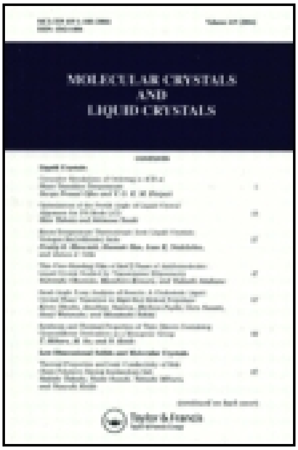

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Mean Field Study of Effects of Longitudinal Flow on Nematic Polymer Solutions

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Mean Field Study of Effects of Longitudinal Flow on Nematic Polymer Solutions

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The effect of steady longitudinal flow on nematic polymer systems is investigated using a simple mean-field approximation. Employing a connection between the shear rate and polymer chain extension we find that as the shear rate is increased in the nematic phase, the consequent chain extension significantly modifies the orientational order of the nematic monomers. In particular if a continuous (discontinuous) coil-stretch transition occurs above a critical shear rate in an ordered comb-like nematic polymer system, the birefringence changes sign continuously (discontinuously). We also examine the effect of pretransitional nematic ordering on the entropic elastic constant for chain extension in small shear flow.

INTRODUCTION

Under shear flow polymer molecules in solution exhibit a deformation of their average configuration, or shape, away from spherical symmetry.[1] As the shear rate is increased beyond a critical value a coil-stretch transition may occur,[2,3] provided the shear stress is applied for a sufficiently long time compared to a molecular relaxation time (Zimm) $\tau_0 \sim 10^{-3}$ sec.

Although the above effect has usually been discussed in the context of dilute linear polymers with ideal chains[2] or with inclusion of excluded volume effects,[4] it seems reasonable to assume a similar transition might occur for nematic polymer solutions. Finkelmann's[5] review of nematic polymer systems discusses some physical properties of main-chain and side-chain (comb-like) liquid crystalline polymers (Figure 1).

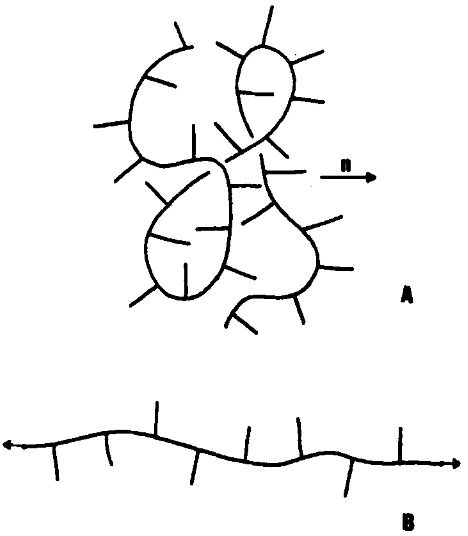

FIGURE 1 Schematic picture of a comb-like nematic polymer: (A) The coiled state with *n* as the director. (B) Polymer of (A) in the stretched state. The arrows represent the force applied on the chain by the longitudinal flow gradient.

In this paper we present a simple model which accounts for the effect of chain extension in longitudinal shear flow on the nematic order parameter at constant polymer concentration. We qualitatively examine effects of the coil-stretch transition on the birefringence for $T < T_{\mathrm{NI}}$ (T_{NI} is the nematic isotropic transition temperature), and also the influence of nematic order for $T \geq T_{\mathrm{NI}}$ on the configuration free energy of the molecule.

In the elongational velocity field $\mathbf{v} = (-\kappa/2x, -\kappa/2y, \kappa z)$ the chain extends in the $\hat{z}$ direction. We call this extension **r**. [We ignore contraction of the chain perpendicular to r. If the deformation is assumed affine, then the contraction can be written in terms of $|r|$.]

The elastic free energy connected with an isotropic configuration of an ideal polymer coil consisting of Z monomers each of length a is written (in analogy to a spring stretched a distance r),[2]

$$F_e = \tfrac{3}{2}TE(\vec{r}/R_0)^2 = \tfrac{3}{2}TE(L/R_0)^2\lambda^2 \qquad (1)$$

where $R_0 = Z^{1/2}a$ the mean square end to end length of the molecule, $\lambda = r/L$, and $L = Za$ is the extended length of the molecule. The factor E takes into account the nonlinear dependence of F on λ for high chain extension. It is[6]

$$\begin{aligned} E &\approx 1, & \lambda &\ll 1 \\ E &\approx 1/[\lambda(1-\lambda)], & \lambda &\sim 1 \end{aligned} \tag{2}$$

One problem discussed by deGennes[2] and Daoudi[3] is the relation between the extension λ and the shear rate κ. This relation is schematically reproduced in Figure 2. An analogy with a *P-V* diagram[2] for a liquid gas transition is useful but not quantitative.

