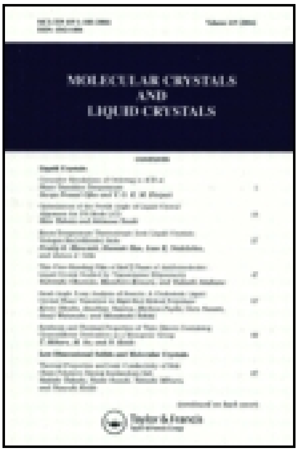

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Molecular Order in the Nematic Melt of a Semiflexible Polyether by Deuteron NMR

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MOLECULAR ORDER IN THE NEMATIC MELT OF A SEMIFLEXIBLE POLYETHER BY DEUTERON NMR

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Abstract: The conformations and orientational order of decamethylene spacer units in the nematic melt of a semiflexible polyether, based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane and 1,10-dibromodecane-d_{20}, have been studied by deuteron NMR methods. The quadrupole echo spectrum obtained *immediately* after rapid cooling to the nematic melt phase around 20 K below the isotropic-nematic transition yields a motionally averaged Pake pattern scaled by a factor of 1/3 relative to that obtained at low temperature in the rigid solid. This result indicates that *all* the C-D vectors of the decamethylene units, while undergoing rapid reorientational motions in this nematic melt, always maintain the same orientational angle of ca. 70° to the local nematic director axis. This condition is satisfied by a model where the decamethylene spacers adopt highly extended *alternate trans* conformations with nearly perfect orientational order with respect to the local nematic director. Slow cooling through the isotropic-nematic phase transition results in an oriented sample and its spectrum is characterized by an asymmetrically broadened doublet at all temperatures, exhibiting the same quadrupolar splitting for all the five distinct ^{2}H 's. The magnitude of the splitting increases with increasing supercooling and reaches a maximum of about 85 kHz while still in the fast motional limit. These deutron NMR patterns for the oriented samples indicate that the *alternate trans* conformational order remains nearly unchanged at all temperatures, but the orientational order continues to increase with increasing supercooling and reaches a nearly perfect order at $\Delta T \sim 20$ K. These results are in good agreement with recent theoretical predictions (D. Y. Yoon and P. J. Flory, *MRS Symp. Proc.* **134**, 11 (1989)) that the polymer chains adopt nearly fully extended conformations in the nematic melt. The asymmetric broadening of the doublet can be explained by assuming slow fluctuations and the resulting distribution in local nematic director orientations with respect to the magnetic field direction.

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INTRODUCTION

Polymer liquid crystals have been widely studied in recent years due to the scientific and potential technological importance of these materials.[1–4] Semiflexible liquid crystalline polymers, with backbones comprised of rigid and flexible sequences in alternating succession, are particularly well suited for experimental studies since they have well defined isotropic-mesomorphic transitions that occur at easily accessible temperatures.

Recently, Percec and coworkers have established that the liquid crystalline behavior of main-chain semiflexible polyethers can be tailored by controlling the relative fractions of rigid and flexible groups.[5] The polyethers TBP-n (Fig. 1) based on the reaction of 1-(4-hydroxy-4'-biphenyl-2-4(4-hydroxyphenyl)butane and α,ω-dibromoalkanes have been synthesized for the methylenic spacers with the number of methylene units n in the range from 4 to 20. The number average molecular weights of these polyethers are sufficiently high that the phase transition temperatures are independent of molecular weight; thus the phase transition characteristics can be studied as a function of the number of carbons in the flexible spacer. This series of compounds show an oscillating odd-even dependence of both the enthalpy and the temperature of the nematic-isotropic transition as a function of n, the number of methylene units in the spacer sequence.

The conformational order of the flexible spacers is thought to be very important in the overall ordering of the nematic phase, and has been the subject of theoretical papers.[6–8] In this regard, deutron NMR measurements on polymer samples with deuterated polymethylene spacers have been shown to be a very powerful technique in delineating the conformations of the spacer groups in the nematic phase.[9–13] However, previous NMR studies, carried out mostly for polyester systems, have been hampered by the persistent presence of isotropic lines even at temperatures well below the isotropic- nematic transition, most likely due to the high polydispersity in their molecular weights due to transesterification reactions. In this regard, the semiflexible polyethers provide definite advantages in that a rather high molecular weight system can be prepared and maintained with a relatively narrow distribution in molecular weight. This work reports one dimensional deuteron NMR studies of TBP-10 (see Fig. 1) with completely deuteriated decamethylene spacers (TBP-10D).

