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Molecular Organization in Nematic Polymers. 1. Biphasic Structures vs the Nematic Phase

Samuel I. Stupp,* John L. Wu, Jeffrey S. Moore, and Philip G. Martin

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 West Green Street, Urbana, Illinois 61801

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ABSTRACT: The objective of this work has been to investigate how molecules are organized in nematic polymers within the temperature range between melting of the solid phase and complete isotropization. The main experimental technique in this study has been broad-line proton NMR and the polymers used were a sequentially aperiodic aromatic–aliphatic copolymer and its isomeric periodic compound. The study included also calculations of conformational energy and molecular shape in seven-mer chemical sequences present in the polymers investigated. NMR measurements as a function of temperature on the aperiodic copolymer provided evidence for the segregation of chains by chemical composition in the nematic and isotropic regions of biphasic patterns observed at high temperatures. The more flexible chains of the system congregate in isotropic regions whereas nematic regions retain the more rigid ones. Experiments at lower temperatures where biphasic patterns are no longer observed by optical microscopy suggest that nematic polymers form orientationally ordered phases that tolerate isotropic motion in their molecular segments. We propose that these motions can occur through "nematic–isotropic fluctuations" with spatial and temporal periodicities which depend on temperature and molecular structure. The physical origin of these fluctuations is not known but molecular weight distribution and the aperiodicity of chemical sequences could be important factors.

Introduction

Many if not most polymer molecules which form liquid crystalline phases are not rod-like objects but have significant conformational flexibility. The mechanism by which these entropy preserving long molecules organize into phases with orientational order may therefore differ from that involved in the formation of classical nematic structures. We must therefore continue to question the basic premise behind nematic organization in polymeric phases. Questions must also be raised about the global vs local nature of nematic ordering and also about the dynamic nature of nematic ordering. Our understanding of such problems and their impact on structure–property relations in these new materials is still in its early stages.

Over the past two years our laboratory reported on phase separation in main chain LCPs consisting of chemically aperiodic backbones.[1,2] As temperature increases, these fluids can phase separate gradually into isotropic and nematic regions observable by light microscopy. The biphasic range can be very broad and we attributed this behavior to the system's "polyflexibility". Given the importance of polyflexibility in understanding molecular organization in nematic polymers we summarized below some of its basic principles.

The term polyflexibility describes the concept of a distribution in molecular flexibility among chains of a system given their chemical dissimilarity. The nature of chemical dissimilarity linked to polyflexibility may involve variations among chains in composition, sequence, or molar mass. Therefore, polyflexibility will occur most likely but not exclusively in random copolymers derived from monomers differing in torsional energies. The distribution in persistence length or elastic bending constant among chains of a polyflexible system may also arise simply from a molar mass distribution. Nonetheless a universal connection does not exist between a flexibility distribution and a chain-length distribution. The relationship between these two distributions is clearly dependent on chemical structure. Finally it is important to recognize that in a polyflexible system individual chains can "potentially" explore varying fractions of conformational space. Exactly what fraction of that space they explore will depend of course on the environment surrounding the chains. The implication is that the form of the flexibility distribution is both system and phase dependent. Also this idea couples the flexibility distribution to intra- and intermolecular interactions between monomeric units.

Our conclusion on the role of polyflexibility in the biphasic structure of nematic polymers was based on the remarkable contrast observed between a chemically ordered polymer and its isomeric system of chemically disordered chains. In spite of a molar mass distribution the periodic polymer was found to undergo its nematic to isotropic phase transition sharply over a temperature range which was 25 to 40 times narrower than that of the disordered isomer. Following our experimental observations, a computer simulation and theoretical calculations were also consistent with the concept that chemically disordered chains were organizing by molecular flexibility. Even though the microscope revealed the organization as the separation of molecules into two phases, an invisible more complex state of segregation could exist in these fluids. In this regard one must point out that Gibb's phase rule is not violated by the presence of more than one phase provided these sequentially random polymers of finite length are regarded as *n*-component systems.

The biphasic structure revealed by the light microscope disappears at low temperatures and the fluid becomes uniformly birefringent as one may expect for a classical liquid crystal. It remains an open question what might be the nature of organization among the long molecules as isotropic regions shrink to invisible size scales. In this work we report on both experiments and calculations that are relevant to this question. The liquid crystal polymer was probed in a magnetic field at temperatures above and below the onset of the microscopic biphase. The study was carried out on a family of polymers synthesized in our laboratory and the experimental technique was broad-line proton NMR.

Experimental Section

We described in earlier publications the synthesis and characterization of the liquid crystal polymers used in this work.[3,4]

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The viscosity average molecular weight of the chemically aperiodic polymer varied within the range 6 400–21 000 and that of the chemically periodic polymer was 7 900. Viscosities of the polymer samples were measured with a Ubbelohde type viscometer at 30 ± 0.01 °C using solutions of the polymers in tetrachloroethane. Flow times were obtained at four different concentrations with dilutions made directly in the viscometer bulb. Limiting viscosity at infinite dilution, $[\eta]$, was taken as the average value of the least-squares intercept of η_{sp}/c vs c and ln (η_r/c) vs c curves. Gel permeation chromatography utilized a Waters HPLC model 600 equipped with a refractive index and diode array detector. The solvent used was 1,1,2,2-tetrachloroethane (TCE) at a flow rate of 0.5 mL min^{-1} and a temperature of 40 °C. Columns were obtained from Polymer Laboratories (500 Å, 10^3 Å (5 μm)) and calibrated with polystyrene standards in TCE.

