Statistical model of polar nematic polymers

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The interaction in specially designed polymers may be dominated by the first rank $P_1(\cos\beta)$ type potential instead of the second rank $P_2(\cos\beta)$ type, as in conventional liquid crystal polymers ($P_1(\cos\beta)$ and $P_2(\cos\beta)$ are the first and second Legendre polynomials, respectively of the angle made by the polymer segments with respect to the preferred direction or director). The ordering of the polymers is envisaged in terms of the worm-like theory. The polymers show a polar nematic phase, that is a ferroelectric phase. These polymers have certain interesting properties, such as a second order polar nematic–isotropic transition, and related critical features. These materials are expected to exhibit giant dielectric responses. For more general polymer systems with interactions of both $P_1(\cos\beta)$ and $P_2(\cos\beta)$ types, we predict a peculiar phase behaviour.

1. Introduction

In recent years, the study of liquid crystal polymers is of increasing interest in both science and industry [1] These polymers are made up of mesogenic groups incorporated into the chain back bone or as side chain elements connected by suitable links to the main chain. In most of the liquid crystal polymers found so far, the dominant interacting potential between the monomers is quadrupolar in nature. However, in polar nematic polymers, the interest of the paper, the dipole interaction may be more important. As is well-known ferroelectricity has not been discovered in low molecular mass nematic liquid crystals. It does exist in chiral smectic liquid crystal phases such as S_C^* and S_I^* [2]. However the S_C^* phase has to be forced to unwind to give the usual ferroelectric properties. In contrast, no such unwinding is needed in the hypothetical ferroelectric nematic [3] and so attempts to find ferroelectric nematic liquid crystals have not disappeared. This paper is concerned with examining the possibility of their existence in main chain, semiflexible polymers and, if they exist, to predict their phase behaviour. The formation of a ferroelectric nematic depends on the dominance of the dipole interaction over the quadrupole interaction and the requirement that the energy of the dipole interaction, which is about the order of p^2/d^3 (where p is the dipole moment, d the average distance between the dipoles) has to be of the same order of magnitude as the thermal energy kT_c (where T_c is the transition temperature to the ferroelectric state). Unfortunately, with the possible exception of bowlic molecules [3], when the molecules have very large dipole moments they tend to form dimers with opposite directions of the dipole moments, which prevents the appearance of the spontaneous polarization.

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In consequence, semiflexible polymers, synthesized with large dipole moments in a sequence carried by the monomers along the chains in the same direction, may be better candidates for forming a polar nematic phase than the monomers. They have less tendency to form dimers after polymerization since two monomers of different chains being antiparallel does not imply in semiflexible chains that all other monomers in the two chains are also in contact with antiparallel monomers. Polar nematic polymers have been discussed by Lam [4] in terms of a lattice model, but only very dilute systems were discussed.

This paper is concerned with the nature of the phase transition between the polar nematic and isotropic phases, the character of the order of the polar nematic polymers, and their electric response.

2. The model

In this section, we apply the functional integral technique to describe orientational distribution of the tangent to the polymers and then map the problem into a diffusion equation of a particle on the surface of a unit sphere in a dipolar mean field. Because the polymer system is of the second type, as discussed later, its order parameters in the vicinity of the transition are small and hence a perturbation approach is a useful method in this region to examine the phase transition and the critical features of the system; at low temperatures the polar field becomes large and the asymptotic method is appropriate. In addition a numerical calculation is also carried out to give the complete dependence of the order parameter on temperature.

The functional integral technique, proposed by Feynman and Hibbs [5] to deal with questions in quantum mechanics, is naturally applied to the study of the statistical mechanics of the polymer system [6]. The functional integrals relate the configurations of a polymer to the paths of a particle when the particle is undergoing brownian or diffusive motion. If the chain is worm-like, the bending of the chain will cost an energy

$$\int_0^L \frac{\varepsilon}{2} \left[\frac{d\mathbf{u}(s)}{ds} \right]^2 ds, \tag{1}$$

where ε is the bending constant, L is the length of the polymer, and $\mathbf{u}$ is the tangent unit vector along the chain at arc length s so that

$$\mathbf{u} \cdot \mathbf{u} = 1. \tag{2}$$

We assume that such a main chain semiflexible polymer favours a long range order of parallel alignment, after summing along the chain, the dipolar potential is given by, in the mean field approximation,

$$U_q = - \int_0^L b\bar{P}_1 P_1(\cos \theta) \, ds, \tag{3}$$

where b is the coupling constant and is positive in this case, $P_1(\cos \theta) = \cos \theta$ is the first Legendre ploynomial, and $\bar{P}_1$ is the polar nematic order parameter.