DEUTERON NMR

The application of deuteron NMR to studies of molecular order and dynamics, especially in anisotropic systems, is well established.[14–17] To a good approximation, the spin states of ^{2}H are governed only by the Zeeman interaction and the interaction of the quadrupole moment with the electric field gradient (EFG) tensor. In a nematic phase aligned with a magnetic field, the ^{2}H spectra reflect the orientational anisotropy of the molecule, and the resulting lineshapes depend on the microscopic molecular dynamics as well as the overall orientational characteristics of the sample.

For aliphatic deuterons, the EFG tensor is nearly axially symmetric with the unique principal axis along the C-D bond. The angular frequencies of the two ^{2}H NMR transitions depend on the polar angle Θ between the C-D bond vector and the magnetic field direction and are given by

$$\omega = \omega_0 \pm \delta \frac{(3\cos^2\Theta - 1)}{2} \tag{1}$$

with

$$\delta = \frac{3e^2qQ}{4\hbar} \tag{2}$$

The static quadrupole coupling constant for aliphatic deuterons is given by $\delta/2\pi = 125$ kHz.[18]

In a system composed of C-D bonds that are undergoing rapid isotropic reorientation for which the correlation time $\tau_c << 2\pi/\delta$, the quadrupole interaction vanishes, and a single line obtains at $\omega = \omega_0$. This is the characteristic spectrum of the isotropic phase of a liquid crystal.

A system containing rigid, randomly oriented C-D bonds yields a lineshape function that is the well known Pake powder pattern[19] centered about ω_0 with principal frequencies[20]

$$\omega_{\parallel} = \pm\delta \tag{3}$$

and

$$\omega_{\perp} = -\frac{\omega_{\parallel}}{2} \tag{4}$$

If the C-D bonds are undergoing anisotropic reorientational motional process for which the instantaneous orientation distribution function has three fold or higher axial symmetry about a local director, and if the correlation time for this motion is in the fast limit ($\tau_c << 2\pi/\delta$), the averaged EFG tensor is axially symmetric about the local director, and the averaged quadrupole coupling constant is given by

$$\bar{\delta} = \frac{\delta}{2}\langle 3\cos^2\beta - 1\rangle \tag{5}$$

where β is the instantaneous angle between the C-D bond vector and the local nematic director. The brackets in Eq. 5 denote the time average. The lineshape obtained from an ensemble of local directors uniformly distributed on a sphere is again a Pake pattern with motionally averaged principal frequencies[21]

$$\bar{\omega}_{\parallel} = \pm\bar{\delta} \tag{6}$$

and

$$\bar{\omega}_{\perp} = -\frac{\bar{\omega}_{\parallel}}{2} \tag{7}$$

Alternatively, if the local directors are perfectly aligned along the magnetic field direction, the lineshape is a doublet given by

$$\omega = \omega_0 \pm \bar{\delta} \tag{8}$$

For a nematic liquid crystalline polymer aligned in a magnetic field, the orientation of local nematic directors may be undergoing fluctuations, very slow relative to the fast EFG averaging process discussed above, that are axially symmetric about the field. This will lead to a distribution of local nematic directors $P(\theta)$, and the probability that a given local director lies in the interval between θ and $\theta + d\theta$ is given by $P(\theta)\sin(\theta)d\theta$. If the form of the probability distribution function is known, the ^2H lineshape can be simulated numerically. Conversely, if some assumption is made about the form of the orientation distribution function, it can be used to fit the experimental lineshape in order to yield the adjustable parameters that describe this function.

EXPERIMENTAL

Materials

The semiflexible polyether TBP-10D (Fig. 1) was synthesized as described previously for TBP-10,[5] except 1,10-dibromodecane-d_{20} was substituted for the protonated analog. The polymer was purified by precipitation from solution into methanol, further purified by precipitation from chloroform solution into acetone, and put through two successive precipitations from tetrahydrofuran solution into water. There was no significant difference in thermal behavior between the deuteriated and protonated spacer compounds.

M_n= 10,000, M_w/M_n = 1.9 (GPC); M_n= 9000 (VPO), 13,000 (NMR). Differential scanning calorimetry (DSC) traces (Fig. 2), along with polarizing microscopy, show a very well-defined nematic phase range from 315 K to 370 K. The enthalpy of the isotropic to nematic transition is 21 J/g, surprisingly large for linear semiflexible liquid crystals.

