Chain conformations of liquid-crystalline polymers

A. M. Gupta* and S. F. Edwards
Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK
(Received 23 November 1992; revised 26 March 1993)

We extend our mean-field theory of backbone liquid-crystalline polymers (LCPs) to calculate chain anisotropy in nematic phase. The LCP theory applies to semiflexible, worm-like polymers and we use the Kratky–Porod formalism with a self-consistent mean-field approximation. We calculate the end-to-end distance of a polymer chain in the nematic phase as a function of concentration and temperature. For sufficiently long or sufficiently flexible polymers, we find for the ratio of z to x components of the end-to-end distance: $(1+2S)/(1-S)$, where S is the order parameter and z the director axis. At the transition this has a universal value of 2. The order parameter is described by the equation: $(1-S)^2(1+2S)^2/(2+S)=27/8\varepsilon uc$.

(Keywords: semiflexible polymers; liquid-crystalline polymers; nematics; chain conformations)

Introduction

Liquid-crystalline polymers (LCPs), as a consequence of partial ordering of long chains, manifest intriguing phenomena[1,2]. In the interest of processability it is desirable to introduce some flexibility along the polymer backbone and in this paper we consider semiflexible, worm-like polymers. Such polymers have a gradual curvature along their contour and we expect that they are mathematical models for polymers with partially hindered backbone rotations.

With the goal of describing the complex LCP dynamics, a simple self-consistent formulation of polymer statics is required. We have recently proposed a mean-field description of the nematic state in semiflexible LCPs[3]. Both lyoptropic and thermotropic systems are addressed and the simplicity of the final thermodynamic description offers promise of amenability to more difficult problems.

In this paper we apply our mean-field theory of nematic polymers to calculate the chain conformations. It is expected that as a result of ordering, the polymer chains are extended along the director axis (z axis) and explore proportionally less space in the other two directions. This anisotropy was recently probed in a polyester nematic phase by neutrons[4]. We discuss these experiments in relation to our work.

Review of mean-field theory of LCP

Here we enunciate the salient features of our mean-field theory which predicts successfully the backbone liquid-crystalline (LC) behaviour of semiflexible long chain polymers[3]. Two concepts are fundamental to any LC description: an inherent or induced rigidity in the polymer chain and an anisotropic polymer–polymer interaction. We consider the Hamiltonian $\mathscr{H}$ of partition function $\mathscr{Z}$:

$$\begin{aligned}\mathscr{Z} &= \int \mathscr{D}[R(s)] \exp(-\mathscr{H}/k_{\mathrm{B}}T) \\ &= \int \mathscr{D}[R(s)]\left\{\exp\left[-\varepsilon/2 \int \mathrm{d}s\ddot{R}^2(s)\right] \prod_{\alpha} \delta[\dot{R}^2(s_\alpha)-1]\right\} \\ &\quad \times\left\{\exp\left[-(u_{\mathrm{n}}/2)\int\int \mathrm{d}s_\alpha\,\mathrm{d}s_\beta[\dot{R}(s_\alpha)\times\dot{R}(s_\beta)]^2\right.\right. \\ &\quad \left.\left. \times\,\delta[R(s_\alpha)-R(s_\beta)]\right]\right\} \qquad (1)\end{aligned}$$

We have dropped the isotropic excluded volume term since at the level of presentation in this paper it has no bearing on the LC behaviour. However, if fluctuations were to be discussed, the term $(w/2)\int\int \mathrm{d}s_\alpha\,\mathrm{d}s_\beta\,\delta(R_\alpha-R_\beta)$ would be included in the Hamiltonian. The first term in equation (1), for the non-interacting chain contour $R(s)$, describes the chain backbone as a path that has a continuous tangent $\dot{R}(s)$ and a curvature $\ddot{R}(s)$. The simplification introduced is to allow the tangent magnitude to fluctuate locally but to remain unity on an average. This is consistent with the other approximation in our model, of a mean-field nematic interaction, and affords a simple analytic solution. We rewrite the unit magnitude constraint as:

