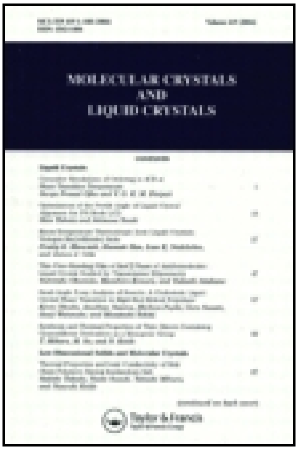

Molecular Crystals and Liquid Crystals

Liquid Crystalline Behavior Of Two-Component Molecular Adducts From Bifunctional Molecules-II

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LIQUID CRYSTALLINE BEHAVIOR OF TWO-COMPONENT MOLECULAR ADDUCTS FROM BIFUNCTIONAL MOLECULES–II

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The phase behavior is reported for five two-component systems based on two different bifunctional molecular species (4,4′-(1-,4-butanedioxy)diphenol-bis (pyridinecarboxylate) and 4-acetylpyridinazine) characterized by the presence of pyridinic nitrogen and capable of interacting with carboxylic acids via hydrogen bond. The evidence of a drastic influence of this interaction in the solid and liquid phase is shown. For four systems, thermotropic liquid crystal behavior is found on the basis of differential scanning calorimetry and polarized optical microscopy at controlled temperature.

Keywords: mesogenic complexes; hydrogen bonded mesogens

INTRODUCTION

The formation of supramolecular liquid crystalline complexes via hydrogen bonding is a well-known feature which may involve one-component as well as multicomponent systems [1–7]. In a recent paper [8] it was shown how the formation of a liquid crystalline phase in low molecular weight two-component systems may be accompanied by a peculiar and sometime complex phase behavior when the two components exert on each other a strong and specific interaction via hydrogen bonds. In particular, for systems containing one dibasic component such as isonicotinic acid diester **B** (Scheme 1) and one dicarboxylic acid such as hexyloxy terephthalic

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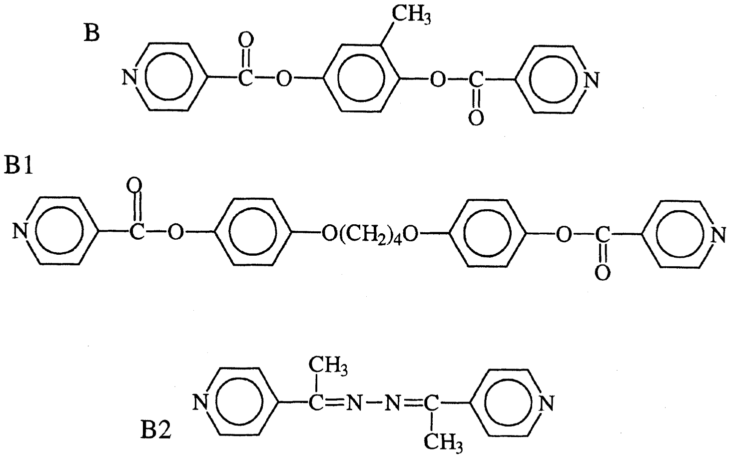


SCHEME 1

acid, the intercomponent interaction can have dramatic effects even at temperatures lower than the melting temperature of both components. A new solid phase is formed which eventually melts into a liquid crystal, although none of the components is mesogenic in itself. However, the complementary bifunctional character of the two molecular species does not seem to be capable by itself of producing hydrogen-bonded topologically polymeric –**A**–**B**–**A**–**B**– structures stable enough to have a very significant effect on the thermal stability of the mesophase as compared to nonpolymeric analogues. A somewhat different picture comes out from the behavior of analogous systems reported by Griffin [9] with the formation of heteromeric liquid crystalline polymers via hydrogen bond connections. In this article, we report the results of an investigation on the phase behavior of systems based on the use of two different difunctional basic molecules, **B1**, **B2** (Scheme 1) and some carboxylic acids. Compound **B1** was selected with the expectation that its twin structure and the moderate conformational mobility of the aliphatic spacer would combine to allow linear molecular adducts with larger axial ratios to be realized, obtaining higher mesophase stability because of that. A homologue of **B1**, with much longer spacer ($n = 10$), was used by Griffin[10] in combination with tetraethyleneglycol di-p-benzoic acid. Compound **B2** was selected as a further example of an entirely rigid molecular segment and also because of its structural analogies with a 4,4′-dihydroxy,α,α′-dimethyl benzalazine, whose promesogenic qualities have been investigated since it is both a low molecular weight [11] and polymeric [12] substance.

