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EFFECT OF MOLECULAR STRUCTURE ON MESOMORPHISM. 16.[1] NEMATIC-ISOTROPIC THERMODYNAMICS FOR OLIGOMER MODELS OF LIQUID CRYSTALLINE POLYMERS

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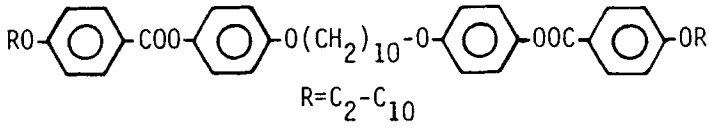
Abstract: Thermodynamic measurements of ΔH and ΔS for the nematic-isotropic transition for a homologous series of Siamese Twin diester liquid crystals are reported. These diesters are structurally related as conceptual dimers in the monomer →oligomer →polymer sequence of liquid crystals with a 4,4'-disubstituted phenyl benzoate mesogenic moiety. Both ΔH and ΔS values show an odd:even alternation with carbon number intermediate in magnitude between those for the monomeric and the polymeric mesogens. It is concluded that the Twin diesters are good models for these oligomers in the monomer →oligomer →polymer progression.

INTRODUCTION

With an interest in understanding structure:property relations in both small molecule liquid crystals and polymeric liquid crystals we have recently synthesized and reported[2] transition temperatures and phase behavior of a "dimeric" series of mesogens, 1, below. These compounds can be considered as dimers in the conceptual tail-to-tail coupling of two (monomeric) 4-alkoxyphenyl 4'-alkoxybenzoate mesogens, 2. As such these compounds, 1, are related as Siamese Twin mesogens to 2. Our interest in these Twin dimers is that they are examples of conceptual (but not actual) oligomers in the incremental progression of monomer →oligomer →polymer liquid crystals. The actual oligomers in the polycondensation reactions to form main chain liquid crystalline polymers are dominated by reactive ends (such as COOH, COCl, OH) and are therefore unrelated to both the high molecular weight polymer liquid crystal



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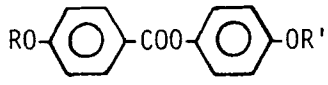

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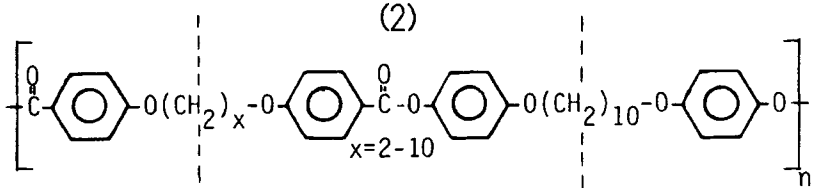


(3)

and the small molecule liquid crystal analogous to these polymers. Conceptual oligomers such as 1 on the other hand are related to the repeating mesogenic unit in the polymers, 3[3], and to the small molecule related to this repeating mesogenic moiety, 2. In the structures above the dashed lines indicate the 4-alkoxyphenyl 4'-alkoxybenzoate mesogenic moiety in the polymeric repeat unit of 3.

We wish to report here the nematic-isotropic transition enthalpies (ΔH) and transition entropies (ΔS) for Twin dimers 1 as a function of the length of the alkoxy chain at the ends of the molecule. In addition we present a comparison of similar nematic-isotropic data for monomeric compounds 2 and the related polymeric materials 3 in an effort to examine the potential use of compounds such as 1 as models for oligomers in the monomer → oligomer → polymer sequence of liquid crystalline materials.

EXPERIMENTAL

Compounds 1 and 3 have been synthesized and characterized by us previously.[2,3] Thermodynamic data for polymers 3 and monomers 2 were taken from the literature. For monomers 2 the paper of Demus *et al*[4] was used. Concerning the choice of which OR' to use for 2 we chose decyloxy primarily because the data for most of these compounds was more easily obtained (by extrapolation) than for pentyloxy as OR'. We are not suggesting that decyloxy is a better model than pentyloxy

for OR' in 2, but rather that we have greater confidence in the validity of our extrapolated ΔH and ΔS values for the decyloxy homologues. For comparison of nematic-isotropic enthalpies and entropies among the three series of compounds the calculations were made as described below to normalize each to one 4-alkoxyphenyl 4'-alkoxybenzoate segment:

polymers,3	J/g was taken from the literature and converted to a per "mole" of phenyl benzoate segment basis using half the mass of the formal polymeric repeat unit as the conversion factor.
Twin dimers,1	J/mole divided by two
monomers,2	J/mole taken from the literature as described above.