$$\prod_{\alpha} \delta[\dot{R}^2(s_\alpha)-1] = \mathscr{N}_1 \int \mathscr{D}[\lambda(s)] \exp\left\{-i\int \mathrm{d}s\lambda(s)[\dot{R}^2(s)-1]\right\} \qquad (2)$$

where $\mathscr{N}_1$ is the normalization and $\lambda(s)$ is a field. The second term in equation (1) is the polymer–polymer nematic interaction, which is also approximated as a polymer-field interaction – details may be found in the original paper[3]. If $\sigma^{ij}(r)=\int \mathrm{d}s\dot{R}^i(s)\dot{R}^j(s)\,\delta[r-R(s)]$ is the ijth component of the orientation tensor and $\psi(r)$ the corresponding conjugate field, we write the field-

---

*To whom correspondence should be addressed

0032-3861/93/143112–03

dependent Hamiltonian:

$$\int \mathscr{D}[R(s)] \exp\left(-\frac{\hat{H}}{k_B T}\right)$$

$$= \mathscr{N} \int \mathscr{D}[R(s)] \left\{ \exp\left[-\int \mathrm{d}s\left(\frac{\varepsilon}{2}\ddot{R}^2 + i\lambda \dot{R}^2 + i\dot{R}\psi\dot{R}\right)\right] \right.$$

$$\times \exp\left(i \int \mathrm{d}s\lambda\right) \exp\left(i \int \mathrm{d}^3 r \psi\sigma\right)$$

$$\left. \times \exp\left[-\frac{u_n}{2} \int \mathrm{d}^3 r(\sigma^{ii}\sigma^{jj} - \sigma^{ij}\sigma^{ji})\right] \right\} \tag{3}$$

The self-consistent approximation is to take $\lambda(s)$, $\sigma(r)$ and $\psi(r)$ at their means. We interrogate the phase behaviour by minimizing the free energy with respect to the fields (after performing the Gaussian integral over all polymer paths), obtaining the system state, polymer concentration and temperature dependent mean value of the fields. Quoting the results obtained in our previous paper[3]:

$$\sigma_\alpha = \frac{c}{4} \frac{1}{\sqrt{\varepsilon/2}} \frac{1}{\sqrt{\tilde{\psi}_\alpha + \tilde{\lambda}}} \tag{4a}$$

$$1 = \frac{1}{4} \frac{1}{\sqrt{\varepsilon/2}} \sum_\alpha \frac{1}{\sqrt{\tilde{\psi}_\alpha + \tilde{\lambda}}} \tag{4b}$$

$$\tilde{\psi}_\alpha = u_n \sum_\beta \sigma_\beta - u_n \sigma_\alpha \tag{4c}$$

where c is the polymer concentration. The subscripts α and β represent the eigenvalues of the tensors and the notation $\tilde{\psi}$, $\tilde{\lambda}$ shows that the imaginary number i has been absorbed in the new definitions.

These equations display the correct form of phase change in LCPs. In two dimensions we get a second-order phase transition and in three dimensions the phase transition is first order, uniaxial. The equation for the order parameter S is:

$$\frac{(1+2S)^2(1-S)^2}{(2+S)} = \frac{27}{8\varepsilon u_n c} \tag{5}$$

The formulation describes both concentration-driven liquid crystals (lyotropic) and temperature-sensitive alignment (thermotropic). The simplest temperature dependence is the Boltzmann term in the bending energy ε, and we use the pseudo-potential to the first virial coefficient $T_s = U/u$; $u_n = u(1 + T_s/T)$ for the nematic interaction. U represents the soft aligning interactions of the van der Waals' type, as in most aromatic backbones, and u arises from steric constraints. The condition for phase change is:

$$c_c u \frac{\varepsilon}{T_c}\left(1 + \frac{T_s}{T_c}\right) \cong 6 \tag{6}$$

The order parameter has the universal value 0.25 at the transition and its growth thereafter is given by equation (5). When the soft aligning forces dominate, $T_s \gg T_c$, $T_c \sim (cU\varepsilon)^{(1/2)}$. If the polymers have insignificant quadrupolar inducement to liquid crystallinity, $T_s \ll T_c$, $T_c \sim (cu\varepsilon)$. In lyotropic liquid crystals the biphasic regime is spanned between the concentrations, $0.9813c_c \leqslant c \leqslant 1.0267c_c$; c_c is the critical polymer concentration at the transition, from equation (6). The order parameter in the nematic phase during the coexistence regime is 0.306. We find that the order parameter S in semiflexible polymers is much smaller than for rod-like LCPs. This is to be expected given the flexibility of the backbone, which encourages local alignment but then the polymer can wander off.

