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INFLUENCE OF MOLECULAR WEIGHT ON PHASE TRANSITION ENTROPIES OF A THERMOTROPIC NEMATIC POLYESTER

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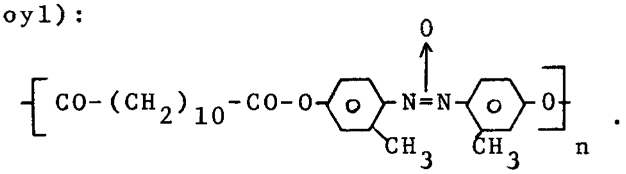
ABSTRACT

We report the values of isotropisation enthalpies and entropies of some model compounds, oligomers, and polymers of poly(2,2'-methyl-4,4'-oxyazoxybenzene dodecanedioyl), a thermotropic nematic polymer with moderately low transition temperatures and regularly alternating rigid-flexible units in the main chain. The values of ΔH_{IN} and ΔS_{IN} increase rapidly with increasing molecular weight, to reach a plateau at $\overline{M}_n$ >3,000 g/mole. Results are interpreted in terms of increasing participation of the flexible aliphatic spacer units in the ordering process of the nematic phase. In the polymer, the entire repeating unit is aligned by the nematic potential.

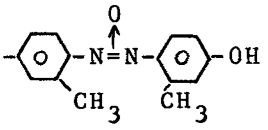
We have recently described the synthesis and properties of a series of poly(4,4'-oxyazoxybenzene alkanedioyls) and poly(2,2'-methyl-4,4'-oxyazoxybenzene alkanedioyls) which display thermotropic nematic phases (1,2,3,4). These polymers are polyesters in which rigid azoxybenzene mesogenic core regularly alternates in the main chain with a flexible alkanedioate "spacer group". Preliminary investigation indicates a drastic influence of molecular weight and molecular weight distribution on transition temperatures, mesophase stability (3), and degree of alignment of the polymer in magnetic (3,5) and shear fields (3).

In order to help delineate the transition from high molecular weight to standard low molecular weight nematic phases based on the azoxybenzene mesogenic moiety, we present here the results of a calorimetric investigation of a series of model compounds, oligomers and polymers of poly(2,2'-methyl-4,4'-oxyazoxybenzene dodecanedioyl):



The polymer, labelled DDA-9 and consisting of a regular sequence of flexible-rigid units, has moderately low transition temperatures and a nematic stability range of 45-50°C (2). In a sample of $\overline{M}_n$ = 11,700, for example, the phase transitions are K118N162I, a temperature range which allows measurement of enthalpies and entropies of transition without fear of sample decomposition.

EXPERIMENTAL:

Monomers and polymer samples of varying molecular weight were prepared as described elsewhere (2,3,4). Oligomers were prepared by room temperature solution polymerization in pyridine. Oligomer chains were terminated by $-COOCH_3$ or by  (9-end capped) moieties, the latter largely predominent, as shown by NMR spectroscopy. Fractionation was carried out by a combination of non-solvent precipitation and chromatographic techniques. Synthesis and characterization of model compounds has been described elsewhere (6). Molecular weights of polymers DDA-9-T and DDA-9-SP were measured as described in ref.(3); molecular weights of samples DDA-9-L, DDA-9-E, and DDA-9-I were determined by end group titration using ^{1}H NMR spectroscopy.

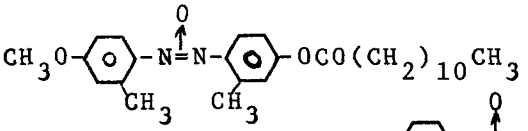
Thermal analysis was performed with a Perkin Elmer 2C Differential Scanning Calorimeter. A high purity indium standard was employed for calibration of the heats of transition. The temperature scale was corrected for instrumental lag by calibration with the indium sample. All DSC measurements were made under nitrogen atmosphere.

In order to provide a consistent thermal history, each material studied was first heated to at least 20 degrees above the crystal to isotropic or nematic to isotropic transition. DSC traces were obtained by cycling the sample between that temperature and $240^{o}K$. The heating and cooling rates were 10 degrees/min.