Recent experimental studies by Chauveteau and Moan[7] on polymer solutions in converging flows indicate a rather sharp but not discontinuous increase in viscosity above a critical shear rate $\sim 2 \times 10^3$ sec^{-1}. They interpret their results as a coil-stretch transition.

It must be remembered that the studies of Refs. 2, 3, 4 were confined to an isolated macromolecule; therefore a mean-field approximation was employed and reference to finite size effects were neglected. Finite size effects would tend to smooth out the transition region.[8]

Also neglected in Refs. 2, 3 were effects of internal friction. It may not be justifiable to neglect internal friction (Cerf) in nematic polymer systems, in particular for side-group or comb-like nematic polymers. For instance, the Cerf friction[2] caused by monomer-monomer contact should be larger because the protruding structure of the monomers allows the chains to interlock. Variations in the length of the side group, and distance between side groups on the main chain may be used to control this interaction.

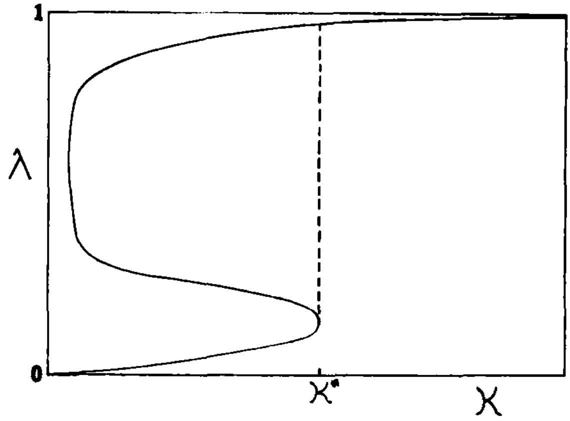

FIGURE 2 Schematic behavior of chain extension λ vs. shear rate κ (after Refs. 2, 3). The abscissa is not to scale. We define the absolute limit of instability as κ^* ($\sim 10^3$ sec^{-1}).

In absence of shear the nematic phase is caused by partial parallel alignment of monomers on the polymer chain.[5] The nematic state is pictured in Figure 1a for comb-like or side chain polymers. The ordering of the side chains in turn affects the average configuration of the main chain. The degree of alignment S can be derived from birefringence, Δn, measurements. The temperature dependence of $|\Delta n|$ follows approximately that predicted by the Maier-Saupe theory of thermotropic nematics.[5] Tsvetkov *et al.*[10] discuss molecular polarizabilities of nematic polymers, and Blinov *et al.*[11] have given a preliminary report of flow birefringence in comb-like nematic polymers.

The above mentioned polymeric nematic phases are generally one-component systems and as such we can expect a large number of entanglements to be present. This complication can be reduced if the nematic polymer is diluted in a compatible solvent. The study of Brochard[12] suggests a nematic solvent of a similar structure to the nematic monomer of the polymer. Her results in this case give a reasonably wide temperature region where the nematic phase is stable over a range of concentrations of nematic polymer in nematic solvent, provided the stability of a glass or crystalline phase is not increased.

Other factors which should be considered are limits on the shear rate due to viscous dissipation and turbulence effects. The energy dissipation for an incompressible fluid neglecting surface effects[13] and neglecting internal friction of the polymer caused by conformation change and monomer-monomer contact,

$$\dot{E} = -\frac{1}{2}\eta_s \int dV (2V_{ik})^2$$

where η_s is the solvent viscosity and $v_{ik} = \frac{1}{2}(\partial v_i/\partial x_k + \partial v_k/\partial x_i)$ is the velocity gradient tensor. Assuming longitudinal flow $v = (-\kappa/2x, -\kappa/2y, \kappa z)$ we arrive at

$$\frac{\dot{E}}{V} = -3\eta_s \kappa^2 \tag{3}$$

where V is the volume of the system exposed to the flow gradient.

