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DDA9. The physical reasons why these polymers behave differently at large masses may be related to the molecular arrangement of the macromolecules in the nematic phase. AZA9 polymer is less ordered than DDA9 polymer for comparable masses (odd–even effect is S[6,10]) and is a usual nematic, whereas DDA9 is a cybotatic nematic.[6] It is possible that for DDA9, this extra order would shift the change in molecular mass behavior to values of M higher than 8500, but this question remains open.

Finally, it must be noted that the twist viscosity coefficient γ_1 studied in this paper is of different nature than the oscillatory shear viscosity η^* previously measured[14] in the same polymers. This latter coefficient is smaller by several orders of magnitude than the corresponding γ_1. In fact, as suggested by rheooptical experiments on a similar polymer,[15] the values of η^* measured in the experimental conditions of ref 14 (high angular frequency velocities) are probably close to those of the second Miesowicz shear viscosity coefficient η_b (nematic director along with line of constant velocity). This coefficient is predicted to be much less sensitive to chain length than γ_1.[12] This may explain why the values of η^* are comparable for both polymers (within a factor smaller than 2 related to differences in nematic ordering), even for masses as large as 15 000.[14]

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Registry No. DDA9 (SRU), 79079-27-9; DDA9 (copolymer), 120667-65-4.

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Biaxiality of Molecular Ordering in Some Main-Chain Nematic Polymers: A Combined NMR and Magnetic Susceptibility Study

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ABSTRACT: The biaxiality of molecular orientational order of main-chain thermotropic nematic polymers ME9-Sn, poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(α,ω-dixo-α,ω-alkanediyl)], has been studied by combined proton NMR, deuterium NMR, and magnetic measurements. The main result is that the well-established increase of order (S_{zz}) with chain length is essentially caused by an increase of the biaxiality $S_{xx} - S_{yy}$ via a decrease of S_{yy}, with S_{xx} remaining constant. In other words, the increase of order is due to a progressive reduction of the orientational fluctuations of the aromatic core in one plane only; fluctuations in the perpendicular plane are not affected. An odd–even effect with the number n of methylene groups in the spacer, in phase with that of S_{zz}, is found for $S_{xx} - S_{yy}$. This behavior is directly linked to the particular structure of the repeating unit, in which the plane of the mesogenic core makes a large dihedral angle with the plane of the linkage ester group.

Introduction

An important aspect in the study of (uniaxial) nematic phases is the description of the molecular orientational order. For rigid, noncylindrical, elongated molecules, this order is characterized by two parameters. The first-order parameter S_{zz} (uniaxial term) pictures the average orientation of the main principal axis $0z$ of the ordering matrix ($0z$ is the "long molecular axis") with respect to the mean director and the second-order parameter $\delta = S_{xx} - S_{yy}$ (biaxial term) reflects the difference in ordering of the two minor principal (short) axes $0x$ and $0y$. The quantity $\eta_s = \delta / S_{zz}$ is the anisotropy parameter of the molecular orientational order and is directly related to the difference between the amplitudes of librations around the $0x$ and $0y$ axes.

The earlier mean-field theories[1,2] predict that for the uniaxial phase, both S_{zz} and δ depend on molecular shape but that $\delta = 0$ for molecules with cylindrical symmetry.

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A similar result has been obtained recently in a generalization of these theories.[3] From the experimental side, the situation is complicated because real molecules are generally nonrigid and because it is not possible to measure separately the two order parameters. In practice, simultaneous analysis of data obtained by different techniques is required to obtain convincing results concerning the magnitude of these order parameters. For low molecular mass nematics (LMN), there are so far only three examples of neat phases for which it has been unambiguously shown that δ is nonzero in the whole nematic phase, namely, 4-pentyl-4'-cyanobiphenyl (5 CB),[4,5] 2-fluorenyl 4-(tetradecyloxy)benzoate (FLOC 14),[6] and *p*-azoxyanisole (PAA).[5,7,8] However, it seems that the same situation holds for most real nematics.[9] For polymer liquid crystals (PLC), this question has been the focus of some attention recently.[10] For main-chain thermotropic polymers of the $(RF)_x$ type, where R is a rather rigid mesogenic unit and $F = (CH_2)_n$ is a flexible spacer, it was suggested that "linking successive cores together via a flexible spacer could very well amplify biaxial librations of the mesogenic cores".[11] The possibility of a pronounced odd–even effect oscillation in δ with the parity of *n*, similar to that observed for S_{zz},[12,13] was also suggested.[11] Some results exist for model compounds of such polymers of the RFR type (siamese twins). For α,ω-bis[(4'-cyanobiphenyl-4-yl)oxy]alkane twins, it has been shown that, at the clearing point, S_{zz} is considerably larger for members of the homologous series with *n* even that with *n* odd (oscillation in S_{zz}) and that δ is nonzero and independent of *n* within experimental accuracy.[14] For members $n = 7$ and $n = 10$ of α,ω-bis[[[4-[(4-methoxy-2-methylphenyl)azoxy]-5-methylphenyl]oxy]carbonyl]alkane twins, which are model compounds of poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(α,ω-dioxo-α,ω-alkanediyl)] (polymers of the ME9-Sn series[12,13,15-21]), it has been found that, in the entire nematic phase, η_s is probably much smaller than that of PAA.[8]

In this paper, we present a detailed study of the biaxiality of molecular ordering of some ME9-Sn polymers using combined proton NMR (^{1}H NMR), magnetic susceptibility, and deuterium NMR (^{2}H NMR) measurements. The results clearly show that (i) the biaxiality increases with both temperature and chain length, (ii) an even–odd effect in δ, in phase with that of S_{zz}, seems to exist, and (iii) the increase of order with increasing chain length is essentially due to a progressive reduction of the orientational fluctuations of the mesogenic core in one plane, the fluctuations in the perpendicular plane not being affected.