Transition enthalpies for series 1 Twin dimers were obtained on a Du Pont model 990 thermal analyzer equipped with a model 910 cell for differential scanning calorimetry. The sample chamber was continuously purged with nitrogen during all runs (a minimum of four runs per data point). A Perkin-Elmer AD-2 microbalance was used to weigh the samples. Indium was used as enthalpic standard. Peak areas were measured using extrapolation of monotonic baseline on both sides of the transition to the transition temperature (taken as point of maximum rate of change of heat capacity; endothermic maximum). The resulting area was measured by accurately weighing multiple standardized photocopies and comparing these weights to indium peak weights.

RESULTS AND DISCUSSION

All polymers, 3, and all Twin dimers,1, are enantiotropic nematic materials having the nematic phase as the only mesophase.[2,3] The monomeric phenyl benzoates, 2, have phase behavior typical of many mesogenic homologous series, i.e., nematic only when alkoxy tail(s) are short, both smectic and nematic at intermediate chain lengths, and smectic only when tails are long.[4,5] Comparisons of nematic-isotropic temperatures among the three series have been made previously[2] with the conclusions that:

i) The polymeric mesogens, 3, have high T_{N-I} with a large odd:even alternation in T_{N-I}. There is a

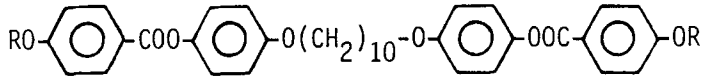
gradual descending trend as the carbon chain length X is increased.

ii) The monomeric materials, 2, have low T_{N-I} with a small, but perceptable odd:even effect in a gradually ascending fashion as carbon chain length (OR) is increased.

iii) The Twin dimeric mesogens, 1, have T_{N-I} at intermediate values with a distinct odd:even alternation in the same sense as that in the polymers, 3. There is also a gradual descending trend in T_{N-I} as the tails (RO) increase in length.

The intermediate T_{N-I} with its distinct odd:even alternation and exclusively nematic mesophase behavior of the Twin dimer family, 1, suggest a strong connection between phase type and mesophase ordering in both Twin dimers, 1, and polymers, 3. Blumstein *et al.*[6,7] have recently reported synthesis and thermodynamic data for both polymers, model compounds and actual oligomers related to poly(azoxyesters). Their results indicate "polymeric" behavior begins at about six repeating units per chain for their system.

Thermodynamic data for the N-I transition for the Twin dimer series, 1, are presented in Table 1. Figures 2 and 3 show N-I enthalpies and entropies, respectively, for compounds 1,2, and 3 using the derivations as described in the experimental section. Both figures show remarkable similarity indicating a strong coupling between intermolecular forces and structural ordering in each of these systems. With the exception of X=4 in series 3 (which we now believe to be an incorrect data point) there is an odd:even alternation in each series. Alternation in the polymer series, 3, is the most prominent and on a "monomer" basis the polymeric mesogens exhibit the greatest intermolecular binding (ΔH) and mesophase order (ΔS). This is made even more significant by the fact that in our calculations the flexible segments are effectively halved thus the actual enthalpic and entropic values of an exactly analogous polymer would be even larger than those shown. The phenyl benzoate series, 2, has a sharply ascending odd:even alternation with the least degree of intermolecular bonding and structural ordering (at least until X=10). The twin dimers, 1, have a regular odd:even alternation for both ΔH and ΔS with an intermediate (relative to 2 and 3) amount of both intermolecular attraction and mesophase ordering. For both enthalpy and entropy changes the general trend is toward increasing values as the tails (RO) become longer.



