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Structure and substitution effects on the thermotropicity of some polyesters and model compounds

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The variations which occur in the thermal stability of the nematic mesophase as a function of the structure of the mesogenic moiety are considered here for the role played by three types of modifications. These are changes in the chemical nature of the mesogenic group, variation of the axial ratio of the rigid core and the presence of lateral substituents on the aromatic rings. Low molecular weight and polymeric liquid crystals of similar chemical nature have been investigated in order to see if parallel structure–property relationships exist between the two groups of compounds. In particular, starting from a mesogenic group built up of three aromatic rings connected by ester bonds, we have introduced the following modifications: (i) substitution of the central $-COOC_6H_4OOC-$ with the –CH=N–N=CH– group; (ii) addition of two oxybenzoic end units to increase the length of the mesogenic moiety; (iii) introduction of two or more lateral methoxy substituents on the aromatic rings. The compounds were obtained by low temperature solution esterification between acyl chlorides and phenolic derivatives in the presence of a tertiary amine. Syntheses generally took place through the preliminary preparation of suitable intermediates. The thermal stability and the nature of the mesophases have been examined by different techniques. An interpretation of the results on the basis of the axial ratio and the strength of orientation dependent mutual attractions is attempted for model compounds. As far as polymers are concerned thermodynamic parameters follow the expected trend, if compared with those of low molecular weight analogues. Qualitatively models and polymers exhibit a similar dependence of mesophase stability on geometrical and electronic effects.

1. Introduction

A large variety of segmented thermotropic polymers have been synthesized in recent years [1–10]; however, in spite of intensive research activity in preparing and characterizing these materials, the relationship between structure and liquid crystal properties is one of the problems which continues to demand additional and systematic investigation. Following our previous reports [11, 12], devoted to a better understanding of some aspects of this relationship, we have investigated a series of model compounds and polymers with systematically modified mesogenic moieties. In particular, starting from a rigid core built up of three aromatic rings connected by ester bonds, we have introduced the following modifications: (i) substitution of the central –COOC6H4OOC– with the –CH=N–N=CH– group; (ii) addition of two oxybenzoic end units to increase the length of the mesogenic moiety; (iii) introduction of two or more lateral substituents on the aromatic rings. The compounds obtained have been

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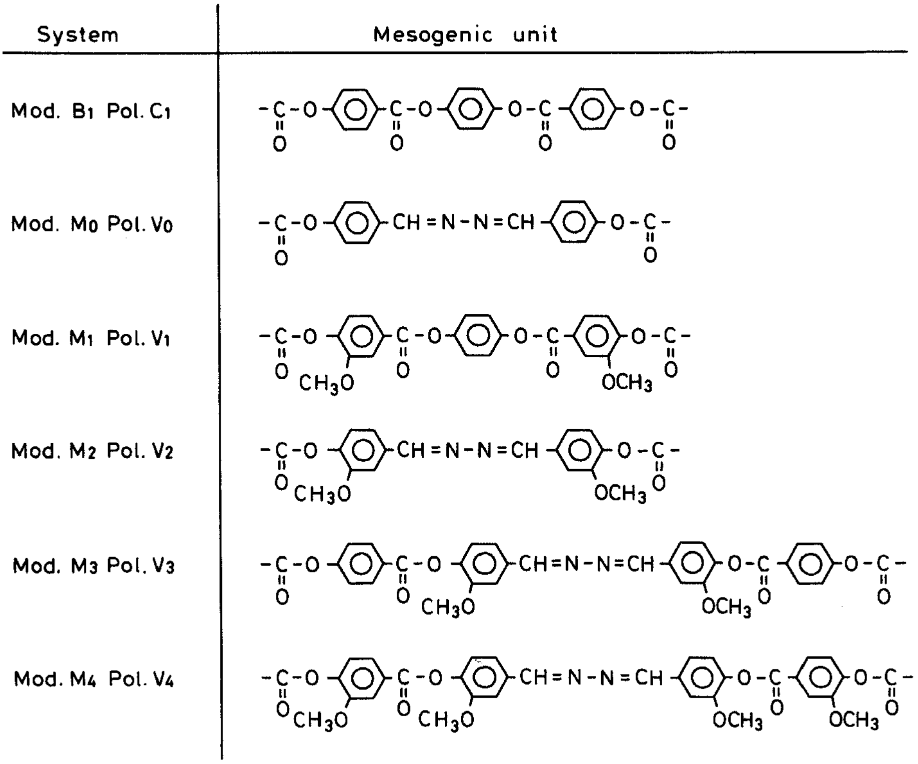

