Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Behavior of Two-component Molecular Adducts from Bifunctional Molecules

V. Ambrogi [a], U. Caruso [a] & A. Sirigu [a]

[a] Univerita' di Napoli Federico II, Dipartimento di Chimica, Via Mezzocannone, 4 80134, Napoli, Italy

Version of record first published: 24 Sep 2006

To cite this article: V. Ambrogi, U. Caruso & A. Sirigu (1998): Liquid Crystalline Behavior of Two-component Molecular Adducts from Bifunctional Molecules, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 325:1, 145-156

To link to this article: http://dx.doi.org/10.1080/10587259808025391

Mol. Cryst. Liq. Cryst., Vol. 325, pp. 145–156
Reprints available directly from the publisher
Photocopying permitted by license only

Liquid Crystalline Behavior of Two-component Molecular Adducts from Bifunctional Molecules

V. AMBROGI, U. CARUSO and A. SIRIGU*

Univerita' di Napoli Federico II, Dipartimento di Chimica, Via Mezzocannone, 4 80134 Napoli, Italy

(Received 15 April 1998)

The phase behavior of some binary systems formed by the nicotinic acid diester of methylhydroquinone and some dicarboxylic acids based on terephthalic acid has been examined. A strong interaction takes place between the two components leading, for some of them, to the formation of a liquid crystalline phase at temperatures lower than the melting temperature of both components in the pure state. Liquid crystal glasses may be formed on cooling at room temperature. With terephthalic acid, interaction takes place above the melting temperature of the nicotinic acid diester producing a new solid phase, which melts to give an isotropic liquid. No monotropic mesomorphism is detectable for this system.

Keywords: Mesogenic complexes; hydrogen bonded mesogens

1. INTRODUCTION

In principle, the formation of a liquid crystalline phase in a multi-component system does not require the occurrence of specific interactions among different molecular species. It is not even necessary that any single component exhibits liquid crystalline properties in the pure state either enantiotropically or monotropically [1]. In fact, the destabilization of the solid state may lead virtual mesogenic properties to show up in enantiotropic way. A typical example of this event is afforded by the liquid

*Corresponding author. Tel: 49-81-5476 555, Fax: 49-81-5527 771, e-mail: sirigu@chemna.-dichi.unina.it

crystal behavior of the system formed by anisal-*p*-phenetidine and *p*-nitrophenylidene-*p*-phenetidine [2]. In a similar way, and for analogous reasons, a random binary copolymer may show liquid crystalline properties notwithstanding the absence of liquid crystallinity in the phase behavior of the corresponding parent homopolymers [3]. Nonetheless, the occurrence of specific and strong interactions (in the most frequent cases, intermolecular hydrogen bonds) may powerfully contribute to the onset of liquid crystalline properties in systems (even one-component systems) whose constituent molecules are characterized by structural parameters, such as dimension, anisometry, conformational mobility, that would suggest an intrinsically low mesogenic potential. Benzoic acid or cinnamic acid derivatives are very simple examples [4] of such monofunctional [hereinafter, terms monofunctional and bifunctional will be used to indicate the presence in the molecules of one or two atomic groups capable to be involved in strong intermolecular interactions], one-component systems showing liquid crystalline behavior. For these compounds, the formation of dimeric structures, *via* hydrogen bond, leads to "effective" mesogens having (statistically defined) axial ratio much larger than that of the monomer.

Bifunctional molecules open wider possibilities, even in the case of one-component systems, depending on the nature of the functional groups and on the strength of the reciprocal interactions. We have examined the phase behavior of binary systems characterized by the presence of a dicarboxylic acid (ARA) and a diester of isonicotinic acid (BR′B). In this system, strong intermolecular hydrogen bonds may occur between two carboxylic groups or between a carboxylic group and a pyridyl nitrogen while only weak interaction are possible between two pyridyl groups. Therefore, it might be envisaged the formation of statistical linear interaction patterns which can be schematically represented as for a "topological" copolymer: -((BR′B-ARA)$_n$-(ARA-ARA)$_m$-)$_x$ containing ...-BR′B-ARA-... and ...-ARA —ARA-... but no -BR′B —BR′B-sequences [5, 6]. Of course, the formation of much more complex network-like labile structures cannot be excluded.