Using $N = N_s + rN_p$, where N_s is number of solvent molecules and N_p is number of polymer molecules with r monomers in the considered volume, and dividing Eq. (3) by NkT, we define an inverse time

$$\frac{\dot{E}}{NkT} = -\frac{3\eta_s \kappa^2}{nkT} \equiv \tau_D^{-1} \tag{4}$$

where k is Boltzmann constant, T is temperature and n is the number density of monomer + solvent. The heat generated by viscous dissipation within the volume of sample undergoing longitudinal shear must have time to equilibrate so that a limit to the shear rate is given in order of magnitude by setting

$$\tau_D \approx \tau_T \tag{5}$$

where $\tau_T \approx l^2/\chi$ is a thermal relaxation time.[13] χ is the thermal diffusivity of nematic solvent and l is the radius of the constriction in the capillary. We obtain

$$\kappa^2 \approx \frac{nkT\chi}{3\eta_s l^2} \tag{6}$$

Taking $n \approx .5 \times 10^{22}$ cm^{-3}, $T = 400$ K, $\eta_s \approx 10^{-1}$ poise, $\chi \approx 1.0 \times 10^{-3}$ cm^2/sec,[14] $l \approx 100$ μ we find $\kappa \sim 10^5$ sec^{-1} as an upper limit to the shear rate for the considered solution.

Turbulent flow of incompressible liquids in pipes is thought to occur for Reynolds numbers above ≈ 34.[13] For our system the Reynolds number

$$\mathrm{Re} = \frac{\rho v l}{\eta_s} \approx \frac{\rho \kappa l^2}{\eta_s} \tag{7}$$

Using $\kappa \sim 10^3$ sec^{-1}, $l \approx 10^{-2}$ cm, $\rho \approx 1$ gm/cm^3, $\eta_s \approx 10^{-1}$ poise, we find Re ~ 1. At higher polymer concentrations we should replace $\eta_s \to \eta_s + c[\eta]$, where c is the polymer concentration and $[\eta]$ is the intrinsic viscosity.[15] The gradient dependence of $[\eta]$ has been discussed by Peterlin.[16]

It appears reasonable to assume the coil-stretch transition can be reached before turbulence sets in, again provided the molecule is exposed to the shear stress for times sufficiently long compared to the Zimm relaxation time τ_0.[2]

Model

We consider a dilute solution of comb-like nematic polymer molecules exposed to a steady state longitudinal flow field $\mathbf{v} = (-\kappa/2x, -\kappa/2y, \kappa z)$. Flow fields similar to this can be constructed by four-roll mill,[17] or a constricted tube.[7]

In this case we consider the flow field as a static applied field,[18] which modifies the one-particle distribution function. For $T < T_{NI}$ and $\kappa = 0$ we define the director, n, as the direction of preferred orientation of the side-groups and place the director parallel to the $\hat{z}$ direction of the flow field. This is compatible with the symmetry of the flow field.

In the mean-field approximation the orientational free energy for the side groups, at constant volume fraction of polymer, in the presence of an external field ϕ is

$$\Delta F = \frac{N^2}{2}\int d^3r_1\, d\Omega_1 \int d^3r_2\, d\Omega_2\, U_{12} f(\Omega_1) f(\Omega_2)$$
$$+ NT\int d^3r\, d\Omega\, f(\Omega)\ln(4\pi f(\Omega))$$
$$+ N\int d^3r\, d\Omega\, \phi(\Omega) f(\Omega) \tag{8}$$

The integrals are taken over the volume of sample, V, exposed to the shear gradient ($V \gg R_0^3$), U_{12} is the two particle interaction energy and N is as defined above Eq. 4. U_{12} is assumed for simplicity to be the same for monomer-solvent, and solvent-solvent interactions. From here on we set Boltzmann's constant to unity. The distribution function in this approximation has the form

$$f(\Omega) = A^{-1}\exp(-[V_1(\Omega) + \phi(\Omega)]/T) \tag{9}$$

with normalization constant A.

Assuming uniaxial symmetry we have,

$$V_1(\cos\theta) = -\beta S P_2(\cos\theta)$$

where θ is the angle between the director at zero shear flow and a side-group and $S = \langle P_2(\cos\theta)\rangle$ with the thermal average taken over f. The constant β has already been renormalized to include the effect of the nematic polymer on the nematic solvent. We have $\beta = \beta_0 - 2\chi_1\phi kT$ according to Brochard;[12] ϕ is volume fraction of polymer and χ_1 ($|\chi_1| \approx \beta_0$ for similar chemical structure of monomer and solvent) is monomer-solvent interaction parameter. $\chi_1 < 0$ for nematic solvent + nematic polymer. In the nematic phase the molecular side groups encounter an uniaxial energy barrier $\sim 4\ kT$ favoring the orientation $\theta = 0, \pi$. We assume the average directions of the side-chains of the comb-like polymer are perpendicular to the main chain. This assumption becomes weaker with increasing flexibility of the spacer chain attaching the mesogenic monomer to the main chain.