flexible spacers $(CH_2)_8$ in polymers

end tails $CH_3(CH_2)_3$ in models

Figure 1. Chemical structure of the mesogenic units of the model compounds and of the polymers.

characterized by optical microscopy and thermal analysis. The structure of the mesogenic units are shown in figure 1, together with the reference marks. Model compounds have *n*-butyl end groups, whereas polymers have flexible spacers of eight methylene units.

2. Experimental

2.1. *Materials*

The structures of the intermediates **I–V**, used to synthesize the model compounds and polymers, are shown in figure 2. 4-Hydroxybenzoic acid and 4-hydroxy-3-methoxybenzoic acid were recrystallized from water; hydroquinone was recrystallized from toluene and valeryl chloride was purified by distillation under reduced pressure. Sebacoyl chloride (99+per cent from Aldrich) and 4,4′-dihydroxy-3,3′-dimethoxybenzaldehydazine **I** (vanillin azine 99 per cent from Aldrich) were used as received. 4-Valeryloxybenzoyl chloride **II** was synthesized as described previously [13]; 4-valeryloxy-3-methoxybenzoic acid (recrystallized from *n*-hexane, melting point 103·9°C) and its chloride **III** were synthesized according to the same method. 4,4′-(Sebacoyldioxy)dibenzoyl dichloride **IV** was obtained as reported elsewhere [13], following the method of Bilibin *et al.* [14]. The same procedure was adopted to obtain 4,4′-(sebacoyldioxy)-3,3′-dimethoxydibenzoic acid (recrystallized from 1,4-dioxane,

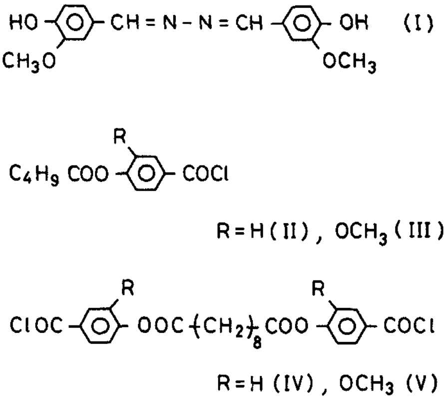

Figure 2. Structures of intermediates I–V used to prepare the model compounds and polymers.

melting point 185·1°C) and the corresponding acid dichloride **V** (recrystallized from *n*-hexane, melting point 83·8°C).

2.2. *Synthesis of the model compounds*

The preparation of model B1 is described elsewhere [12].

Model M1 was obtained by dissolving 4-valeryloxy-3-methoxybenzoyl chloride **III** (5·5 mmol) and hydroquinone (2·2 mmol) in 1,1,2,2-tetrachloroethane (TCE) (overall amount 20 ml) using 29·2 mmol of freshly distilled triethylamine (Et_3N) as an acid acceptor. The reaction mixture was maintained under stirring in a nitrogen atmosphere for 24 h at room temperature. The resulting compound was recrystallized twice from *n*-hexane. Yield 70 per cent.

Model M2 was prepared by adding slowly to a solution of valeryl chloride (6·7 mmol) in 10 ml of tetrahydrofuran (THF) 2·2 mmol of vanillin azine **I** in 0·48 ml of pyridine (Py). The mixture was stirred for 24 h under nitrogen; after reducing the solution volume to a third by evaporation under vacuum, the product was precipitated with a large amount of water, isolated and twice recrystallized in *n*-hexane. Yield 73 per cent.

