Experimental Evidence of Chain Extension at the Transition Temperature of a Nematic Polymer

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Studies by small-angle neutron scattering have been conducted on a main-chain thermotropic nematic polymer composed of alternating mesogens and flexible spacers. The anisotropy of chain conformation in the nematic phase was measured in the melt and in a dilute nematic solution. The variation as a function of degree of polymerization and spacer length is discussed. The results agree favorably with a mean-field theory of wormlike chains.

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We report on small-angle neutron scattering in a main-chain liquid-crystalline polymer to establish the change of chain extension at the transition from the isotropic to the nematic phase. Liquid-crystalline polymers have been investigated recently because of their important technological applications in high modulus fibers and composites, nonlinear optics, synthetic membranes, and as candidates for sensor and other electronic devices. In all these applications, a maximum chain extension in the ordered phase would lead to an enhancement of the mechanical or optical properties of interest. A spontaneous change in the chain shape at the transition has been predicted, leading to an increase in the chain dimension parallel to the average orientation and a decrease in the perpendicular direction.[1,2]

Satisfactory methods for the measurement of the degree of chain extension are still being explored. Small-angle neutron scattering on a partially labeled material is well adapted to the problem[3,4] and two systems were considered in this study.

(1) Dilute solutions of a protonated polymer liquid crystal in a perdeuterated conventional low-mass liquid crystal. The polymer concentration was chosen to be well below the critical concentration for the onset of entanglements.

(2) A polymer melt of a 50/50 (weight ratio) mixture of protonated polymer with the same polymer selectively deuterated on the aliphatic spacer. This system was chosen to obtain maximum scattered coherent intensity. Molecular masses of the protonated (*P*) and selectively deuterated (*D*) chains were closely matched.

The polymer liquid crystals have the structure shown in Fig. 1. The flexible spacer length was $n=10$ {poly[oxy(3-methyl-1,4-phenylene) azoxy(2-methyl-1,4-phenylene) oxy(1,12-dioxo-1,12-dodecanediyl)] (DDA-9)} and $n=7$ {poly[(oxy(3-methyl-1,4-phenylene) azoxy(2-methyl-1,4-phenylene) oxy(1,12-dioxo-1,12-nonanediyl)] (AZA-9)}; the mesogen is closely related to the well-known low-mass nematic *p*-azoxyanisole (PAA). Commercially available perdeuterated PAA-*d*14 was used. Polymers were synthesized and characterized as described previously.[5,6] The degree of polymerization ranging from 15 to 50 repeating units per chain and fractions with polydispersity <1.1 were studied. Phase transition temperatures are moderate and the polymer can be maintained at constant temperature in the isotropic and anisotropic phases for extended periods of time without appreciable degradation. The molecular mass dependence of transition temperature is given in Ref. 5. Isotropization temperatures of DDA-9 samples, for example, range from 110 to 160 °C.

The physical properties of the polymers are well documented and numerous experimental studies have been performed on these model systems.[7,8] Both polymers are totally miscible with PAA in the nematic phase.

The experiments were made on the Paxy spectrometer of the Orphé reactor (Commissariat à l'Energie Atomique-CNRS Laboratoire Léon Brillouin, Saclay). The sample was placed in the oven at a temperature regulated to 0.2 °C. A magnetic field of 14 T was used to achieve uniform orientation parallel to the magnetic field in the nematic phase. The incident wavelength used was 15 Å and the distance between the detector and the sam-

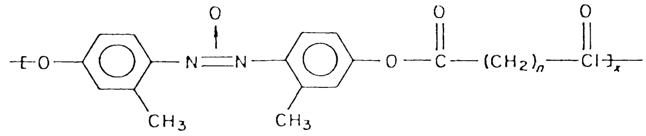

FIG. 1. Schematic structure of the polymer liquid crystals.

ple was 2 m. The range of scattering wave vector q studied was $5\times10^{-3}<q<7\times10^{-2}$ Å^{-1}. The scattering intensity $I(q)$ was obtained by a multidetector consisting of an array of cells, and the spectra were recorded separately along both the X and Y directions perpendicular to the beam.

In the limit of small scattering wave vectors the scattering intensity $I(q)$ can be expressed as a function of the average chain extension $R_\parallel$, the projection of the radius of gyration parallel to the magnetic field, and $R_\perp$, the projection of the radius of gyration perpendicular to the magnetic field. For a scattering wave vector $q_\parallel$ parallel to the magnetic field,

$$I^{-1}(q_\parallel)=I^{-1}(0)(I+q_\parallel^2R_\parallel^2),$$

and for a wave vector $q_\perp$ perpendicular to the magnetic field,

$$I^{-1}(q_\perp)=I^{-1}(0)(I+q_\perp^2R_\perp^2).$$

In the isotropic phase

$$I^{-1}(q)=I^{-1}(0)(I+q^2R_G^2/3),$$

where R_G is the isotropic radius of gyration.

