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Nematic Order of Semiflexible Thermotropic Polymers from NMR Data. Further Developments of a Previous Analysis

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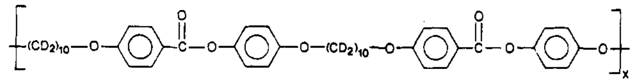
ABSTRACT: The approach, adopted in a previous paper for interpreting the observed ^{2}H NMR spectra of poly(oxyphenylenecarbonyloxyphenyleneoxydodecanediyl-d_{20}) in the nematic state is developed in order to take into account the different time scales affecting conformational jumps and uniaxial reorientations of the chain around the director. Results show that by decoupling these two kinds of motion, the model is no longer critical to geometry. A very local additional order parameter is in fact required and it accounts for all geometrical features which describe the connection of the spacer to the mesogen unit while the structure of the ^{2}H NMR spectrum is solely determined by the conformational mobility of CD$_2$ groups.

Introduction

Recently a paper (hereafter referred to as paper 1) has been published on the NMR study of nematic order of semiflexible thermotropic polymers[1] where it was shown that a proper choice of the conformer population which survives upon the phase transition from the isotropic to the nematic state can explain the ^{2}H NMR observed spectrum of poly(oxyphenyleneoxycarbonyloxyphenyleneoxydodecanediyl-d_{20}) (PDCB-d_{20}) with perdeuteriated alkyl spacers (n = 10 methylene units) shown in Chart I. The conformational model which allowed a successful interpretation of experimental data can be briefly referred to as the "alternate model" and includes the ensemble of highly elongated conformers which is obtained by fixing in the trans rotational isomeric state (RIS) every second bond (starting from the O–CH$_2$ attached to the rigid (phenylene) unit), while intermediate bonds can take on all conformations among the three available RIS of a polymethylene chain (see Figure 1). Orientational order parameters were independently obtained from ^{2}H NMR and ^{1}H NMR spectra recorded at different temperatures, showing a very encouraging self-consistency. Some criticisms have been expressed, however, after the publication of this work, which stimulated, in our opinion, the need of a more detailed analysis of the model adopted for the interpretation of observed NMR data.

The criticisms, involving some geometrical features of the model, are substantially two: (i) the rather arbitrary choice of the O–phenylene–O direction as representing the average chain axis and (ii) the smallness of the phenylene–O–CH$_2$ valence angle χ (see Figure 1) which was set at 112° (i.e., the same value used for the methylene groups), while many crystallographic model compounds indicate, as more likely, a value in the range 117–120°. These two remarks are only apparently different, while both of them involve, as a consequence, a revision of the orientation of both the rigid units and the flexible spacers with respect to the average chain axis.

Chart I



The differences involved are, in this case, on the order of few degrees and are therefore expected to produce only small changes in the calculated spectra, but this is not true. As an example we report in Figure 2 the ^{2}H NMR spectrum calculated by setting the valence angle at the oxygen atom at 112° (a), as already done in paper 1, and 120° (b) (an order parameter of 1 is assumed for both calculations). The effect is quite large on the quadrupolar splitting of the α-CD$_2$ groups, so that we see no longer a single splitting, as experimentally observed, but two.

The critical role played by geometry in our model is a consequence of the assumption that conformational jumps occur on the same time scale as the uniaxial reorientations of the single chain around the nematic director. This assumption was not explicitely stated in paper 1 but it became implicitly active as soon as we decided that the same order parameter must describe both the orientations of C–D bonds and those of the average chain axis.

The observed profile shows one single quadrupolar splitting for all five (in principle) motionally distinguishable CD$_2$ groups. Under the previous asssumptions we were able to reproduce these data only be defining the average chain axis along a direction which is parallel to the CD$_2$–CD$_2$ bonds which, according to the alternate model, can undergo transitions among the three available RIS's. The valence angle at the oxygen was set at 112° so that the rigid units lay parallel to the average chain axis.

