30)	26.2	71	–	–	–	118.3 (113.9)	0.48	1.2
3	$C_8H_{17}OPh$–CNS–$PhOCH_3$	100.4 (73.17)	30.7	82	–	–	–	119.0 (118.2)	0.63	1.6
4	$C_{10}H_{21}OPh$–CNS–$PhOCH_3$	89.11 (74.66)	18.5	51	–	–	–	112.2 (111.3)	0.63	1.6
5	$C_8H_{17}OPh$–CNS–$PhOC_2H_5$	94.22 (82.89)	32.2	88	–	–	–	125.3 (125.6)	0.28	0.7
6	$C_8H_{17}OPh$–CNS–$PhOC_3H_7$	72.99 (65.32)	13.0	38	–	–	–	114.4 (113.9)	0.87	2.1
		Crystal–smectic (C–S)								
7	$C_{12}H_{25}OPh$–CNS–$PhOCH_3$	90.74 (76.44)	56.6	156	96.95 (96.60)	0.40	1.1	113.4 (112.8)	0.85	2.2
8	$C_8H_{17}OPh$–CNS–$PhOC_4H_9$	70.77 (66.36)	9.46	28	99.82 (99.03)	1.14	3.1	123.1 (122.3)	1.14	2.9
								Smectic–isotropic (S–I)		
9	$C_8H_{17}OPh$–CNS–PhF [b]	77.60	28.7	82	–	–	–	124.0	8.60	22
10	$C_8H_{17}OPh$–CNS–PhCl	96.33 (89.59)	37.1	100.6	–	–	–	155.7 (154.5)	8.76	20
11	$C_8H_{17}OPh$–CNS–PhFCl [c]	–	–	–	–	–	–	–	–	–

[a] Compound 1 only forms a monotropic nematic mesophase.

[b] Cooling run was not performed.

[c] Compound 11 is not a mesogen.

both F and Cl atoms in the *ortho*-position of the benzene ring may destroy the molecular symmetry by damaging the uniform cross-section of the molecule; compound 11, therefore, no longer has any mesogen property [7].

It can be seen that the transition temperatures from mesophase to liquid phase, T_{NI}, decrease with an increase in the length of the terminal alkyl group, and in a series with both even and odd carbon chain members, the T_{NI} decrease alternately with $T_{NIeven} > T_{NIodd}$. These observations are in good agreement with those reported in the literature [8]. But the transition temperatures from the crystalline to the mesophase state do not appear to change in any regular way.

From Table 1, one can see that the ΔH and ΔS values for transitions from crystal to mesophase are without exception higher than from mesophase to liquid. The ΔS_{CS} and ΔS_{NI} of compound 7 are especially high, which indicates that the compound is stable in both crystalline and mesophase states.

Supercooling is a common, if not universal, feature of mesomorphic transitions, particularly in the case of the transition related to the crystal phase. This is usually atributed to the fact that the mesophase has the lowest transition temperature and so is easily frozen in a glassy state. In our experiment, the cooling runs were carried out for all the samples, see Table 1. It is noticeable that, with a few exceptions, the supercooling decreases with increasing length of alkyl chains. In order to obtain more information on the effect of the cooling rate on supercooling, measurements at various scanning rates, 2.5–20 °C min^{-1}, were performed for some samples. Figure 1 shows the results for one of the samples, which indicate that the above-mentioned effect exists but is not considerable: liquid crystal transitions are more easily nucleated in comparison with some other substances [9,10].

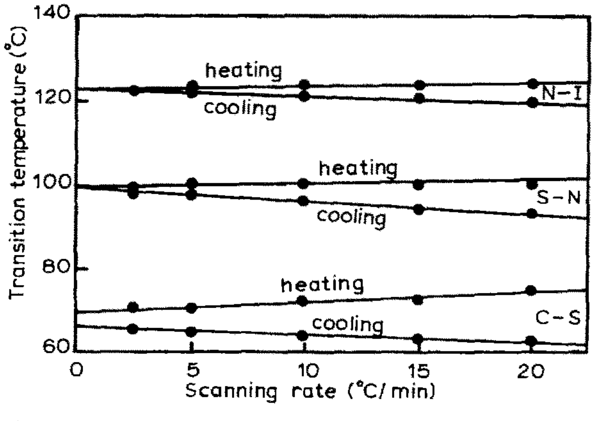

Fig. 1. The effect of scanning rate on the supercooling phenomenon.

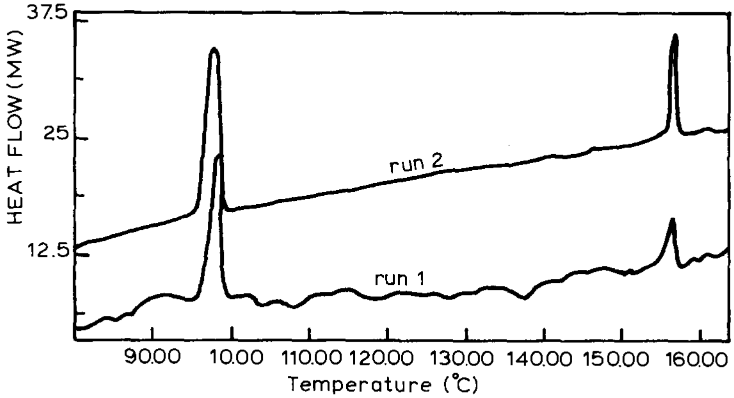

Fig. 2. A comparison of the curves of compound 10: 1, direct measurement; 2, measurement after heating and cooling.

It is interesting to note that, for the compounds in this study, the transition temperatures and enthalpy changes obtained by direct measurement of the samples are almost exactly the same as those obtained by measuring the samples after heating and cooling; any slight differences are still within the normal instrumental error range. Measuring the samples the latter way is preferable because the base line of the curves is much smoother; the cycle of heating and cooling makes the size of the sample particles and the packing density of the samples more even which improves the transmission of heat through the samples. Figure 2 clearly shows this phenomenon.

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