Journal of Thermal Analysis, Vol. 30 (1985) 1317—1324

MESOPHASIC PROPERTIES OF LOW MOLECULAR WEIGHT ANALOGUES OF NEMATOGENIC POLYCARBONATES

C. Carfagna, P. Iannelli, A. Roviello and *A. Sirigu*

DIPARTIMENTO DI CHIMICA, UNIVERSITÀ DI NAPOLI,
VIA MEZZOCANNONE, 4—80134 NAPOLI, ITALY

The mesophasic behaviour of the following compounds has been investigated by DSC, X-ray diffraction and optical microscopy methods:

$CH_3(CH_2)_4—CO—R—A_n—R—CO—(CH_2)_4—CH_3$, $n = 9 \rightarrow 14, 16$
$CH_3(CH_2)_4—CO—R—B_n—R—CO—(CH_2)_4—CH_3$, $n = 2, 3$
$A_n = —CO—O—(CH_2)_{n-4}—O—CO—$, $B_n = —CO—(OCH_2CH_2)_n—O—CO—$,
$R = —O—\varnothing—C(CH_3){=}N—N{=}(CH_3)C—\varnothing—O—$, $\varnothing = —C_6H_4$

They have been assumed to be low molecular weight models of homologous nematogenic polymers.

All the examined compounds exhibit nematic mesomorphism. On complete analogy with the corresponding polymers, the thermodynamic data relative to the nematic-isotropic phase transition show a very reduced, if any, odd-even fluctuation. These data are compared with those obtained for very similar compounds, both polymeric and non-polymeric, containing ester linkages between the rigid and flexible groups, to provide evidence of the reliability of the dimeric compounds as models of the polymeric homologues.

In a recent paper [1] we showed that the mesophasic properties of two homologous series of low molecular weight compounds, whose structure is characterized by the presence of two rigid mesogenic groups connected by a flexible portion (which will be called "dimers"), qualitatively reproduce the peculiarities of the nematic phase of polymers of which dimers represent (with some approximations) two connected monomer units.

In fact, these model compounds exhibit nematic properties with enhanced odd-even fluctuations both in the isotropization temperatures and in the molar isotropization enthalpies, as the corresponding polymers do as a function of the length of the flexible spacer.

Their formula is as follows:

$$DP_n = CH_3(CH_2)_4CO—R—P_n—R—CO(CH_2)_4CH_3$$

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

where

$R = \text{—O—}\varnothing\text{—C(CH}_3\text{)=N—N=(CH}_3\text{)C—}\varnothing\text{—O—}, \quad \varnothing = \text{—C}_6\text{H}_4$

$P_n = \text{—OC—(CH}_2)_{n-2}\text{—CO—}, \quad n = 4 \rightarrow 16$

The corresponding polymers have formula [2]:

$(P_nR)_x, \quad n = 8 \rightarrow 14$

The relevance of the model compounds is connected with i) the possibility of obtaining them in a very purified form, ii) their unequivocally defined molecular weight, iii) the low melt viscosity and the relatively low melting temperatures that make easier (as compared with the polymers) their macroscopic alignment in a magnetic field of moderate strength. This allows a better determination of the degree of order in the nematic phase.

These measurements have been performed with dimeric compounds in a few cases with different techniques.

Griffin and coworkers [3] measured the degree of orientational order as a function of the temperature for a compound with formula:

$$\text{CH}_3(\text{CH}_2)_4\text{—O—}\varnothing\text{—COO—}\varnothing\text{—O—(CH}_2)_{10}\text{—O—}\varnothing\text{—OOC—}\varnothing\text{—O—(CH}_2)_4\text{CH}_3$$

by measuring the anisotropy of the magnetic susceptibility. Blumstein and coworkers [4] investigated similar dimeric model compounds by NMR methods; the authors measured order parameters in the nematic phase of magnetically oriented samples of DP_n compounds by measuring the x-ray diffracted intensity along the principal halo [5]. The results agree in showing that the order parameters extrapolated at the isotropization temperature are significantly higher for compounds containing an even number of carbon atoms in the flexible spacer than for the odd-type molecules or for the "monomeric" analogues (i.e. compounds containing a single rigid group in the molecule). The order parameters measured for the even-type molecules, however, are lower than those found for the corresponding polymeric analogues.