The results from NMR relaxation data[2] and Monte Carlo simulations referred to a real time scale through comparison of the effect of a large number of steps with the overall diffusion rate[3] show that conformational changes occur with correlation times much smaller than those affecting chain reorientations. At the high temperature considered (≅480 K) the correlation time for conformational isomerizations can be estimated[2] on the order of 10^{-10} s while chain reorientations occur with a

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[†] This work was partially carried out while the author was at the Max-Planck-Institut fur Polymerforschung, Mainz, FRG, as visiting scientist.

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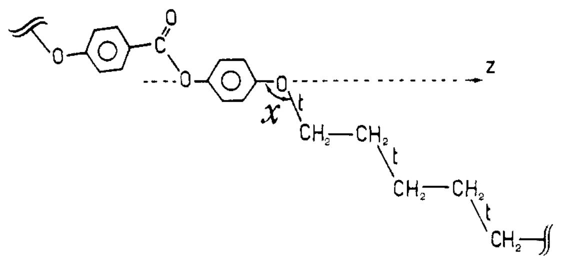

Figure 1. Schematic illustration of a fragment of PDCB-d_{20} with the estimated average chain axis z according to paper 1 indicated (see text). Angle χ is expected to be in the range 117–120°. Bonds labeled with "t" are fixed trans according to the highly elongated conformational model (alternate model) proposed in paper 1 for the spacer in the nematic state.

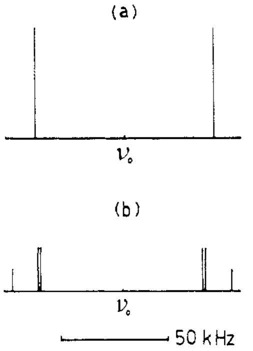

Figure 2. Quadrupolar splittings calculated by setting χ equal to 112° (a) and 120° (b). The average chain direction z is defined in Figure 1. T = 480 K and an orientational order parameter S = 1 is assumed.

correlation time of the order of 10^{-5} s. This large difference suggests immediately that the solution to the problem of the critical influence of geometry on the calculated ^{2}H NMR spectra is to decouple one kind of motion from the other. We can then preaverage the mobility of C–D bonds due only to conformational jumps and we can do this with reference to the direction along which this mobility shows an uniaxial symmetry, i.e., the direction z_c defined by all CD_2–CD_2 bonds, which, according to the alternate model, are allowed to undergo conformational isomerizations. The conformation-dependent result of this preaveraging procedure can then be multiplied by the order parameter connected with reorientational motions of the monomer around the average chain axis, and finally we can take into account, as usual, the overall orientational order parameter which describes the uniaxial reorientation of the whole chain (or portion of chain) around the director; further projection through β_0 on the direction of the external magnetic field was neglected since in nematics (with $\Delta\chi > 0$) β_0 is null.[4] This procedure, compared with the previous one, is schematically reported in Figure 3.

Results

According to the procedure outlined above we can compare the two expressions for calculating the quadrupolar splittings, the previous approach and the present one. In paper 1 the splitting due to the kth C–D bond was calculated as

$$\begin{aligned}\Delta\nu_k &= 3/2\delta\langle P_2(\cos\theta_k)\rangle_{\text{conf}}P_2(\cos\beta)\\ &= 3/2\delta\langle P_2(\cos\theta_k)\rangle_{\text{conf}}S \qquad (1)\end{aligned}$$

where $\delta = (e^2qQ)/h$ is the quadrupolar coupling constant. In the present approach the same splitting is calculated as

$$\begin{aligned}\Delta\nu_k &= 3/2\delta\langle P_2(\cos\theta_{1,k})\rangle_{\text{conf}}P_2(\cos\theta_2)P_2(\cos\beta)\\ &= 3/2\delta\langle P_2(\cos\theta_{1,k})\rangle_{\text{conf}}S' \qquad (2)\end{aligned}$$