Samples for broad-line proton NMR were prepared in standard 5-mm-diameter tubes, each containing 0.4 g of the polymer. The tubes were filled in stages with five equal portions and heated to 200 °C for 2 min after each addition. A glass rod was used to lightly pack each of the portions in NMR tubes. Filled tubes were evacuated, purged with dry nitrogen gas, and heated to 200 °C for various periods of time. Proton NMR measurements were carried out either with a Varian XL-200 instrument equipped with a variable-temperature probe or a Brucker 300-MHz instrument. In the Varian instrument a spectral width of 80 kHz, pulse width of 1.0 μs (90° pulse width = 13 μs), and acquisition times of 100 ms were used for data collection. The Fourier transformation utilized 256 data points, and the magnetic field and radiation frequency were 4.7 T and 200 MHz, respectively. In NMR experiments carried out to resolve aliphatic and aromatic components of the central resonance peak the temperature was maintained at 190 °C. The range of experimental error in these measurements is approximately 11%. Experiments in the Brucker instrument utilized a spectral width of 83 kHz and a magnetic field of 7.05 T; the number of points in the Fourier transformation and acquisition times were also 256 and 100 ms, respectively. Experiments used to study the stability of the macroscopically aligned mesophase were also carried out in the Varian XL-200 instrument. For this experiment we constructed a special furnace that would keep samples for 15 min at 190 °C once removed from the instrument's magnetic field. The furnace was kept next to the magnet and the sample tube was rapidly placed in it as it was removed at high temperature from the magnet's bore. Special samples were prepared to measure the integrated intensity of the central resonance between room temperature and 190 °C. Before NMR experiments were carried out, these samples were first macroscopically aligned in the nematic state under the influence of a strong magnetic field. This was carried out in facilities of the Francis Bitter National Magnet Laboratory at MIT utilizing a 15-T magnetic field. These samples, previously packed in 5-mm-diameter tubes, were inserted in 8-mm-diameter glass tubes which fit precisely within the superconducting magnet's bore. The samples were heated to 190 °C under the influence of the field and then kept for 15 min under the field at this temperature. Samples were then allowed to cool under the field at an approximate rate of 15 °C/min. ^{13}C NMR spectra from polymer solutions were recorded at 75 MHz on a General Electric QE-300 spectrometer.

Results and Discussion

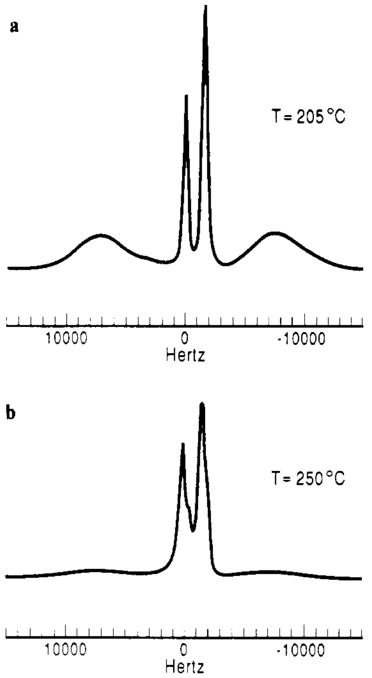


Figure 1. Broad-line proton NMR spectra of the aperiodic copolymer in the nematic phase at 205 °C (a), and in the biphasic region at 250 °C (b).

Biphasic Structures. As mentioned before we had concluded that biphasic patterns (nematic–isotropic) observable by optical microscopy in the molten state of the aperiodic copolymer form because chains varying in molecular flexibility phase separate. This conclusion was based on the observed contrast between the periodic and aperiodic isomers and was supported by a computer simulation of the system which included calculations of isotropization temperatures in aperiodic copolymers. In order to understand the molecular basis of the observed gradual phase separation, into nematic and isotropic regions, one would want to probe chemically the microscopic regions of the two phases for molar mass distribution, structural unit distribution and nature of chemical sequences. These experiments are not feasible now but might be in the future as new instruments become available. In this work we have carried out one experiment which is possible and is of qualitative value in searching for evidence of the chemical fractionation that would occur if chains were separating by molecular flexibility.

Using the 300-MHz instrument we obtained the broad-line proton NMR spectrum of the aperiodic copolymer and were able to resolve the aromatic and aliphatic components of the central peak at various temperatures in the biphasic range. The central peak of the spectrum is linked to the isotropic component in the sample and one would therefore expect the isotropic regions of the biphasic structure to contribute to this signal. Figure 1 shows two broad-line spectra of the aperiodic copolymer at 205 and 250 °C revealing clearly the aliphatic and aromatic contributions to the isotropic signal. The symmetric broad bands in the spectrum obtained at 205 °C are signals corresponding to the magnetically aligned nematic phase, whereas unaligned nematic phase should appear as a broad band overlapping with the sharper signals corresponding to the isotropic component.[5] It is therefore clear that magnetic alignment of the nematic component is not sustained in the biphasic range even though this copolymer does exhibit orientation in the field at lower temperatures. It is interesting that macroscopic magnetic alignment disappears rapidly at the temperatures the isotropic phase becomes visible by optical microscopy implying some coupling of flows in nematic and isotropic regions (no evidence of alignment is observed at 260 °C).

Figure 2 shows a plot of the ratio of areas obtained by integration of the aromatic and aliphatic peaks as a function of temperature. This curve was obtained as the biphasic fluid of the aperiodic copolymer was cooled in the NMR probe. The plot shows that as cooling proceeds the isotropic component becomes richer in aliphatic structural units. This is expected since the more rigid fraction of the flexibility distribution would undergo first the isotropic to nematic transition. The data provide

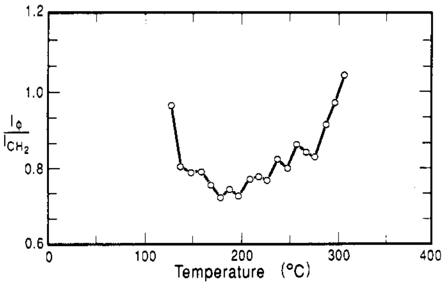


Figure 2. Temperature dependence of the ratio of aromatic to aliphatic resonance intensity measured upon cooling of the aperiodic copolymer from the biphasic range to the nematic phase.

evidence of chemical fractionation in the biphasic range and thus of molecular organization according to backbone flexibility. The absolute values of the aromatic/aliphatic ratios in the plot of Figure 2 might be modified somewhat by the contributions of unaligned nematic to the central resonance peak. However, the importance of the plot is that it reveals chemical fractionation as the volume fraction of isotropic component decreases.