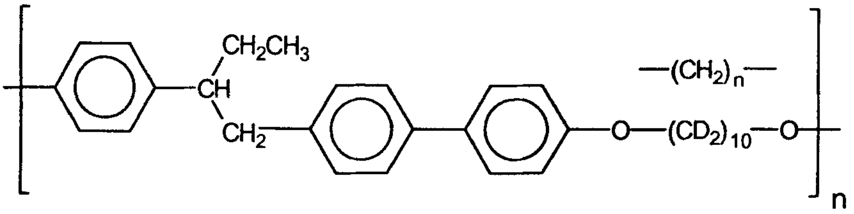

Figure 1. Schematics of chemical repeat structures of TBP-n and TBP-10D.

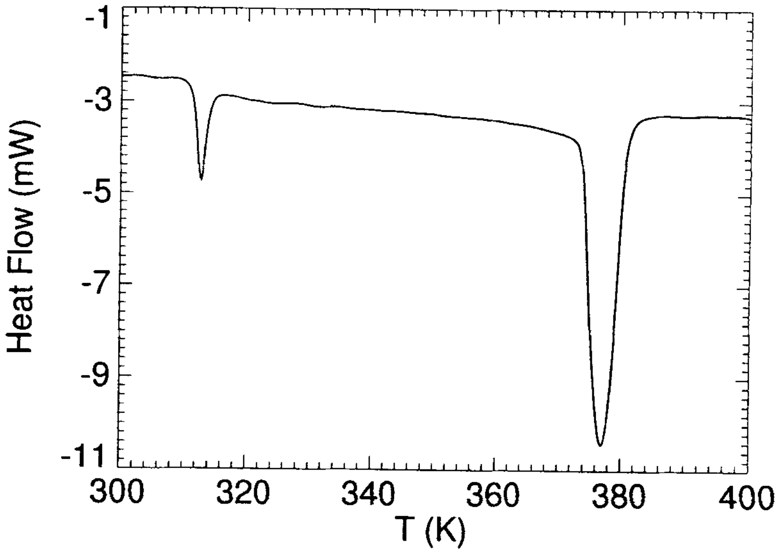

Figure 2. Differential scanning calorimetry measurement of TBP-10D.

Apparatus and Techniques

Deuteron NMR experiments were done on a Bruker AM500 spectrometer operating at a frequency of 76.7 MHz which corresponds to a field of 11.7 T. The spectrometer was extensively modified for increased bandwidth by installing the Bruker SE 451 broad band transmit-receive unit in conjunction with Bruker BC-140 fast 9 bit analog to digital converters. Low pass filtering of the analog audio frequency signal before digitization was performed using a Kron-Hite model 3202 tunable active filter. An Intech model PA10-90 solid state linear MOS FET rf amplifier capable of delivering a pulsed power output of 1 kW was used for final amplification of the rf pulses. A home-built $\lambda/4$ cable duplexer was employed in conjunction with a Doty Scientific LN-1 preamplifier as part of the receiver circuit.

The probe was constructed within the shell of a narrow bore Bruker probe body. The single tuned design incorporated commercial high voltage rf variable capacitors and a 5 mm ID horizontal solenoid coil which accepts shortened 5 mm sample tubes. A carbon resistor was placed in parallel with the sample coil in order to lower its Q to a value of approximately 100. The original Dewar inserts were left intact giving the probe a serviceable operating range of 150 K to 400 K. Temperature control was performed using a Bruker VT-100 controller. Sample temperatures were determined using the fiber-optic sensor of a Fluoroptic® thermometer which was held in contact with the sample tube. Temperature variations were typically less than ± 0.5 K during the course of data acquisition.

The quadrupole echo pulse sequence was used to obtain one dimensional spectra.[22,23] In a typical experiment, 64 acquisitions were averaged using a 2.5 μsec $\pi/2$ pulse width, an interpulse spacing of 20 μsec, a 3 μsec dwell time and a repetition rate of 0.5 sec. The low temperature powder pattern was obtained by averaging 256 acquisitions with a 1.5 μsec dwell time and a repetition rate of 3 sec.

Data analysis and presentation were performed using routines written in PV WAVE. Simulation and fitting programs were written in FORTRAN, making extensive use of subroutines from the IMSL library. All of the software was implemented on an IBM POWERstation 220 running the AIX operating system.

Differential scanning calorimetry was done on a duPont Model 2100, at a heating rate of 5 K/minute.