Griffin *et al.* [5, 6] have recently reported that molecular complexes, presumably of polymeric structure, are formed in binary systems of tetraethyleneglycol di-*p*-benzoic acid and hydroquinone-bis(4-pyridinecarboxylate), leading to mesomorphic phases as found for covalent semiflexible mesogenic polymers.

We report here on the phase behavior of binary systems containing the isonicotinic acid diester of methylhydroquinone as the difunctional base (**B**) and several dicarboxylic acids based on terephthalic acid, including terephthalic acid itself. The use of components containing substituents at

the aromatic core has been suggested by the opportunity of reducing melting temperatures.

2. EXPERIMENTAL

Isonicotinic Acid Diester of Methylhydroquinone (B)

The synthesis has been performed following a procedure suggested by Stupp *et al.* [7] and modified by Griffing *et al.* [5].

9.4 g methylhydroquinone and 6.9 g isonicotinic acid are dissolved in 200 mL dichloromethane (previously dried over alumina) together with 6.8 g 4-dimethylamino-pyridine and 10.6 g monohydrate *p*-toluensulfonic acid. To this solution, 9.2 g diisopropylcarbodiimide are added. The reaction takes place at room temperature during 20 h. yield 74%. The ^{1}H-NMR spectrum is consistent with the expected formula.

Substituted Terephthalic Acids (Substituents: -O(CH$_2$)$_n$CH$_3$)

The synthesis of **A1**(n = 5), **A4**(n = 2) and **A5**(n = 9), has been performed according to a precedure already described [8]. A standard method has also been applied for the synthesis of 4-hexyloxybenzoic acid (**A2**).

Chemical nature and purity of all synthesized compounds was ascertained by ^{1}H-NMR spectrometry. A Mettler TGA 50 apparatus was utilized to investigate on the thermochemical stability of pure compounds and binary systems at the temperature conditions relevant in the study of their phase behavior. The phase behavior was examined by means of differential scanning calorimetry (DSC-7 Perkin Elmer apparatus, nitrogen atmosphere), polarizing microscopy (Leitz microscope, Linkam temperature controled hot stage, nitrogen atmosphere) and X-ray diffraction means (photographic flat film camera, CuKα radiation).

3. RESULTS AND DISCUSSION

Phase Behavior of System (A1 + B)

The phase behavior of system (**A1** + **B**) has been investigated starting from a finely powdered equimolar mixture of solution crystallized components. Neither **A1** or **B** alone exhibit liquid crystalline properties. Solution crystallized **B** undergoes a solid phase transition at 173.8°C followed by

melting to an isotropic liquid at 178.5°C. [It should be noticed that the isonicotinic acid diester of unsubstituted hydroquinone has been reported by Griffin *et al.* [5] as melting at 231°C]. The total enthalpy change is $144.2\,Jg^{-1}$. The melt crystallized sample undergoes two low enthalpy (total $\Delta H < 8\,Jg^{-1}$) solid phase transitions at 123.6°C and 167.3°C and melts to an isotropic liquid at 178,5°C with an enthalpy change of $84.8\,Jg^{-1}$. Cooling the molten sample does not reveal any monotropic mesomorphysm. Crystallization takes place at ~ 153°C ($10\,Kmin^{-1}$ cooling rate) with an enthalpy variation of $-81\,Jg^{-1}$. The X-ray diffraction patterns of solution crystallized and melt crystallized samples are both characterized by a high intensity Bragg diffraction corresponding to a lattice distance of 0.582 ± 0.005 nm. This diffraction has been monitored to detect the presence of unaltered **B** in the (**Al + B**) systems subjected to a thermal treatment.