Gel permeation chromatography data offers additional evidence for the concept that nematic–isotropic phase separation is controlled by compositional and therefore flexibility differences among chains. In spite of the great differences in width of the biphasic range between the periodic and aperiodic polymers both materials were found to have broad distributions of molecular weight. The solution polymerized periodic polymer did have nonetheless a lower value of polydispersity relative to the melt polymerized aperiodic polymer (1.62 vs 2.46). However, the most important evidence for the link between the broad biphasic range and polyflexibility is offered by GPC analysis of the periodic polymer after transesterification is allowed to occur. We annealed the periodic polymer for 1 h above its nematic–isotropic transition (290 °C) under a nitrogen atmosphere. This thermal treatment is known to cause randomization of the periodic polymer[6] and therefore the rather narrow thermal range of the nematic–isotropic transition becomes extremely broad. Interestingly, GPC analysis indicates that the polymer's polydispersity remains unchanged (1.63) as the narrow isotropization becomes extremely broad.

The idea that compositional differences among chains control the nematic–isotropic phase separation implies that the biphasic range would narrow as degree of polymerization increases. This is the point made by the three-dimensional plot shown in Figure 3. The plot was generated from a computer simulation similar to that described in an earlier publication from our group and shows a decrease in the biphasic range as degree of polymerization increases for systems having different global chemical compositions. According to this simulation, the width of the biphasic range, ΔT_{NI}, is inversely proportional to degree of polymerization to the power 0.46, where

$$\Delta T_{NI} = 6(\Delta T_{NI})_{50}\bar{X}_n^{-0.46} \qquad (1)$$

$(\Delta T_{NI})_{50}$ is the width of the biphasic range at an average degree of polymerization of 50. The details of this simulation can be found elsewhere.[7]

Theoretical support for the concept of chains segregating by molecular flexibility in the biphasic range was provided recently by Fredrickson and Leibler.[8] These authors constructed a quantitative theory for an aperiodic nematic copolymer with A and B structural units with dissimilar bending constants. The theory showed that a nematic–isotropic biphasic range could result from differences in flexibility among structural units of the aperiodic chains. The Landau expansion of the free energy in this theory contains a negative term which couples the nematic order parameter, S, and a compositional order parameter, Q:

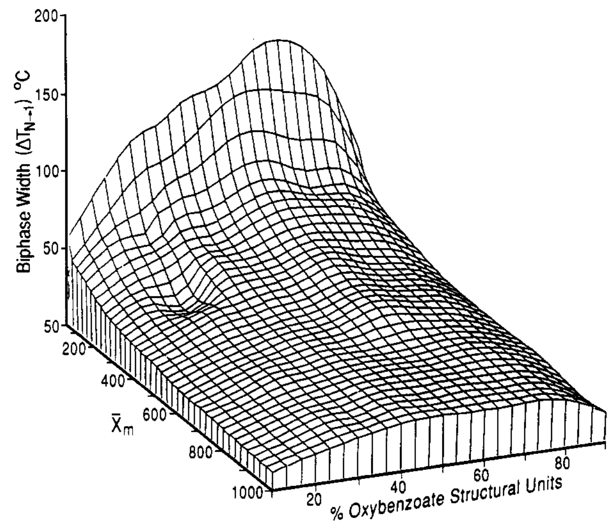


Figure 3. Calculated three-dimensional plot showing the effect of degree of polymerization and global chemical composition of an aperiodic copolymer on the width of the biphasic range. The global chemical composition is expressed as the mole % of oxybenzoate structural units, the most rigid mer in the backbone.

$$f(S,Q) = [A_2 - \nu]S^2 - A_3S^3 + A_4S^4 + [B_2 - \chi]Q^2 - B_3Q^3 + B_4Q^4 - C_2S^2Q \qquad (2)$$

where ν represents the strength of interactions among monomers, χ is the Flory–Huggins parameter, and the coefficients of the expansion depend on variables such as degree of polymerization, the overall volume fraction of each monomer, and the bending constants of the structural units. Most importantly to the present discussion the coefficient C_2 of the coupling term is given by

$$C_2 = 15\Delta/\bar{\kappa} \qquad (3)$$

where $\Delta = \kappa_A - \kappa_B/\bar{\kappa}$, κ_A and κ_B are the bending constants of monomers A and B, and $\bar{\kappa}$ represents a mean bending constant for the aperiodic chains.

From the sign of the coupling term in eq 2 it is clear that segregation of chains rich in the rigid monomer within highly ordered nematic regions will lower the free energy (both S and Q would approach 1). Thus this work offers theoretical support for the experimental evidence presented here that organization of chains by chemical composition is behind the formation of the biphasic structures. The point that cannot be precisely demonstrated so far by theory or experiment is whether segregation is driven by the flexibility differences per se and the corresponding entropic implications or if segregation of chains differing in flexibility is driven by composition-dependent interactions among chains. The entropic driving force linked to flexibility differences can be rationalized on the basis that chains rich in units with low torsional energies (e.g., aliphatic spacers) cannot explore all their potential conformational space when surrounded by the stiffer chains (the ones in which aromatic units appear more frequently). An enthalpic driving force, on the other hand, would argue for intermolecular interactions that depend on chain composition. However, an important question is whether these two driving forces can be in effect separated. That is, can one consider the interactions among chains to be decoupled from the flexibility of chains when structural units differ significantly in bending

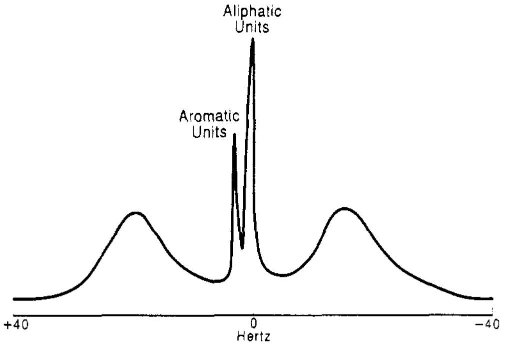


Figure 4. Broad-line NMR of the random copolymer in the nematic phase at 190 °C.

constant. We leave here the topic of biphasic structures with the conclusion that molecular organization involves segregation of chains by chemical composition resulting in the presence of the more flexible chains in isotropic regions. Our attention turns now to the challenging problem of understanding molecular organization in these polymers when the optical microscope sees a uniform nematic phase at lower temperatures.