For strong extension of the polymer chains in the $\hat{z}$ direction, as after a coil-stretch transition, the side groups of the polymer become oriented in the x-y plane. If the orientational coupling between the polymer side groups and the nematic solvent is large (see Appendix), then the long axis of the side-groups (and solvent molecules) is forced perpendicular to the $\hat{z}$ direction by the chain extension. We note here that a biaxial state can exist upon further ordering of the side groups in the x-y plane.

The above situation can be described most simply by assuming the applied field can be expanded as

$$\phi(\lambda,\theta) = \frac{T}{2}\{A_1(\lambda)\cos\theta + A_2(\lambda)P_2(\cos\theta) + \cdots\} \tag{10}$$

where the P_l are Legendre polynomials. The symmetry of the flow field imposes $A_l = 0$ for l odd.

The distribution function becomes

$$f(\theta,\lambda) = A^{-1}\exp\left\{\frac{\beta}{T}\left[S - \frac{T\delta\lambda}{2\beta}\right]P_2(\cos\theta)\right\} \tag{11}$$

where $\delta \equiv \lambda^{-1}A_2(\lambda)$, and only the A_2 term has been retained. We may expect that δ has a similar behavior as a function of λ as E of Eq. (2), i.e., as $\lambda \to 1$, $\delta \gg 1$. In this limit the distribution function of the orientations of the side-groups has a maximum at $\theta = \pi/2$. In the opposite limit of $\lambda \to 0$ we assume $\delta \to 1$. This behavior would be obtained if the function $A_2(\lambda)$ is the inverse Langevin function $l^{-1}(\lambda)$.[6]

The function $\lambda(\kappa)$ is model dependent; therefore, as a first step instead of solving self consistently the relation connecting (S, δ, λ) to κ, we examine the effect of the parameter $x = \delta\lambda$ on the order parameter S. This is a simple calculation. Typical behaviors of the order parameter and the free energy are plotted vs. x in Figures 3 and 4. In Figures 3 and 4 the temperature is lowered to below T_{NI} with $x = 0$; the temperature is then held fixed at the indicated values and x is increased corresponding to the flow gradient stretching the chain. From Figure 4 we note the free energy is positive for ($.3 \lesssim x \lesssim 2.5$) for $T/\beta = .2150$. This indicates the isotropic phase is the most stable in this region of x. However, the maximum free energy difference

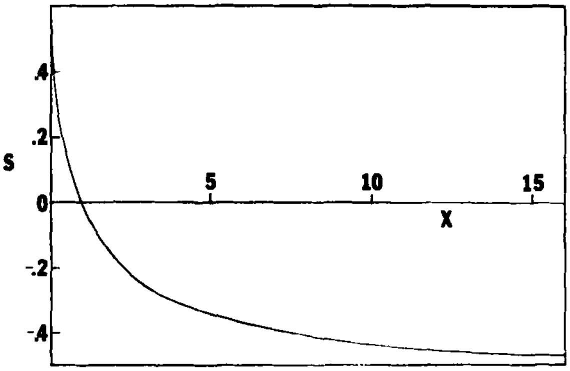

FIGURE 3 Nematic order S vs. $x = \delta\lambda$ at the fixed value $T/\beta = .2150$. At this temperature $S(x = 0) = .50$.

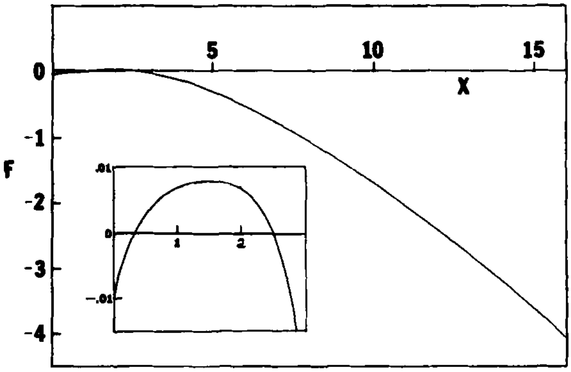

FIGURE 4 Orientational free energy F (Eq. 8) vs. x for $T/\beta = .2150$. Inset shows detail of free energy.