In Fig. 2 the intensities of the cells of the multidetector at two different temperatures in the isotropic phase and in the nematic phase are given. The central spot corresponding to the incident beam has been eliminated. The shade of the cell is a measure of the scattered intensity at that point; a darker cell corresponds to a stronger intensity. We thus obtain direct visualization of fluctuations in intensity and of the dissymmetry due to the anisotropy. In the isotropic phase, the plots show no directional variation. In the anisotropic liquid-crystal phase the spectra are highly anisotropic indicating orientation of the macromolecules along the magnetic field.

The spectra were recorded as a function of temperature in both the isotropic and nematic phases in the vicinity of the transition temperature. From the scattered intensities, $I^{-1}(q_i)=f(q_i^2)$ can be plotted for $q_i=q$, $q_\parallel, q_\perp$. From the linearity in the range of R_i, $q_i<I$, the values of $R_i=R_G$ (isotropic), $R_\parallel$ and $R_\perp$ (nematic) can be obtained. The error is estimated to be 5%–10%. The data given in Figs. 2 and 3 correspond to 15 to 20 experimental values of $I(q)$ aligned in a range of at least $6\times10^{-3}<q<5\times10^{-2}$.

In Fig. 2 the chain dimensions for two different molecular weights ($M_n=6000$ and 18600) are shown as a function of temperature, for a dilute solution of DDA-9 in PAA-d14. The N/I transition is very sharp and the clearing temperature very close to T_c of pure PAA-d14, in agreement with a previous observation.[7] The effect of molecular weight is striking. An increase of the radius of gyration in the isotropic phase and of $R_\parallel$ in the nemat-

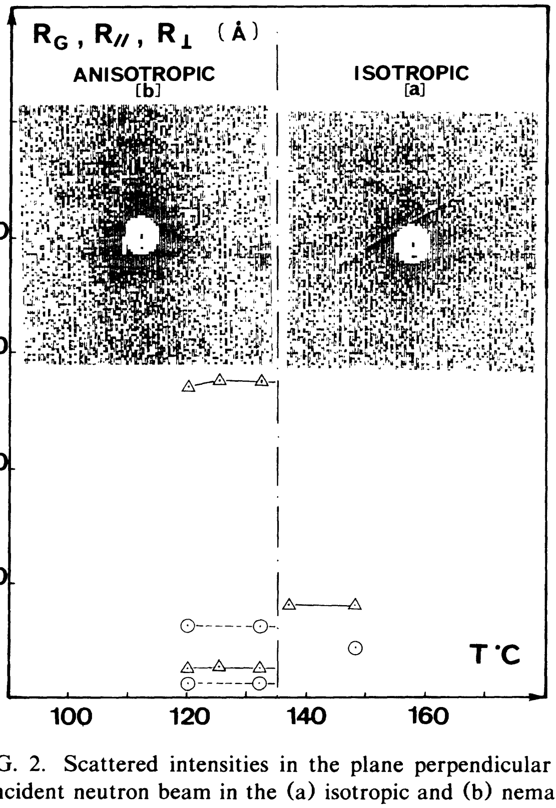

FIG. 2. Scattered intensities in the plane perpendicular to the incident neutron beam in the (a) isotropic and (b) nematic phase for DDA-9, $M_n=6000$. Radius of gyration as a function of temperature for 9% (by weight) DDA-9 $M_n=6000$ (○) and for 5.7% DDA-9 $M_n=18600$ (△) both in PAA-d14.