In analogy to the P_2 case discussed by Warner *et al.* [7] and Wang and Warner [8], the angular diffusion equation in the dipole potential is given by, with $\beta = 1/kT$,

$$\left[\frac{\partial}{\partial s} - \frac{1}{2\beta\varepsilon} \nabla_\mathbf{u}^2 - \beta b\bar{P}_1 P_1(\cos \theta) \right] G(\mathbf{U}, \mathbf{U}'; s, s') = \delta(\mathbf{U} - \mathbf{U}')\delta(s - s'), \tag{4}$$

where $G(\mathbf{U}, \mathbf{U}'; s, s')$ is the Green function for the diffusion equation and $\delta(x - x')$ is the Dirac delta function. Note that in G the argument is the arc position s instead of time, $1/(2\beta\varepsilon)$ acts like a rotational diffusion coefficient and we denote $1/(2\beta\varepsilon)$ by D later on; D^{-1} is the persistence length. For a uniaxial system G becomes, assuming the s-dependent factor $\exp(-\lambda_n D|s - s'|)$,

$$\left[\lambda_n + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) + gP_1(\cos\theta)\right]\psi_n(\theta) = 0, \tag{5}$$

where λ_n are the eigenvalues and the coupling constant $g \equiv \beta b \bar{P}_1/D = 2\bar{P}_1/\tilde{T}^2$ with the reduced temperature $\tilde{T} = kT/(b\varepsilon)^{1/2}$. The eigenfunctions are $\Psi_n(\theta)$ and so the Green function is

$$G(\theta, \theta'; s, s') = \sum_{n=0}^{\infty} \psi_n(\theta)\psi_n(\theta')\exp(-\lambda_n D|s - s'|). \tag{6}$$

Knowing the Green function we are able to obtain the statistical properties of the chain, e.g. the polar order parameter. By definition the order parameter, which is the ensemble average of $P_1(\cos\theta)$, is expressed in terms of the Green function as

$$\bar{P}_1 = \frac{1}{L}\left\langle \int_0^L ds P_1(z) \right\rangle$$

$$= \int_0^L \frac{ds}{L} \frac{\iiint dz\,dz'\,dz''\, G(z', z; L, s)G(z, z''; s, 0)P_1(z)}{\iiint dz\,dz'\,dz''\, G(z', z; L, s)G(z, z''; s, 0)}, \tag{7}$$

where $z = \cos\theta$.

We first investigate the phase behaviour of the polymers in terms of the analytic approach, that is the perturbation approach for the temperature region at the polar nematic–isotropic transition and the asymptotic method for low temperatures, and these are followed by numerical calculations.

2.1. *Perturbative approach*

Considering $gP_1(\cos\theta)$ as a perturbation term, the unperturbed differential equation is the Legendre equation. Therefore, to first order in g, the eigenfunctions of the operator in equation (5) are given by

$$\left.\begin{aligned}
\psi_0(\theta) &= \frac{1}{\sqrt{2}}P_0 + \frac{g}{2\sqrt{2}}P_1(\cos\theta), \\
\psi_1(\theta) &= -\frac{g}{2\sqrt{6}}P_0 + \sqrt{\left(\frac{3}{2}\right)}P_1(\cos\theta) + \frac{g}{2\sqrt{6}}P_2(\cos\theta).
\end{aligned}\right\} \tag{8}$$

If the chain is long enough the ground state ($n = 0$) dominates in G because of the exponential dependence on L. Putting Ψ_0 into equation (6) and then into equation (7) we immediately obtain the second order polar nematic–isotropic (P–I) phase transition which occurs at $\tilde{T}_c = (2/3)^{1/2} = 0.816$.