Model M3 was synthesized by reacting 4-valeryloxybenzoyl chloride **II** (4·5 mmol) and vanillin azine **I** (1·5 mmol) in 40 ml of THF and 6 mmol of Py. The product was precipitated with water and twice recrystallized from ethylacetate. Yield 65 per cent.

Model M4 was obtained by mixing under stirring 2·24 mmol of 4-valeryloxy-3-methoxybenzoyl chloride **III** and 0·89 mmol of vanillin azine **I** in 20 ml of TCE and 0·95 ml of Py. The resulting compound, precipitated in ethanol, was recrystallized from toluene. Yield 67 per cent.

2.3. *Synthesis of the polymers*

The preparation of polymer C1 is reported in [12].

Polymer V1 was obtained by adding slowly to a solution of hydroquinone (3 mmol) and Et_3N (15 mmol) in dry TCE (15 ml) an equimolar amount of 4,4′-(sebacoyldioxy)-3,3′-dimethoxydibenzoyl dichloride **V** dissolved in 15 ml of TCE. The mixture was stirred under a nitrogen atmosphere for 48 h at room temperature; the polymer was precipitated in acetone, carefully washed to remove the tertiary amine hydrochloride and finally dried under vacuum. Polymers V2 and V3 were prepared with the same procedure, by mixing vanillin azine **I** and sebacoyl chloride or vanillin azine **I** and 4,4′-(sebacoyldioxy)dibenzoyl dichloride **IV**, respectively.

Conventional interfacial polymerization conditions were used for the preparation of polymer V4; 2 mmol of 4,4′-(sebacoyldioxy)-3,3′-dimethoxydibenzoyl dichloride **V** in 20 ml of chloroform were added to a solution of vanillin azine **I** (2 mmol) in 4·5 ml of 1 N NaOH and 0·034 mmol of benzyltriethylammonium chloride. After stirring at room temperature for 4 h the reaction mixture separated into two phases; the organic layer was washed four times with water and finally precipitated in methanol.

2.4. *Characterization*

Conventional tests of structural identification were performed on the reaction intermediates and on the model compounds (elemental analysis, IR and NMR spectroscopy). Intrinsic viscosities of the polymeric samples were determined at 25°C in TCE or TCE/phenol 40:60 (v/v). Microscopic observations were carried out with a Polyvar Pol Reichert polarizing microscope, equipped with a Mettler FP 82 hot stage (control unit FP 80) and a Linkam THMS 600/TMS 91 system. Transition temperatures and enthalpies were determined by DSC thermograms recorded with a Mettler TA 3000 system (measuring cell DSC 30) with sample weights from 5 to 10 mg. Heating and cooling rates of 10 or 20 K min^{-1} were generally used. Thermal profiles were recorded on an Epson mod. PC AX 2 disc memory device and the standard data analysis programs were used to evaluate enthalpies and transition temperatures. The thermal stability of the polymeric samples was studied by using a Perkin–Elmer TGS 2 analyser, with heating rates of 20 k min^{-1}.

3. Results and discussion

3.1. *Model compounds*

First we shall examine the results obtained on the model compounds. The elemental analysis characterization is reported in table 1; IR spectra for all of the samples and ^{1}H NMR for compounds M2 and M4 appear to be consistent with the expected chemical structure. The transition temperatures were determined both by DSC measurements and optical observations.

Model B1, as reported elsewhere [12], exhibits a wide nematic range (about 100°C). We did not investigate model M0, since its thermal behaviour is reported in the literature (nematic between 142·2 and 158·4°C) [15]. Model M1 appears to be monotropic: during the first heating cycle it melts with a double endotherm into an isotropic phase; on cooling a nematic phase appears at about 100°C and crystallization occurs around 86°C. Depending on the cooling rate either needles or spherulites are observed. By heating a sample previously crystallized at a rate as slow as -2 K min^{-1}, a single endotherm is observed, meaning that the shape of the melting profile is related to the crystalline form of the sample. Only a crystal–isotropic transition has been found for model M2, whereas models M3 and M4 exhibit an enantiotropic and a monotropic nematic phase, respectively.