In a previous paper [2], two of the authors showed that polymers containing the rigid group R connected by flexible spacers of formula $\text{—COO—(CH}_2)_{n-4}\text{—OOC—}$ also exhibit nematic behaviour, like the already-mentioned polyesters, but with a considerably reduced odd-even fluctuation of the relevant thermodynamic parameters. This appears to be caused by the presence, as linking group between the rigid and flexible parts, of carbonate groups instead of ester groups.

In the present paper we report on a study of the mesophasic properties of "dimeric" model compounds containing such carbonate linkages. Two classes of dimeric compounds have been investigated:

DA_n = $CH_3(CH_2)_4$—CO—R—A_n—R—CO—$(CH_2)_4CH_3$
where
A_n = —CO—O—$(CH_2)_{n-4}$—O—CO—, $n = 9, 10, 11, 12, 13, 14, 16$,
which correspond to polymers $(A_nR)_x$; and
DB_n = $CH_3(CH_2)_4$—CO—R—B_n—R—CO—$(CH_2)_4CH_3$
where
B_n = —CO—$(OCH_2CH_2)_n$—O—CO—, $n = 2,3$,
corresponding to polymers $(B_nR)_x$, [6] which also exhibit nematic mesogenicity.

Experimental

Compounds DA_n and DB_n were synthetized following the procedure described in [1], with some modification concerning their purification. Bis-chlorocarbonate Cl—A_n—Cl (or Cl—B_n—Cl) was added dropwise at room temperature to a solution of $CH_3(CH_2)_4$—CO—R—H (in slight excess with respect to the stoichiometric value) in an anhydrous mixture of dioxane and pyridine. After one hour the reaction mixture was poured into cool 95% ethanol, filtered and washed with 95% ethanol. Further purification was carried out on a silica gel column. The chemical natures of the compounds were confirmed by NMR spectroscopy.

Thermal analysis was performed with a Mettler TA-3000 differential scanning calorimeter. For calibration an indium Fluka 99.999% sample was utilized. With a 10 deg/min scanning rate, the melting interval of the indium standard is 2 K. With the same scanning rate, the melting and isotropization intervals are $\leqslant 4$ K and $\leqslant 2.5$ K, respectively, both for DA_n and for DB_n. The mesophasic properties were also examined by polarizing microscopy at variable temperature. The nature of the mesophase was investigated by X-ray diffraction techniques and by miscibility studies with a nematogenic standard [7]:

$$CH_3(CH_2)_2\text{—COO—}\emptyset\text{—CH}{=}\text{N—N}{=}\text{CH—}\emptyset\text{—OOC—}(CH_2)_2CH_3$$

Results and discussion

DA_n and DB_n each show thermotropic mesophasic behaviour. The X-ray diffraction pattern recorded within the range of stability of the mesophase rules out any smectic structure having a periodicity $\leqslant 50$ Å. Conclusive evidence of the nematic nature of the mesophase exhibited by DA_{10} and DB_2 is given by the phase

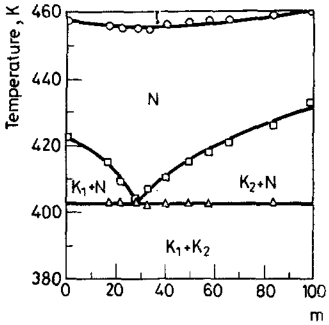

Fig. 1 Phase diagram of the binary mixture formed by DA_{10} and $CH_3(CH_2)_2$—COO—∅—CH=N—N=CH—∅—OOC—$(CH_2)_2CH_3$. $m/100$ = mole fraction of DA_{10}; K = solid phase; N = nematic phase; I = isotropic phase

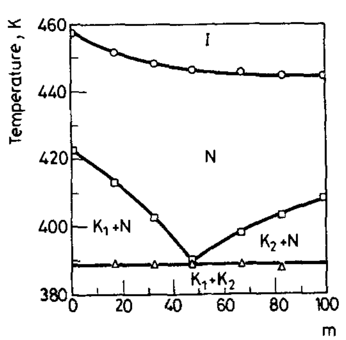

Fig. 2 Phase diagram of the binary mixture formed by DB_2 and $CH_3(CH_2)_2$—COO—∅—CH=N—N=CH—∅—OOC—$(CH_2)_2CH_3$. $m/100$ = mole fraction of DB_2