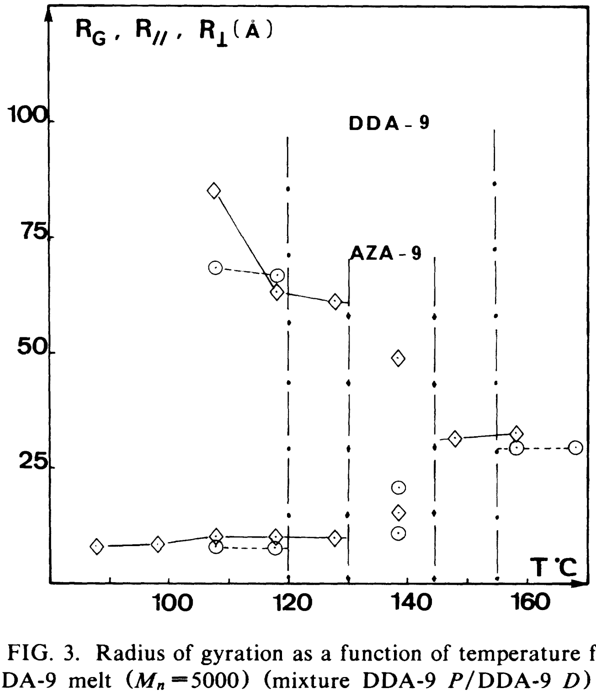

FIG. 3. Radius of gyration as a function of temperature for DDA-9 melt ($M_n=5000$) (mixture DDA-9 P/DDA-9 D) ○ AZA-9 melt ($M_n=6000$) (mixture AZA-9 P/AZA-9 D) ◇. The low-temperature values of R cannot be determined with sufficient accuracy and lie above 150 Å.

ic phase is found. For $M_n = 18\,600$ the parallel component $R_\parallel$ even approaches the value of the total contour length (600 Å) as the temperature is decreased.

In Fig. 3 the chain dimensions are given in the melt of DDA-9 (molecular weight 5000). Excluding the wide biphasic gap of 35 °C because of polydispersity we find an important increase of $R_\parallel$ in the melt. Compare, for example, the $M_n = 6000$ sample in Fig. 2. In Fig. 3 the chain dimensions are also given for an AZA-9 of mass $M_n = 6000$ investigated in the melt. Because crystallization of AZA-9 can be bypassed by rapid cooling to a glassy nematic, this polymer can be studied over a large range of temperatures. The component $R_\parallel$ tends to increase rapidly as the temperature is lowered, possibly as a result of freezing out of hairpins[9] or to the presence of crystallites in the gradually cooled melt. By working in the presence of a magnetic field the anisotropy can be frozen at room temperature and persists for several days after removal of the field.

These experiments were compared with calculations on semiflexible chains. The polymers are treated as inextensible wormlike chains characterized by a bend constant X and an inherent persistence length $Q = X/kT$.[10-12] In a first step, only the effect of an orientational mean field u, for the pure melt, is considered. All thermodynamical properties of the chain can be calculated from a probability function $G(R', R'', L)$ for a chain conformation with initial tangent vector to the curve R', final tangent vector R'', and total contour length L. This function is shown to fulfill a simple partial differential equation. The equation is easily solved by an expansion in spherical harmonics and the chain dimensions can then be calculated. A perturbation expansion is justified in the rigid-rod limit $L/Q \rightarrow 0$ by scaling all lengths with respect to L and use of the small dimensionless parameter uL/kT. The flexible-coil limit $Q/L \rightarrow 0$ is treated as usual by scaling with Q and use of the parameter uQ/kT.[10]

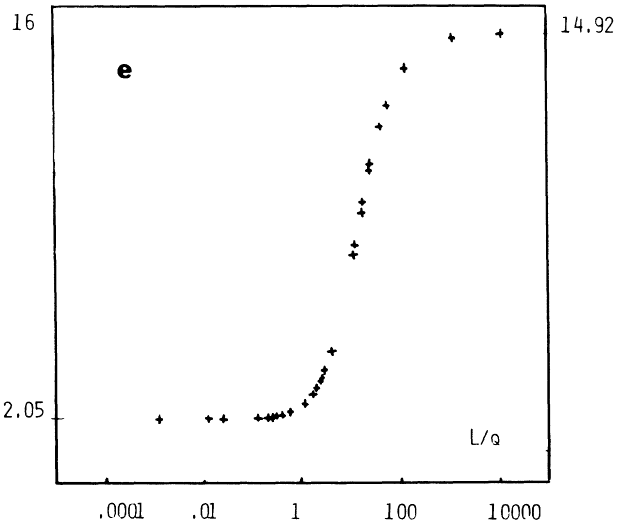

FIG. 4. Model calculations of the anisotropy $e = R_\parallel^2/R_\perp^2$ of the components of the radius of gyration at the transition as a function of L/Q, where L is the total contour length and Q is the persistence length of the wormlike chain.