The results of DSC analysis are summarized in table 2; they indicate that, as the central –COOC6H4OOC– unit is substituted for the shorter –CH=N–N=CH– bridging group, the stability range of the nematic phase is substantially reduced (see models B1 and M0). The introduction of two lateral methoxy substituents decreases both the melting point and the nematogenic character of the molecule: as a

Table 1. Elemental analysis of model compounds.

	Percentage C		Percentage N		Percentage H	
Sample	Calculated	Found	Calculated	Found	Calculated	Found
B1 [12]	69·52	69·29	—	—	5·79	5·80
M1	66·31	65·94	—	—	5·86	5·98
M2	66·64	66·49	5·97	6·00	6·88	6·91
M3	67·67	67·58	4·25	4·10	5·71	5·73
M4	65·62	65·38	3·65	3·51	5·73	5·82

Table 2. Transition temperatures and enthalpies for the model compounds.

Model	T_m/°C	T_{NI}/°C	ΔH_m/kJ mol^{-1}	ΔH_{NI}/kJ mol^{-1}
B1 [12]	166·5	261·5	28·5	1·88
M0 [15]	142·2	158·4	—	—
M1	106·8–114·0	(100·1)	29·9	(0·64)
M2	127·3	—	34·5	—
M3	229·9	274·8	61·6	3·99
M4	206·1	(194·3)	66·5	(2·31)

Brackets indicate monotropic transitions.

consequence model M1 is only monotropic and model M2 is not liquid-crystalline. However, upon increasing the length of the rigid moiety by adding two oxybenzoic units, the nematic character is restored (model M3) and persists even if two more methoxy groups are appended to the aromatic rings (model M4).

In order to correlate the observed thermal properties with the geometry of the molecules, the mean axial ratios $\langle x \rangle$ of the mesogenic units, given in figure 1, were evaluated from bond lengths and angles [16, 17], assuming van der Waals radii equal to 1·2 and 2·0 Å for H and CH_3, respectively. To simplify the problem, coplanarity of the ester, phenylene and –CH=N–N=CH– groups has been assumed, even though it has been reported that significantly planar azines, such as anisaldehyde azine, are not completely so [18] and steric interactions in methoxylated models could introduce departures from coplanarity. The mean diameters for models M1–M4 have been calculated by averaging the values estimated by considering substitution on the 3 or 5 position of the 4-hydroxybenzoic acid ring. The mean axial ratios $\langle x' \rangle$ of the whole molecules have been calculated by assuming for the terminal *n*-butyl chains conformations which approach most closely a rod-like shape [12]. The results are listed in table 3, where l and l', $\langle x \rangle$ and $\langle x' \rangle$ refer to the mesogenic unit and to the whole molecule, respectively, and T^* is the characteristic temperature of the Flory–Ronca theory [19], deduced from $\langle x' \rangle$ and T_{NI}. Methoxy substitution increases the diameter of the mesogenic unit going, for example, from 7·54 Å, for unsubstituted B1, to a mean value of 9·76 Å for substituted M1; this value is averaged taking into account that methoxy groups can lie on the same side or opposite with respect to the ideal axis of the rod and that free rotation around the ring–oxygen bond is possible. Molecular broadening in M1 and M2 increases the mean diameter by about 20–25 per cent as compared to unsubstituted analogues, while a smaller increase, of the order of 4–5 per cent, arises from the comparison of disubstituted M3 with tetrasubstituted M4.

Table 3. Lengths and axial ratios of the mesogenic unit (l, $\langle x \rangle$) and of the molecule (l', $\langle x' \rangle$). Estimation of T^* from the Flory–Ronca theory [19].