The Nematic Phase at Low Temperatures. At low temperatures (below 200 °C) the isotropic phase of the biphasic regime is not visible by optical microscopy. However, the broad-line NMR spectrum still reveals at these low temperatures a central peak indicating the occurrence of isotropic motion. Therefore if this motion originates from the presence of an isotropic phase in the system such regions must be of submicron dimensions. We reported earlier broad-line proton spectra of our experimental polymer in this temperature range revealing a well-resolved central resonance peak in a magnetically aligned sample.[5] The presence of this peak was interpreted as evidence for the presence of molecular segments which are more mobile and disordered than those in liquid crystalline regions. This central peak has been observed in other liquid crystal polymers[9,10] and associated with an isotropic component in the samples. In this work we characterized the peak at 190 °C with higher resolution than before and found clear evidence of chemical shift corresponding to both aromatic and aliphatic protons. A typical spectrum at this temperature revealing the chemical shift in the central peak at 190 °C is shown in Figure 4. This observation confirms our earlier suggestions that the central resonance peak results from mobile chain segments and not simply from the flexible aliphatic units of the mesogens. We also measured here the fraction of isotropic resonance as a function of temperature in samples that were prealigned in a magnetic field of 15 T and solidified in the oriented state. The data are shown in Figure 5 revealing the appearance of the isotropic signal above 50 °C and a rapid increase of the signal above melting of the solid phase near 140 °C. Interestingly, the slope of the curve increases further around 170 °C, and it is above this temperature that it becomes possible to induce macroscopic alignment of the nematic phase in a magnetic field.[5]

Characterization of two experimental polymers by solution ^{13}C NMR yielded the global structural unit compositions given in Table I. Using these values we calculated the theoretical ratio of aromatic to aliphatic resonance intensity and found it within experimental error equal to ratios measured from the central peak (the higher values measured in studies within the biphasic range are possibly linked to the oxidation of aliphatic units at the higher temperatures). The magnitude of the ratio implies that below the onset of the biphase observed by optical microscopy the central peak is not associated with a component of composition different from that of the global composition of the system. It is still possible to postulate that the isotropic signal originates from a phase-separated low molecular weight component or material contained within defects of the texture. However, this description of molecular organization in the system is not compatible with data discussed below.

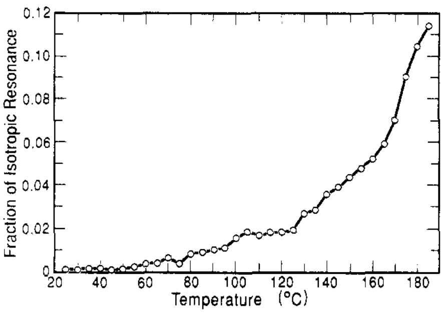
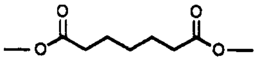
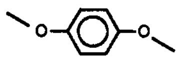
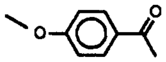


Figure 5. Fraction of isotropic resonance as a function of temperature in the random copolymer. The data were obtained from a sample aligned previously in a high magnetic field of 15 T.

It is not clear what type of molecular organization in the nematic phase would tolerate the isotropic molecular flexibility that the NMR reveals once the biphasic structures are no longer visible. One must consider the possibility of phase separation by molecular weight leading to an isotropic microphase. The problem with this possibility is that on theoretical grounds nematic order is expected to increase with chain length. It is then difficult to understand why the level of isotropic motion increases with average molecular weight. Evidence to support this statement was presented in one of our earlier publications and has been reproduced in a new set of data for the same polymer presented in the second paper of this series. The data in the next paper also shows that the isotropic motion does not decrease appreciably with aging of the mesophase. On the other hand it is known that the textures of polymeric liquid crystals coarsen with time[11] and therefore the motions of molecules within defects of the texture is not a good explanation for the central peak.

NMR measurements using the chemically periodic isomer of the aperiodic copolymer offer some insight on the origin of the central peak in the nematic phase. Figure 6 shows the broad-line NMR spectrum of the chemically periodic polymer revealing resolution of the sharp signals for aromatic and aliphatic protons. We also measured the fractional area of the spectrum under the central resonance as a function of temperature on both heating and cooling, and these data are shown in Figure 7. The area under the central resonance should have contributions from both the sharp signals attributed to isotropic motion and also from the broad component characteristic of the nematic phase if macroscopic magnetic alignment is not complete. Therefore the increase or decrease of fractional area with temperature does not reflect exclusively the growth or loss of isotropic signal but also the increase or loss of macroscopic magnetic alignment. In this context we attribute the initial drop of fractional area in the heating curve to magnetic alignment of the sample above the crystal to liquid crystal transition (around 200 °C). At the same time the abrupt rise near 260 °C probably reflects the isotropization of the entire sample with the complete disappearance of the broad component (this is the range of the isotropization transition by DSC and optical microscopy). The gradual increase between 215 and 260 °C reflects both an increase in sharp isotropic signal and

Table I
Calculated and Experimental Values of Aromatic and Aliphatic Contributions to the Isotropic Motion

	structural unit compositions[a]				
	PI (C)	DOP (A)	OB (B)		
$\bar{M}_v$				I_ϕ/I_{CH_2}[b] (calc)[c]	I_ϕ/I_{CH_2} (exp)
7 300	0.38	0.35	0.27	0.655	0.653
10 000	0.37	0.36	0.28	0.695	0.637

[a] Values obtained from solution ^{13}C NMR. [b] Intensity ratio of aromatic to aliphatic resonance. [c] These calculations are outlined in ref 3.