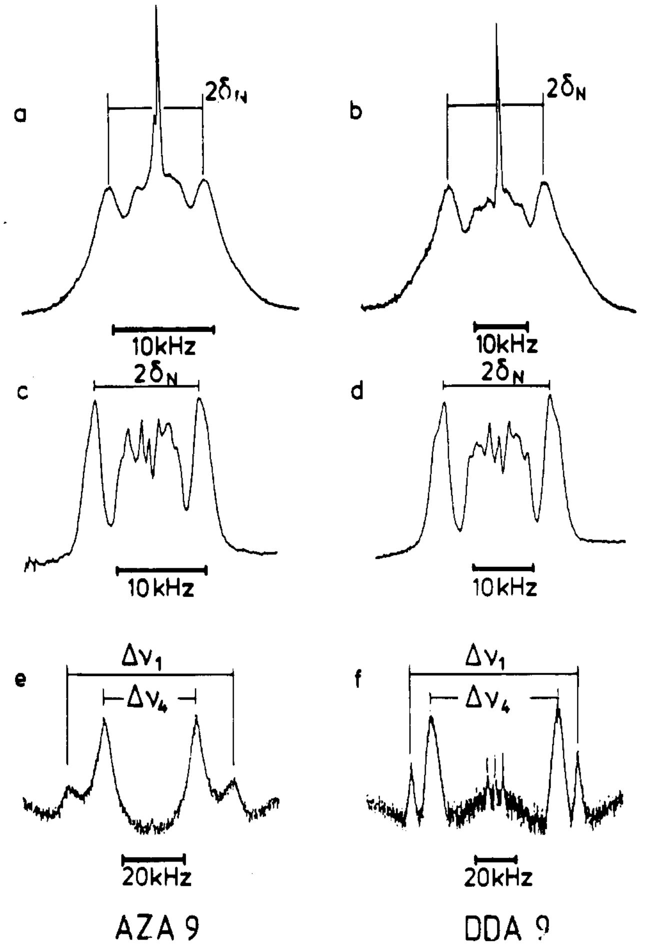
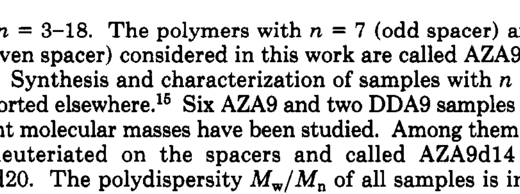


Figure 1. Typical NMR spectra of AZA9 and DDA9 polymers in the nematic phase at comparable reduced temperature. (a, b) ^{1}H NMR spectra of normal samples; (c, d) ^{1}H NMR spectra of spacer deuteriated samples 7 and 8; (e, f) corresponding ^{2}H NMR spectra of samples 7 and 8. The sharp central lines in spectra a and b correspond to the isotropic component (N + I biphase).

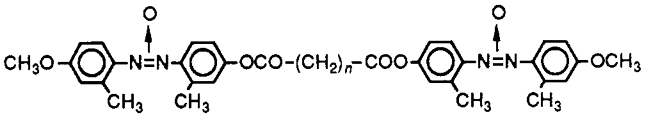
Materials and Methods

Polymers of the ME9-Sn series[15,16] are main-chain thermotropic nematic polyesters of general formula



where $n = 3$–18. The polymers with $n = 7$ (odd spacer) and $n = 10$ (even spacer) considered in this work are called AZA9 and DDA9. Synthesis and characterization of samples with $n \leq 14$ are reported elsewhere.[15] Six AZA9 and two DDA9 samples with different molecular masses have been studied. Among them, two were deuteriated on the spacers and called AZA9d14 and DDA9d20. The polydispersity M_w/M_n of all samples is in the range 1.2–1.3. All these polymers exhibit a nematic plus isotropic (N + I) biphase of width ΔT_{NI} between the pure isotropic (I) and pure nematic (N) phases. Detailed studies of the biphasic aspects of these polymers have been reported.[18] The clearing temperature T_{NI} is conveniently defined as the middle of the N + I biphase, where the nematic fraction f_N, as measured by NMR,[12,13,17] is just 0.5.

The above-mentioned twin model compounds of formula



with $n = 7$ (9AZA9) and $n = 10$ (9DDA9) are also of interest in the present context. The main results of a previous[8] similar study on these two compounds, and on PAA, will also be reproduced here for comparison. Table I summarizes the physical data of all samples considered in the present work.

Generally, the experimental conditions were essentially the same as described previously.[8] The NMR spectra were obtained with a Brüker CXP90 spectrometer working at 90 MHz for proton and a Brüker WM 250 spectrometer working at 38.4 MHz for deuterium. The samples (~50 mg) were contained in 5-mm-diameter tubes and the spectra recorded by slow cooling by steps of 1–3 °C, after equilibrating during at least 20 min at a temperature well inside the pure isotropic phase. Figure 1 shows typical PMR and DMR spectra of these polymer samples, whose breadth is characteristic of aligned nematic phases.[19,21]

The magnetic measurements were performed by using a SHE Corporation SQUID magnetometer working at 4 T. The same samples as in the NMR experiments were held in plastic containers which were dried during ~1 day at ~100 °C. Thermal contact of the samples with the regulating temperature device was achieved with helium gas. The presence of helium depressed the clearing temperature by a few degrees so that comparison with

Table I
Physical Data of Samples Used

	sample	M_n	$\bar{X}$	$T_{NI}{}^a$	ΔT-(N + I)^b	$\bar{\chi}^c$	$\bar{\chi}$
	1	7300	18.0	142.5	12	−5.70^d	−234^{d,e}
	2	3700	9.0	119.2	19	−5.69	−233^e
AZA9	3	3100	7.5	110.4	20	−5.63	−231^e
	4	2300	5.6	99.2	30	−5.70	−234^e
	5	1800	4.4	81.4	30	−5.70	−234^e
DDA9	6	2250	5.0	111	∼40	−5.49	−248^e
AZA9d14	7	4300	10.1	131.0	20		
DDA9d20	8	2500	5.6	128.5	30		
9AZA9	9	696		50.5	10	−6.17	−215^f
9DDA9	10	738		99	4	−6.08	−224^f
PAA	11	256		136	<1	−5.83	−150^g

[a] In °C, defined at $f_N = 0.5$. [b] In °C, full width of biphasic range. [c] In 10^{-7} cm^3/g. [d] Estimated. [e] In 10^{-6} cm^3/mru. [f] In 10^{-6} cm^3/half-mol. [g] In 10^{-6} cm^3/mol.

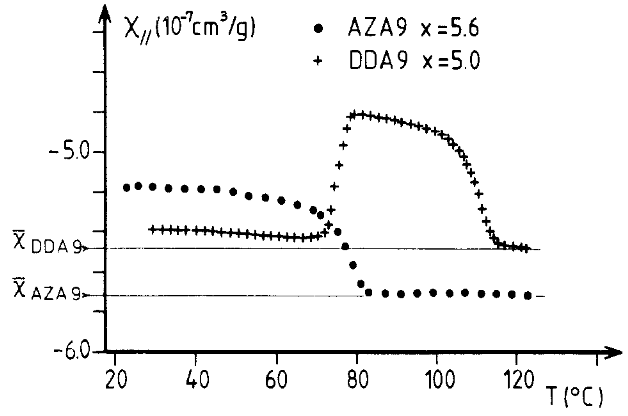


Figure 2. Typical temperature dependences of magnetic susceptibility: (●) AZA9 polymer (sample 4); (+) DDA9 polymer (sample 6).