Model	l/Å	$\langle x \rangle$	l'/Å	$\langle x' \rangle$	T_{NI}/K	T^*/K
B1 [12]	19·53	2·59	31·66	3·82	534·5	325
M0	15·84	2·10	27·97	3·38	431·4	336
M1	19·53	⟨2·00⟩	31·66	⟨2·95⟩	(373·1)	368
M2	15·84	⟨1·62⟩	27·97	⟨2·61⟩	—	—
M3	28·32	⟨2·96⟩	40·45	⟨3·85⟩	547·8	328
M4	28·32	⟨2·83⟩	40·45	⟨3·69⟩	(467·3)	308

If we try to discuss qualitatively T^* values, we observe that the comparison between models B1 and M1 indicates that, as already suggested for methyl substituted mesogenic esters [12], the strength of the orientation dependent mutual attraction between molecules, measured by T^*, is enhanced also by the presence of methoxy groups on the rings. If a similar increase of T^* due to the introduction of two methoxy groups on model M0 is considered, a T^* value of 380 K can be estimated for M2 with an isotropization temperature of about 318 K (45°C). This temperature is quite close to the value of 35°C, determined by extrapolating the nematic–isotropic transition line in the phase diagram for a binary system of model M2 with nematic p-azoxyanisole (PAA) (see figure 3). Geometric factors appear to play the main role in stabilizing the nematic phase of models M3 and M4.

3.2. *Polymers*

As for the polymers corresponding to the models just described, their yields and intrinsic viscosities are listed in table 4 and the thermodynamic properties are summarized in table 5.

Polymer C1 shows a wide nematic range (about 80°C) and a good thermal stability (up to 400°C); on cooling the nematic melt the DSC profile indicates crystallization at 250°C (see figure 4). Fast cooling of the sample from the isotropic state demonstrates that both the transitions are reversible; however, under these conditions, crystallization is shifted to lower temperatures (about 200°C, curve c of figure 4). This behaviour agrees with a model for crystallization of thermotropic polymers, recently proposed [20].

Polymer V1, with two methoxy groups on the external rings, is nematic between 200·5 and 230·7°C; the liquid crystal range is substantially reduced since substitution seems to affect T_{NI} more than T_m. On cooling only the isotropic–nematic transition is observed at 219·5°C and during the second heating cycle a cold crystallization occurs at 99·9°C, followed by melting at 116·6°C and isotropization at 227·6°C (see figure 5). Thermogravimetric analysis demonstrates that the polymer is stable up to 380°C.

Polymers V2, V3, V4, obtained from vanillin azine and different acid dichlorides, show a reduced thermal stability (up to 300°C); in spite of our attempts to optimize the experimental conditions, the intrinsic viscosities of the polymers did not exceed 0·2–0·3 dl g^{-1}. The DSC profile of sample V_2 shows a broad endotherm at 159·6°C, corresponding to a crystal–isotropic transition; on cooling at -10 K min^{-1} no crystallization occurs. This polymer crystallizes during the second heating run at 107·8°C and melts at 151·3°C. Sample V3, with two oxybenzoic units at the ends of the rigid segment, melts with a double endotherm at 202·8/229·3°C and becomes isotropic at about 300°C (see figure 6). The enthalpy associated with the N–I transition is probably underestimated, since this peak is very close to the degradation threshold. On

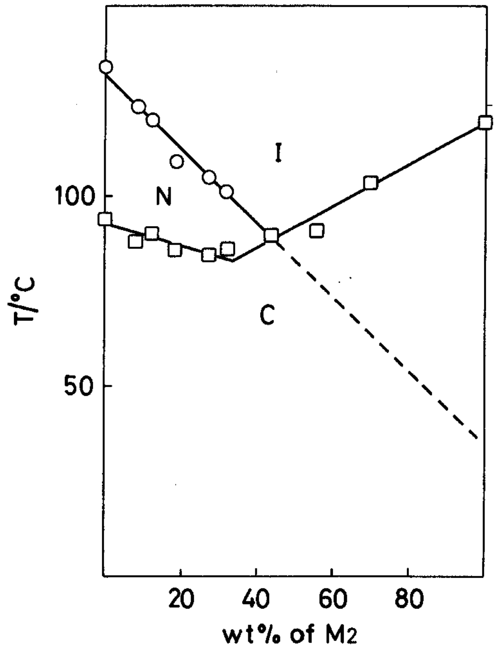

Figure 3. Phase diagram for the miscibility study of mixtures of model M_2 and PAA (C, crystal; N, nematic; I, isotropic liquid). The open circles indicate the N–I transition, the open squares the melting temperatures.