GPC analysis was carried out with a Perkin-Elmer Series 10 LC equipped with an LC-100 column and a Nelson Analytical 900 series data station. The measurements were made using the UV detector, chloroform as a solvent (1 ml/min, 40 C), two PL gel columns of 5×10^2 and 10^4 Å, and a calibration plot constructed with polystyrene standards.

A Wescan Instruments Model 233 was used for the vapor phase osmometry measurements, which were carried out at 50 °C using o-dichlorobenzene as the solvent. A polystyrene standard was used for calibration.

Solution ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer using deuterochloroform as the solvent. M_n was calculated from the ratio of the intensities of the signals of the methine proton (next to the phenyl) and the methylene protons (next to the biphenyl ring in the repeating unit) divided by the intensity of the terminal methylene group (next to the oxygen).

RESULTS AND DISCUSSION

Figure 3a shows the quadrupole echo spectrum obtained *immediately* after rapid cooling from 393 K in the isotropic phase to 348 K in the nematic phase. A second spectrum taken at 163 K after rapid cooling from the isotropic phase is shown in Fig. 3c. The Pake pattern of Fig. 3c is consistent with a rigid matrix of randomly oriented aliphatic deuterons as is expected for the unoriented frozen solid at low temperature. Calculated lineshapes obtained by least squares fitting to the experimental spectra of Figs. 3a and 3c are shown in Figs. 3b and 3d respectively. The best-fit parameter values are listed in Table 1. It is seen that the Pake pattern of Fig. 3b is scaled by a factor of approximately 1/3 relative to that of Fig. 3d, which is the same for all the five distinct C-D bonds (i.e., α, β, γ, δ, ε C-D bonds in Fig. 4). According to Eqs. 3. 5, and 8, this indicates that *all* the C-D bonds maintain a constant orientation angle of ca. 70 ° (to be consistent with valence geometry) with respect to the local director axis during their *rapid* reorientational motions. This narrowing requires that rapid cranklike motions[15] occur only about C-C bonds that are oriented along the local director axis.

The conformational and orientational order such motions require are very stringent. In this regard, the highly extended *alternate trans* conformations, proposed previously on the basis of both thermodynamic[8,10]and ^{2}H NMR experiments,[10,11] perfectly fit the requirements. As shown schematically in Fig. 4, in this model the rapid exchange between trans and gauche conformations occur only for the C-C bonds denoted by bold lines, while all the remaining skeletal bonds in the $O(CD_2)_{10}O$ sequence are fixed at trans conformations. Such alternate trans conformations keep all the C-C bonds which undergo rapid conformational transitions aligned parallel to the aromatic mesogenic sequences that they are attached to. Therefore, if the mesogenic groups are aligned parallel to the local nematic director, the rapid motions in the decamethylene spacer sequences always occur at a fixed orientation, by 71°, for *all* the C-D bonds with respect to the local director. According to Eq. 5, such motions result in a reduction in width of

Pake pattern to about 34% of the value for the frozen solid, in excellent agreement with the experimental value of 31% in Table 1.

TABLE 1. Fitting parameters from analysis of unoriented TPB-10D powder patterns in the rigid glass and nematic phase.

	T (K)	$\lvert\bar{\delta}\rvert/2\pi$	GB (kHz)	LB (kHz)
glass	163	124.1	5.3	
nematic	348	38.8	1.8	2.4