NMR results was performed by plotting the data versus reduced temperature $T - T_{NI}$. The chosen thermal history was the same as in the NMR experiments. The contribution to the magnetization of the container was measured in a prior experiment performed under the same experimental conditions and subtracted from the raw data. The masses of the samples were measured before and after the experiments and variations of a few percent were observed, associated essentially with degasing. The accuracy on absolute values of susceptibilities is estimated to this amount (cf. Table I). Figure 2 shows two typical magnetic susceptibility curves for DDA9 and AZA9 polymers of comparable lengths. The increase of the susceptibility when going from the isotropic to the nematic phase reveals molecular alignment along the static magnetic field of the magnetometer. The smaller variation for AZA9 compared to DDA9 is an indication of a poorer order (odd–even effect on S_{zz}[12,13]). The relatively sharp decrease to a value close to that in the isotropic phase at the nematic–solid transition, and observed for all DDA9 polymers and for model compound 9DDA9, confirms the result inferred by NMR[19] that solidification is accompanied by loss of macroscopic order. On the contrary, macroscopic alignment can be preserved until rather low temperatures for AZA9 polymers and model compound 9AZA9.

Results and Qualitative Analysis

General Procedures. In a uniaxial phase, NMR dipolar or quadrupolar interactions and diamagnetic susceptibility are monomolecular, second-rank tensorial quantities, whose average value is simply related to the matrix order $\tilde{\mathbf{S}}$. If $\tilde{\mathbf{Q}}$ is such a tensor, it can be shown that the average value $\bar{q}$ of the component of $\tilde{\mathbf{Q}}$ along the mean director $\bar{n}_0$ is given by

$$\bar{q} = \bar{Q}_{n_0 n_0} = \tfrac{1}{3}\,\mathrm{Tr}\,(\tilde{\mathbf{Q}}) + \tfrac{2}{3}\,\mathrm{Tr}\,(\tilde{\mathbf{Q}}\tilde{\mathbf{S}}) \qquad (1)$$

where Tr symbolizes the trace of the corresponding matrix.

Expressing the trace in the principal frame of $\tilde{\mathbf{S}}$ and using the fact that $\tilde{\mathbf{S}}$ is traceless, algebraic manipulation of eq 1 shows that if $\tilde{\mathbf{Q}}$ is also traceless, we can write

$$\bar{q} = \tfrac{2}{3}S_{zz}(A_Q + B_Q\eta_S) \qquad (2)$$

in which A_Q and B_Q are related to the diagonal components of $\tilde{\mathbf{Q}}$ in the principal frame of $\tilde{\mathbf{S}}$ by

$$A_Q = Q_{zz} - \tfrac{1}{2}(Q_{xx} + Q_{yy}) \qquad (3)$$

$$B_Q = \tfrac{1}{2}(Q_{xx} - Q_{yy}) \qquad (4)$$

Note that A_Q and B_Q can be considered as the uniaxial and biaxial component of $\tilde{\mathbf{Q}}$, in the principal frame of $\tilde{\mathbf{S}}$, respectively.

If the molecular is nonrigid but if an ordering matrix can still be defined for the average molecule (implying decoupling between internal and external motions), the components Q_{ij} of $\tilde{\mathbf{Q}}$ should be replaced in eq 2–4 by their averages $\langle Q_{ij}\rangle$ over the internal motions.

Equation 2 shows that two independent experiments are in principle sufficient to determine S_{zz} and η_S. However, because $\langle A_Q\rangle$ and $\langle B_Q\rangle$ are generally not known with sufficient accuracy and may be not constant with temperature, additional independent data are required. If S_{zz} can be estimated independently (^{1}H NMR in the present case as will be seen below), then the behavior of $\bar{q}/S_{zz}$ versus temperature, where $\bar{q}$ is either the anisotropy of diamagnetic susceptibility or a quadrupolar splitting, can give rather accurate information concerning η_S and/or $\langle A_Q\rangle$ and $\langle B_Q\rangle$, that is on the anisotropy of molecular ordering and/or on the molecular structure and conformation. The results obtained from ^{1}H NMR, magnetic measurements, and ^{2}H NMR are now described and discussed in detail.

^{1}H NMR. The ^{1}H NMR line shapes in Figure 1 are rather complicated due to the large number of proton spins with dipolar interactions. Approximate simulations of these spectra have been attempted.[19] The main feature is the existence of a main doublet $2\delta_N$, which originates essentially from dipolar interaction between spins in the ortho position on the phenyl rings. Since the ortho direction is nearly parallel to the long axis 0*z* of the mesogenic core, this interaction will a priori be little affected by possible biaxial fluctuations, the reason being that the averaging effect will be practically the same for fluctuations occurring around the short 0*x* or 0*y* axes (expressed mathematically this means that we have $\langle Q_{xx}\rangle \approx \langle Q_{yy}\rangle$ in eq 4 implying $\langle B_Q\rangle \approx 0$). It is also not affected by rotation of the rings around their para axes so that $\langle A_Q\rangle$ in eq 3 is independent of temperature. Thus this dipolar interaction is practically proportional to S_{zz} only. The splitting $2\delta_N$, which measures the distance between two maxima of the spectrum, does not represent exactly this interaction. The exact position of these maxima depends on the shape of the lines. This shape is determined by the other dipolar interactions, which do depend on η_S. However, we have checked quantitatively with *p*-azoxyanisole (PAA) that the positions of the maxima move by less than 1% for η_S, varying from 0 to 0.3.[7] Such variation is within experimental error, and since η_S in these polymers is not expected to vary significantly more than 0.3 within the nematic range, we can assume that $2\delta_N$ is practically proportional to S_{zz}. The actual relationships that have been used in this (and previous) studies and justified by comparison with PAA are

$$2\delta_N\ (\mathrm{KHz}) \approx 24.08S_{zz} \qquad \text{(nondeuteriated samples)} \qquad (5)$$

$$2\delta_N\ (\mathrm{KHz}) \approx 22.74S_{zz} \qquad \text{(samples deuteriated on the spacers)} \qquad (6)$$

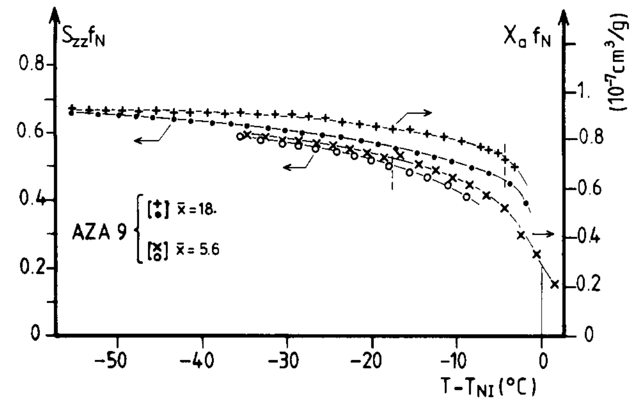


Figure 3. Variations of $S_{zz}f_N$ (left-hand scale) and $\chi_a f_N$ (right-hand scale) versus reduced temperature for two AZA9 polymers of different lengths (samples 1 and 4). Note the different dependences of both quantities. The dashed vertical lines indicate the limit of the N + I biphase.