Table 4. Yields and intrinsic viscosities of the polymers.

Polymer	Yield/%	$[\eta]$/dl g^{-1}
C1	98	0·97†
V1	96	0·84‡
V2	88	0·20‡
V3	90	0·34‡
V4	92	0·20‡

† Measured in TCE/phenol 40:60 (v/v) at 25°C.
‡ Measured in TCE at 25°C.

Table 5. Thermodynamic properties of the polymers.

Polymer	T_m/°C	T_{NI}/°C	ΔH_m/kJ mol^{-1}	ΔH_{NI}/kJ mol^{-1}
C1	287·1	369·7	15·8	4·6
V1	200·5	230·7	11·8	3·6
V2	159·6	—	14·9	—
V3	229·3	297·9	19·1	2·1
V4	240·4	(231·3)	20·0	(3·3)

Brackets indicate monotropic transitions.

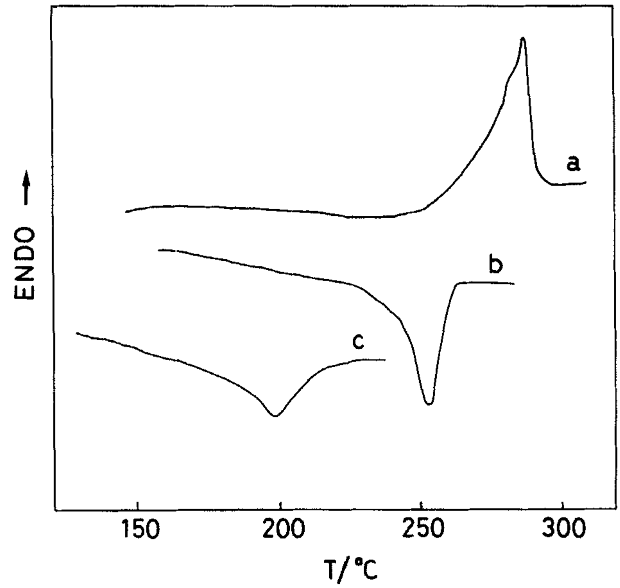

Figure 4. DSC traces of polymer C1 (a, melting profile; b crystallization of the nematic melt; c, crystallization of a sample quickly cooled from the isotropic state; scan rate 20 K min^{-1}).

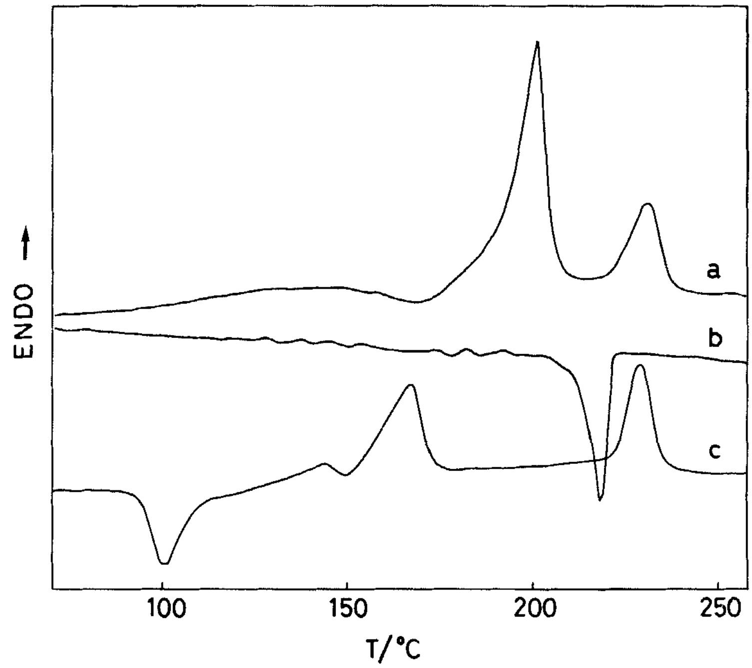

Figure 5. DSC traces of polymer V1 (a, first heating profile; b, cooling trace; c, second heating run; scan rate 10 K min^{-1}).