EXPERIMENTAL

Materials

Synthesis of B1

B1 was synthesized by reaction of isonicotinic acid with 4,4′-butanoxybisphenol. In a typical preparation, 8.2 mmol of the bisphenolic reagent (previously obtained by standard methods from 4,4′-dibromobuthane and hydroquinon) and 16.4 mmol isonicotinic acid are dissolved in 100 mL anhydrous dichloromethane together with 16.4 mmol anhydrous p-toluensulfonic acid and an equal amount of 4-dimethylaminopyridine in the presence of 20.5 mmol diisopropylcarbodiimide. The reaction is let go at room temperature for 24 h under stirring. The solvent is then distilled off and the solid product washed several times with a water-ethanol mixture. Crystallization of the final product is operated from chloroform solution. The ^{1}H-NMR spectrum is in accordance with the expected structure. B1 is a crystalline solid melting at 210°C with an enthalpy change of 149 J/g, as measured by differential scanning calorimetry (DSC) technique. Optical polarizing microscopic observations show that B1 melts to an optically isotropic liquid. Melt-crystallized samples undergo a low-enthalpy phase change which is reversible on heating at 170°C. No monotropic liquid crystalline behavior is detectable. TGA measurements show that the compound is chemically stable under $\sim$250°C (Td(5%) = 248°C under nitrogen atmosphere).

Synthesis of B2

In a typical preparation, to 0.120 mol of 4-acetylpyridine are dissolved in 100 mL absolute ethanol and a less than stoichiometric amount (0.040 mol) hydrazine monohydrate is added. The reaction is let run under reflux for 5 h. **B2** is obtained by solvent elimination and is further crystallized from methanol/water solution. The ^{1}H-NMR spectrum is consistent with the expected formula. **B2** is a pale yellow crystalline substance melting at 129.5°C (ΔHm = 119 J/g). Td(5%) measured under nitrogen atmosphere is 179°C. DSC analysis and polarizing optical microscopy indicate the occurrence of solid state polymorphism for melt-crystallized samples. The phase behavior is to same extent dependent on the thermal history. However, in any case, the melting phase does not depend on the thermal history: melting temperature and enthalpy are invariant. Figure 1 shows the most common case occurring.

Carboxylic acids: the following carboxylic acids (Scheme 2) have been prepared following standard procedures: **A1**=hexyloxybenzoic acid; **A2** = hexyloxyterephthalic acid; **A3**=1,10-decanedioic acid was purchased (Aldrich) and utlized as such (as verified by optical microscopy, melting to

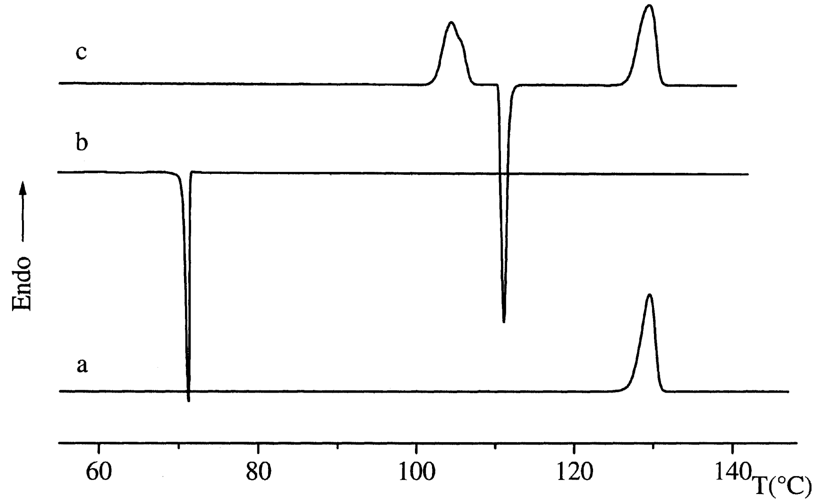
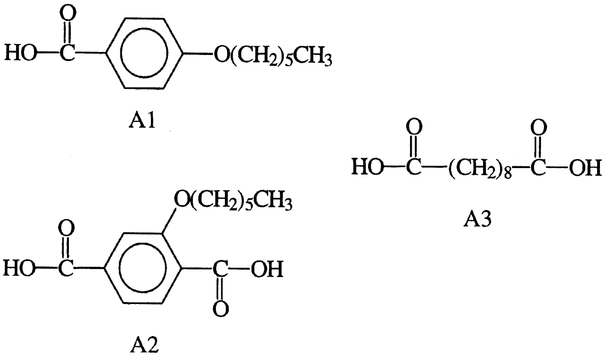