In Fig. 4, the variation of the quantity $e = R_\parallel^2/R_\perp^2$ at the transition temperature is given for the pure melt as a function L/Q. In agreement with results on the end to end distance by other authors[2,11,12] an increase of anisotropy of the radius of gyration is found with increasing degree of polymerization L for a given persistence length Q. The effect at the transition is found to be significant even in the rigid-rod limit, because of, in this case, ordering and simply an increase in the projection of the chain on the director. Temperature dependence is predicted to be weak. From intrinsic viscosity measurements the persistence length is estimated to be on the order of 1 so that L/Q is of the order of 10 to 40 for the samples measured. Comparing the experimental values of Fig. 3 with the theoretical calculations, we find that experimentally much higher anisotropies are obtained in the melt. A similar discrepancy also occurs for the nematic order parameter. The value calculated within the wormlike chain model lies significantly below the published value obtained by NMR.[7]

The model has also been extended to mixtures and in particular to a mixture in a conventional liquid-crystal solvent.[11] The effective mean-field interaction on a monomer is then $xU_{AA}S_A + (1-x)U_{AB}S_B$ where x is the polymer concentration, U_{AA} and U_{AB} are the interactions between polymer monomers or the monomers and the liquid-crystal molecules, and S_A and S_B are the order parameters of the polymer and the liquid-crystal, respectively. In the limit of a very dilute polymer solution the chain dimensions are then determined by the (weaker) field of the liquid crystal leading to an effective decrease of anisotropy.

The dependence on temperature and chain length of the average radius of gyration will be affected by screening or the ability of the chain to adapt to the isotropic and orientational fields. In ordinary flexible extensible chains, resulting scaling laws for R_G^2 are well established but not for the wormlike chain. The effects of excluded volume are predicted to become appreciable only at sufficiently large values of L/Q. In this case a decrease of R_G^2 on increasing temperature and decreasing degree of polymerization is proposed.[10,13,14]

In conclusion, we have presented for the first time, by neutron scattering, experimental proof of the appearance of anisotropy in chain dimensions for a main-chain liquid-crystal polymer. Although this has also been demonstrated in the case of comblike polymer liquid crystals,[15-17] the coupling between the mesogens on the side chains and the flexible backbone is more complex is such materials. Depending on the type of flexible chain (polysiloxane or polyacrylate) and the type of liquid-crystal phase (nematic or smectic) extension is either parallel or perpendicular to the direction of the average orientation and the effect is much weaker than that observed in the present case.

Spontaneous chain extension will affect many physical properties. As an example, the ratio of the viscosity for a flow parallel or perpendicular to the average orientation has been predicted[18] to be a direct measure of the anisotropy and a weak anisotropy ($e = 2.2$) as was measured by this method in a side chain polymer in dilute solution in a low-mass liquid crystal.[19] Measurements along these lines in the present systems would be of interest.

At low temperatures the nematic field becomes large and an exponential increase in chain dimensions with decreasing temperature has been predicted.[12] Careful low-temperature measurements on a liquid-crystal polymer melt are required. The AZA-9 system would be well adapted to this type of study, but in contrast to the present work where cooling occurred over a period of hours, rapid cooling of the sample is necessary to avoid partial crystallization.

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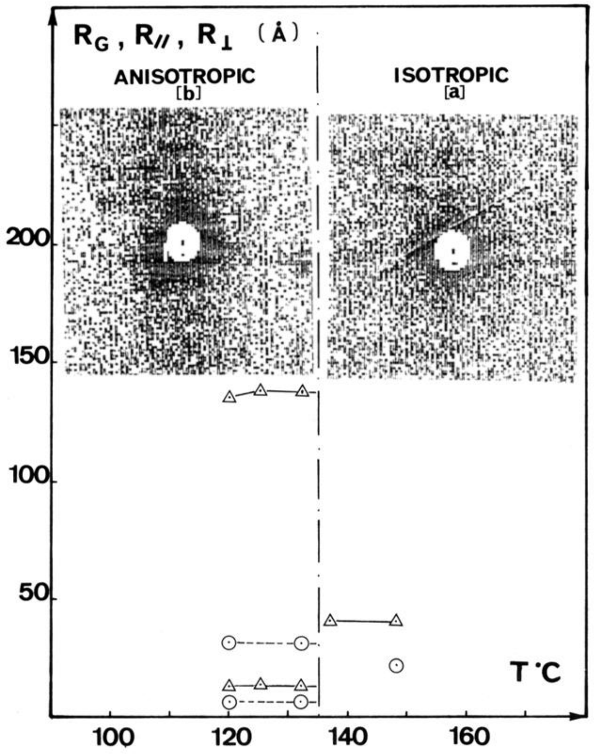

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