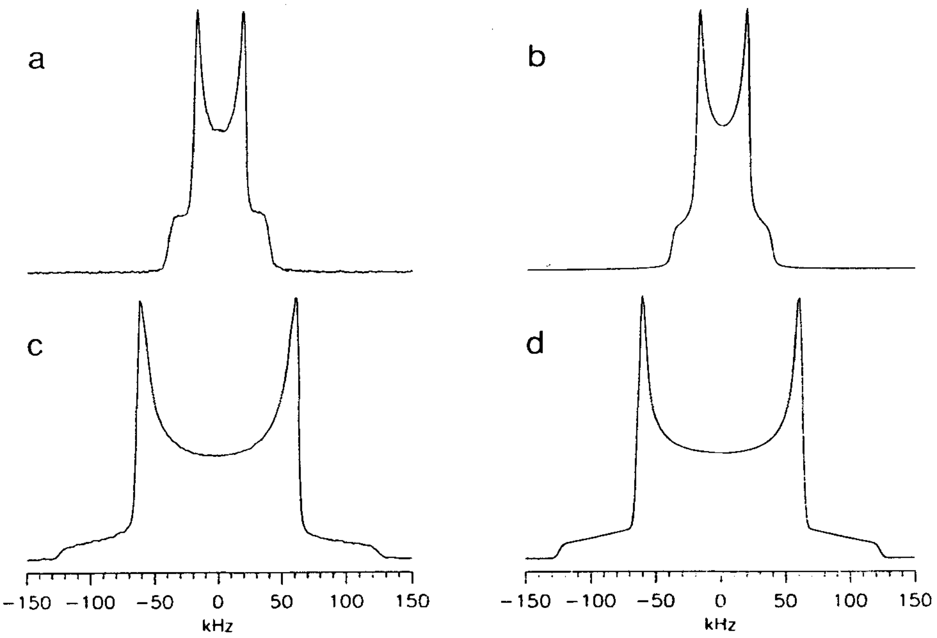

Figure 3. (a) Deuterium quadrupole echo spectrum of TBP-10D in the nematic phase at 348 K, immediately after rapid cooling from the isotropic phase. (b) Best-fit simulation of powder pattern shown in (a). (c) Deuterium quadrupole echo spectrum of TBP-10D in the glassy state at 163 K, after rapid cooling from the isotropic phase. (d) Best-fit simulation of powder pattern shown in (c). No line broadening was applied to the experimental spectra.

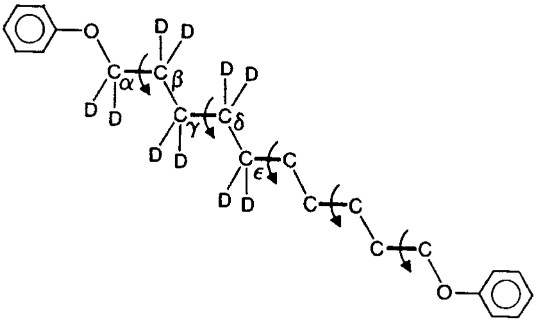

Figure 4. Schematic diagram of the *alternate trans* decamethylene spacer conformations in the nematic state of the semiflexible polyether TBP-10D. The bold lines with arrows denote the bonds around which rapid transitions between the trans and the gauche states are allowed, while all the other bonds in the $O(CD_2)_{10}O$ spacer group are always in the trans conformation.

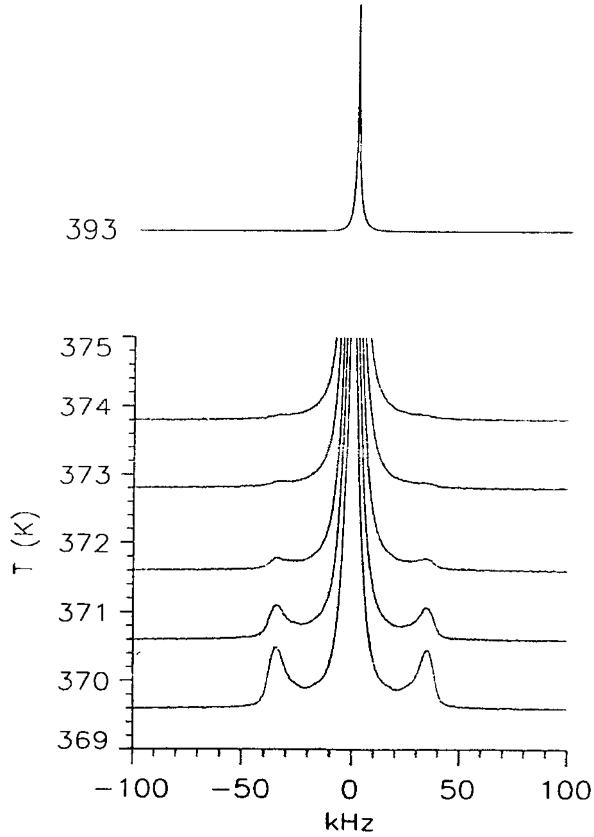

Figure 5. Temperature dependence of the quadrupole echo spectra of TBP-10D in the vicinity of the isotropic-nematic phase transition.