FIGURE 1 Thermal behavior of **B2**. DSC heating run of a solution-crystallized sample (curve a); successive cooling run (curve b); second heating run (curve c).

an isotropic liquid takes place at $Tm = 135°C$, $\Delta Hm = 213\,Jg^{-1}$). **A1** melts at 108.6°C ($\Delta H = 62.9\,Jg^{-1}$) producing a nematic liquid. Isotropization occurs at 153.7°C with an enthalpy change of $12.3\,Jg^{-1}$. A low enthalpy ($27.3\,Jg^{-1}$) solid state transition is observed at 71°C (some modification of the solid state behavior ($T = 74°C$, $\Delta H = 47\,Jg^{-1}$) may be observed for finely powdered samples by grinding). This phase behavior is consistent with previously reported data in the literature [13]. **A2** does not exhibit any



SCHEME 2

liquid crystalline behavior. Melting to an isotropic liquid takes place at 200.5°C ($\Delta H = 134.5\,Jg^{-1}$) for solution-crystallized samples and at 222°C ($\Delta H = 116\,Jg^{-1}$) for the melt-crystallized ones. Solution-crystallized samples exhibit a solid phase transition at 169°C with an enthalpy change of $60\,Jg^{-1}$.

Characterization Methods

The phase behavior of compounds and their mixtures, previously finely ground at room temperature, was examined by DSC (Perkin Elmer DSC7, nitrogen atmosphere, 10 K/min scanning rate), and polarizing microscopy (Leitz microscope, Linkam temperature-controlled hot stage, nitrogen atmosphere). Thermochemical stability of single compounds and of binary mixtures was monitored by use of a Mettler TGA 50 apparatus. The chemical identity of synthesized compounds was checked by ^{1}HNMR spectrometry (Varian XL-200; Bruker AC 250 spectrometers).

RESULTS AND DISCUSSION

Systems (2A1 + B1) and (2A1 + B2)

A1 is a typical and well-known example of a low molecular weight compound whose mesogenic behavior has to be ascribed to the formation of hydrogen-bonded molecular pairs. In our preceding article[8], the phase behavior of system (2**A1**+**B**) was described. It was shown that a strong interaction between **A1** and **B** takes place at temperatures across the melting range of **A1**, but well below the melting temperature of **B**, leading to a new solid phase which melts at 134°C into a homogeneous liquid crystal (nematic) phase. Rather surprisingly, the thermal stability of the nematic phase is only slightly higher than that measured for pure **A1**, notwithstanding the considerably higher axial ratio that might be assigned to the **A1**–**B**–**A1** segment as compared to the **A1**–**A1** pair. A qualitative explanation was suggested assuming a higher angular mobility of the **A1**–**B** hydrogen bond as compared to the more rigid carboxylic coupling of two **A1** molecules. In order to collect further data that might help to evaluate the generality of this phenomenon the phase behavior of systems (**2A1** + **B1**) and (**2A1** + **B2**) has been investigated. Figures 2 and 3 show the DSC behavior of the **B1** and **B2** containing systems, respectively. In both cases, the low temperature endothermic signal in the DSC curve pertaining to the first heating run is likely due to a solid phase transition of the **A1** fraction. This feature, which is also observed for the solution-crystallized pure acid, is to some extent dependent on the thermal history