The difference between the proportionally constants is due to the existence of a fine structure in the lines of the main doublet of the partially deuteriated samples, which shifts the two maxima inward. Note that if absolute values of these constants may be off by a few percent, their relative value is much more accurate.

In the N + I biphase, a sharp line superimposes on the spectra, corresponding to the isotropic component, as seen in Figure 1a,b. The value of the nematic fraction f_N can be deduced from these spectra by following the decrease of the amplitude of this isotropic component from the pure isotropic phase to the pure nematic phase, so that not only S_{zz} but also f_N has been deduced from the ^{1}H NMR experiments.[20,21] These quantities have been determined for all samples of Table I. As will be seen below, a more interesting quantity for comparison with magnetic data is $S_{zz}f_N$. Figure 3 shows typical variations of $S_{zz}f_N$ versus reduced temperature for two AZA9 samples.

Magnetic Susceptibility. The magnetic susceptibility of usual organic molecules around or above room temperature is always negative and originates essentially from the diamagnetism of the chemical moieties, which is stronger by 2–3 orders of magnitude than the paramagnetism due to the nuclear spins. The anisotropy of diamagnetic susceptibility χ_a of the nematic phase is defined as[8]

$$\chi_a = \tfrac{3}{2}(\chi_\parallel - \bar{\chi}) \qquad (7)$$

where $\chi_\parallel$ and $\bar{\chi}$ are the susceptibilities measured in the nematic and isotropic phases, respectively. Note that the value of χ_a is much more accurate than $\chi_\parallel$ or $\bar{\chi}$ separately because systematic errors on absolute values cancel in the difference.

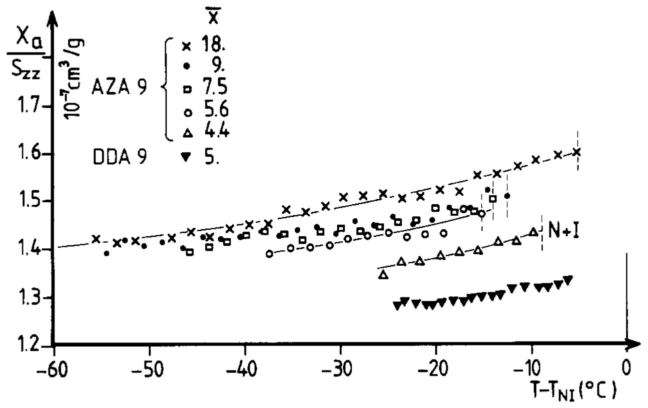


Figure 4. Ratio of anisotropy of diamagnetic susceptibility to main order parameter versus reduced temperature for samples 1–6. Note the increase with temperature and chain length.

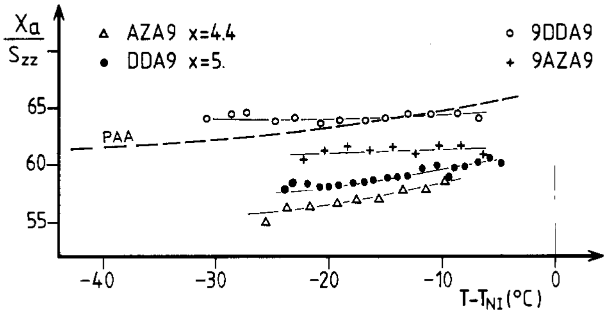


Figure 5. Ratio of anisotropy of diamagnetic susceptibility to main order parameter versus reduced temperature for two polymers AZA9 and DDA9 of comparable lengths (expressed in 10^{-6} cm^3/mru), for the two twin model compounds 9AZA9 and 9DDA9 (expressed in 10^{-6} cm^3/half-mol), and for PAA (expressed in 10^{-6} cm^3/mol). Note the similarity between AZA9 and DDA9 polymers and the much weaker temperature dependence for the model compounds.

In the N + I biphase, it is easy to show that the second member of eq 7 represents $\chi_a f_N$. Since f_N has been measured by ^{1}H NMR, it is possible to determine χ_a provided a careful renormalization of the temperature scales between both experiments is made. It turns out that such renormalization is rather easy, due to the sharp decrease of $S_{zz}f_N$ and $\chi_a f_N$ around T_{NI}. The temperature dependence of $\chi_a f_N$ has been determined for all nondeuteriated samples of Table I. Figure 3 shows examples of variations of $\chi_a f_N$ for the same two samples as for ^{1}H NMR. It is observed that although similar, the temperature dependences of $\chi_a f_N$ and $S_{zz}f_N$ are not exactly the same. This difference is observed for all samples studied and is larger for long polymers than for shorter ones. Figure 4 shows χ_a/S_{zz} versus reduced temperature for all AZA9 polymers studied, deduced from plots such as those of Figure 3. It is observed that this ratio increases with increasing temperature and with molecular length. Since the magnetic susceptibility is mainly due to the phenyl rings, according to eq 2, this result is a first indication that the ordering of the mesogenic core is biaxial. It is possible to be more quantitative. Combining eq 2 and 7 and by analogy with the analysis developed for PAA, assuming that the internal motions are simply librations of the rings around their para axes, we have[8]

$$\chi_a/S_{zz} = \Delta\chi_1^{(0)} + \Delta\chi_2^{(0)}\langle\cos 2\varphi\rangle\eta_S \qquad (8)$$