R	T[a]	ΔH[b]	ΔS[c]	R	T[a]	ΔH[b]	ΔS[c]
C_2H_5	451.0	7.18	7.96	C_7H_{15}	416.2	6.98	8.39
C_3H_7	433.3	6.89	7.95	C_8H_{17}	419.3	8.31	9.91
C_4H_9	433.1	7.00	8.09	C_9H_{19}	406.2	7.28	8.97
C_5H_{11}	422.2	6.84	8.10	$C_{10}H_{21}$	409.4	9.21	11.3
C_6H_{13}	422.7	7.49	8.86				

a) T_{N-I} in K b) ΔH_{N-I} in kJ/mole c) ΔS_{N-I} in J/mole · K

TABLE 1. Thermodynamic data for N - I transition in Twin dimers 1.

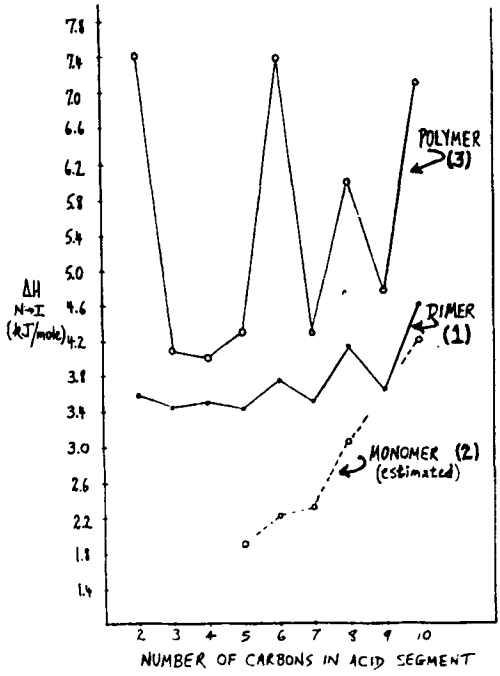


FIGURE 1. Comparisons of nematic-isotropic enthalpies for series 1,2 and 3 mesogens.

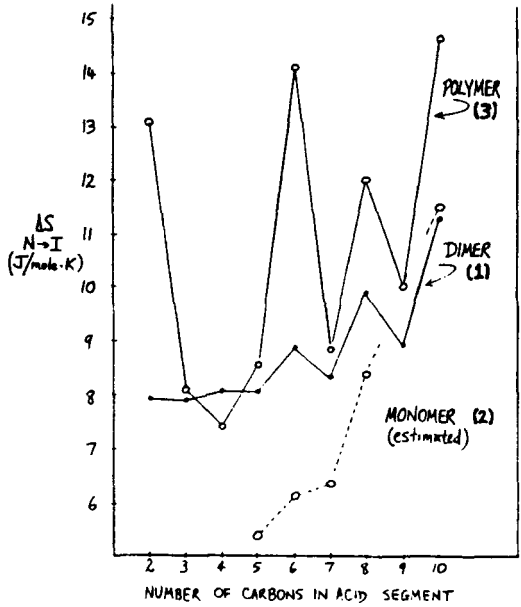


Figure 2. Comparisons of nematic-isotropic entropies for series 1,2, and 3 mesogens.

For this series, 1, the average value of both ΔH and ΔS (especially for the lower members) is quite above that for the monomers, 2, even considering the fact that OR'=decyloxy not pentyloxy for the monomer series. The odd:even alternation in 1 appears as a secondary effect superimposed on a large basal value of approximately ΔH=3.4 kJ/mole and ΔS=8 J/mole • K, i.e. the coupling of the OR' alkoxy chains imposes a large ordering (and enthalpic) effect on the Twin dimers with the odd:even effect as a minor variation on this major theme. There is a curious increase in the extent of alternation of both ΔH and ΔS. Both values show a much greater degree of alternation as the tail length increases. We currently have no suitable explanation to offer for this behavior. It therefore appears that the thermodynamics of the nematic-isotropic transition support the proposal that model compounds such as 1 are useful to study the conceptual intermediates in the monomer→oligomer→polymer sequence as well as being interesting mesogens in their own right having flexible centers.

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