The free energy F per chain is given to fourth order in the perturbation by

$$F/(kTLD) = \lambda_0 + \frac{\bar{P}_1^2}{\tilde{T}^2} \cong -\frac{g^2}{6} + \frac{\bar{P}_1^2}{\tilde{T}^2} + \frac{11}{1080}g^4$$

$$= \left(\tilde{T}^2 - \frac{2}{3}\right)\frac{\bar{P}_1^2}{\tilde{T}^4} + \frac{22}{135}\frac{\bar{P}_1^4}{\tilde{T}^8};$$ (9)

F is always less than zero in the polar phase as $\tilde{T} < \tilde{T}_c (=(2/3)^{1/2})$ and so the polar phase is stable.

Minimization of the free energy in (9) gives the polar order parameter $\bar{P}_1$ for the temperature range immediately below the transition. The result is

$$\bar{P}_1 = \alpha\tilde{T}^2\left(1 - \frac{3}{2}\tilde{T}^2\right)^{1/2},$$ (10)

where α is a constant $= \sqrt{(45/22)}$.

2.2. Finite chain

If the chains are not very long, the excited states become important. For the sake of simplicity we include one higher excited state only and so the P–I transition occurs at

$$\tilde{T}_c(L) = \tilde{T}_c(\infty)\left[1 - \frac{1}{2LD}[1 - \exp(-2LD)]\right].$$ (11)

The term in the square brackets is actually the ratio of the mean square dimension relative to its value when L is infinite at the isotropic state, i.e. $\langle R^2 \rangle/(LD^{-1})$. The equation implies that the transition temperature is proportional to the mean square dimension of the polymer. The neglect of even higher terms does not change the result significantly. The term from the second excited state is only 2 per cent of that from the first excited state even when LD is as small as unity. Equation (11) gives the long chain result if $L \gg D^{-1}$.

2.3. Asymptotics

In the strong polar nematic limit, either at low temperature or with a strong polar potential, θ is confined around the region near a pole, e.g. $\theta = 0$. We may then solve the problem asymptotically and approximately for small θ. In this limit equation (5) is rewritten as

$$\left[\frac{d^2}{d\theta^2} + \cot\theta\frac{d}{d\theta} - \frac{g}{2}\theta^2 + (\lambda + g)\right]\psi = 0,$$ (12)

which is equivalent to equation (6.1) of [7] despite the up-down symmetry of the director being absent in our case since we are interested only in states close to one pole of the tangent's sphere. Since then these states are similar to those in the nematic problem we obtain

$$\bar{P}_1 = 1 - \frac{1}{\sqrt{2g}} = 1 - \frac{\tilde{T}}{2\sqrt{\bar{P}_1}}$$ (13)

which is a cubic equation in $\bar{P}_1^{1/2}$. There are three real roots of the cubic, two of which are discarded on physical grounds. The relevant solution for $\bar{P}_1$ is given by

$$\bar{P}_1 = \frac{4}{3}\cos^2\left[\frac{1}{3}\cos^{-1}\left(-\frac{3\sqrt{3}}{4}\tilde{T}\right)\right]. \tag{14}$$

2.4. *Numerical results*

We also calculate the polar order parameter numerically. Following the approach used in solving the problem for conventional nematic polymers [8] we expand the eigenfunctions in terms of Legendre polynomials as

$$\psi_n = \sum_{m=0}^{\infty} c_{n,m} P_m(z). \tag{15}$$

Substituting equation (15) back into equation (5) we obtain a set of linear equations for the expansion coefficients $c_{n,m}$, viz.

$$\frac{m}{2m-1}gc_{n,m-1} - m(m+1)c_{n,m} + \frac{m+1}{2m+3}gc_{n,m+1} = \lambda_{n,m}c_{n,m}. \tag{16}$$

Putting equation (15) into equation (7) for $\bar{P}_1$ and using ground state dominance, we obtain

$$\bar{P}_1 = \int_{-1}^{1} z[\psi_0(z)]^2 \, dz \bigg/ \int_{-1}^{1} [\psi_0(z)]^2 \, dz$$

$$= \sum_{m=0}^{\infty} \frac{c_{0,m}}{2m+1}\left[\frac{m}{2m-1}c_{0,m-1} + \frac{m+1}{2m+3}c_{0,m+1}\right]. \tag{17}$$

The numerical results are shown as the dark line in figure 1, while the dashed line and the dotted line are the perturbation results and asymptotic calculation, respectively. It demonstrates that the perturbation and asymptotic approaches work well around the transition and in the low temperature region, respectively.