Solution crystallized **A1** shows a solid state transition at 169°C ($\Delta H = 60\,Jg^{-1}$). Melting to an isotropic liquid takes place at 220.5°C with an enthalpy change of $134.5\,Jg^{-1}$. The crystallization of the sample on cooling corresponds to a DSC endothermic signal peaked at 216°C but formed by two coalescent signals with a total enthalpy change of $-116\,Jg^{-1}$. The optical observation excludes that the crystallization might be preceded by an isotropic–liquid crystal phase transition. Melting of the melt crystallized sample occurs at 222°C with an enthalpy change of $116\,Jg^{-1}$.

The phase behavior of (**A1 + B**) as prepared is drastically different (Fig. 1). Although the components are in the solid state, a strong interaction takes place at temperatures far lower than the melting temperature of both of them leading to a liquid phase. Melting of the mixture occurs essentially within the range 125–145°C forming an anisotropic liquid exhibiting a very mobile schlieren texture.

Isotropization takes place at ~ 150°C. Melting of a small fraction of the system (as prepared (**A1 + B**) is a heterogeneous two-solids system) is detectable up to ~ 160°C. Above this temperature the system is homogeneously liquid and isotropic. The DSC analysis on cooling (Fig. 1, curve b) shows an exothermic signal peaked at ~ 145°C ($\Delta H = -6\,Jg^{-1}$) that corresponds to the optically detected anisotropization of the liquid, showing a schlieren texture indicative of a nematic structure. This liquid phase transition is reversible. However, cooling down to ambient temperature ($10\,Kmin^{-1}$ cooling rate) the quenching of the liquid crystalline phase may be accompanied by the crystallization of a small fraction of the sample. The X-ray diffraction pattern recorded at room temperature for a sample previously brought at 165°C and quickly cooled down is indicative of very scarce crystallinity, if any. The diffraction pattern is characterized by a

broad halo centered around $\sin(\theta)/\lambda = 1.20\,nm^{-1}$ with a slight equatorial polarization. No Bragg diffraction indicative of the presence pure **B** is detectable. The schlieren pattern, exhibited by the fluid nematic phase, is also quenched down adding evidence to the formation of a glassy liquid crystalline structure. Crystallization to a new low-temperature melting system takes place on heating (Fig. 1, curve c) and, finally, the homogeneous liquid crystalline phase is recovered.

No significant thermochemical problems are detectable by TGA analysis within the outlined temperature range (5% weight loss temperature is 240°C under nitrogen).

As far as the basic feature is concerned (*i.e.*, the formation of a mesophasic liquid out of non mesogenic components) the phase behavior of (**A1** + **B**) is consistent with that reported by Griffin *et al.*, for an equimolar mixture of tetraethyleneglycol di-*p*-benzoic acid and the nicotinic acid diester of hydroquinone. However, in our case no smectic mesomorphism has been observed and no modification of the behavior was detected after repeated thermal cycles.

Component **A1** has three chemical-structural features which had been hypothetically considered to be influential on the phase behavior of the