between the isotropic and nematic phases in this region is $\simeq .008$ (the isotropic free energy is defined to be zero), and the isotropic state is not strongly preferred. Since we are mainly concerned with the behavior of S for $x \ll 1$ ($\delta \simeq 1, \lambda \ll 1$), or $x \gg 1$ ($\delta \gg 1, \lambda \simeq 1$), i.e. below and above a coil stretch transition, we shall not discuss this region further. At large x the nematic state with $S < 0$ is strongly preferred.

Keeping x finite ($x \ll 1$) we find (see discussion after Eq. (19)) upon lowering the temperature that $S < 0$ always results. In Figure 5 we sketch S vs. shear rate κ assuming δ to behave similarly to E as a function of λ. The values of λ correspond to Figure 2.

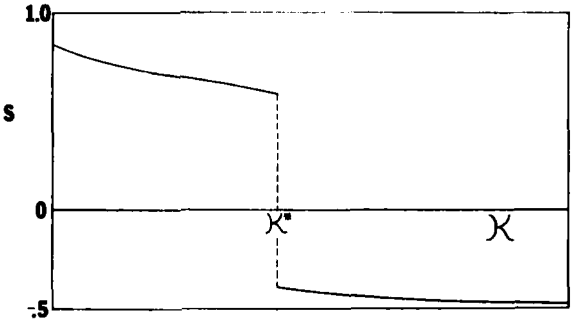

FIGURE 5 Nematic order S vs. κ. κ^* is defined in caption of Figure 2.

DISCUSSION

The reversal of the sign of the order parameter above a critical shear rate should be observable as a change in the sign in the birefringence, $\Delta n = n_e - n_0$. If one chooses the solvent to have the same optical anisotropy as the side chains, and for simplicity the same magnitude of polarizabilities, the Lorenz-Lorentz equation yields the order parameter S

$$\Delta n = \frac{\bar{n}^2 + 2}{n_e + n_0} \frac{4\pi}{3} n \, \Delta\alpha \, S \qquad (12)$$

$\bar{n} = \frac{1}{3}(n_e^2 + 2n_0^2)$, $\Delta\alpha$ is the anisotropy of polarizability of a side group (or solvent molecule), n is the number density of monomer + solvent.

We have assumed also in writing Eq. (12) that: (1) solvent and polymer order are strongly coupled, and (2) the polarizability of the bonds along the main chain is neglected. Assumption (1) is justified by the argument of the Appendix. Assumption (2) is justified by the fact that the polarizabilities of the side chains (containing aromatic groups and dipoles) are much larger ($\sim 10^2$) than the polarizability of the main chain.

The above considerations apply for polymers of high Z (high molecular weight) so that the number of different conformations of the main chain compatible with a nematic ordering of the side-groups is large. However, for some low molecular weight polymers with $L < e$ (e is the persistence length for bending the main-chain), the birefringence, for $T < T_{\mathrm{NI}}$ ($\kappa = 0$), may be of opposite sign than the birefringence of high molecular weight polymers at the same monomer concentration.[10] Possibly an ordering of the comb-like oligomers or "stars", similar to disk-like molecules, with the side groups perpendicular to the optical axis is favorable in this case.

To examine the system for $T > T_{NI}$ and $\lambda \ll 1$ ($\delta \sim 1$), we expand the total free energy Eq. (8) and (1) in powers of S and λ.

$$\begin{aligned} F_T &= F_e + \frac{1}{2}\beta\left(S^2 - \frac{T\delta}{2\beta}\lambda S\right) - T\ln A \\ &= \frac{1}{2}A'S^2 + \frac{1}{2}TB\lambda^2 + TCS\lambda + \cdots \end{aligned} \tag{13}$$

where F_e is given by Eq. (1) and

$$\begin{aligned} &A' = \beta\left(1 - \frac{T^*}{T}\right), \qquad T^* = \frac{1}{5}\beta \\ &B = 3(L/R_0)^2 - \delta^2/20 \\ &C = \frac{\delta}{4}\left(\frac{2T^*}{T} - 1\right) \end{aligned} \tag{14}$$

Stability puts $A' > 0$, $B > 0$ and $A'B - TC^2 > 0$.