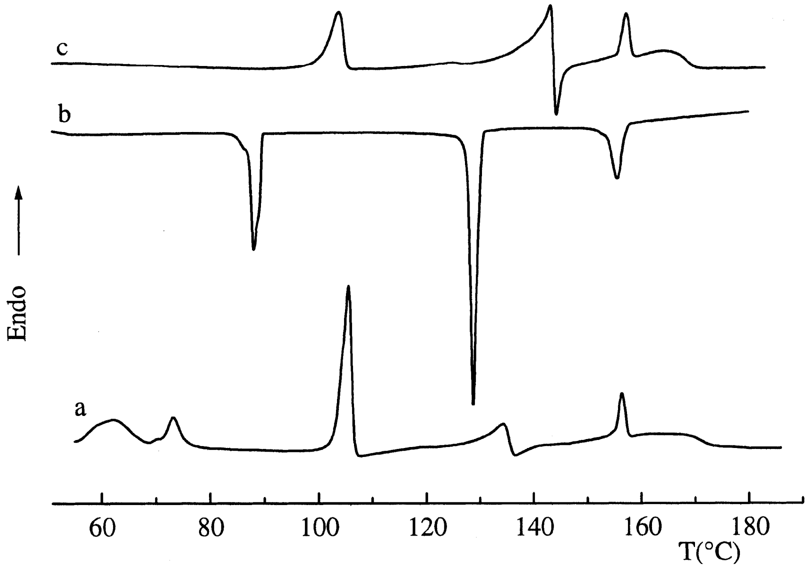


FIGURE 2 Thermal behavior of system (**2A1**+**B1**). DSC heating run of an as-prepared mixture of solution-crystallized components (curve a); successive cooling run (curve b); second heating run (curve c).

of the sample. The phase behavior at higher temperatures is different for the two systems. A fraction only of system (**2A1** + **B1**) melts at ~106°C. On further heating, the eterophasic system is transformed entirely into a homogeneous isotropic liquid at temperatures close to 180°C. The system may be observed as a monophasic liquid crystal (nematic) on cooling the isotropic liquid (Figure 2, curve b). Successive heating performed in the absence of crystal phase allows the isotropization transition to be observed and the thermodynamic parameters to be measured: Ti = 160°C, ΔHi = 13.7 J/g. On the contrary, in the range 98–108°C (close to the melting temperature of **A1**) the entire (**2A1**+**B2**) system transforms, with an almost negligible enthalpic change, into a single new solid phase which eventually melts to a monophasic smectic liquid at 128°C (ΔHi = 59 Jg^{-1}), changes to a nematic phase at 147°C, and finally becomes isotropic at 157°C (ΔHi = 10.0 J/g). Curves b and c of Figure 3 show that the phase behavior of the system after the first heating run is fairly well reversible. The phase behavior of this system is very similar to that exhibited by (**2A1** + **B**) [8]. However, a most remarkable difference concerns the liquid crystalline state: only the nematic phase is observed, with isotropization temperature at 154°C.