End-to-end distance of a chain

Any average property of a chain, $f(R)$, for a given Hamiltonian $\mathscr{H}$ is:

$$\langle f(R) \rangle = \frac{\int \mathscr{D}[R] f(R) \exp(-\beta\mathscr{H})}{\int \mathscr{D}[R] \exp(-\beta\mathscr{H})} \tag{7}$$

The end-to-end distance of a semiflexible chain, $f(R) = \langle R_{\mathrm{L0}}^2 \rangle = \langle [R(L) - R(0)]^2 \rangle$, subject to a nematic interaction, can be calculated by using the field-dependent Hamiltonian given in equation (3). We calculate the αth projection of the end-to-end distance, $\langle R_{\mathrm{L0}}^2 \rangle_\alpha$, by working in the discrete Fourier space and then considering the limit of a sufficiently long polymer such that we can use the continuous modes:

$$\langle R_{\mathrm{L0}}^2 \rangle_\alpha$$

$$= \mathscr{Z}^{-1} \left\{ -\frac{\partial^2}{\partial\mu^2} \left(\int \mathscr{D}[R] \right.\right.$$

$$\times \exp\left[-\frac{\varepsilon}{2} \int_0^L \mathrm{d}s\ddot{R}^2 - i(\lambda + \psi_\alpha) \int_0^L \mathrm{d}s\dot{R}^2 \right.$$

$$\left.\left.\left. + i\mu \int_0^L \mathrm{d}s\dot{R} \right] \right) \right|_{\mu=0} \right\}$$

$$= -\frac{\partial^2}{\partial\mu^2} \left(\exp\left(-\frac{\mu^2}{8\pi} \int_{-\infty}^{+\infty} \mathrm{d}q \right.\right.$$

$$\left.\left.\left. \times \frac{[\exp(iqL) - 1][\exp(-iqL) - 1]}{(\varepsilon/2)q^4 + i(\lambda + \psi_\alpha)q^2} \right) \right) \right|_{\mu=0}$$

$$= \frac{1}{2i(\lambda + \psi_\alpha)} \left\{ L - \frac{1}{\sqrt{2i[(\lambda + \psi_\alpha)/\varepsilon]}} \right.$$

$$\left. \times [1 - \exp(-L\sqrt{2i(\lambda + \psi_\alpha)/\varepsilon})] \right\} \tag{8}$$

If the persistence length in the α direction is defined as $b_\alpha = 3/2i(\lambda + \psi_\alpha)$, then using the fields as evaluated in equations (4a)–(c):

$$b_x = 12\varepsilon\left(\frac{1}{3} - \frac{S}{3}\right)^2 \tag{9a}$$

$$b_y = b_x \tag{9b}$$

$$b_z = 12\varepsilon\left(\frac{1}{3} + \frac{2S}{3}\right)^2 \tag{9c}$$

We rewrite equation (8):

$$\langle R_{\mathrm{L0}}^2 \rangle_\alpha = \frac{b_\alpha}{3} \left[L - \frac{\sqrt{b_\alpha} \sum_\beta \sqrt{b_\beta}}{6} \right.$$

$$\left. \times \left(1 - \exp\left(-\frac{6L}{\sqrt{b_\alpha} \sum_\beta \sqrt{b_\beta}} \right) \right) \right] \tag{10}$$

The average magnitude of the tangents is unity.

