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Orientational Order in the Nematic Phase of Low Molecular Weight Analogues of Nematic Polymers

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Received February 13, 1985

ABSTRACT: The nematic order parameter as a function of the temperature has been measured by X-ray diffraction methods for some compounds having the formula $CH_3(CH_2)_mCOOROOC(CH_2)_mCH_3$ (m = 3, 4) or $CH_3(CH_2)_4COOROOC(CH_2)_nCOOROOC(CH_2)_4CH_3$ with n = 7–10, R = $-C_6H_4-C(CH_3){=}HC-C_6H_4-$. Dimeric compounds with even n afford order parameters higher than for any other of the examined compounds. Extrapolation to the isotropization temperature leads to a limiting value of ~0.58. No significant difference has been found between dimers with odd n and monomeric compounds. Order parameters extrapolated at the isotropization temperature approach the Maier–Saupe limit. The behavior of the dimeric compounds is coherent with the pattern defined for the thermodynamic data concerning their isotropization and with the behavior of structurally homologous linear polymers also showing nematic mesomorphism.

Introduction

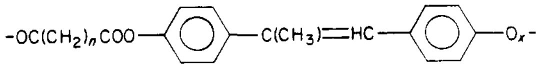
The study of mesophasic properties of semiflexible polymers has attracted interest on the problem concerning the reciprocal influence between contiguous rigid and flexible parts of the same molecule.

Recent results point out that orientational order of the rigid parts and conformational structure of the flexible portions play complementary roles. High levels of orientational order of the rigid parts in a nematic phase are more compatible with the extended conformations of the flexible parts.[1] The odd–even fluctuations of the thermodynamic quantities connected to the isotropization transition appear to be a consequence of this. Theoretical calculations[2] and some experimental investigations[3,4] are fairly convergent to the conclusion that for these semiflexible polymers the degree of order at the nematic–isotropic phase transition should be only moderately higher than for ordinary low molecular weight "monomeric" nematogens.

Low molecular weight nematogens whose molecules are structurally characterized by a "rigid–flexible–rigid" sequence have been examined as the most simple models for polymeric homologues.[5] Series of such "dimeric" model compounds having a variable number of carbon atoms in the flexible spacer reproduce the main features observed for the nematic phase of homologous series of polymers, namely, a relatively large molar isotropization enthalpy, particularly for the even-type molecules (i.e., those molecules having an even number of atoms in the backbone chain of the flexible spacer), a very much greater odd–even fluctuation of this quantity than observed for low molecular weight nematogens having a single rigid group in the molecule ("monomers"), and a greater thermal stability of the mesophase as compared with that exhibited by these monomeric homologues.

In a recent study Griffin, Sigaud, and Yoon,[3] on the basis of magnetic susceptibility measurements, have shown that the orientational order parameter at the nematic–isotropic phase transition for an even-type dimer has an intermediate value between those found for the homologous monomer and polymer.

We have measured by X-ray diffraction methods the degree of orientational order in molten fibers of semiflexible polymers of the formula



(ref 6)

In this paper the results of an investigation on the degree of order characterizing the nematic phase of dimeric and monomeric homologues are discussed.

0024-9297/85/2218-2773$01.50/0

Experimental Section

The following compounds have been examined:

$$\mathrm{Dn} = \mathrm{CH_3(CH_2)_4COOROOC(CH_2)_{n-2}COOROOC(CH_2)_4CH_3}$$
$$n = 9\text{–}12 \text{ and } \mathrm{R} = -\mathrm{C_6H_4{-}C(CH_3){=}HC{-}C_6H_4}-$$

(in this and in the following formulas $-C_6H_4-$ = *p*-phenylene).

$$\mathrm{Mn} = \mathrm{CH_3(CH_2)_{n-2}COOROOC(CH_2)_{n-2}CH_3} \qquad n = 5, 6$$

Compounds Dn and Mn will be also referred to as dimers and monomers, respectively. Their syntheses have been described elsewhere.[5,7]

In addition to these, a dimeric compound with the formula

$$\mathrm{DG10} = \mathrm{CH_3(CH_2)_4OC_6H_4COOC_6H_4O(CH_2)_{10}O{-}C_6H_4OOCC_6H_4O(CH_2)_4CH_3}$$

has been examined in order to make a closer comparison with the results obtained by Griffin, Sigaud, and Yoon[3] on the same compound but with a different experimental method. Compound DG10 was synthesized by the reaction of $CH_3(CH_2)_4OC_6H_4COOH$ (which was prepared by standard procedures) with $HOC_6H_4O(CH_2)_{10}OC_6H_4OH$ following a procedure described by Griffin and Havens.[8]

The orientational order parameter within the nematic range was measured by X-ray diffraction methods on samples aligned in a 0.3-T magnetic field.