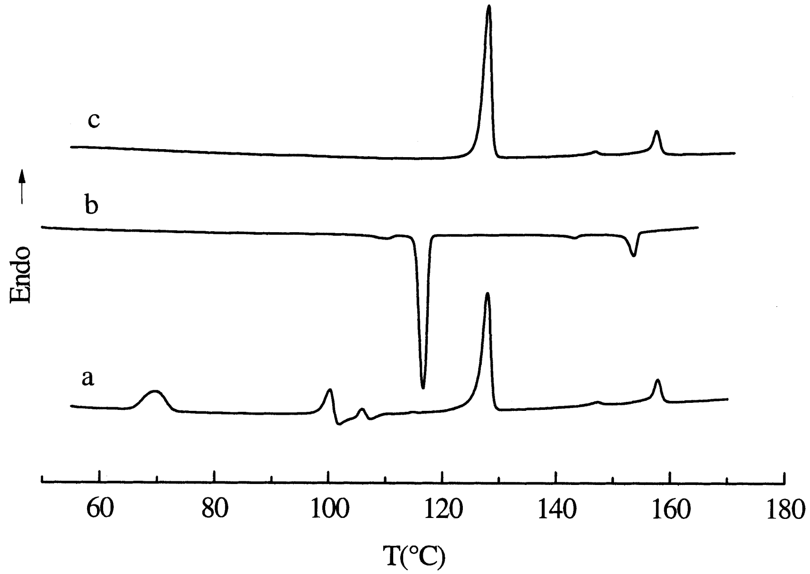


FIGURE 3 Thermal behavior of system (**2A1**+**B2**). DSC heating run of an as-prepared mixture of solution-crystallized componenets (curve a); successive cooling run (curve b); second heating run (curve c).

Systems (A2 + B1) and (A2 + B2)

Figure 4 shows the thermal DSC behavior of (**A2** + **B1**). Curve a, relative to the first heating run, is characterized by two endothermic signals peaked at 154°C ($\Delta H = 20\,Jg^{-1}$) and at 176°C ($\Delta H = 108\,Jg^{-1}$). Polarizing microscopy indicates that no melting takes place at temperatures corresponding to the first DSC signal. Therefore, it may reasonably correspond to the solid phase transition undergone by the acid component. This occurs at 159°C for pure **A2**. The measure of $20\,Jg^{-1}$ for the transition enthalpy in the equimolar mixture containing 30% by weight of **A2** is consistent with the value found for pure **A2** ($61\,Jg^{-1}$). The optical observation indicates that melting of the mixture to give an isotropic liquid takes place in the range ~175–200°C. Above this temperature, which is lower than the melting temperature of both components, the system is monophasic liquid and isotropic. Curve b of Figure 4 is characterized by a couple of signals corresponding to phase transitions detectable also with the microscopy observation. The second heating run (curve c) shows the behavior of melt-crystallized mixtures. The phase behavior of successive thermal cycles is entirely reproducible. The optical observation of the phase contiguous to

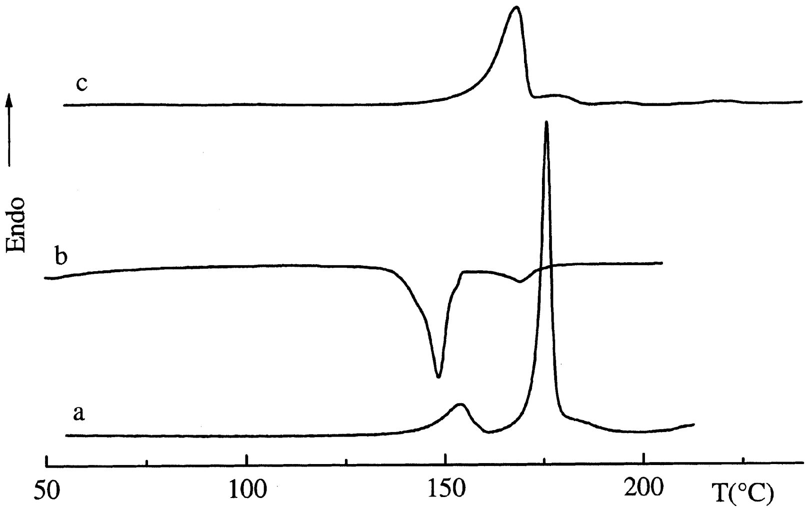


FIGURE 4 Thermal behavior of system (**A2** + **B1**). DSC heating run of an as-prepared mixture of solution-crystallized components (curve a); successive cooling run (curve b); second heating run (curve c).