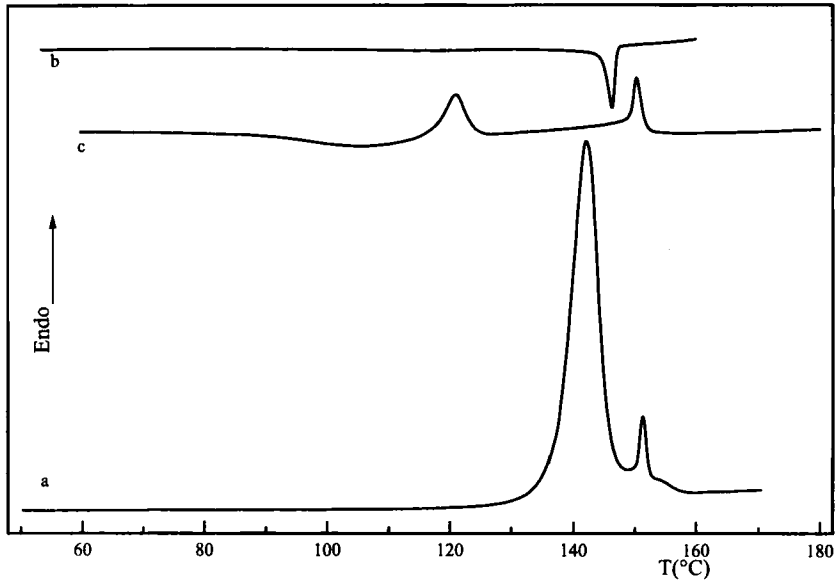

FIGURE 1 Thermal behavior of system (**A1** + **B**). DSC heating run of an as prepared mixture (curve a); successive cooling run (curve b); second heating run (curve c).

equimolar mixture with **B**: (i) is bifunctional, therefore capable in principle to be engaged in the formation of arrays of connected molecules; (ii) it has a rigid core, therefore likely to produce "statistical mesogens" with a reduced number of **A1B** sequences; (iii) it has a flexible substituent on the core, therefore melts at reduced temperature and is more likley to afford homogeneous liquid systems in combination with **B** at moderate temperatures. The results reported above appear to be qualitatively consistent with these expectations. However, in order to gain some additional insight, some correlated compositions were examined: (**2A2 + B**) [**A2** = 4-hexyloxybenzoic acid]; (**A3 + B**) [**A3** = terephthalic acid]; (**A4 + B**) [**A4** = propyloxyterephthalic acid]; (**A5 + B**) [**A5** = decyloxyterephthalic acid].

The examination of system (**2A2 + B**) gives interesting suggestions. The phase behavior of **A2** has been already reported [9]. The characterization parameters of our sample, prepared by standard methods, are consistent with those reported in the literature. It melts at 108.6°C ($\Delta H = 62.9\,Jg^{-1}$) to a nematic liquid which isotropizes at 153.7°C ($\Delta H = 12.3\,Jg^{-1}$). A solid state transition is detectable at 71°C with an enthalpy change of $27.3\,Jg^{-1}$.

The DSC behavior of (**2A2 + B**) at the first heating run of a previously untreated, finely powdered sample, with **A2/B** = 2 molar ratio is shown in Figure 2 (curve a). The evidence of a strong interaction between the components is detectable in the temperature range 102–113°C, that is across the melting range of **A2**. The optical observation indicates that a new solid phase is formed out of liquid **A2** and the solid **B**. The endothermic ($\Delta H = 93.6\,Jg^{-1}$) signal peaked at 134°C corresponds to the melting of the new phase to a homogeneous anisotropic liquid with a very mobile schlieren texture whose sharp isotropization takes place at 154.2°C with an enthalpic change of $6.8\,Jg^{-1}$. On cooling at 10°C/min cooling rate (Fig. 2, curve b), anisotropization takes place at ~150°C and crystallization at 95°C ($\Delta H = -81.0\,Jg^{-1}$). No solid state transition is detected either on cooling or during the successive heating run and no phase change takes place on heating before melting at 134°C. The melting DSC endotherm is considerably sharp: 3°C half-width at 10°C heating rate, compared to 2°C found for pure **A2**. This behavior, as well as the liquid–liquid transition, is entirely and repeatedly reversible. Apparently, crystallization of liquid (**2A2 + B**) produces a single stoichiometrically invariable phase containing both components.

The stability of the liquid crystal phase of (**2A2 + B**) is only slightly larger than that of pure **A2**. This is an intriguing point and a purely qualitative answer might be found in the different degree of rigidity of the molecular aggregates stemming from hydrogen bond geometry. In fact, hydrogen bond