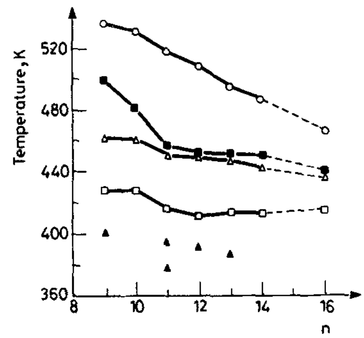

Fig. 3 Melting and isotropization temperatures of polycarbonates $(A_nR)_x$ (□, △, ▲(K—K)) and model compounds DA_n (■, 0)

diagrams shown in Figs 1 and 2, respectively, relating to binary mixtures with the above-mentioned nematogenic standard. Complete miscibility is observed in the nematic phase.

Same relevant thermodynamic data for the series DA_n are reported in Table 1, together with the corresponding data concerning the homologous polymers.

The close correspondence between the dimeric molecules and the polymers is clear in Fig. 3.

The virtual absence of odd-even fluctuations is at sharp variance with the behaviour of the corresponding ester compounds, both dimeric and polymeric.

A strictly parallel correspondence is shown in Fig. 4 for the molar isotropization entropies. The same drastic reduction of the odd-even fluctuations as observed for the polycarbonates as compared to the corresponding polyester series is to be observed for the dimeric homologueses. Even the pattern of the relative magnitude of the entropies is replicated. The enthalpy ratios $\Delta H_i/\Delta H_t$ (ΔH_i = molar isotropization enthalpy; ΔH_t = molar enthalpy change for the (virtual) transition solid phase stable at room temp. →isotropic liquid) for DA_n and DP_n are compared in Fig. 5.

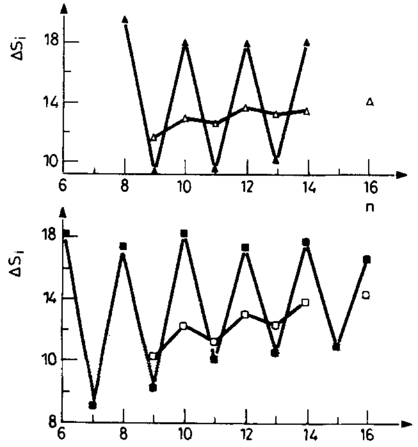

Fig. 4 Molar entropy changes at the isotropization for polyesters $(P_nR)_x$ (▲), polycarbonates $(AnR)_x$ (△), model compounds DP_n (□) and model compounds DA_n (□)

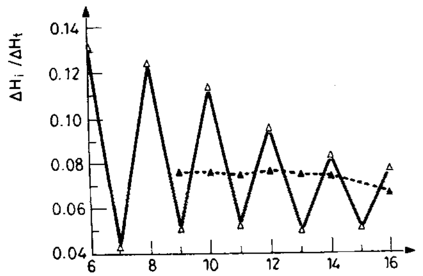

Fig. 5 $\Delta H_i/\Delta H_t$ ratios as a function of spacer length for model compounds DP_n (△) and DA_n (▲)

Once again, the data relating to DA_n show no really significant odd-even fluctuation. The correspondence between the thermodynamic data and the order parameter needs to be ascertained particularly in connection with two points: the reduced odd-even fluctuation and the intermediate position between odd and even classes of DP_n compounds.

Table 1 reports some thermodynamic data on compounds DB_2, DB_3 and the corresponding polymers. The similarity between the dimers and polymers is apparent. For both compounds the mesophase is of nematic type and the molar isotropization entropy is significantly smaller than for the series DA_n, in close analogy with the corresponding polymers $(B_nR)_x$ and $(A_nR)_x$. The same is true for the melting and isotropization temperatures. The ratios $\Delta H_i/\Delta H_t$ are also definitely smaller than those found for DA_n, although only slightly lower than for the odd members of the series DP_n. For the latter, the order parameter at the isotropization temperature is found to be very close to the Maier–Saupe limit [5].