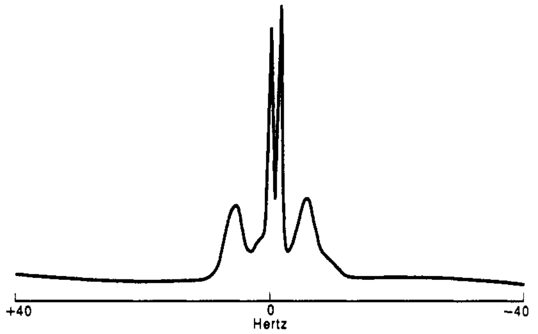


Figure 6. Broad-line proton NMR spectrum of the sequentially periodic nematic polymer at 240 °C.

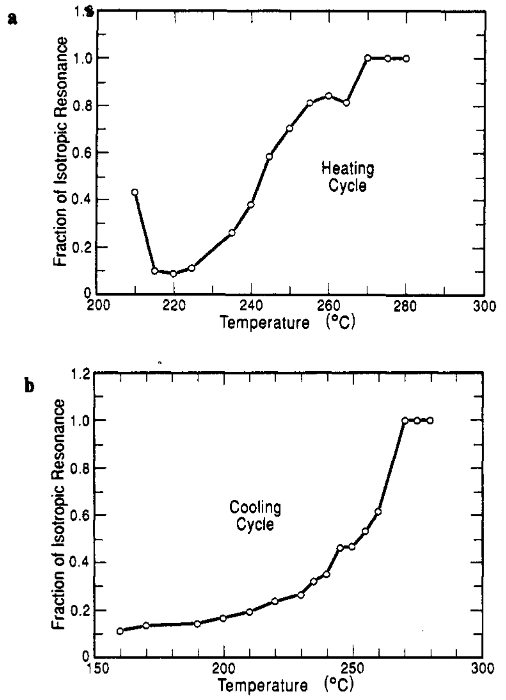


Figure 7. Fraction of isotropic resonance measured upon heating (a) and cooling (b) in the periodic nematogen.

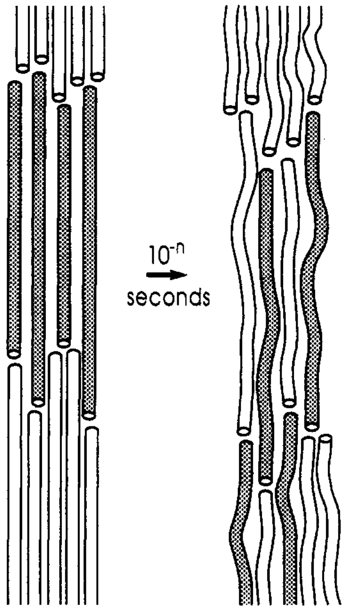


Figure 8. Schematic drawing of a polymeric nematic phase which experiences isotropic fluctuations over characteristic time scales. The drawing illustrates one of several possible driving forces for the fluctuation, namely, changes in molecular environment around segments as chains translate in the nematic fluid.

loss of magnetic alignment. Upon cooling the initial sharp drop should be due to the reappearance of the nematic phase and the consequent gain in the broad component. The further decrease in central area must be linked to alignment of the sample in the magnetic field which judging from the spectra is complete near 240 °C. Thus we estimate that the contribution from isotropic motion in the central resonance is roughly 10–20%. This is effectively in the range of the aperiodic isomer as measured when complete magnetic alignment of the fluid is achieved.[5] *The periodic polymer has a well-defined and narrow isotropization range. Therefore, the detection of sharp signals in the central resonance well below the nematic to isotropic transition would support the view that the isotropic or "pseudoisotropic" motion detected by NMR is characteristic of this polymeric nematic phase and not simply explained by phase-separated isotropic regions or the presence of impurities.* This possibility questions the validity of the traditional theoretical approach used to understand nematic organization of polymers. We discuss below a model we term the "liquid fringed micelle" in which isotropic motion is tolerated by orientationally ordered chains.

In the liquid fringed micelle we envision segments of chains commuting over some characteristic time between regions of high orientational order and more disordered regions of high mobility. One may think of the liquid fringed micelle as a nematic fluid undergoing pseudoisotropic "fluctuations" in which translational freedom of molecular segments throughout the structure allows the system to retain fluidity. In fact, *changes in the nature of molecular segments collected in a given space and time could be an important driving force for the fluctuation. Such changes in the nature of molecular segments could easily occur in random copolymers where there are local variations in the chain's bending constant associated with quenched chemical disorder. In chemically periodic chains molar mass polydispersity could impact on the preference of a specific population of segments in a given space and time to exist in highly ordered nematic environments or in more disordered regions.* A drawing is shown in Figure 8 as a visual aid to picture the system. In this specific drawing some chains have been labeled and shown to commute in space and create neighborhoods where highly disordered nonnematic organization prevails. Flexible segments when surrounded by similar segments would explore a larger fraction of conformational space relative to an isolated flexible segment surrounded by more rigid ones. Flexible segment bundles would create a pseudoisotropic environment whereas an isolated flexible segment surrounded by rigid sequences could exist in a nematic environment. In this case the effective rigidity of the flexible segment is induced by its surrounding nematic field. It is also possible for individual chains to translate through existing nematic and pseudoisotropic regions. During this translation segments would gain or lose conformational entropy depending on their environment at any given instant in time. Isotropic fluctuations could be important also in the spatial translation of domains and director fluctuations within domains. They may also impact on the formation of new domains by coalescence of existing domain sectors. As discussed below the nature of the fluctuations in the liquid fringed micelle would change with temperature and molecular structure of the nematogens.