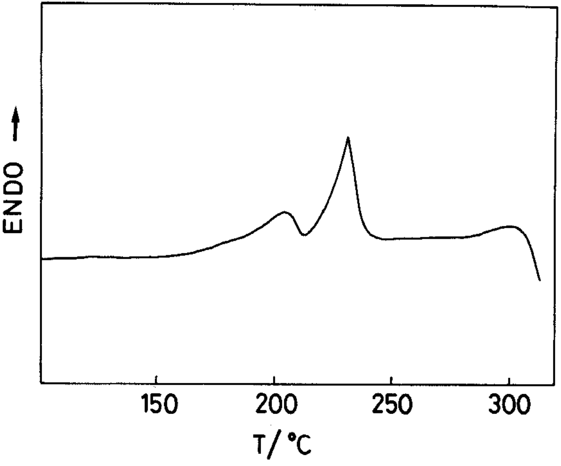

Figure 6. DSC heating profile at 20 K min^{-1} of polymer V3.

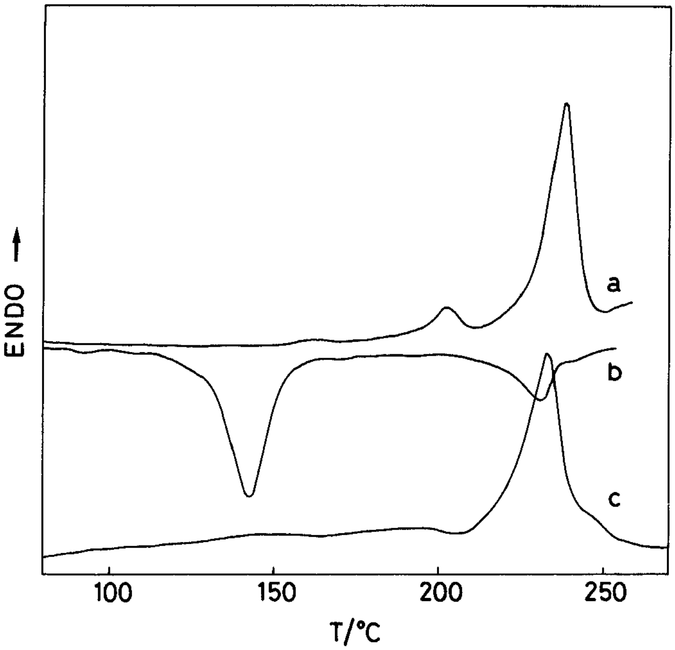

Figure 7. Thermal behaviour of polymer V4 (a, DSC heating profile; b, cooling trace; c, second heating, scan rate 20 K min^{-1}).

cooling from the nematic phase crystallization occurs at 183°C; in a second heating cycle the polymer melts at 226·9°C Polymer V4 exhibits a monotropic nematic phase; it melts in the first cycle at 240·4°C to an isotropic liquid, but on cooling it becomes nematic between 231·3 and 148·6°C. In a second run the crystal–isotropic transition appears at 237·5°C. (see figure 7). Since no nematic phase has been found on heating by optical microscopy, the high temperature shoulder at about 245°C (curve c) must be related to a complex melting behaviour.

4. Conclusions

The comparison between the thermal behaviour of model compounds and polymers indicates that, qualitatively, these two groups of compounds exhibit parallel structure–property relationships; however, polymers generally exhibit an enhanced stability of the mesophase. Indeed, whereas samples B1 and C1 are nematic over a wide range, both the methoxy substituted compounds M1 and V1 have a substantial decrease of the mesophase stability; nevertheless the model compound is monotropic and the polymer enantiotropic. Transition enthalpies follow the expected trend, since polymers C1 and V1 have larger isotropization and lower melting enthalpies than the model compounds B1 and M1. Substitution of the central $-COOC_6H_4OOC-$ nucleus with the shorter $-CH=N-N=CH-$ group in methoxy substituted compounds M2 and V2 deletes any liquid crystal property, but the nematic character is stabilized in M3 and V3 by the increased length of the rigid moiety and persists, in spite of the presence of several methoxy lateral substituents, in M4 and V4. Enantiotropic and monotropic nematic phases are shown by compounds M3/V3 and M4/V4, respectively; in this case the polymeric nature of sample V4 seems to be ineffective in improving mesophase stability, through this effect might arise from the low intrinsic viscosity of the polymer. Indeed, it has been shown that the molecular weight affects the values of the transition temperatures of polymeric materials [21, 22].