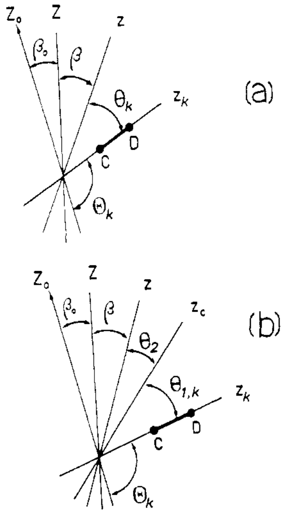

Figure 3. Schematic definitions of the angles involved in the anisotropic reorientations within an uniaxial liquid crystal. Definitions a refer to the approach adopted in paper 1 while definitions b belong to the present approach. $\mathbf{Z}_0$ ($\equiv\mathbf{Z}$ in a macroscopically oriented sample) is the direction of the external magnetic field. **Z** is the nematic director. z is the average polymer chain axis. z_k is the direction of the kth C–D bond. z_c is the direction of uniaxial symmetry for conformational motions.

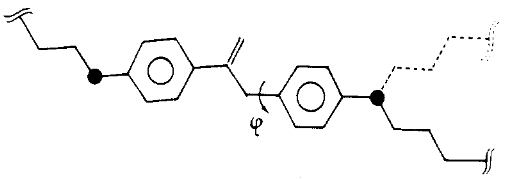

Figure 4. Conformational degrees of freedom in the mesogen units are mainly due to ϕ (±65°; ±115°). The two filled circles define the new estimate of the direction of the average chain axis. A transoid and a cisoid enchainment of the spacers is shown by full lines and dashed lines, respectively.

By comparing eq 2 with eq 1 we see that the difference is in the meaning to be attributed to the two factors S and S'. In eq 1 S gives directly the orientational order parameter which is common to both the C–D bonds and the average chain axis, while in eq 2 S' takes into account also the effect of $P_2(\cos\theta_2)$ connected with the local reorientations of monomers around the average chain axis. Since in this case the two factors have the same value we must conclude that the effect of decoupling the two kinds of motions is that of increasing the overall orientational order parameter $P_2(\cos\beta)$ by a factor of $1/P_2(\cos\theta_2)$.

We can now define the average chain axis z without the need of preserving, around it, uniaxial symmetry for conformational motions. The most reasonable choice is that of the long molecular inertial axis for the mesogen unit as shown in Figure 4, where it is also shown that the 4-fold rotation ϕ around the CO–O-phenylene bond (±65° and ±115° as result of an average estimate from crystalline aromatic esters[5]) allows for a substantial equivalence of transoid and cisoid connections of the spacers astride each mesogen unit. This equivalence involves, on the average, a propagation of the chain along a direction parallel (or nearly parallel) to the orientation of the single mesogen. This situation is schematically shown in Figure 5, where a portion of chain in the nematic state is shown. All mesogens are parallel to each other due to the highly extended conformations of the spacers while the coexistence of transoid and cisoid junctions astride each rigid unit defines a direction of propagation which is substantially parallel to the direction of the single mesogens. Any choice of z as connecting two subsequent rigid units could lead,

Macromolecules **1988,** *21,* 635–643

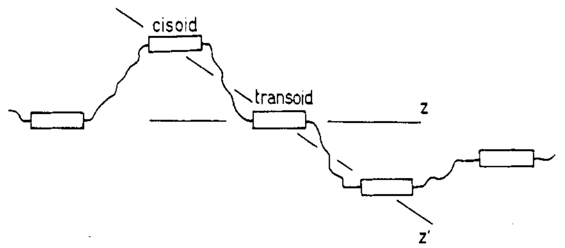

Figure 5. Schematic picture of the situation of a chain in the nematic state. The coexistence of equivalent transoid and cisoid enchainments astride mesogen units gives rise to an average chain axis z substantially parallel to the rigid units. Any z', connecting two subsequent mesogens, can lead, in the case of polymers, to unlikely estimates of this axis.

in case of polymer chains, to unreliable estimates of the average chain axis.