In the mid-nematic range the order fluctuations should have some characteristic spatial and temporal wavelength depending on molecular structure. As temperature decreases toward solidification the isotropic fluctuations may decrease in frequency and amplitude and would be localized in very small regions. If interactions among similar units are favored at lower temperatures, amplitudes and spatial wavelengths could increase. In fact when aperiodic chains solidify some sequence segregation by flexibility could be frozen in. As temperatures climb to the far-nematic range close to isotropization one could expect that the least globally rigid "chains" and not just "segments" congregate in space and form enlarging pockets of conformational entropy which do not exchange as easily by translation with strongly nematic neighborhoods. The result is an increase in spatial wavelengths for nematic order and pseudoisotropic motion. The increased resistance to commute results eventually in the appearance of phase-separated isotropic regions. This description establishes a possible physical link between the microscopically visible biphasic structure and the "fluctuating" nematic phase. Finally, we expect of course that these fluctuations will cease as the nematogens become increasingly rigid. For example the fluctuations may be of less significance in nematogens with all aromatic backbones given their high torsional energies.

We performed an experiment on magnetic orientation to gain further insight on molecular organization and especially to test the concept of the liquid fringed micelle. In this experiment we aligned macroscopically a sample of the aperiodic copolymer in a high magnetic field at the temperature where the isotropic signal is well defined and the fluid is nematic and not biphasic by optical microscopy. The tube of material was definitely aligned macroscopically by the field as indicated by the broad-line proton spectrum in Figure 9. When the sample was removed from the field but kept at the same temperature for 30 min the macroscopic alignment disappears completely (see Figure 9). If this high molecular weight sample would have been organized as a classical nematic of long rod-like chains one might have expected retention of the alignment for longer periods of time. However, in the absence of the guiding external force the nematic–isotropic fluctuations envisioned for these polymeric nematics would drive the system rapidly to the macroscopically unaligned polydomain state.

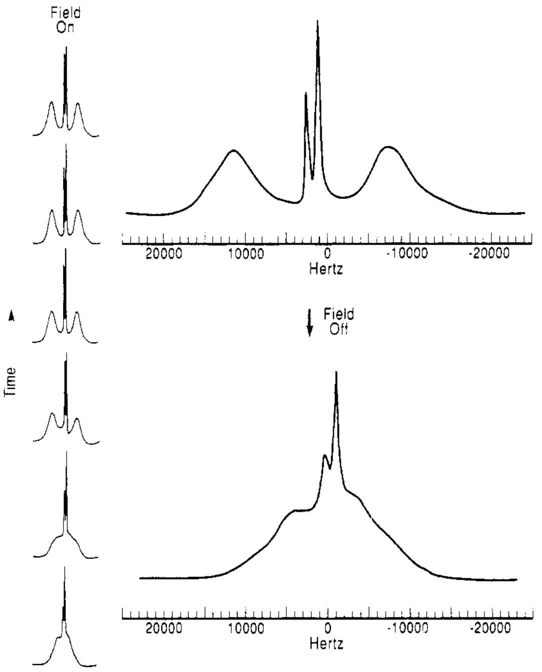


Figure 9. Changes in the broad-line proton NMR spectra as the nematic fluid acquires macroscopic orientation in the external magnetic field (left). Within 30 min with the field off the aligned polymeric nematic disorients to a vanishingly small macroscopic order parameter.

The fluctuating structure of the liquid fringed micelle would be favored when molecular segments have conformational "versatility" to commute dynamically between nematic and isotropic environments. We have therefore carried out here a conformational analysis of relevant chemical sequences. We approached the analysis of conformational versatility through calculations of shape and energy for conformers available to chemical sequences. The aliphatic spacer present in the experimental polymer (the pimeloate structural unit) is the major source of conformational flexibility. The local flexibility of a chain segment will thus strongly depend on its spacer content. For example, at the triad level we expect sequences containing zero, one, and two spacers to be present in molar fractions of 0.15, 0.70, and 0.15, respectively. The three central structural units of heptad sequences shown in Figure 10 are considered to be representative of mono- and dipimeloate triads. Our calculations were therefore performed on these two heptads and details of the calculations are explained below.

Yoon and Bruckner[12] reported earlier on conformational calculations for a number of repeating units of mesogenic polymers. By using Boltzmann factors calculated with known torsional energies their calculations yielded the frequency of conformers with different molecular extensions. The energy and order parameter distributions associated with conformers were also presented in their work. We have utilized here a somewhat different method to calculate these parameters and have also calculated two molecular shape parameters. Distributions of uniaxial ratio and biaxiality were generated here for each of the two populations of conformers. We explain first the details of these calculations and how they differ from those reported previously. We then discuss their implications to the understanding of molecular organization in nematic polymers.

The computational procedure considers all rotational isomeric states of the spacer for the two sequences of Figure 10. The geometrical parameters and torsional energies used for individual structural units in the sequence can be found in ref 12. For each conformational state, the shape of the heptad sequence is approximated by an ellipsoid with a characteristic semimajor axis of length *a* and semiminor axes of lengths b and c. The method used to construct the ellipsoids follows the approach of Taylor et al.[13] used to generate an ellipsoidal approximation to the shapes of protein molecules; the method can be summarized as follows. We consider the origin of the coordinate system to be the first atom in the heptad sequence. Obtaining the self-direct product of all the vectors that connect the origin and each of the carbon and oxygen atoms in the heptad one can generate an ellipsoid which describes the shape of the conformer. The inertial properties of the ellipsoid correspond in fact to the mass distribution of the conformer.[13] One obtains the principal ellipsoid frame through the second moment matrix S, given by

$$S_i = (\vec{r}_i \otimes \vec{r}_i^{\mathrm{T}}) = \begin{bmatrix} x_i^2 & x_i y_i & x_i z_i \\ y_i x_i & y_i^2 & y_i z_i \\ z_i x_i & z_i y_i & z_i^2 \end{bmatrix} \tag{4}$$

where x, y, and z represent the Cartesian coordinates of r vectors connecting the origin of an arbitrary frame and atoms in the heptad. The tensorial sum of self-direct products corresponding to atoms in the sequence yields the matrix **S**,

$$\mathbf{S} = \sum_i S_i \tag{5}$$

The eigenvectors of **S** yield instead the principal ellipsoid axes whose semiaxis lengths are equal to the square root of their corresponding eigenvalues. The matrix **S** is related to **M**, the matrix of moments and products of inertia, by the following relation:

$$\mathbf{M} = R^2 I - \mathbf{S} \tag{6}$$

where I is the inertial moment and R is a radius of gyration.