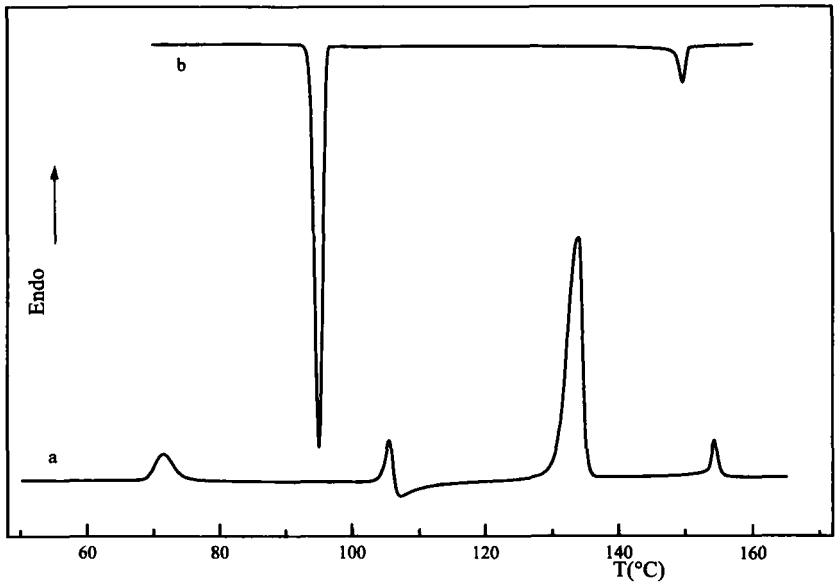

FIGURE 2 Thermal behavior of system (**2A2** + **B**). DSC heating run of an as prepared mixture (curve a); successive cooling run (curve b).

interactions in the liquid phase should lead basically to three molecular aggregations in statistical equilibrium: **A2-B-A2**, **A2-B** and **A2-A2**; the latter is responsible of the liquid crystalline property of pure **A2**. The geometry of these species may be described as a rigid rod-like core connected to two terminal flexible segments, for **A2-B-A2**, and **A2-A2**, or to a single such segment, for **A2-B**. As to **A2-A2**, due to the carboxylic acid double hydrogen bond, the -O-Φ-COOH—HOOC-Φ-O- (Φ = *p*-phenylene) group should be considered as the "mesogenic" core and groups $-(CH_2)_5CH_3$ as the flexible segments. For **A2-B-A2** and **A2-B**, the hydrogen bond between acid and base does not require a particularly rigid alignment of the O-H—N direction with the N—C-COO- axis of the isonicotinic moiety. This means that the entire **A2** group might be taken as a "flexible" segment with respect of the linear rigid core **B**. This feature would considerably shorten the axial ratio of the **A2-B-A2** aggregate with respect to the rigidly linear geometry consequently reducing its mesogenic potential.

Otherwise, for a rigidly linear -O-Φ-COOH—**B**—HOOC-Φ-O- core the stability of the liquid crystal phase of (**A2-B-A2**) should be expected to be definitely higher than for pure **A2**. However, it should be remarked that the lability of the molecular aggregates in the liquid must have a depressive

effect on the stability of the mesophase. It may be worth noticing that a similar phenomenon has been reported by Kato *et al.* [10] concerning an equimolar complex between **A2** and 4-propoxy,4′-stilbazole. In that case, isotropization of the nematic phase occurs at 155°C. Taking into account that the axial ratio of 4-stilbazole moiety is rather close to that of **B**, due to the larger average cross sectional area of the latter, qualitative explanation might be analogous to that outlined above.

The DSC behavior of a previously untreated (**A3** + **B**) system is shown in Figure 3 (curve a). No calorimetrically detectable interaction of the two components takes place before melting of **B**. However, the enthalpy change connected to the melting transition is significantly lower then one would expect if any interaction between **A3** and **B** were absent (measured 87 Jg^{-1}, expected 96 Jg^{-1}). Actually, a clearly exothermic interaction is detectable at temperatures higher than ~210°C with a broad DSC signal peaked at ~225°C followed by a large endotherm peaked at 241°C. The DSC heating behavior of a system previously brought at 220°C and kept at that temperature for 10 min, then cooled at room temperature, does not show neither the melting signal of **B** nor the successive exothermic effect but only