where $\Delta\chi_1^{(0)}$ and $\Delta\chi_2^{(0)}$ are the uniaxial and biaxial components of the diamagnetic susceptibility tensor of the repeating unit, in the principal frame of $\tilde{S}$ (cf. eq 3 and 4), the superscript (0) referring to the most probable conformation. The internal average $\langle\cos 2\varphi\rangle$ pictures the mean libration amplitude of the rings. Since $\Delta\chi_1^{(0)}$ and $\Delta\chi_2^{(0)}$ are essentially positive quantities,[8] which depend only on the nature of the repeating unit and not on chain length, the result in Figure 4 means that $\eta_S\langle\cos 2\varphi\rangle$ increases with both increasing temperature and molecular length. Since, in addition, $\langle\cos 2\varphi\rangle$ can only decrease (or remain constant) with increasing temperature, the above results essentially reflect a corresponding increase of the biaxiality parameter η_S in AZA9 polymers. For DDA9 polymers, which differ by the parity (and number) of methylene groups in the spacers, similar detailed experiments could not be performed because of the limitation toward high temperatures of our magnetometer (clearing temperatures are significantly higher for DDA9). However, the results with sample 6 (the only DDA9 polymer studied) show a very similar behavior. Figure 5 shows χ_a/S_{zz} expressed per mole of repeating unit (mru) (rather than per gram as in Figures 3 and 4) versus reduced temperature for this DDA9 sample, together with the corresponding curve for sample 5 (an AZA9 polymer of comparable length). Taking into account the (positive) contribution to χ_a of the three additional CH_2 group in DDA9 ($\sim 1 \times 10^{-6}$ cm^3 per mol of CH_2[22]), it can be considered that the two curves superpose within experimental accuracy, suggesting that η_S is the same for the two polymers. For comparison, also shown on the same figure are the curves for model compounds 9AZA9 and 9DDA9 and for PAA (extracted from ref 8). The curves for the two models can also be considered as superposable within experimental accuracy for the same reason as for the two polymers. The difference between absolute value of χ_a/S_{zz} for the polymer and the corresponding model comes from the (negative) contribution of a few 10^{-6} cm^3/mol[22] of the extra carbonyl group in the repeating unit of the polymer (negative because C=O is at a large angle with the long molecular axis, see below). The small difference between PAA and models (or polymers) comes from the rough compensation between the positive contribution of the spacers and the negative contribution of carbonyl groups. The overall variation of χ_a/S_{zz} in the nematic phase for the polymers is comparable to that of PAA and is much smaller for the model compounds. Concerning a possible odd–even effect in the second-order parameter $S_{xx} - S_{yy}$, the finding that η_S is practically the same for the two models and for two polymers of comparable lengths, associated with the result that a strong oscillation in S_{zz} is observed,[12,13] suggests that an in phase oscillation in $S_{xx} - S_{yy}$ also exists in ME9-Sn polymers. The ^{2}H NMR results that are analyzed below allow a check of these conclusions. They also provide important information about the molecular conformation as well as on the physical origin of the biaxiality in these polymers.

^{2}H NMR. The ^{2}H NMR spectra of DDA9d20 and AZA9d14 polymers (Figure 1e,f) are qualitatively similar and are characterized by two doublets with splittings $\Delta\nu_1$ and $\Delta\nu_4$. Doublet $\Delta\nu_1$ clearly corresponds to methylene deuterons adjacent to the carbonyl groups and $\Delta\nu_4$ to the remaining deuterons. The ^{2}H NMR spectrum of model compound 9DDA9d20 is published elsewhere.[20,21] It is very similar to that of the polymers except that the individual lines of the doublets are much narrower. The increase of the width of the lines with increasing molecular mass can probably be assigned to the increase of the average viscosity.[23] For the present study, the information contained in $\Delta\nu_1$ is of direct interest because the first methylene group reflects to a large extent the ordering of the mesogenic core.

The reason is that at variance with the other methylene groups whose orientation can explore a rather wide solid angle by successive rotations around the C–C bonds, the internal rotation axis of the first methylene group makes a small angle with the long axis $0z$. Consequently, the internal rotations contribute little to the averaging effects. However, because the CD bonds make a large angle with the long axis, the biaxial fluctuations of the core will significantly affect the value of $\Delta\nu_1$. More specifically, assuming that the two methylene deuterons are magnetically equivalent,[28] we can write the following expression:[9]

$$\Delta\nu_1 = {}^3\!/_2 c S_{zz}[|\langle P_2(\cos\beta_1)\rangle + {}^1\!/_2\langle \sin^2\beta_1 \cos 2\phi_1\rangle\eta_S|] \qquad (9)$$

where $c = e^2qQ/h \approx 172$ KHz is the quadrupole coupling constant for methylene deuterons and (β_1,ϕ_1) are the polar and azimuthal angles of one CD bond in the principal frame of $\tilde{S}$. Defining a reduced splitting $\Delta\nu^*_1$ by $\Delta\nu_1/(^3/_2)c$, the quantity $\Delta\nu^*_1/S_{zz}$ represents the expression between brackets in eq 9. The value of S_{zz} was deduced from the ^{1}H NMR spectra via eq 6 and $\Delta\nu^*_1/S_{zz}$ was deduced by combining these results with the ^{2}H NMR splittings. As for the magnetic measurements, a careful renormalization of the temperature scales between ^{1}H NMR and ^{2}H NMR is required to obtain reliable numbers. This renormalization is achieved very accurately by measuring f_N as a function of temperature by both methods and superposing the two curves. Figure 6 shows $\Delta\nu^*_1/S_{zz}$ versus reduced temperature for the two partially deuteriated polymer samples, as well as for model compound 9DDA9d20. In this latter case, the data are taken from ref 20. In that reference, the values were overestimated by ~8% due to an offset of ~2 °C in the temperature scales between the ^{1}H NMR and ^{2}H NMR experiments.

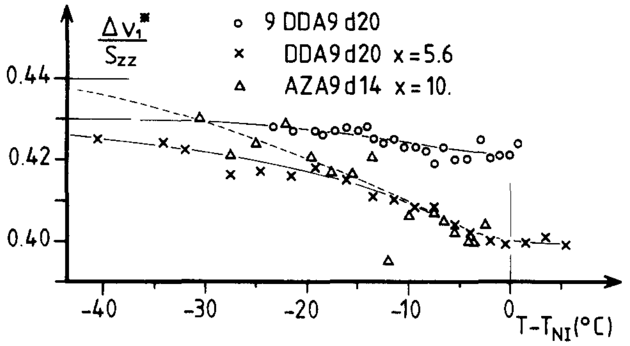


Figure 6. Ratio of reduced ^{2}H NMR splitting $\Delta\nu^*_1$ to main order parameter S_{zz} versus reduced temperature for the two spacer deuteriated samples 7 and 8 and for model compound 9DDA9d20. The limiting value at low temperature is ~0.43 for DDA9 and ~0.44 for AZA9. Note the similarity with Figure 5.