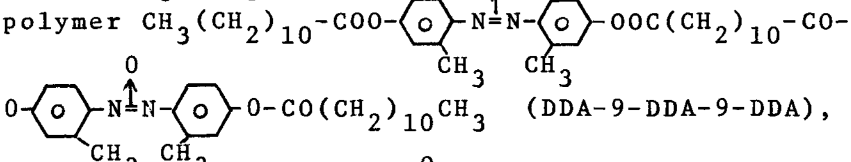
The transition temperatures were read directly from the maximum or minimum position of the peak on the temperature scale. Textures of the materials were studied using a Leitz Ortholux polarizing microscope equipped with a hot stage and a Mettler FP-52 temperature programmer.

RESULTS AND DISCUSSION:

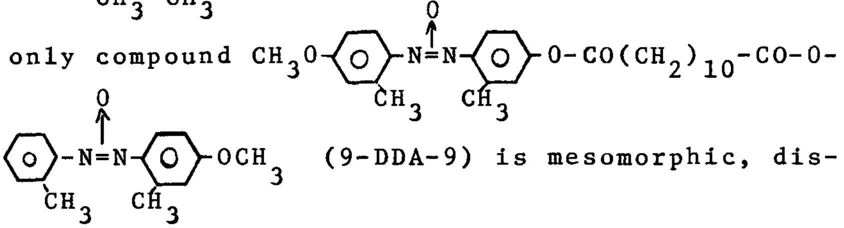
Enthalpies and entropies for the isotropic to nematic transition are listed in Table I. The units KJ/mole of backbone atoms and J/mole of backbone atoms-degree, are used to eliminate the effect of different lengths of structural units(7). Although the values obtained on heating and cooling were usually the same, the enthalpies reported here were calculated from the areas under the cooling curves for two reasons: compounds 9-DDA-9 and DDA-9-I are monotropic nematics and show no mesophase transition on heating; horizontality of baseline is better during the cooling cycle. The values of ΔH_{IN} and ΔS_{IN} for 4,4'-methoxyazoxybenzene (PAA) and 4,4'-decyloxyazoxybenzene (DAB) are taken from the data of Arnold (8), as the corresponding 2,2'-methylazoxybenzene derivatives are not mesomorphic. Indeed, of all the model compounds of DDA-9 which we have synthesized (6), including a model of the repeating unit



(9-DDA) and a prepolymer



(DDA-9-DDA-9-DDA), only compound



(9-DDA-9) is mesomorphic, displaying a monotropic nematic phase on cooling to 100°C. Oligomer DDA-9-I, a mixture composed predominantly of units 9-DDA-9-DDA-9, also displays a monotropic nematic phase. The rest of the samples listed in Table I are nematic on both heating and cooling.