Discussion

For an isotropic liquid the order parameter is zero and the end-to-end distance is the same in each direction. At

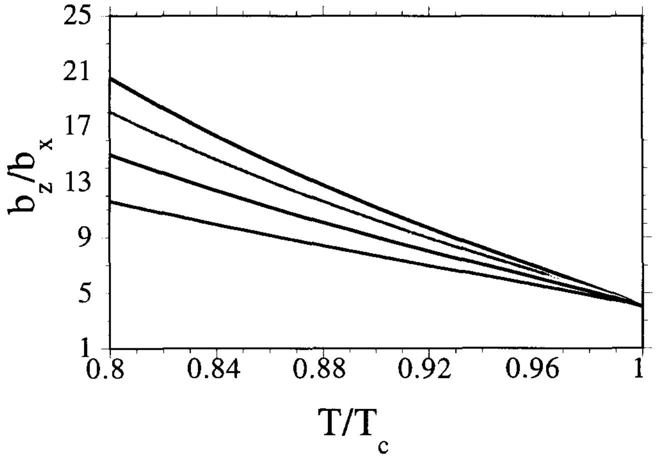

Figure 1 Ratio of persistence lengths as a function of reduced temperature. From the top curve down: $T_s/T_c=\infty$, 10, 1 and 0

the transition the material becomes preferentially oriented in the z direction, and then the z component of the end-to-end distance grows over the other two as in equation (10). The choice of the director axis is arbitrary in the absence of external effects such as fields or surface boundaries. If we consider the limit of very long chains, or small persistence lengths, we find that the anisotropy in the square end-to-end distance is proportional to the ratio of the persistence lengths: $\langle R^2\rangle_z/\langle R^2\rangle_x \sim b_z/b_x = (1+2S)^2/(1-S)^2$. The polymers for which our theory is manifestly applicable are in this limit. We show how the anisotropy grows as a function of reduced temperature, T/T_c, for different values of T_s/T_c in *Figure 1*.

In the limit of complete alignment, the x and y components of the end-to-end distance vanish and the chain extends like a rigid rod in the z direction. Then considering the implicit temperature dependence of ε ($\varepsilon \sim 1/T$), we obtain $\langle R_{\mathrm{LO}}\rangle_z = L$.

Experimental innovations in neutron scattering have made possible the measurement of chain anisotropy in LCPs. A recent study of polyester nematics motivated this paper[4]. The authors found that R_z/R_x increased from 1.5 to 2.1 from 196 to 175°C. Definitive comments cannot be made with this limited information on the applicability of our theory. The molecular weights of the polyesters were low, the degree of polymerization was about 10 and therefore not suitable for our theory which applies to long polymers. Further, it is not clear that it is valid for us to treat these polyesters as worm-like. The polyester backbone consists of alternating rigid and flexible units. If the flexible units are long, such that the polymer forgets the persistence of the previous rigid unit, it is more realistic to model these chains as a collection of freely hinged rods. An additional complication in these systems is the transesterification reaction.

Our theory is similar to a number of other theories of backbone semiflexible LCPs, and our results are in qualitative agreement with these theories[5–7]. Since the model we propose has a simple analytic description, it might be useful for future work on complex problems like polymer dynamics. The experimental results are sparse and at present it is not possible to favour one theory over the other based on experimental validation. At this stage, an experimental programme on well characterized, model, semiflexible, backbone LCPs would be particuarly useful.

References

1 'Polymer Liquid Crystals' (Eds A. Ciferi, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1982
2 'Theory and Application of Liquid Crystals' (Eds J. L. Erickson and D. Kinderlehrer), Springer-Verlag, Berlin, 1987
3 Gupta, A. M. and Edwards, S. F. *J. Chem. Phys.* 1993, **98**, 1588
4 Arrighi, V., Higgins, J. S., Weiss, R. A. and Cimecioglu, A. L. *Macromolecules* 1992, **25**, 5297
5 Wang, X. J. and Warner, M. *J. Phys.* 1986, **A19**, 2215
6 ten Bosch, A., Maissa, P. and Sixou, P. *J. Chem. Phys.* 1983, **79**, 3462
7 Semenov, A. N. and Kokhlov, A. R. *Sov. Phys. Usp.* 1988, **31**, 988