the isotropic liquid indicates that is is an anisotropic phase whose morphology is not unequivocally related to any known liquid crystalline phase. The proximity of the liquid-liquid transition to the transition involving solid and liquid crystal phases has prevented the use of X-ray diffraction techniques to elucidate the phase structure. Figure 5 shows the DSC behavior of (**A2**+**B2**). Curve a refers to the first heating run of the mixture. A single endothermic signal appears (peak temperature T = 168°C, $\Delta H = 135\,Jg^{-1}$) which the optical microscopy observation relates to the melting of the system to an isotropic liquid. On cooling (curve b), the liquid becomes anisotropic at ~145°C, producing a nematic phase easily recognizable by its very mobile schlieren morphology. The reverse isotropization transition occurs at 149°C with an enthalpy change of $11\,Jg^{-1}$. The reversibility of the liquid-liquid transition is unequivocally observable provided the nematic phase is not too deeply cooled down. In that case, as shown in Figure 5 (curve b), crystallization takes place and the successive heating run brings the system directly to melting (curve c, Tm = 167°C, $\Delta H = 122\,Jg^{-1}$), demonstrating the monotropic behavior of the liquid crystalline phase. It has to be noted that in the DSC behavior at the first heating run (curve a), which is relative to the system as obtained by grinding the mixture at room temperature, no thermal signal is detectable pertaining to the melting of **B2** (~130°C). Consistently, no evidence of even partial melting is detectable

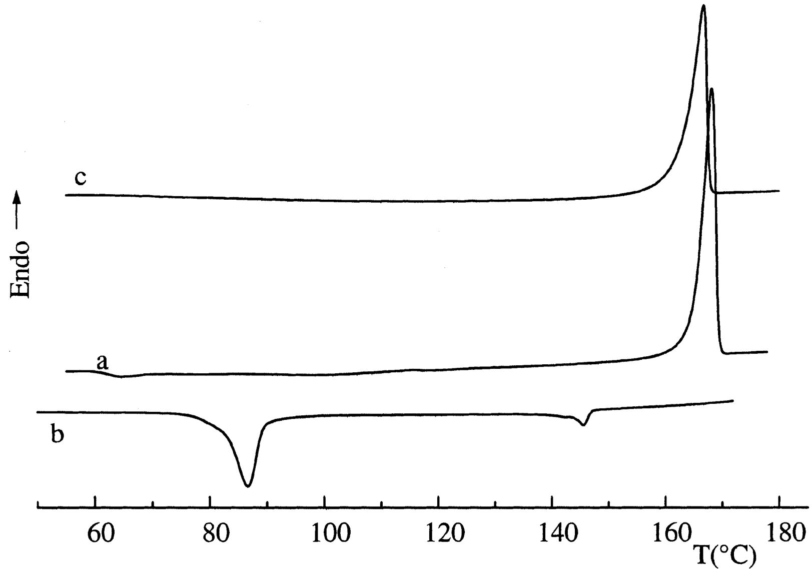


FIGURE 5 Thermal behavior of system (**A2** + **B2**). DSC heating run of an as-prepared mixture of solution-crystallized components (curve a); successive cooling run (curve b); second heating run (curve c).

by polarizing microscopy observation. This feature suggests that some strong interaction may take place between the two components at mixing.

System (A3 + B2)

The DSC thermal behavior of (**A3**+**B2**) is reported in Figure 6. In the first heating run a thermal phenomenon takes place in the range ~120–135°C which is characterized by an endothermic signal peaked at 125°C ($\Delta H = 6.7\,Jg^{-1}$) closely followed by an exothermic signal peaked at 130°C ($\Delta H = -12.3\,Jg^{-1}$). Polarizing optical microscopy shows that although both pure components have melting temperatures within the 120–135°C range, a new solid phase is formed whose melting temperature to an isotropic monophasic liquid corresponds to the endothermic signal peaked at 166°C ($\Delta H = 196\,Jg^{-1}$) shown in Figure 6 (curve a). Crystallization of the molten mixture occurs at 155°C ($\Delta H = 196\,Jg^{-1}$) with no previous DSC or microscopy evidence indicating the formation of a monotropic liquid crystal phase. Melting of the melt-crystallized system (curve c) takes place at 166°C ($\Delta H = 196\ Jg^{-1}$). Successive thermal cycles give entirely reproducible results. System (**A3**+**B2**), unique among the five examined systems, does not exhibit liquid crystalline behavior. Yet, a