The analogy between Figures 5 and 6 is striking. For the two polymers $\Delta\nu^*_1/S_{zz}$ and χ_a/S_{zz} vary with temperature. This variation is very small for the model compounds and increases as the polymer length increases. In terms of eq 9, the finding that $\Delta\nu^*_1/S_{zz}$ decreases with increasing temperature is explained in the following way: since β_1 is expected to be rather large between ~70° for the $0z$ principal axis along the first methylene CC bond and ~90° for $0z$ along the symmetry axis of the spacer in its all-trans conformation), $\langle P_2(\cos\beta_1)\rangle$ is negative, with a value ranging between −0.32 and −0.50. On the other hand, since η_S is by convention a positive quantity and increases with increasing temperature (cf. Figure 5), a decrease of $\Delta\nu^*_1/S_{zz}$ can be observed only if $\langle ^1/_2 \sin^2\beta_1 \cos 2\phi_1\rangle$ is positive, that is, if the angles ϕ_i explored during the internal rotation around the first methylene CC bond mainly range between 0 and 45°.[29] The meaning of this result is easily understood by considering two extreme values of the dihedral angle between the $x0z$ principal plane and the symmetry plane of the first methylene group. In the first case where this angle is 0, ϕ_1 is about 60°, a situation that should be rejected. On the contrary for 90°, we have $\phi_1 \approx 30°$, a situation that is in agreement with the above result.

To summarize, it can be concluded from these ^{2}H NMR results that the $x0z$ principal plane (which is the plane in which the libration amplitude of the core is the largest) makes a large angle with the symmetry plane of the first CH_2 group.

Quantitative Analysis

The above analysis has been essentially qualitative. It is possible to be more quantitative by exploiting in more

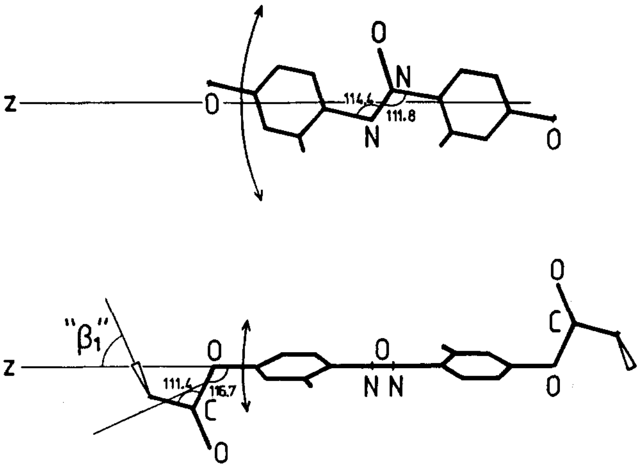


Figure 7. Sketch of two orthogonal views of a possible structure of the repeating unit of ME9-Sn polymers. The plane of the ester group makes a large angle with the plane of the mesogenic unit (roughly located between the two phenyl rings) and a small angle with the symmetry plane of the first methylene group. The arrowed arc circles picture the different libration amplitudes in the two perpendicular planes from which the biaxiality originates. Standard bond angles are also indicated.

detail the results that are summarized in Figures 3–6.

Molecular Structure and Conformation. Not much information concerning the structure of the repeating unit can be a priori extracted from these data. However, using the arguments developed below, a picture like that sketched in Figure 7 can be proposed. First, we reasonably expect that the plane of the ester group is close to the symmetry plane of the first methylene group. Second, the mean dihedral angle between the ester plane and that of the attached ring is probably rather large. This latter situation is indeed found in other compounds containing a similar moiety. In crystalline phenyl benzoate, this angle is 65.1°.[24] In leprolomin, a molecule of biological interest with two phenyl rings and three attached acetate moieties, the three corresponding angles are 89.8°, 90.0°, and 92.6°.[25] Large values are also predicted by conformational energy calculations.[26] Thus, the same situation seems likely for our polymer. Third, the analogy between the central mesogenic core of our polymer and that of PAA suggests that the conformations might be very similar.

Assuming a not too large dihedral angle between the rings (this angle is 22.6° in PAA), the above results suggest that the main plane of the core makes a large angle with the symmetry plane of the first methylene group. That is, this main plane is very close to the xOz principal plane, a situation that is expected for small, flat molecules.[1-3] So far, no data exist about the conformation of the core of our polymer, only quantum chemical calculations,[27] which support the analogy with PAA. A confirmation of this hypothesis can probably be obtained by exact simultation of ^{1}H NMR spectra of the spacer deuteriated polymers, since the shape of these spectra is sensitive to the orientation of the principal plane with respect to the rings.[7]

The mean value of the polar angle β_1 can also be estimated rather accurately for both DDA9 and A7A9 polymers. According to eq 9, $\Delta\nu^*_1/S_{zz}$ gives $|\langle P_2(\cos\beta_1)\rangle|$ for $\eta_S \approx 0$. The magnetic susceptibility data suggest that η_S becomes very small at low temperature. Figure 6 shows that the limiting values of $\Delta\nu^*_1/S_{zz}$ are near 0.43 for DDA9 and 0.44 for AZA9. Since $\langle P_2(\cos\beta_1)\rangle$ is negative, this corresponds to an average value of $\beta_1 \approx 77.5°$ for DDA9 and $\beta_1 \approx 78.5°$ for AZA9. Although very small, this difference of ~1° between the two values is significant, as can be seen in Figure 6.

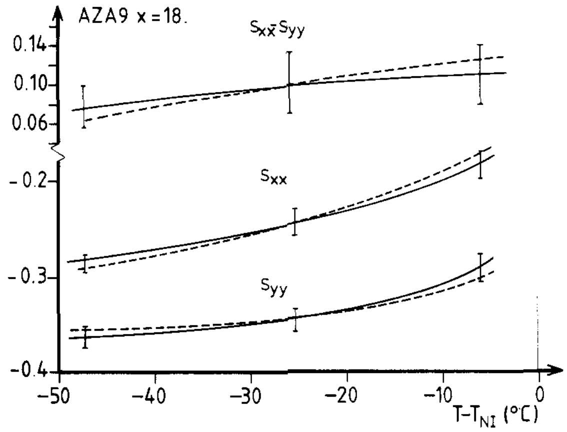


Figure 8. Example of the temperature dependence of S_{xx}, S_{yy}, and $S_{xx} - S_{yy}$ (AZA9 polymers, sample 1). The full lines assume that the libration amplitude of the rings is constant ($\langle\cos 2\varphi\rangle$ = 0.75). The dashed lines take into account some variation of $\langle\cos 2\varphi\rangle$. The extremities of the error bars correspond to $\langle\cos 2\varphi\rangle$ = 1 and 0.5.