We have used the semimajor axis, a, and semiminor axes, b and c, of the ellipsoid to define for each conformer a uniaxial ratio, μ, and biaxiality, β:

$$\mu = \frac{a}{{}^1/_2(b + c)} \tag{7}$$

$$\beta = \frac{b - c}{{}^1/_2(b + c)} \tag{8}$$

The chain segment vectors, $\vec{q}$, shown in Figure 10 are projected onto the major ellipsoid axis to define the conformer's extension. Also the vector $\vec{p}$ in Figure 10 represents the rigid structural units, and its angle with the semimajor axis defines θ. As the rotational isomeric states are enumerated, statistical weights of the conformations are summed within a predetermined interval of extension to yield conformer frequency distributions with respect to uniaxial ratio ($T = 140$ °C) (see Figure 11, parts a and b). Values of conformational energy, orientational correlation of rigid units given by $\langle {}^3/_2 \cos^2\theta - {}^1/_2 \rangle$, uniaxial ratio, and biaxiality are similarly collected for each interval of extension or uniaxial ratio and presented in Figures 12–15.

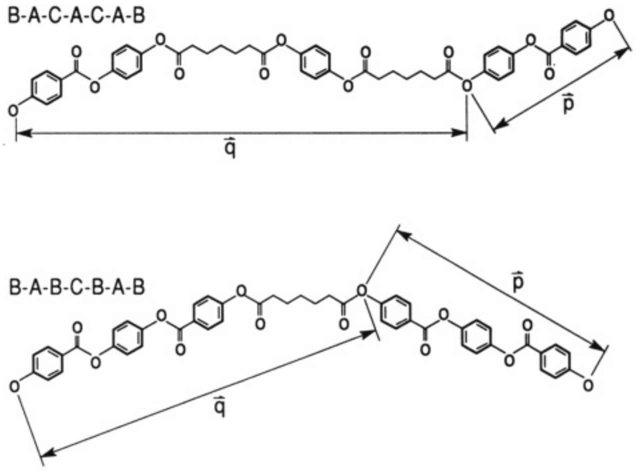


Figure 10. Chemical structure of two common heptads in the aperiodic nematogen. The drawing illustrates the definition of vectors $\bar{p}$ and $\bar{q}$ representing, respectively, the rigid structural units and the segments projected onto the major ellipsoid axis to define chain extension (see text). See Table I for definition of A, B, and C.

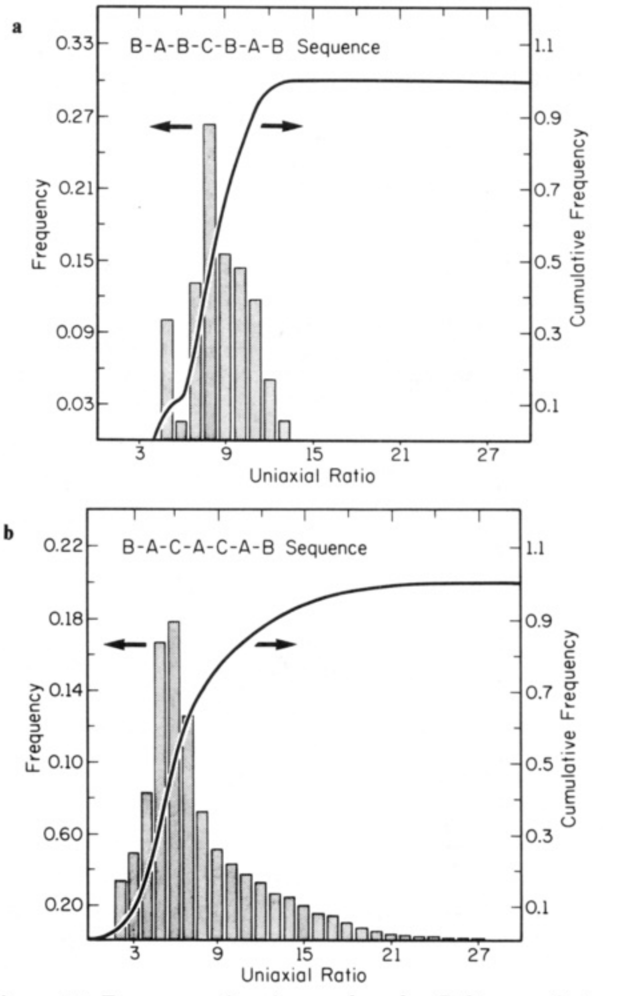


Figure 11. Frequency of conformers based on Boltzmann factors ($T = 140$ °C) for two chemical sequences in the aperiodic nematogen as a function of uniaxial ratio (a) BABCBAB and (b) BACACAB. See Table I for definition of A, B, and C.

The plot of conformational energy as a function of extension or uniaxial ratio in Figure 12 is particularly interesting. This graph invites the thought that polymeric nematogens may exist in which little change in conformational energy occurs as chain segments explore a large fraction of conformational space. That is, heptad sequences in this case can be pictured as extending and contracting with little cost in internal energy from the high uniaxial ratio conformers favored by nematic regions to the more coiled conformers expected in isotropic spaces. This is in fact an important characteristic of molecular segments if they are going to be labeled as conformationally versatile. The versatility, on the other hand, aids the

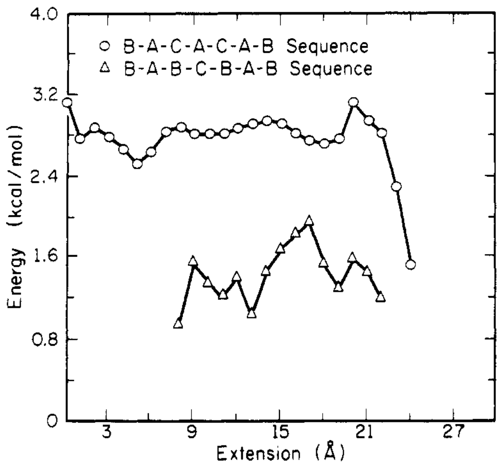


Figure 12. Energy of conformers in two different heptads of the aperiodic polymer as a function of extension in the chemical sequence considered. See Table I for definition of A, B, and C.