In conclusion, modelling polymers by low molecular weight homologues, appears to be a useful approach, at least, as far as general trends are concerned. More reliable data should derive from the investigation of low oligomers, barely considered in the recent literature [23–26].

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References

[1] Roviello, A., and Sirigu, A., 1977, *Gazz. chim. Ital*, **107**, 333.
[2] Ober, C. K., Jin, J. I., and Lenz, R. W., 1984, *Adv. Polym. Sci.*, **59**, 103.
[3] Griffin, A. C., and Johnson, J. F. (editors), 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4 (Plenum).
[4] Lenz, R. W., 1985, *Polym. J.*, **17**, 105.
[5] Blumstein, A., 1985, *Polym. J.*, **17**, 277.
[6] Lenz, R. W., 1985, *Pure appl. Chem.*, **57**, 1537.
[7] Chapoy, L. L. (editor), 1985, *Recent Advances in Liquid Crystalline Polymers* (Elsevier).
[8] Blumstein, A. (editor), 1985, *Polymeric Liquid Crystals* (Plenum).
[9] Noel, C., 1988, *Makromolek. Chem. Makromolek. Symp.*, **22**, 95.
[10] Ballauff, M., 1989, *Angew. Chem. Int. Ed. Engl.*, **28**, 253.
[11] Costa, G., Nora, A., Trefiletti, V., and Valenti, B., 1988, *Molec. Crystals liq. Crystals*, **157**, 79.
[12] Costa, G., Minicucci, A., Trefiletti, V., and Valenti, B., 1990, *Liq. Crystals*, **7**, 629.
[13] Valenti, B., Trefiletti, V., Silanus, F., and Costa, G., 1988, *Molec. Crystals liq. Crystals*, **155**, 511.
[14] Bilibin, A. Yu., Tenkovtsev, A. V., and Skorokhodov, S. S., 1985, *Makromolek. Chem. rap. Commun.*, **6**, 209.
[15] Roviello, A., and Sirigu, A., 1976, *Molec. Crystals liq. Crystals*, **35**, 155.
[16] Sutton, L. E. (editor), 1958, *Tables of Interatomic Distances and Configuration in Molecules and Ions* (The Chemical Society); and 1965, Supplement.
[17] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim) p. 43.

[18] GALIGNÈ, J. L., and FEILGUEIRETTES, J., 1968, *Acta crystallogr.*, **B24**, 1523.

[19] FLORY, P. J., and RONCA, G., 1979, *Molec. Crystals liq. Crystals*, **54**, 311.

[20] CARPANETO, L., MARSANO, E., VALENTI, B., and ZANARDI, G., *Polymer* (in the press).

[21] FEJIOO, J. L., UNGAR, G., OWEN, A. J., KELLER, A., and PERCEC, V., 1988, *Molec. Crystals liq. Crystals*, **155**, 487.

[22] COSTA, G., TREFILETTI, V., VALENTI, B., and GALLOT, B., 1990, *Makromolek, Chem.*, **191**, 791.

[23] CENTORE, R., ROVIELLO, A., and SIRIGU, A., 1988, *Liq. Crystals*, **3**, 1525.

[24] AURIEMMA, F., CORRADINI, P., ROVIELLO, A., and VACATELLO, M., 1989, *Eur. Polym. J.*, **25**, 57.

[25] GRIFFIN, A. C., SULLIVAN, S. L., and HUGHES, W. E., 1989, *Liq. Crystals*, **4**, 677.

[26] OGAWA, Y., and TAKAMIZAWA, K., 1989, *Polym. J.*, **21**, 551.