Treating the system as if it were in thermal equilibrium [shear rate limited by Eq. (6)] we obtain

$$\langle S^2 \rangle = \frac{T}{A' - \dfrac{C^2T}{B}} = \left(\frac{\overline{A'}}{T}\right)^{-1} \tag{15}$$

$$\langle \lambda^2 \rangle = \frac{1}{B - \dfrac{C^2T}{A'}} = \bar{B}^{-1} \tag{16}$$

$$\langle S\lambda \rangle = -\frac{C}{\dfrac{A'B}{T} - C^2} = -\bar{C}^{-1} \tag{17}$$

For $A > 0$ and Z large we have $B \sim Z$ and

$$\langle S^2 \rangle = \frac{T}{A'}\left(1 + \frac{\alpha}{Z} + \cdots\right)$$

where $\alpha = C^2T/A$, which implies the temperature T^* is modified only to order Z^{-1} under small shear rate ($\lambda \ll 1$, $\delta \sim 1$).

As $T \to T^*$ the coefficients of F undergo a modification and in particular the renormalization $\bar{B}$ implies, in the above approximation, that onset of nematic order favors chain extension. The nonlinear factor included in Eq. (1) will limit this extension.

Minimizing Eq. (14) with respect to S we find $S = -TC/A\lambda$. Thus the presence of $\lambda > 0$ for $T \to T_{\mathrm{NI}}$ favors $S < 0$ at all finite temperatures. This is characteristic behavior of systems exposed to an external field.

In summary we argue: (1) if a longitudinal shear induced coil-stretch transition occurs in a comb-like nematic polymer, the birefringence should exhibit a reversal of sign. This is due to the reorientation of the nematic side groups from parallel to the capillary axis to perpendicular to the axis by chain extension, within a constriction or series of constrictions,[3] along the capillary axis; (2) the entropic elastic constant Eq. (1) undergoes a renormalization approaching the N–I transition. The renormalization is such as to favor increased deformation of the coil. [We have not considered the anisotropy of the deformation.] This might be observable (for $T \to T_{\mathrm{NI}}^+$) as a slight anomaly in the intrinsic viscosity[15] at small shear rates which can be written in our case; n_c = number of polymer molecules per unit volume in a dilute solution,

$$[\eta] = \lim_{n_c \to 0} \frac{\eta - \eta_s}{\eta_c \eta_s} \cong \frac{5}{2} \cdot \frac{4\pi}{3} \langle r^2 \rangle^{3/2} = q \langle \lambda^2 \rangle^{3/2} \tag{18}$$

Therefore we arrive at

$$[\eta] = qB^{-3/2}\left(1 - \frac{c^2T^2}{B\beta(T - T^*)}\right)^{-3/2} \tag{19}$$

where $q = 10\pi/3L^3$.

Eq. (18) assumes the coiled polymer looks to the solvent as a hard sphere of radius $\langle r^2 \rangle^{1/2}$, the solvent flow penetrating only a small distance ~ monomer length into the coil.[2] Thus we have assumed the distribution function (Eq. (12)) for small shear has no term directly coupling the monomer order to the shear. For large shear the mechanical coupling of the chain to the monomers, and the orientational coupling of the monomers to the solvent (see Appendix) under stretching dominates the distribution function.

We have not considered the possibility of shear alignment in the nematic solvent (see Appendix B). This would require two order parameters, one for the solvent, S_1, and one for the solute, S_2. We then would have to examine the interactions of S_1 and S_2 with flow gradient. Also necessary is a more detailed study of the relation between chain extension, shear rate, S, and the parameter δ so that more definite statements can be made above the rather tenuous phenomenological connections used joining the behavior of δ to the shear rate κ.

The above analysis can also be carried out for main-chain nematic polymers where the nematic monomers are parallel to the main chain. In this case the parameter $\delta < 0$, and the maxima of the distribution function at $\theta = 0, \pi$ are enhanced with chain extension.