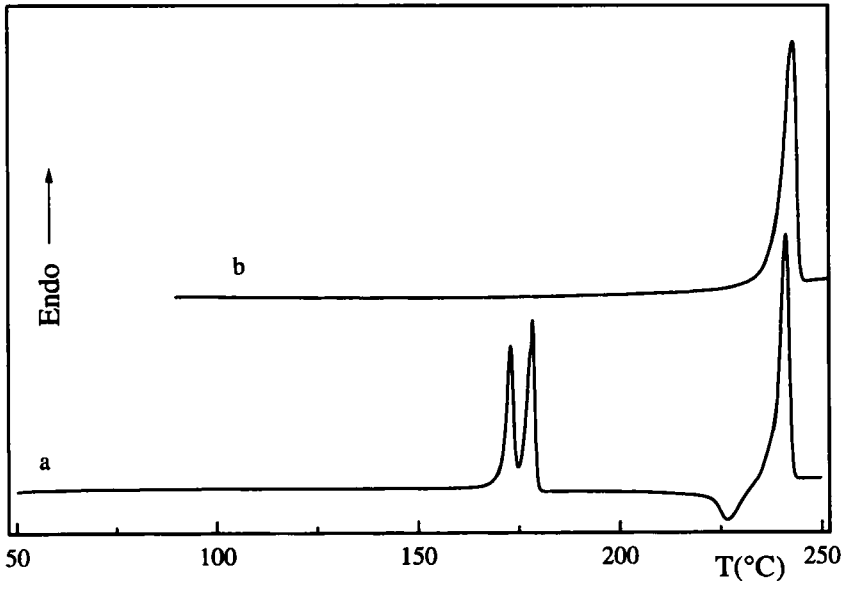

FIGURE 3 Thermal behavior of system (**A3** + **B**). DSC heating run of an as prepared mixture (curve a); DSC heating run of a sample previously brought at 220°C for 10 min then cooled at room temperature (curve b).

the endothermic transition at ~240°C (Fig. 3, curve b). Optical observations indicate that the exothermic region corresponds to the formation of a solid phase which eventually melts at ~240°C to an isotropic liquid. This solid phase (phase **C**) does include the entire amount of **B** originally present but only part of the terephthalic acid is involved; the exceeding fraction remains at the solid state. No transformation of phase **C** is detectable on cooling. The phase behavior of a sample previously brought to $T > 240$°C is to some extent dependent on the successive cooling rate and might also be slightly influenced by thermochemical degradation going on at high temperatures (~2% weight loss under nitrogen at 240°C). However, the formation of a crystal phase melting close to 240°C is still observed.

In conclusion, the phase behavior of (**A3** + **B**) shows some analogy and sharp differences as compared to that of (**A1** + **B**). A strong interaction takes place between the components but only on melting of **B**. The product of this interaction is a solid phase melting at an intermediate temperature between those of the pure components (melting temperature of **A3** is reported to be ~308°C with sublimation). The liquid phase is isotropic and no monotropic mesomorphism is detected on cooling before crystallization takes the start at ~180°C. This means that even in case an hypothetical liquid crystal phase were formed with a thermal stability comparable to that shown by system (**A1** + **B**), it would remain entirely virtual.

The examination of systems (**A4** + **B**) and (**A5** + **B**) adds new information, particularly concerning the role played on the mesophase stability by the substituent at the terephthalic segment. The DSC behavior of an as prepared fine equimolar mixture of **A4** and **B** is shown in Figure 4 (curve a). As for (**A1** + **B**), a strong interaction between the two components takes place in the solid state at temperatures well below the melting temperatures of both (Tm(**A4**) = 239°C). The endothermic signal peaked at 149°C corresponds to the progressive melting of the mixture to a liquid crystalline nematic phase. At 10°C/min heating rate, a small fraction of the solid (most likely **A4**) does not dissolve into the liquid phase until ~185°C. At that temperature the liquid phase is homogeneous and isotropic, isotropization having taken place at 165°C. This transition is thoroughly reversible with only a small supercooling of the isotropic phase (~3°C), as usually observed for low molecular weight nematics. Deep cooling of the nematic phase at 10°C/min cooling rate brings the system to non equilibrium conditions with only partial crystallization (Figure 4, curve b). However, the liquid crystalline phase behavior is entirely reproduced at the successive heating run.