Although only one member for each class, odd or even, has been examined (DB_2 is of odd type), it is apparent from the ΔS_i and $\Delta H_i/\Delta H_t$ data that the odd-even

Table 1 Thermodynamic data of model compounds and corresponding polymers

	DA_n						$(A_nR)_x$		
n	$T_{K\to K}$	T_m	T_i	ΔS_i	$\Delta H_i/\Delta H_T$		T_m	T_i	ΔS_i
9	402	428	462	10.2	0.076		499	536	11.7
10		428	461	12.4	0.076		481	530	13.0
11	369 394	416	451	11.2	0.075		456	517	12.6
12	392	412	450	13.1	0.077		453	508	13.8
13	388	414	448	12.3	0.075		451	495	13.3
14		413	443	13.9	0.074		450	486	13.5
16	388	416	436	14.5	0.067		441	446	14.1
DB_2		410	446	6.8	0.046	$(B_2R)_x$	416	501	5.2
DB_3		385	425	5.9	0.042	$(B_3R)_x$	380	448	4.2

Temperatures are in Kelvin scale

$T_{K\to K}$ = Solid-solid transition temperature

T_m = Melting temperature

T_i = Isotropization temperature

ΔS_i = Molar isotropization entropy in J mol^{-1} K^{-1}

$\sigma(T)/T$ = 0.001

$\sigma\Delta S_i/\Delta S_i$ = 0.06

ΔH_i = Enthalpy variation at the isotropization

ΔH_T = Sum of the enthalpy variations corresponding to the transitions from the most stable phase to the isotropic liquid

Table 2 ΔS_i values for the different series of compounds

Polymers (A)	ΔS_i (B)	Dimers	$\Delta S_i/2$ (B)	Monomers (C)	ΔS_i (B)
$(P_{12}R)_x$	17.9	DP_{12}	8.80	M_6	3.27
$(A_{12}R)_x$	13.8	DA_{12}	6.56	N_6	3.71 (D)
$(B_3R)_x$	3.4	DB_3	2.60		
$(P_9R)_x$	9.3	DP_9	4.10	M_5	2.34
$(A_9R)_x$	11.7	DA_9	5.10	N_5	3.18 (D)
$(B_2R)_x$	5.2	DB_2	3.40		

(A) The first series of values is relative to compounds whose flexible groups are constituted by a chain with 12 atoms; for the second series the chain is constituted by 9 atoms. This is true only for the polymers and the dimers and not for the monomers.

(B) ΔS_i/J mol^{-1} K^{-1}

(C) $M_n = CH_3(CH_2)_{n-2}—CO—R—CO—(CH_2)_{n-2}CH_3$ $n = 5, 6$

and $N_n = CH_3(CH_2)_{n-3}—OOC—R—COO—(CH_2)_{n-3}CH_3$

(D) Unpublished results

effect is either the inverse of that characterizing all the above-mentioned compounds or, much more likely, virtually non-existent.

In fact, the flexibility of the spacer appears to be the critical factor for the occurrence of odd-even fluctuations. An enhanced flexibility of the spacer, either through increase of its length or because of intrinsic stereochemical reasons, tends to diminish the influence of the parity (odd or even). The latter should be the case for dimers DB_n and their polymeric homologues. Table 2 lists some relevant data on homologous classes of polymers, dimers and monomers, to facilitate comparison.

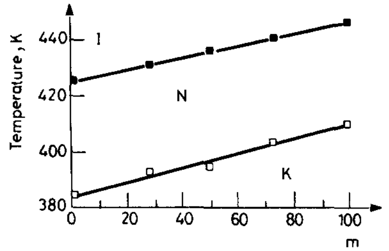

Fig. 6 Phase diagram of the binary mixture formed by DB_2 and DB_3. m/100 = mole fraction of DB_2

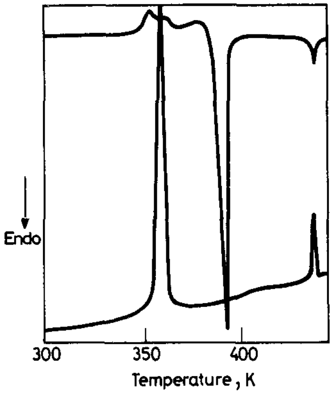

Fig. 7 DSC curves of DB_2-DB_3 equimolar mixture. cooling and b = subsequent heating run

Another reason for studying DB_2 and DB_3 was to investigate the smectic-like structure shown by polymers $(B_2R)_x$ and $(B_3R)_x$ and by related copolymers containing various amounts of the two monomeric units. At room temperature, these polymers display a smectic periodicity detectable by X-ray diffraction measurements which vanishes without any first or second-order thermodynamic discontinuity into a normal nematic structure [6].