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APPENDIX

We wish to show that the orientational coupling between nematic polymer and nematic solvent is strong at high enough polymer concentrations. We use an analogy to a system of colloidal magnetic grains suspended in a nematic matrix.[19]

A slightly non-aligned floating anisotropic particle causes a disturbance in the director field $\delta\mathbf{n}(r)$; $\mathbf{n}_0 \cdot \delta\mathbf{n} = 0$, where $\mathbf{n}_0$ is the direction of the macroscopic optic axis. The distortion $\delta\mathbf{n}(r)$ decays like $1/r$ for large r.[20] In the one-constant approximation the distortion free energy takes the form $F = K/2\int dV(\nabla\mathbf{n})^2$ with $K =$ elastic constant. Setting $\mathbf{n} = (\delta n_x, \delta n_y, 1)$, $\delta\mathbf{n} \ll 1$ we get an Euler equation $\nabla^2\delta\mathbf{n} = 0$ which has a solution at large r; $\delta n_i \sim \text{const.}/r$.

Now suppose we have a suspension of grains or polymer of density c (number of monomers or grains per cm^3) which orient the nematic surrounding them. Call $\mathbf{u}(r)$ the orientation axis of the grain or portion of polymer at r, let $\boldsymbol{\nu}(r) = \mathbf{u} - (\mathbf{n}_0 \cdot \mathbf{u})\mathbf{n}_0$ be the perpendicular projection of $\mathbf{u}$ on $\mathbf{n}_0$. The orientation of nematic material at point r in the absence of a grain at point r is $\mathbf{n}(r) = \mathbf{n}_0 + \delta\mathbf{n}(r)$. Allowing only small distortions transverse to $\mathbf{n}_0$ we have by superposition[19]

$$\delta\vec{n}(\vec{r}) = \sum_{\substack{i \\ \text{(grains)}}} e_i \frac{[\vec{\nu}(\vec{r}_i) - \delta\vec{n}(\vec{r}_i)]}{|\vec{r} - \vec{r}_i|} \qquad \text{(A1)}$$

There is no contributing distortion at an arbitrary point r from a grain at point k if $\boldsymbol{\nu}_k = \delta\mathbf{n}_k$. We set $e_i = e$ for all i, and can identify e with a persistence length of a polymer chain.

Operating on both sides of Eq. (A1) with ∇^2 and assuming uniform density of solute, we get ($\xi^{-2} = 4\pi n_c e$, n_c = number chains per cm^3, $n_c = c/Z$, and c = number of monomers/unit volume.)

$$(\nabla^2 - \xi^{-2})\delta\vec{n}(\vec{r}) = -\xi^{-2}\vec{\nu}(\vec{r}) \qquad \text{(A2)}$$

If $\int_0^\infty |\nu(r)| r^2\, dr < \infty$ we may Fourier transform Eq. (A2) to arrive at

$$(\xi^2 q^2 - 1)\delta\vec{n}_q = -\vec{\nu}_q \qquad \text{(A3)}$$

Thus

$$\delta\vec{n}(\vec{r}) = \sum_{\hat{q}=0}^{1} \frac{\vec{\nu}_{\hat{q}/D}}{\left(1 - (\xi/D)^2 \hat{q}^2\right)} e^{-i\hat{q}\cdot\vec{r}/D} \qquad \text{(A4)}$$

In Eq. (A4) we set $\hat{q} = D\mathbf{q}$, with D as a cutoff under which no variation in δn is allowed.

Hence if $\xi/D \ll 1$ then $\delta\mathbf{n} \simeq \boldsymbol{\nu}$ and the solute and solvent orientation are strongly coupled. This implies the limit on the density n_c which we take as

$$n_c \gg \frac{1}{D^2 e} \qquad \text{(A5)}$$

Letting $D \simeq 50\ \mu$ and $e \simeq 50$ Å,[10] we arrive at $n_c \gg 10^{12}$ cm^{-3} ($c \gg Z \times 10^{12}$ cm^{-3}). Thus very small concentrations of nematic polymer may be used. This is desirable since the width of the nematic-isotropic two-phase region increases with increasing concentration of polymer.[12]

Recent birefringence and dichroism measurements of the nematic order S have been made by Finkelmann *et al.*[21] They conclude for the measured compounds that there is little difference in the temperature dependence of S within the nematic phase of either the LC side chain polymer or the LC monomer.

APPENDIX B

Some final points to be discussed are:

(1) We assumed the bonds between the main chain and the side chains are sufficiently stiff so that the side chains remain on the average perpendicular to the main chain in a strong flow field. In the absence of flow the equilibrium configuration of the chain will probably be disc-like so that a larger fraction of side-chains can point along the director. The viscosity measurements of Ref. (11) corroborate this view.

In our Eqs. (1) and (3) we assumed for simplicity spherical symmetry of chain configuration. This inconsistency may be weakened somewhat by placing the side groups further apart on the main chain and/or using a more flexible main-chain such as a polysiloxane backbone (chemical difficulties might be encountered here).