The behavior of (**A5** + **B**) is to some extent similar. Interaction is calorimetrically detectable at temperatures above ~120°C (Tm(**A5**) = 215°C).

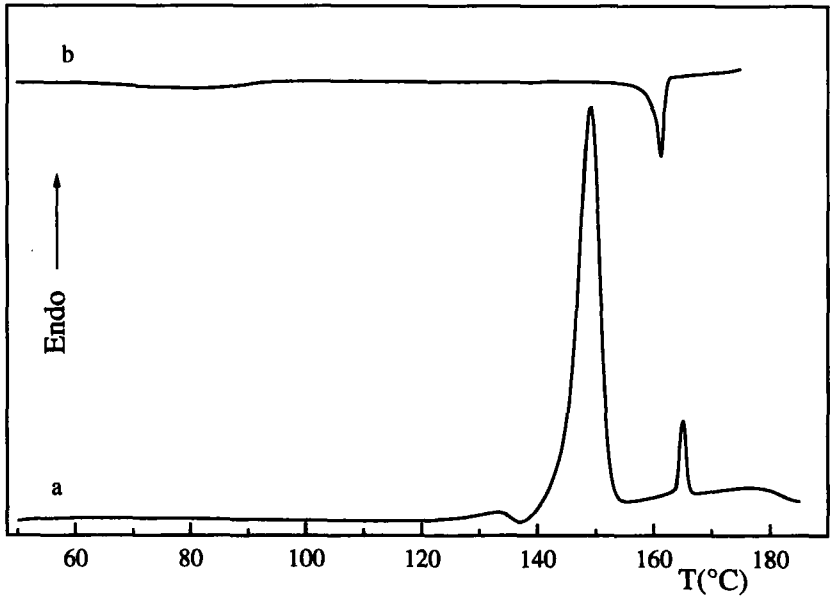

FIGURE 4 Thermal behavior of system (**A4 + B**). DSC heating run of an as prepared mixture (curve a); successive cooling run (curve b).

Melting to an isotropic liquid is completed at ~ 145°C (Fig. 5, curve a). On cooling, a phase transition to a nematic occurs at 135°C. The isotropization temperature measured on heating the liquid crystal is 138°C (Fig. 5, inner squared area). As for (**A4 + B**), cooling to room temperature produces quenching of the nematic phase (Fig. 5, curve b) which eventually undergoes crystallization on heating (Fig. 5, curve c). No attempt has been made to clarify the nature of the solid phase. However, the liquid crystalline behavior is qualitatively and quantitatively reproducible over numerous thermal cycles.

4. CONCLUSIONS

The outlined evidences may be summed up as follows: (a) the phase behavior of all systems examined indicate that a strong interaction takes place between **B** and the carboxylic acid component. For all dicarboxylic acids, but terephthalic acid, the interaction has a dramatic effect even at temperatures lower than the melting temperature of both components; (b) with all acids, but terephthalic acid, the system exhibits an enantiotropic