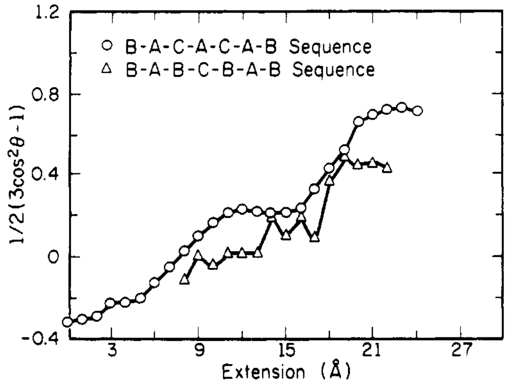


Figure 13. Order parameter as a function of chemical sequence extension. The order parameter is defined through the angle between the rigid structural unit vector $\bar{p}$ and the semimajor axis. See Table I for definition of A, B, and C.

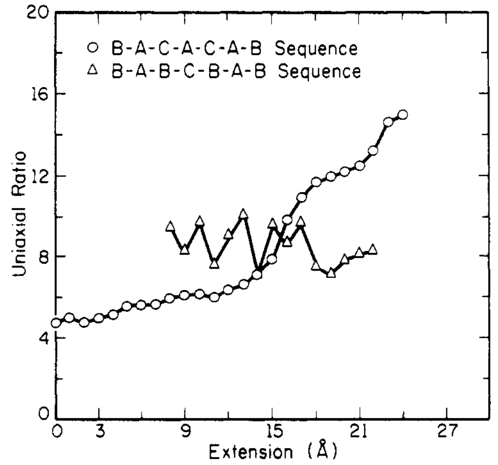


Figure 14. Uniaxial ratio, μ, as a function of chain extension for two different heptad sequences. See Table I for definition of A, B, and C.

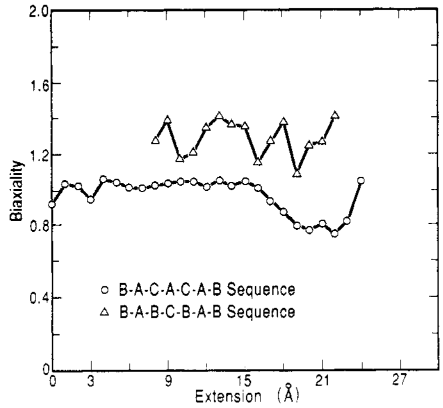


Figure 15. Biaxiality of conformers (see text) for two different heptads as a function of chemical sequence extension. See Table I for definition of A, B, and C.

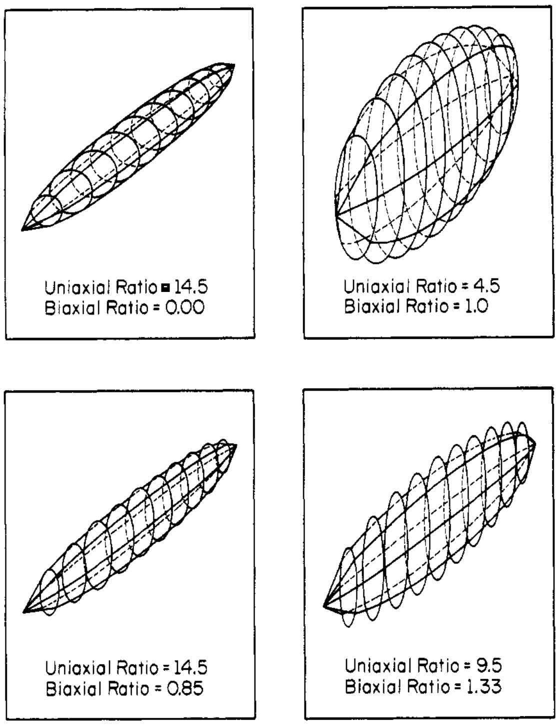


Figure 16. Ellipsoidal constructions for four different conformers having the values of uniaxial ratio and biaxiality indicated.

isotropic fluctuation as the "snapshot" environment around molecular segments changes with translation of chains. As suggested earlier, the segment's environment could change due to lack of periodicity in the chains and also due to molar mass polydispersity in the system. Nonetheless, these structure factors may not be necessary for the nematogens to experience the isotropic fluctuations. More fundamental reasons that are beyond our current understanding of these systems could play a role as well. Also it is not possible to establish at this point if the fluctuation would be driven by entropic or enthalpic factors.

The analysis of molecular shape in heptads isolated in a vacuum, with all its obvious weaknesses, is also helpful in thinking about the concept of conformational versatility and its impact on the fluctuation. First of all Figure 16 shows graphical representations of various ellipsoidal constructions for the heptads and their corresponding values of μ and β. Larger μ values correspond to elongated ellipsoids, whereas low β values are associated with cylindrical shapes and higher ones with board-like shapes. If one considers Figure 15, it is clear that the global biaxiality or global symmetry of the heptads can remain fairly constant as a very large fraction of conformational space is explored. The physical meaning of this result is the suggestion that the chain's conformational versatility can accommodate packing difficulties during nematic-isotropic fluctuations. As the heptad explores conformations in the extension range considered, uniaxial ratio changes from those preferred in pseudoisotropic regions to those preferred in strongly nematic regions.

Conclusions

Nematic polymers form orientationally ordered phases that tolerate isotropic motion in their molecular segments. These motions can occur through nematic–isotropic fluctuations with spatial and temporal periodicities which depend on temperature and molecular structure. The physical origin of these fluctuations is not known but they may occur specially in nematogens with aperiodic chemical sequences or in systems with molecular weight distribution. The molecules in these nematic phases organize at high temperatures into biphasic patterns in which the more flexible chains of the system congregate in isotropic regions whereas nematic regions retain the more rigid ones.

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