Mixtures of DB_2 and DB_3 were examined with the purpose of lowering the melting temperature. However, (Figs 6 and 7), solid solutions are formed with no appreciable depression of the melting temperature. Within the range of stability of the mesophase, no evidence was detected of any smectic-like structure with a periodicity shorter than ~ 50 Å.

* * *

The financial assistance of the Ministero Pubblica Istruzione is acknowledged.

References

1 J. A. Buglione, A. Roviello and A. Sirigu, Mol. Cryst. Liq. Cryst., 106 (1984) 169.

2 A. Roviello and A. Sirigu, Makromol. Chem., 183 (1982) 895.

3 A. C. Griffin, G. Sigaud and Do Y. Yoon, Macromolecules, 16 (1983) 875.

4 A. Blumstein, R. B. Blumstein, E. M. Stickles, M. M. Gauthier and F. Volino, Macromolecules, 17 (1984) 177.

5 R. Capasso, P. Iannelli, A. Roviello and A. Sirigu, to be published

6 A. Roviello, S. Santagata and A. Sirigu, Makromol. Chem. Rapid Commun., 5 (1984) 209.

7 A. Roviello and A. Sirigu, Mol. Cryst. Liq. Cryst., 35 (1976) 155.

Zusammenfassung — Das mesophasische Verhalten der folgenden Verbindungen wurde mittels DSC, Röntgendiffraktion und optischer Mikroskopie untersucht:

$CH_3(CH_2)_4{-}CO{-}R{-}A_n{-}R{-}CO{-}(CH_2)_4{-}CH_3$; $n = 9 \rightarrow 14$, 16

$CH_3(CH_2)_4{-}CO{-}R{-}B_n{-}R{-}CO{-}(CH_2)_4{-}CH_3$; $n = 2$, 3

$A_n = {-}CO{-}O{-}(CH_2)_{n-4}{-}O{-}CO{-}$; $B_n = {-}CO{-}(OCH_2CH_2)_n{-}O{-}CO{-}$;

$R = {-}O{-}C_6H_4{-}C(CH_3){=}N{-}N{=}(CH_3)C{-}C_6H_4{-}O{-}$.

Die Verbindungen wurden als Modelle homologer nematogener Polymere mit niedrigem Molekulargewicht angesehen. Alle untersuchten Verbindungen zeigen einen nematischen Mesomorphismus. Analog zu den entsprechenden Polymeren zeigen die sich auf den nematisch-isotropen Phasenübergang beziehenden thermodynamischen Daten eine, wenn überhaupt, sehr reduzierte ungerade-gerade Fluktuation. Diese Daten werden mit denen verglichen, die für sehr ähnliche, sowohl polymere als auch nicht-polymere Verbindungen mit Esterbindungen zwischen den starren und flexiblen Gruppen erhalten wurden, um Beweise für die Zuverlässigkeit der auf dimeren Verbindungen aufbauenden Modelle für polymere Homologe zu erhalten.

Резюме — Методами ДСК, рентгенофазового анализа и оптической микроскопии исследовано мезофазное поведение соединений со следующей структурой:

$$CH_3(CH_2)_4{-}CO{-}R{-}A_n{-}R{-}CO{-}(CH_2)_4{-}CH_3 \qquad n = 9 \rightarrow 14{,}16$$

$$CH_3(CH_2)_4{-}CO{-}R{-}B_n{-}R{-}CO{-}(CH_2)_4{-}CH_3 \qquad n = 2,\ 3$$

$$A_n = {-}CO{-}O{-}(CH_2)_{n-4}{-}O{-}CO{-}; \qquad B_n = {-}CO{-}(OCH_2CH_2)_n{-}O{-}CO{-}$$

$$R = {-}O{-}\phi{-}C(CH_3){=}N{-}N{=}(CH_3)C{-}\phi{-}O{-} \qquad \phi = C_6H_4$$

Предполагалось, что эти вещества являются низкомолекулярными модельными соединениями гомологов жидкокристаллических полимеров. Все исследованные соединения проявляют жидкокристаллический мезоморфизм. Термодинамические данные относительно фазового перехода нематик — изотроп, показывают очень пониженную, по аналогии с соответствующими полимерами, четную-нечетную флуктуацию. Данные сопоставлены с таковыми, полученными для подобных полимерных и не полимерных соединений, содержащих эфирные звенья между жесткими и гибкими группами, для доказательства достоверности этих димерных соединений как моделей полимерных гомологов.