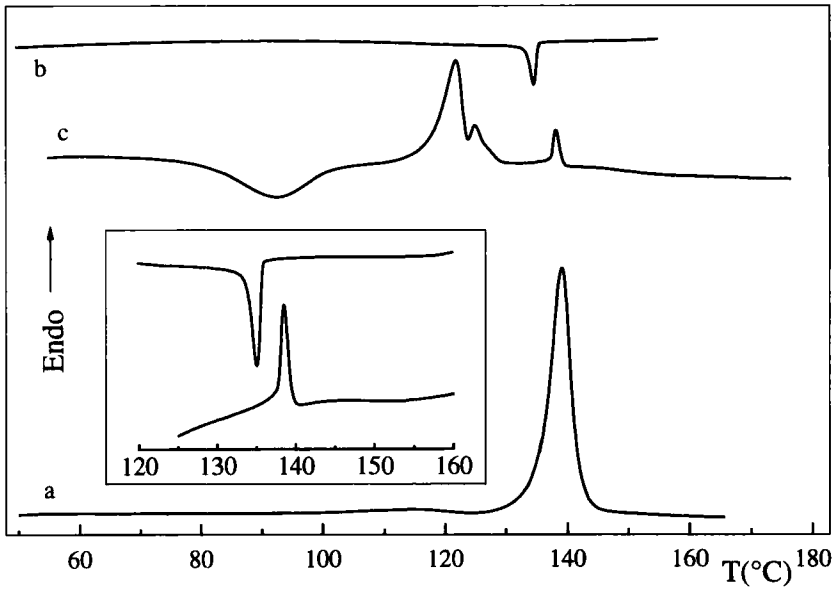

FIGURE 5 Thermal behavior of system (**A5 + B**). DSC heating run of an as prepared mixture (curve a); nematic-isotropic and reverse liquid phase transitions (inner squared area); cooling run from the isotropic phase (curve b); successive heating run (curve c).

TABLE I Phase behavior of examined systems

System	*Tm*(**An**)/°C[a]	*Tm*(**An + B**)/°C[b]	*Phase*[c]	*Ti*/°C[d]
A1 + B	220.5	125–145	nematic	150
2A2 + B	108.6	102–113	nematic	154.2
A3 + B	~308 (subl.)	240	isotropic	
A4 + B	239	149	nematic	165
A5 + B	215	145	isotropic[e]	135

[a] melting temperature of pure **An**; [b] melting temperature of as prepared **An + B**; [c] liquid phase at *Tm*(**An + B**); [d] isotropization temperature; [e] nematic for previously molten samples.

liquid crystal phase of nematic structure; (c) the thermal stability of the nematic phase shown by a system containing substituted terephthalic acid decreases with increasing length of the substituent; (d) the liquid crystalline thermal stability of systems (**An + B**), as compared to that of (**2A2 + B**), or of **A2**, suggests that the difunctional structure of **An** and **B** components might be not particularly effective in producing polymeric segments with comparatively high statistical average axial ratio.

Acknowledgements

This research has been partially supported by Ministero della Ricerca Scientificae Tecnologica of Italy and Consiglio Nazionale delle Ricerche. The authors are grateful to Centro di Metodologie Chimico Fisiche for the use of NMR spectrometry facilities.

References

[1] H. Kelker and R. Hatz, Handbook of Liquid Crystals, Chap. 8, Verlag Chemie GmbH, Weiheim (1980).
[2] J. S. Dave and J. M. Lohar, *Chem.* and *Ind.*, p. 597 (1959).
[3] A. Roviello, S. Santagata and A. Sirigu, *Makromol. Chem., Rapid Commun.*, **4**, 281 (1983).
[4] A. Beguin, J. Billard, F. Bonamy, J. M. Buisine, P. Cuvelier, J. C. Dubois and P. Le Barny (Eds.), Sources of Thermodynamic Data on Mesogens, *Mol. Cryst. Liq. Cryst.*, **115**, (1984).
[5] C. Alexander, C. P. Jariwala, C. M. Lee and A. C. Griffin, *Makromol. Chem., Macromol. Symp.*, **77**, 168 (1994).
[6] C. P. Jariwala, C. M. Lee and A. C. Griffin, *Polymer*, **35**, 4550 (1994).
[7] J. S. Moore and S. I. Stupp, *Macromolecules*, **23**, 65 (1990).
[8] U. Caruso, P. Iannelli, S. Pragliola, A. Roviello and A. Sirigu, *Macromolecules*, **28**, 6089 (1995).
[9] A. J. Herbett, *Trans. Farad. Soc.*, **63**, 555 (1967).
[10] T. Kato, T. Uryu, F. Kaneuchi, C. Jin and J. M. J. Frechet, *Liq. Crystals*, **14**, 1311 (1993).