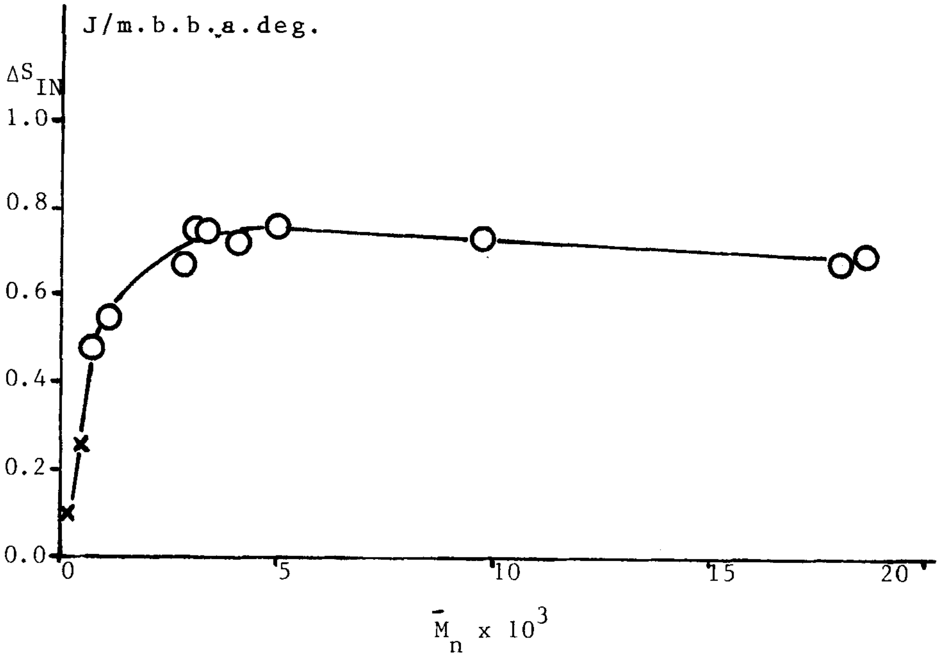


Figure 1. ΔS_{IN} vs. $\bar{M}_n$ for $(DDA\text{-}9)_n$

Fig. 1 illustrates the increase of ΔS_{IN} with increasing molecular weight. Beginning with the values of ΔS_{IN} for PAA and DAB, which are within the usual range for standard low molecular weight nematics (8), the isotropisation entropy per backbone atom increases drastically for the two monotropic compounds 9-DDA-9 and DDA-9-I before levelling off at 0.73 ± 0.03 J/m.b.b.a.deg. Of the samples investigated to date the lowest molecular weight to display an enantiotropic nematic phase is DDA-9-L-I, which contains approximately six repeating units per chain ($\bar{M}_n$=2,800). This seems to be the point at which a "polymeric" system develops as the result of cooperativity between successive repeating units. The values of isotropisation enthalpies and entropies of the "polymers", are unusually high compared to that of standard low molecular weight nematics and reflect the extended conformation of the dodecanedioate spacer in the nematic fluid (3,4).

An x-ray diffraction experiment performed on a quenched oriented nematic phase of sample DDA-9-L was interpreted in terms of a cybotactic nematic model with extended spacer conformation (3), thereby, confirming the calorimetric results. A proton NMR investigation of DDA-9-L sample revealed an unusually high nematic order parameter varying between 0.69 at T_{NI} and o.84 at T_{KN}(5,9); a detailed analysis of the NMR spectrum shows that the spacer aligns with a degree of order comparable to that of the mesogene with a low density of hairpin bend defects (9).

The lower molecular weight samples, on the other hand, appear to be characterized by decreasing participation of the flexible moiety in the nematic ordering process, as evidenced by the decreasing values of ΔS_{IN} . Preliminary measurements of nematic order parameters of samples DDA-9-E, DDA-9-I and 9-DDA-9 appear to bear out this conclusion. Whereas development of the highly organized nematic phase seems to be dependent on the connectivity of at least 5-6 repeating units, existence of a simple monotropic phase appears to require one of two factors: minimum axial ratio of the mesogene <u>or</u> proper sequencing of

TABLE I

ENTHALPIES AND ENTROPIES FOR THE ISOTROPIC TO NEMATIC TRANSITION.

Model Compound	Molecular Weight	T_{IN}(°K)	ΔH_{IN} KJ/*mbba	ΔS_{IN} J/*mbba.°
**PAA	258.3	408.7	0.041	0.10
** DAB	510.7	396.6	0.098	0.25
9-DDA-9	738.8	373	0.17	0.47
DDA(9-DDA)$_2$	1075.4	no mesophase		
Oligomer or Polymer	$\bar{M}_n$			
DDA-9-I	1130	347	0.19	0.55
DDA-9-L-I	2800	401	0.27	0.67
DDA-9-L-III	3080	405.4	0.30	0.75
DDA-9-E	3270	401	0.30	0.75
DDA-9-L	4110	406.6	0.29	0.72
DDA-9-L-II	5000	405.4	0.31	0.76
DDA-9-SP	9700	427	0.31	0.73
DDA-9-T1	18,100	433	0.29	0.67
DDA-9-T2	18,700	435	0.30	0.69

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*mbba = mole of backbone atoms

** data for PAA and DAB are from N⟶I transition.

rigid-flexible units. Thus, model compound DDA-9-DDA-9-DDA (molecular weight:1075.4 g/mole) which is composed of the sequence of units flexible-rigid-flexible-rigid-flexible, is not mesomorphic; on the other hand, 9-DDA-9 (molecular weight: 738.8 g/mole) with a sequence of units rigid-flexible-rigid has a monotropic nematic phase. Model compound 2,2'-methyl-4,4'-acetoxyazoxybenzene is not mesomorphic, but 4,4'-acetoxyazoxybenzene has a narrow monotropic nematic phase illustrating the influence of the axial ratio on mesophase formation.

It is clear from data presented in Table I and Fig. 1 that, as the molecular weight of oligomers and model compounds increases, the flexible part of the molecule takes on an increasingly active role in the process of nematic order formation. Behavior of the DDA-9 polymer cannot be explained in terms of a dispersion of rodlike mesogenic elements in a flexible diluent (10,11).

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