The temperature of the sample, which was contained inside a 3-mm-diameter hole drilled in an aluminum plate, was regulated within 0.5 K. For each compound the measurement has been performed at a minimum of three different temperatures within the nematic range. In order to minimize influences of possible chemical decomposition, each measurement was performed with a new sample. The chemical stability of the samples utilized was eventually monitored by DSC thermal analysis. No evidence of chemical modification was detectable.

The X-ray diffraction pattern was recorded on a flat-film camera (Ni-filtered Cu Kα radiation being used).

The diffracted intensity along the principal halo was measured photodensitometrically by means of a Perkin-Elmer PDS microdensitometer.

The optical density function $I(X)(X = 0$ is the equatorial line), correted for the background radiation, was utilized to calculate the orientation distribution function according to eq 1, which is a slightly modified form of the Kratky formula:[9]

$$I(X) = \int_{\sin^{-1} a}^{\pi/2} N(\psi) \sin(\psi)\, d\psi/(\sin^2(\psi) - a^2)^{1/2} \quad (1)$$

where $a = \cos(\theta_m)\sin(X)$, θ_m is the diffraction angle corresponding to the maximum diffracted intensity along the equatorial line, and ψ = angle between the long molecular axis and the macroscopic orientation axis.

$N(\psi)$ is expanded as a series of Legendre polynomials of even order

$$N(\psi) = \sum_{2i} a_{2i} P_{2i}(\cos(\psi))$$

and its substitution in (1) leads to eq 2

$$I(x) = \sum_{2i} a_{2i} c_{2i} \quad (2)$$

$$c_{2i} = \int_{\sin^{-1} a}^{\pi/2} P_{2i}(\cos(\psi)) \sin(\psi)\, d\psi/(\sin^2(\psi) - a^2)^{1/2}$$

The order parameter $\bar{P}_2 = 4a_2/5 = \langle 3\cos^2(\psi) - 1\rangle/2$ is found by least-squares fitting of (2) with i(max) = 8.

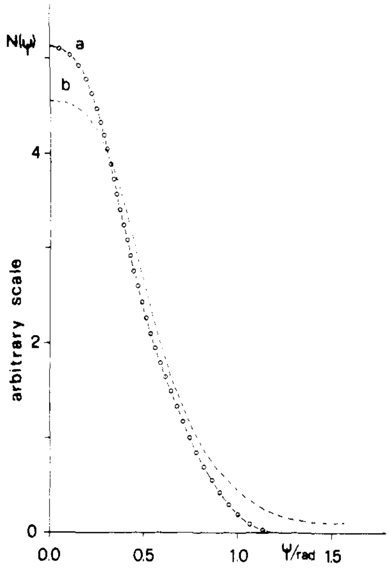


Figure 1. Orientation distribution function $N(\psi)$ for two dimeric compounds: (a) D12, T/T_{NI} = 0.984; (b) D11, T/T_{NI} = 0.962.

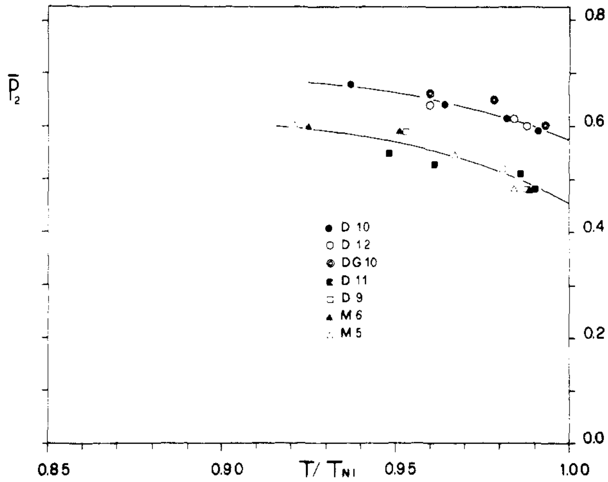


Figure 2. Order parameter $\bar{P}_2$ as a function of the T/T_{NI} ratio (T_{NI} = isotropization temperature).

The calculated orientation distribution function $N(\psi)$ for one odd and one even dimer is reported in Figure 1.

Results and Discussion

Order parameters as a function of the temperature are reported in Figure 2.

The first clear evidence to be remarked on is the sharp distinction between dimeric compounds having even and odd numbers of carbon atoms in the flexible spacer. Such differences, which parallel analogous fluctuations of the isotropization entropies, are by far greater than any other measured or calculated for homologous series of nematogenic compounds containing a single rigid group and one or two terminal tails. In coherence with our results, fluctuations of this amplitude have been calculated by Luckhurst for the core order parameters of homologous bis(4,4′-cyanobiphenyloxy)alkanes.[10]

Comparable experimental results have been found by the authors for the above mentioned polymeric homologues. A difference ranging, according to the temperature, between 0.15 and 0.20 has been found by Blumstein and coworkers[11] between the order parameter of bis[3-methyl-4-[(4-methoxy-2-methylphenyl)azoxy]phenyl] 1,12-dodecanedioate and bis[3-methyl-4-[(4-methoxy-2-methylphenyl)azoxy]phenyl] 1,9-nonanedioate on the basis of NMR data. In both cases the order parameter of the even-type dimers at the isotropization is close to 0.6.