Biaxial Order. According to eq 8, it is possible to estimate η_S if $\Delta\chi_1^{(0)}$ and $\Delta\chi_2^{(0)}\langle\cos 2\varphi\rangle$ are known. An estimate of these two quantities is possible. By extrapolation at low temperature of the data in Figures 4 and 5, we estimate $\Delta\chi_1^{(0)} \sim 51.25 \times 10^{-6}$ cm^3/mru for AZA9 and 54.25×10^{-6} cm^3/mru for DDA9. These numbers are comparable to the value for PAA $\sim 54 \times 10^{-6}$ cm^3/mol[8] and confirm the close similarity of the two central cores. The value of $\Delta\chi_2^{(0)}\langle\cos 2\varphi\rangle$ is more difficult to estimate accurately. For PAA, $\Delta\chi_2^{(0)} \approx (92 \mp 20) \times 10^{-6}$ cm^3/mol.[8] For our core, $\Delta\chi_2^{(0)}$ is expected to be comparable (or smaller if the mean dihedral angle between the rings is larger). The dynamical average $\langle\cos 2\varphi\rangle$ pictures the librations of the rings around their para axes. Estimation of its value can be obtained by analysis of the ^{1}H NMR line shapes. For PAA, reasonable simulations are obtained only for $\langle\cos 2\varphi\rangle$ ranging between 1 and ~0.75.[7b] A similar situation is likely for our polymers. Although the exact value is not known, $\langle\cos 2\varphi\rangle$, being an average over (fast) internal motions within the mesogenic unit, is expected to depend only on the structure of this unit and eventually on absolute temperature T but not, or very weakly, on chain length and/or the (slower) external motions described by matrix $\tilde{S}$, which depend essentially of reduced temperature $T - T_{NI}$. To take into account all the uncertainties, we have somewhat arbitrarily chosen $\langle\cos 2\varphi\rangle \sim 0.75$ and $\Delta\chi_2^{(0)} \approx 92$ (equivalent to $\langle\cos 2\varphi\rangle \sim 1$ and $\Delta\chi_2^{(0)} \approx 69$) and calculated η_S for all polymers at all temperatures. Then, using the values of S_{zz}, the quantities S_{xx}, S_{yy}, and $S_{xx} - S_{yy}$ have been deduced.

The anisotropy parameter can also be deduced from the ^{2}H NMR results of Figure 6 from eq 9 with $\langle P_2(\cos\beta_1)\rangle = -0.43$ for DDA9 and -0.44 for AZA9 and a common value of $\langle\phi_1\rangle \approx 30°$. Writing $\phi_1 = 30° + \Delta\phi_1$ where $\Delta\phi_1$ pictures the (internal) rotation around the first C–C bond of the spacer, we have

$$\langle \tfrac{1}{2}\sin^2\beta_1 \cos 2\phi_1\rangle \approx \frac{1 - \langle P_2(\cos\beta_1)\rangle}{3} \times \cos(60°)\langle\cos 2\Delta\phi_1\rangle \approx 0.24\cos\langle 2\Delta\phi_1\rangle$$

As above, an arbitrary value of $\langle\cos 2\,\Delta\phi_1\rangle \approx 0.75$ has been chosen to estimate a mean value of η_S.

Figure 8 shows an example of the temperature behavior obtained for AZA9 polymer with $\bar{x}$ = 18 (the longest polymer studied) deduced from the susceptibility results. It is observed that S_{xx} and S_{yy} are negative and increase

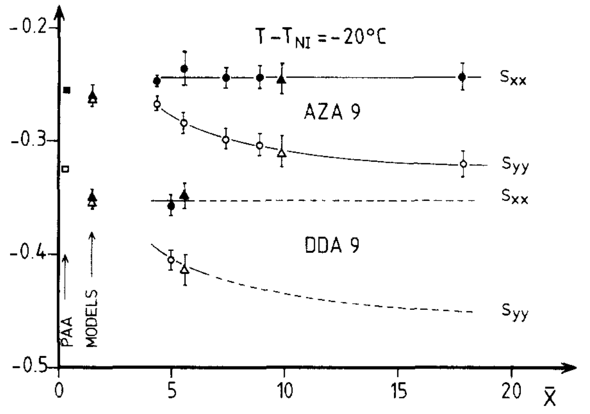


Figure 9. Example of the chain length dependence of S_{xx} and S_{yy} at fixed reduced temperature ($T - T_{NI} = -20$ °C) for AZA9 and DDA9 polymers. Circles are deduced from susceptibility data (Figures 4 and 5); triangles are deduced from ^{2}H NMR data (Figure 6). The values for PAA are also shown (extracted from ref 7). The results for long DDA9 polymers are extrapolated, as indicated by dashed lines. Error bars: same meaning as in Figure 8 for $\langle \cos 2\varphi \rangle$ (susceptibility) or $\langle \cos 2\Delta\phi_1 \rangle$ (^{2}H NMR).

with increasing temperature, indicating that the disorder increases by increasing the fluctuations around both short axes 0x and 0y. The biaxiality $S_{xx} - S_{yy}$ first increases and then tends to flatten off as the clearing point is approached, indicating that the fluctuations in the easy plane increase faster at low temperature but that this trend tends to reverse near the clearing point. The similarity of this behavior with those of LMM FLOC14[6] and PAA[7] is worth noticing and is in agreement with theoretical predictions for LMN.[1-3] The two extremities of the error bars in Figure 8 correspond to $\langle \cos 2\varphi \rangle = 1$ and 0.5. Since a variation between 1 and 0.5 is probably overestimated, the error bars also include part of the uncertainty on the value of $\Delta\chi_2^{(0)}$. The dashed lines are an example of variation assuming that $\langle \cos 2\varphi \rangle$ changes (decreases) with increasing temperature.

More interesting in the present context is the chain length dependence. Figure 9 shows S_{xx} and S_{yy} versus length for $T - T_{NI} = -20$ °C. Again the extremities of the error bars correspond to $\langle \cos 2\varphi \rangle$ or $\langle \cos 2\Delta\phi_1 \rangle$ varying between 1 and 0.5. The most striking feature of these results is that S_{xx} is practically independent of chain length, whereas S_{yy} decreases with increasing length. This means that the amplitude of the fluctuations in the easy x0z plane is constant and depends only on temperature. On the contrary, the amplitude in the y0z plane is reduced when the chain length increases. Thus, the increase of order with chain length is due to a reduction of the fluctuations in the y0z plane, that is, to an increase of order in one dimension only. This order and associated biaxiality decrease with decreasing chain length, and for the model compounds, the fluctuations have nearly cylindrical symmetry.