The valence angle at the ether oxygen is now set at 118°, in agreement with crystallographic data on model compounds. The result of these geometrical changes is that of giving rise to a θ_2 angle of ca. 10° between z and z_c. This increases the orientational order parameter of ca. 5% relative to the values obtained in paper 1. A smaller effect, ca. 2%, is predicted on the orientational order parameter obtained from ^{1}H NMR due to the slight tilting of the phenylene rings with respect to the new average chain axis. The new values range from 0.79 to 0.86 as the temperature decreases from 216 °C (the isotropic–nematic transition temperature) to 180 °C. Such effects are small enough to leave all conclusions drawn in paper 1 substantially unchanged.

Concluding Remarks

Decoupling of coformational jumps from chain reorientational motions rests on the different correlation times of these two kinds of motion. This approach allows for a more realistic definition of the average chain axis and for a more reliable valence angle, at the ether oxygen atom *without any modifications of the calculated ^{2}H NMR spectrum* and only small adjustments of the orientational order parameters obtained from ^{2}H and ^{1}H NMR data. This is due to the fact that polymethylene spacers with an even number of chains atoms keep, in the highly extended conformations, the average chain axis z very close to z_c, with an angle θ_2 on the order of a few degrees. From this observation we can immediately devise an interesting extension of the present analysis to the case of spacers with an odd number of chain atoms. In this case, in fact, the highly extended conformers cannot keep the mesogens parallel to each other but rather tilted at ca. 60°[6] so that a much stronger effect from $P_2(\cos\theta_2)$ is expected on the S' factor (see eq 2), giving rise to smaller observed splittings, while conformational mobilities are not expected to depart substantially from the results of calculations already carried out for the even-membered spacer,[6] where three quadrupolar splittings, with different relative magnitudes, are computed as the elongation of the spacer is changed.

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Registry No. PDCB-d_{20}, 112220-29-8.

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Affinity of Grain Deformation in Mesomorphic Block Polymers Submitted to Simple Elongation

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ABSTRACT: Small-angle X-ray scattering (SAXS) and strain measurements were performed at various orientations with respect to the stretching direction of a polybutadiene-hydrogenated elastomeric polystyrene–polybutadiene–polystyrene (SBS) block polymer cast under the form of either cylindrical or spherical morphology. The two materials consisted of randomly oriented grains having either an hexagonal packing of polystyrene cylinders or a predominant face-centered-cubic packing of polystyrene spheres. Because both these materials exhibited an isotropic and isochoric macroscopic deformation in agreement with the strain ellipsoid model, they were considered as model systems for applying a general relation proposed for testing the affinity of grain deformation in mesomorphic block polymers. In this relation also based on the strain ellipsoid model, the Bragg spacing strain, d/d_0, for a family of planes with their normal at an angle ω with respect to the stretching direction is given as a function of ω and the longitudinal macroscopic strain, α_x, by the formula $d/d_0 = [\alpha_x^2 \cos^2\omega + (1/\alpha_x)\sin^2\omega]^{1/2}$. Upon stretching, the SAXS patterns of both the cylindrical and the spherical SBS-H systems exhibited elliptical lattice reflections from which were computed Bragg spacing strain d/d_0 values in good agreement with the proposed formula. The tests were limited to an upper draw ratio of 2.3 above which the lattice reflections were either severely truncated or nearly superimposed.

Introduction

Thermoplastic two-phase elastomers consisting of block, graft, or segmented polymers exhibit unique mesomorphic structures and mechanical properties that have stimulated a great deal of applied and theoretical works in the literature.[1] Among these materials, styrene–diene polystyrene–polybutadiene–polystyrene (SBS) and polystyrene–polyisoprene–polystyrene (SIS) three-block polymers have been extensively studied. They are known to yield mesomorphic structures in which, depending upon their composition and their preparation, the cross-linking polystyrene microphase takes the form of spheres, cylinders, or lamellae arranged in regular arrays over large domains of the material. In fact, these domains form

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