A series of the spectra taken as the sample is slowly cooled from the isotropic phase into the nematic phase in the vicinity of the isotropic-nematic transition are displayed in Fig. 5. For these experiments, the sample was allowed to come to thermal equilibrium at each temperature before the spectra were acquired. Above the transition, the -$(CD_2)_{10}$- spacers are undergoing isotropic reorientation sufficiently rapidly to cause the quadrupolar interaction to vanish as observed in the top spectrum of Fig. 5. The onset of the nematic phase occurs at 373 K which is in good agreement with the DSC results (see Fig. 2). The continuation of the temperature dependence of the spectra into the nematic phase is shown in Fig. 6a. These spectra are characterized by an asymmetrically broadened doublet with intensity decreasing more gradually toward lower frequency splitting. This broadening is interpreted as being due to fluctuations of local director orientations around the magnetic field direction, occurring very slowly relative to the fast EFG averaging process.

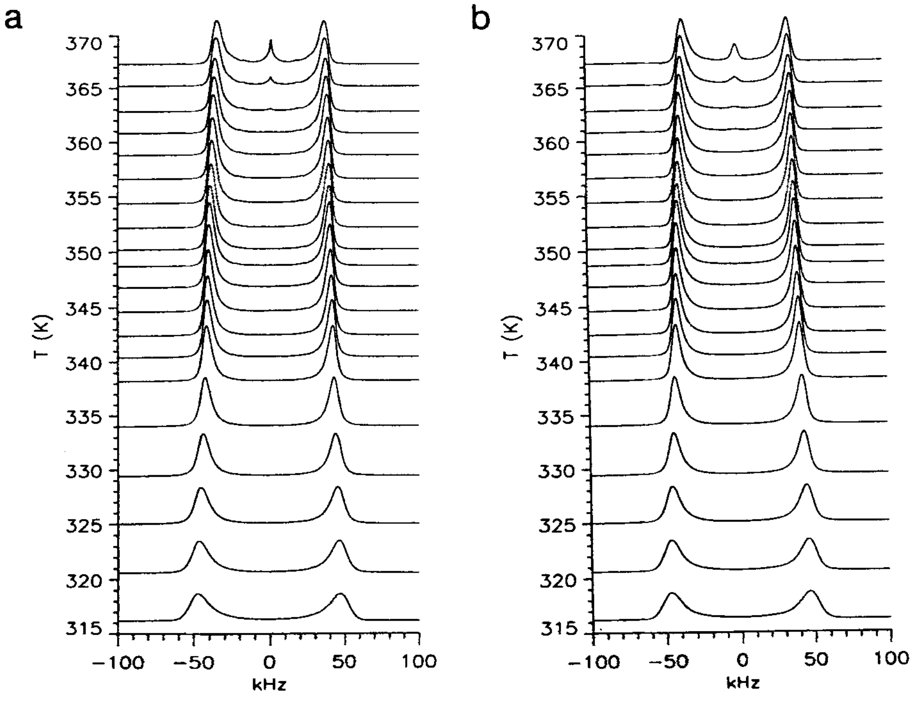

Figure 6. (a) Temperature dependence of the quadrupole echo spectra of TBP-10D below the isotropic-nematic phase transition. (b) Best-fit simulations of the spectra shown in (a). No line broadening was applied to the experimental spectra.

The line shapes of the nematic phase were simulated assuming that the local directors are aligned with respect to the magnetic field direction according to the orientation distribution function

$$P(\theta) = ze^{-\alpha \sin\theta} \tag{9}$$

where θ is now the angle between the unique axis of the motionally averaged EFG tensor (the local director) and the magnetic field, α is an adjustable parameter which determines the width of the distribution and z is a normalization constant. Simulations were least squares fit to the experimental spectra using a one dimensional interpolation scheme[24] to calculate the lineshapes, and the simplex method to find the minimum sum of squares.[25] Four adjustable parameters were incorporated in the fit: the quadrupole coupling constant $\bar{\delta}$ motionally averaged with respect to the local director, the coefficient α describing the width of the distribution function of local directors with respect to the magnetic field direction (Eq. 9), a Lorentzian broadening factor (LB) and a Gaussian broadening factor (GB).