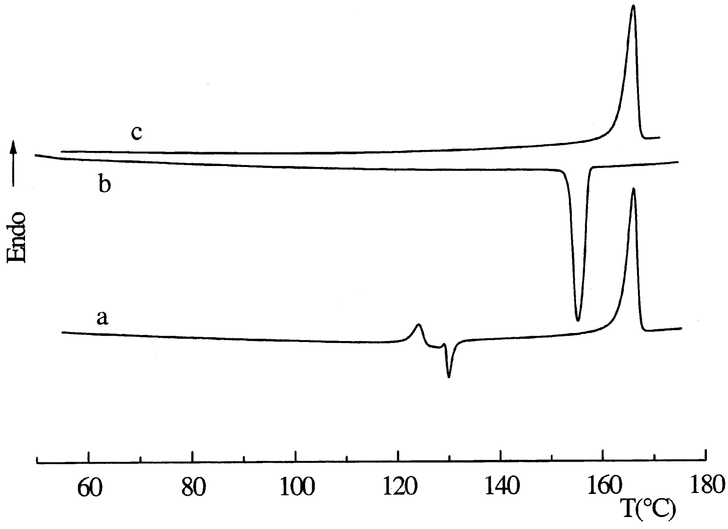


FIGURE 6 Thermal behavior of system (**A3** + **B2**). DSC heating run of an as-prepared mixture of solution-crystallized components (curve a); successive cooling run (curve b); second heating run (curve c).

monophasic liquid is formed around 166°C. The absence of liquid crystallinity may be the consequence of two converging features: (a) the intrinsic low thermal stability of a virtual mesophase, and (b) the comparatively high stability of the crystalline phase (containing both components) accompanied by a short supercooling interval of the isotropic liquid. Feature (a) should be not surprising on account of the conformational flexibility of the carboxylic acid moiety as compared to that of the terephthalic acid group (contained in (**A2**+**B2**)) and the additional mobility steming from the low structural stability of –**A3**–**B2**–**A3**– pseudo-polymeric sequences. The consequence should be a reduction of the statistical axial ratio of the potential mesogenic segment. It may be interesting to note that liquid crystallinity with isotropization temperature as high as 256°C was observed for the linear polyester formed from 4,4′-dihydroxy-α,α′-dimethylbenzalazine and 1,10-decandioic acid [12], while the isotropization transition of the liquid crystalline phase exhibited by the low molecular weight diester containing five carbon atoms in the two terminal flexible segments [11] occurs at 136°C.

CONCLUSION

Experimental results presented in this article afford further evidence of how acid-base interactions occurring via hydrogen bonding between

TABLE 1 Thermal Data for Phase Transitions

System	T_m/°C[a]	ΔH_m/Jg^{-1}[a]	$T_{LC\text{-}LC}$/°C[b]	ΔH/Jg^{-1}[b]	$T_{LC\text{-}I}$/°C[c]	ΔH_I/Jg^{-1}[c]
(2A1+B1)	106[d]	31.0			160	13.7
	104[e]	19.0				
(2A1+B2)	128[d]	59.0	147	< 1	157	10.0
	128[e]	66.0				
(A2+B1)	176[d]	108			not meas.	not meas.
	169[e]	83				
(A2+B2)	168[d]	135			149	11.0
	167[e]	122				
(A3+B2)	166[d]	196				
	166[e]	196				

[a] Melting temperature and enthalpy change.
[b] Smectic-nematic transition temperature and enthalpy change.
[c] Nematic to isotropic liquid transition temperature and enthalpy change.
[d] Solution-crystallized sample.
[e] Melt-crystallized sample.

carboxylic acids and pyridinic bases may substantially influence the phase behavior of stoichiometrically regulated binary molecular systems (Table 1). This influence may involve both solid and liquid states, leading eventually to thermotropic mesomorphism even for those systems whose components are not intrinsically mesogenic. Actually, 4 out of the 5 examined systems have been found to produce mesomorphism. Among these, consistent with the expectations although not very remarkable, appears the relatively higher thermal stability of the mesophase shown by mixtures containing **B1** as the base. This feature may likely depend on the possibility for **B1** molecules to produce higher statistical axial ratios by taking the most extended conformation. Also significant appears the nonmesogenic behavior of system (**A3** + **B2**). This peculiarity should probably be ascribed to the high conformational flexibility of **A3** molecules.

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