The proximity of a smectic phase will also enhance anisotropy in the average chain configuration, and in this case the results of this study will be qualitatively modified. In any case future study should include anisotropy in chain configuration, and interaction of this anisotropy with shear.

(2) Alignment of the solvent molecules in the elongational flow will tend to counteract the orientation induced by the coil-stretch transition in the polymer chain. At zero shear rate the director $\mathbf{n}\|\hat{z}$. When the coil-stretch transition occurs $\mathbf{n}$ rotates to the x-y plane. In a real system this rotation of the director may take place continuously. Treating the effect of the polymer solute as a body force analogous to a magnetic field $\mathbf{H}$ we can qualitatively illustrate the competition between flow alignment of the solvent and alignment through coil-stretch transition of solute by the following argument.

Flow exerts a torque Γ on the director.

$$\Gamma = \mathbf{n} \times \left\{ \gamma_1 \left(\dot{\mathbf{n}} - \tfrac{1}{2} (\nabla \times \mathbf{v}) \times \mathbf{n} \right) + \gamma_2 \hat{A} \mathbf{n} \right\} \tag{B1}$$

Here A_{ij} is the velocity gradient tensor, $\mathbf{v} = (-\kappa/2x, -\kappa/2y, \kappa z)$, $\nabla \times \mathbf{v} = 0$. Out of equilibrium this torque must equal the torque $\mathbf{n} \times \mathbf{h}$, exerted by the molecular field $\mathbf{h}$;[20]

$$\Gamma = \mathbf{n} \times \mathbf{h} \tag{B2}$$

From Eqs. (B1) and (B2) we may derive an equation for small transverse excursions of the director in the x-y plane. Putting the magnetic field $\mathbf{H} = H_0\hat{z}$ we have in the one-constant approximation k = Frank elastic constant,

$$h_\alpha = -\left(kq^2 + \chi_a H_0^2\right) n_\alpha, \qquad \alpha = x, y.$$

Assuming the spatial gradients of n are small ($\dot{\mathbf{n}} = \partial\mathbf{n}/\partial t + (\mathbf{v}\cdot\nabla)\mathbf{n} \approx \partial\mathbf{n}/\partial t$), we find the equation,

$$\gamma_1 \dot{n}_\alpha - \gamma_2 \frac{\kappa}{2} n_\alpha + \chi_a H_0^2 n_\alpha = 0 \tag{B3}$$

Letting $n_\alpha \sim \exp(-i\omega t)$ we get,

$$-i\omega\gamma_1 - \gamma_2 \frac{\kappa}{2} + \chi_a H_0^2 = 0$$

or

$$i\omega = \frac{1}{\gamma_1}\left\{|\gamma_2|\frac{\kappa}{2} + \chi_a H_0^2\right\} \tag{B4}$$

where we have written $\gamma_2 = -|\gamma_2|$.[20]

For the case of interest $\chi_a < 0$, the inequality

$$2\left|\frac{\chi_a}{\gamma_2}\right|\frac{H_0^2}{\kappa} > 1 \tag{B5}$$

implies n_α increases and the optical axis starts to rotate to the x-y plane.

Our parameter δ gives the strength of the orienting force of the polymer, and an inequality analogous to (B5) may be derived from Eq. (11)

$$\frac{T\delta\lambda}{2\beta S} > 1 \tag{B6}$$

When (B6) is satisfied the maximum of the distribution function for the orientation of the side groups shifts to $\theta = \pi/2$.

A self-consistent calculation including the flow orientation of the solvent probably increases the critical shear rate κ^* at which the coil-stretch transition takes place. The increase in order due to flow in the solvent increases the energy barrier the polymer side-groups must surmount during reorientation under stretching; therefore κ^* is increased.

Since the coil-stretch transition is mainly caused by energy transfer from center of mass motion of the solvent molecules into distortion of polymer configuration the effect of solvent flow orientation on κ^* should be small.

(3) If the preferred configuration of nematic polymer in the anisotropic state is disc-like with the side groups perpendicular to the disc [as in remark (1)], it is conceivable that flow orientation of the disc could cause the birefringence to change sign without the chains being stretched. In this case the polymer could be treated within a swarm model. The anisotropic Flory parameters $R_\perp$ and $R_\parallel$ being the radius and thickness of the swarm respectively.

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