A lower ($\sim$0.5) value has been measured by Griffin, Sigaud, and Yoon[3] on DG10, which is a dimeric compound of even type. However, our measurements on this compound give order parameters very close to those found for even dimers Dn.

The order parameters of odd-type dimers and both even- and odd-type monomeric compounds are included in a band of values that, on the average, lay 0.1 below the even dimeric compounds. Extrapolation to $T = T_{NI}$ leads to a limiting value that is close to the Maier–Saupe limit.

A conclusive remark arises both from the experimental results and from the theoretical calculations: the coupling of two rigid molecular sections (either as such or as a part of a polymeric chain) via a conformationally flexible spacer tends to increase the nematic orientational order, as compared to the monomeric homologues, only when the spacer has an even number of atoms along the backbone chain, producing, as a consequence, an enhancement of the odd-even fluctuation of the order parameter. Although some available thermodynamic measurements may allow reasonable extrapolations, no significant direct experimental evidence is available as yet concerning the extent of the connection of this phenomenon with the stereochemical nature and length of the flexible spacer.

Acknowledgment. Financial support by Ministero della Pubblica Instruzione is acknowledged. We are grateful to P. Izzo for technical assistance in the building of part of the experimental apparatus.

Registry No. $CH_3(CH_2)_4COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_3CH_3$, 65224-17-1; $CH_3(CH_2)_3COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_3CH_3$, 65224-16-0; $CH_3(CH_2)_4COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_7COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_4CH_3$, 98585-84-3; $CH_3(CH_2)_4COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_{10}COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_4CH_3$, 98585-86-5; $CH_3(CH_2)_4O$-*p*-C_6H_4-COO-*p*-C_6H_4-$O(CH_2)_{10}O$-*p*-C_6H_4-OOC-*p*-C_6H_4-$O(CH_2)_4CH_3$, 78352-90-6; $CH_3(CH_2)_4$-COO-*p*-C_6H_4-$C(CH_3){=}CH$-C_6H_4-*p*-$OOC(CH_2)_9COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_4CH_3$, 98585-85-4; $CH_3(CH_2)_4COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_8COO$-*p*-C_6H_4-$C(CH_3){=}HC$-*p*-C_6H_4-$OOC(CH_2)_4CH_3$, 98585-87-6.

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Notes

A Semiempirical Equation of State for Molten Polymers and Hydrocarbon Liquids

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In a previous paper,[1] we proposed a new expression for the free volume applicable to polymer and low molecular weight hydrocarbon mixtures. It was coupled with the well-known UNIFAC model[2] as the free volume term. The newly proposed UNIFAC-FV model was found to be successful to predict solubilities of various hydrocarbon gases and vapors in molten polystyrene, polypropylene, polyethylene, and polybutadiene[1,3] from the contributions of each group contained in the molecules.

In the present study, a semiempirical equation of state applicable to liquid states is derived from the partition function containing the free volume term mentioned above. The equation of state derived is applied to predict specific volumes of low molecular weight hydrocarbon liquids and molten polymers.

Partition Function and Equation of State

Details of derivation for the partition function have been previously reported.[1] In brief, the partition function Z has been derived based on the concept of Flory[4] and is given by the equation

$$Z = Z_{\text{comb}}\left(\frac{\nu^*}{\Lambda^3}\right)^{crN}(\tilde{v}_{\text{f}})^{crN}(q_{\text{int}})^{rN} \times \exp\left\{\frac{s\eta rN \exp(0.3\tilde{v})}{2k\tilde{v}^{1.66}T^{1.23}}\right\} \tag{1}$$

where

$$\tilde{v}_{\text{f}} = (\tilde{v} - 1) \exp\left\{-\frac{18(\tilde{v} - 1)^2 + 9(\tilde{v} - 1) + 2}{6(\tilde{v} - 1)^3}\right\} \tag{2}$$

$$\tilde{v} = v/v^* \tag{3}$$

The functional form of Z was empirically determined by using the PVT and heat of vaporization data of low molecular weight hydrocarbons. In the above equations, Z_{comb} is the combinatorial partition function, ν^* is the hard-core volume per segment, Λ is the de Broglie wavelength, c is the one-third external degrees of freedom per segment, r is the number of segments per molecule, and N is the number of molecules. Further, $\tilde{v}_{\text{f}}$ is the reduced free volume, q_{int} is the partition function arising from internal rotation and vibration degrees of freedom, s is the number of intermolecular contact sites per segment, η is a constant characterizing the energy of interaction for a pair of neighboring sites and having the dimensions of $JK^{0.23}$, $\tilde{v}$ is the reduced volume defined by eq 3, v is the molar volume, v^* is the hard-core volume per mole, k is the Boltzmann constant, and T is the temperature.

0024-9297/85/2218-2775$01.50/0