Figures 8 and 9 show that despite the inherent uncertainties, the results are rather accurate. In particular, the values deduced from susceptibility and ^{2}H NMR are nicely consistent with one another, as can be appreciated on Figure 9. This observation allows us to extrapolate the results for DDA9 polymers, for which data on long polymers are lacking, as shown by dashed lines in Figure 9. The magnitude of the odd–even effect shows up clearly in this figure. Note that this magnitude depends on the implicit assumption that the 0z principal axes of all compounds, in particular those of odd and even polymers, have the same direction with respect to the mesogen backbone. However, the order parameters being significantly different, it might be expected that the principal frames are not exactly the same. We have estimated that misorientations of ~15° between 0z axes induce changes of ~10% in S_{zz} and of less than ~5% in $S_{xx} - S_{yy}$. These changes are of the same order as the other uncertainties and do not affect the semiquantitative character of the results.

A Simple Model of Main-Chain Polymers

The above results suggest the following simple model of these $(RF)_x$ polymers. The first important ingredient of this model is the fact that the spacer, or at least the parts of it including the ester group and the first methylene group, is not colinear with the long axis of the mesogenic unit (Figure 7). The second ingredient is the fact that the x0z principal plane makes a large dihedral angle with the plane of the ester group. For a given extended polymer chain, the orientational fluctuation by an angle θ of one mesogenic unit necessarily involves a translational displacement of the rest of the chain toward this unit. With the above geometry, simple considerations show that the amplitude of this displacement is much smaller for fluctuations perpendicular to the plane of the ester group (second order in θ) than parallel to it (first order in θ). Consequently, the orientational fluctuations of largest amplitude will occur in a plane (by definition the x0z principal plane of **S**) that is nearly perpendicular to the plane of the ester group, as has been found. This fluctuation, involving small displacement of the chain, is expected to be little affected by chain length, explaining that S_{xx} is constant. On the contrary, a fluctuation in the y0z plane, involving larger displacements, is expected to be more difficult as chain length increases, explaining the decrease of S_{yy}.

Summary and Concluding Remarks

By combining NMR and magnetic measurements, we have been able to propose a rather fine description of the molecular conformation and orientational order at the level of the mesogenic unit and linkage to the spacer in these ME9-Sn polymers. The most important and novel result that has emerged is that the increase of order with chain length essentially originates from an increase of the biaxiality, that is, from a reduction of the orientational fluctuations in one plane only. The very small biaxiality found for the model compounds suggests that the intrinsic biaxiality of the mesogenic unit is relatively weak compared to that of PAA. This feature is presumably due to the presence of the two additional methyl groups substituted on the two phenyl rings. The basic difference between PAA and these polymers is that in the former, the biaxiality is caused by the departure from cylindrical symmetry of the molecule, whereas in the polymers, the biaxiality of the mesogenic core is induced by the polymeric character. For a given polymer length, the temperature dependence of $S_{xx} - S_{yy}$ suggests similar structure and conformation of the repeating unit of odd and even polymers, as revealed also by the close similarity of the line shapes in Figure 1. The higher order in even polymers is probably due to a better molecular packing (polymers are cybotactic nematics[13]). All these results support the conjecture made in ref 11 about the nature of the order in main-chain polymers.

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Registry No. AZA9 (SRU), 82851-48-7; AZA9 (copolymer), 120667-64-3; DDA9 (SRU), 79079-27-9; DDA9 (copolymer), 120667-65-4.

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(28) The molecule being not flat, this equivalence can only be obtained by fast exchange between the actual conformation and the conformation deduced by symmetry with respect to a plane, by rotation around all the single covalent bonds (racemization).
(29) The referee has suggested a possible different explanation for the observed decrease of $\Delta\nu^*{}_1/S_{zz}$, namely, that $\langle\cos 2\phi_1\rangle$ is negative and decreases in such a way that it overcompensates the corresponding increase of η_S. Such a possibility is unrealistic since an increase of η_S of $\sim$0.1 between low and high temperature (consistent with the magnetic results) implies a variation of $|\langle\cos 2\phi_1\rangle|$ larger than 1 in the same temperature range. Changing the convention concerning the sign of η_S changes the meaning of the angle ϕ_1 in eq 9 and the sign of $\Delta\chi_2{}^{(0)}$ in eq 8 but clearly not the physical situation.

Synthesis and Characterization of Poly(oxy-2,6-naphthalenediylcarbonyl)

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ABSTRACT: The synthesis of oligomeric and high molecular weight polyesters of 6-hydroxy-2-naphthoic acid in therminol is described. The polyesters are characterized by X-ray, DSC, TMA, light microscopy, and SEM. Close analogies are found to exist between the polycondensation reaction, thermal transitions, and solid-state structures of poly(oxy-2,6-naphthalenediylcarbonyl) and poly(oxy-*p*-phenylenecarbonyl). The composition versus $T_{c\rightarrow n}$ diagram for the copolyesters of 6-hydroxy-2-napthoic acid and 4-hydroxybenzoic acid is described.

Introduction

The structure and properties of the copolyesters of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) have been examined by a number of different workers in considerable detail during the past few years.[1-10] Similarly, the homopolyester of HBA has been the subject of many investigations concerning its polymerization,[11,12] its crystal structure,[13-15] and the nature of its thermal transitions.[16,17] On the other hand, very little information has been published on the homopolyester of HNA other than preliminary studies by Calundann[18] and Cao and Wunderlich.[2] Much of the scientific interest in poly(HBA) arises from its tendency during polycondensation to precipitate out at a low degree of polycondensation ($\bar{P}_n$) in the form of single crystals.[11] The poly(HBA) has been shown to display two reversible transitions at about 350 and 440 °C.[17] The first has been characterized as a crystal–(one-dimensional) plastic crystal (or highly ordered smectic)[19] and the second as a crystal–nematic transition.[17]

Our attention was drawn to poly(HNA) from a study undertaken to characterize the kinetics of copolycondensation of the HBA/HNA system.[20] It was observed that HNA oligomers precipitated early in the polycondensation reaction in a manner similar to the HBA system. In addition, poly(HNA) displayed two transitions in the DSC very close to those of poly(HBA). Consequently, we undertook to synthesize and better characterize the HNA homopolyester and to establish more definitively the structure of the material and particularly the nature of the high-temperature transitions.

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