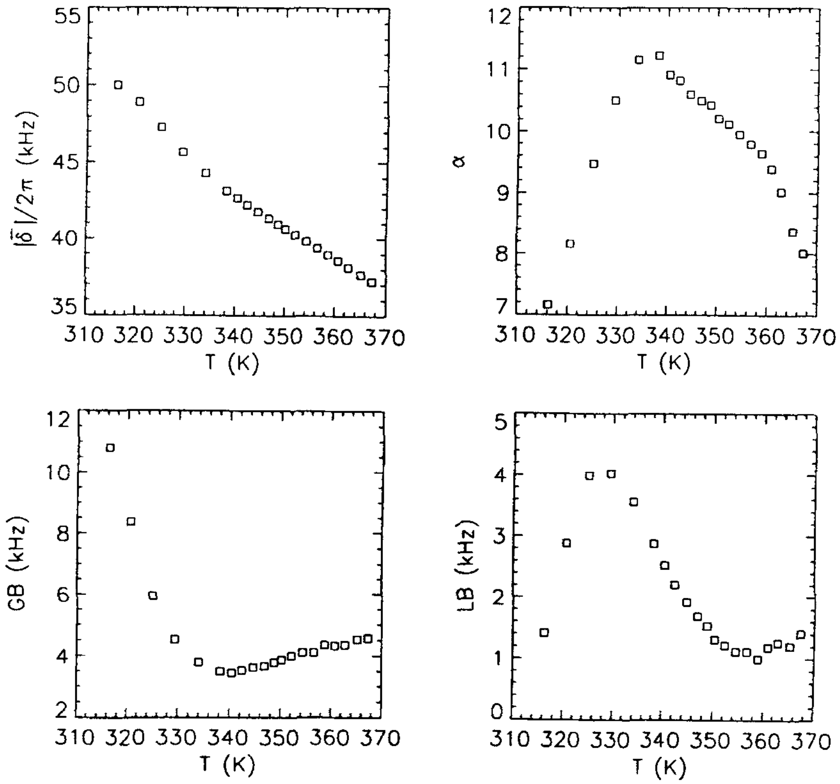

Figure 7. Temperature dependence of the fitting parameters: see the text.

The best-fit simulations are shown in Fig. 6b. The best-fit parameters are plotted in Fig. 7 as a function of temperature. It is evident from these plots that an abrupt broadening of the line shape occurs below approximately 340 K. This is interpreted as a slowing of the rate of conformational or rotational exchange from the fast motion limit into the intermediate exchange regime. As the model used to simulate the lineshapes does not hold in the intermediate exchange regime, it is fortuitous that the lineshapes are so well reproduced below 340 K.

The absolute value of the C-D bond orientational order parameter, S_{mot}, motionally averaged over all the conformations and orientations with respect to the director of the domain, is given by the ratio $|\bar{\delta}|/|\delta|$. The order parameter of the domains, S_{dom}, with respect to the field is given by

$$S_{dom} = z\int_{0}^{\pi} P_2(\cos\theta)\, e^{-\alpha\sin\theta}\sin\theta d\theta \tag{10}$$

Then, the overall total orientational order parameter, S_{tot}, for the local chain segments, in an alternate trans conformation, can be defined

$$S_{tot} = \frac{S_{mot}S_{dom}}{S_{mot}^{max}} \tag{11}$$

where S_{mot}^{max} is the motionally averaged order parameter of C-D bonds when the segmental axis of an alternate trans conformation (see Fig. 4) is perfectly aligned along the local domain director. Taking the usual ∠CCD valence of 109°, we obtain S_{mot}^{max}= 0.341, in excellent agreement with the value of S_{mot}= 0.344 at 340 K, determined from the fit of the ^{2}H-NMR spectra. The values of the total overall orientational order parameter S_{tot} of chain segments are plotted (squares) as a function of temperature in Fig. 8. Also shown in the figure (triangles) is the orientational order parameter with respect to the nematic director, i.e., S_{tot}/S_{dom}. The total order parameter is very high for this nematic polymer, and the order parameter within the nematic domain is found to be considerably higher, ca. 0.9 even at the isotropic - nematic transition and approaching unity at ΔT greater than 20 K.

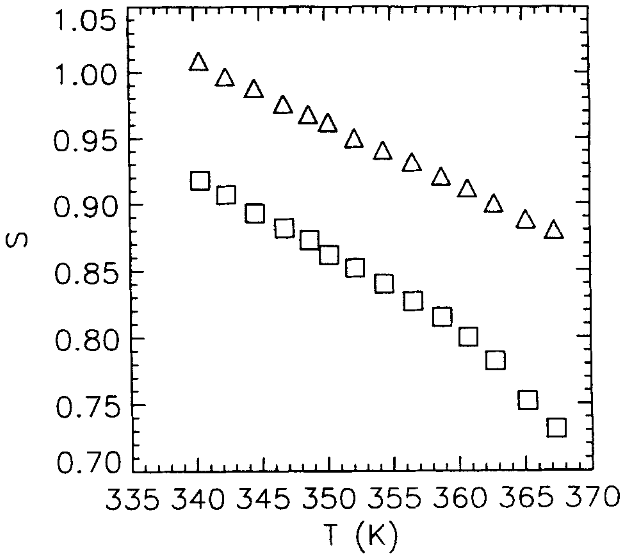

Figure 8. Temperature dependence of the overall order parameter S_{tot} (squares) and the order parameter with respect to the nematic director, i.e., S_{tot}/S_{dom} (triangles).

CONCLUSIONS

The deutron NMR study of a semiflexible polyether TBP-10D with decamethylene sequence spacers strongly supports the model of highly extended *alternate trans* conformations of the decamethylene spacers in nematic melts. The orientational order parameter continues to increase with increasing supercooling, and reaches a nearly perfect orientational order at ca. 20 K supercooling. These findings are in good agreement with recent theoretical predictions.[6,7]

The asymmetry in the doublet for the sample aligned by the magnetic field has been explained by assuming fluctuations of local nematic director orientations around the field direction. This differs from previous conclusions that assume different conformational degrees of order along the spacer units, i.e., the middle section versus the ones adjacent to the mesogenic groups. In this regard, two dimensional NMR investigations will be very helpful in clarifying this problem as well as delineating the conformational defects in nematic polymer melts. Moreover, the NMR results could be correlated with small-angle neutron scattering experiments which can determine the overall radius of gyration and its components along the aligning magnetic field and in the plane perpendicular to the field as function of temperature.

REFERENCES

1. A.M. Doanld and A. H. Windle, *Liquid Crystalline Polymers* (Cambridge University, New York, 1992).
2. *Liquid Crystalline Polymers,* R.A. Weiss and C.K. Ober, Eds., ACS Symposium Series 435 (American Chemical Society, Washington, DC, 1990).
3. *Polymeric Liquid Crystals,* A. Blumstein, Ed., (Plenum, New York, 1985).
4. *Polymer Liquid Crystals,* A. Ciferri, W.R. Krigbaum and R.B. Meyer, Eds., (Academic, New York, 1982).
5. V. Percec and M. Kawasumi, *Macromolecules* **24,** 6318 (1991).
6. P.J. Flory, *MRS Symp. Proc.* **134,** 3 (1989).
7. D.Y. Yoon and P.J. Flory, *MRS Symp. Proc.* **134,** 11 (1989).
8. D.Y. Yoon and S. Bruckner, *Macromolecules* **18,** 651 (1985).
9. E.T. Samulski, M.M. Gauthier, R.B. Blumstein and A. Blumstein, *Macromolecules* **17,** 479 (1984).
10. D.Y. Yoon, S. Bruckner, W. Volksen, J.C. Scott and A.C. Griffin, *Faraday Discuss. Chem. Soc.* **79,** 41 (1985).
11. S. Bruckner, J.C. Scott, D.Y. Yoon and A.C. Griffin, *Macromolecules* **18,** 2709 (1985).
12. A. Abe and H. Furuya, *Macromolecules* **22,** 2982 (1989).
13. L. Abis, V. Arrighi, A.L. Cimecioglu, J.S. Higgins and R.A. Weiss, *Eur. Polym. J.* **29,** 175 (1993).
14. H.W. Spiess, *Chem. Rev.* **91,** 1321 (1991).
15. H.W. Spiess, *Adv. Polym. Sci.* **66,** 23 (1985).
16. L.W. Jelinsky, in *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk,* R.A. Komoroski, Ed., (VCH, Deerfield Beach, 1986), Chap. 10.
17. C.A. Fyfe, *Solid State NMR For Chemists (*CFC, Guelph, 1983), Chap.3.
18. H.W. Spiess, *Colloid & Polymer Sci.* **261,** 193 (1983).
19. G.E. Pake, *J. Chem. Phys.* **16,** 327 (1948).
20. H.W. Spiess, *NMR Basic Principles and Progress* **15,** 55 (1978).
21. D.A. Torchia and A.S. Szabo, *J. Magn. Reson.* **64,** 135 (1985).
22. R. Hentschel and H.W. Spiess, *J. Magn. Reson.* **42,** 157 (1979).
23. M. Bloom, J.H. Davis and M.I. Valic, *Can. J. Phys.* **58,** 1510 (1980).
24. D.W. Alderman, M.S. Solum and D.M. Grant, *J. Chem. Phys.* **84,** 3717 (1985).
25. J.A. Nelder and R. Mead, *Computer Journal* **7,** 308 (1965).