3. Field effects and critical features

Low molecular mass nematic liquid crystals are well-known [9–13] to respond to external fields which couple either to the positive diamagnetic anisotropy of molecules or their anisotropy of molecular polarizability in the electric field case. Among these Palffy-Muhoray *et al.* [13] have examined the possibility of ferroelectric nematics. The field effects were also studied for a conventional nematic polymer [14, 15].

In the underlying polar nematic polymer system, when an electric field **E** is applied, its contribution to the energy is given by

$$U_f = -\int_0^L \boldsymbol{\mu} \cdot \mathbf{E}\, ds = -\mu E \int_0^L P_1(\cos\theta)\, ds, \tag{18}$$

where μ is the dipole moment which is along the tangent of the chain. Instead of equation (5), in this case we have

$$g = 2(\bar{P}_1 + \gamma)/\tilde{T}^2 \tag{19}$$

where $\gamma \equiv \mu E/b$. A procedure similar to those in the field-free case and in the conventional nematic case when an external field is applied [15] is carried out. The order parameter $\bar{P}_1$ can be obtained straightforwardly for a long chain. In an applied
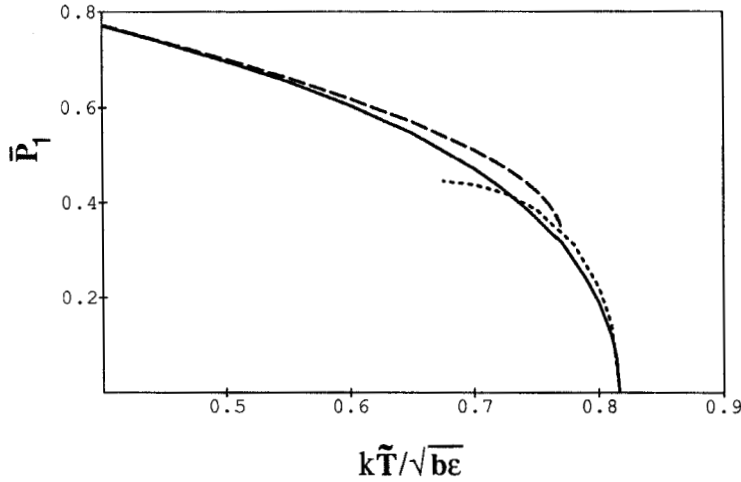
Figure 1.   The order parameter $\bar{P}_1$ as a function of scaled temperature $\tilde{T}$. The dotted and dashed lines show the perturbation and asymptotic results, respectively. The full line is the numerical result.
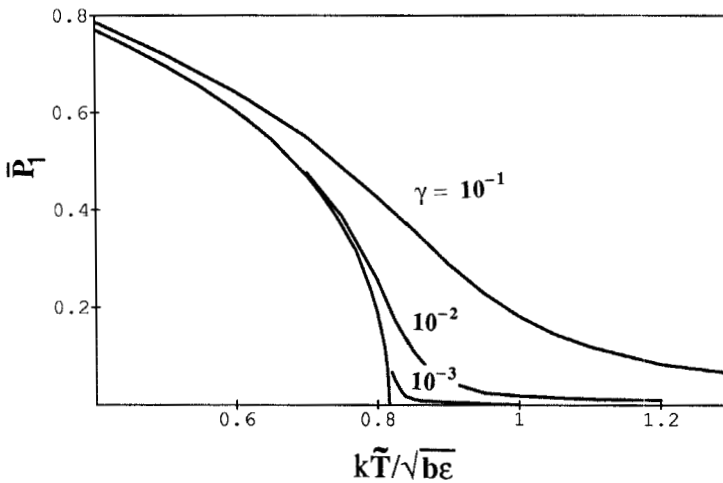

Figure 2.   The order parameter as a function of the normalized temperature and the external electric field.

field $\bar{P}_1$ is not only a function of T, but also of γ as well. Figure 2 presents the numerical results. In an applied electric field the phase gap disappears. The order parameter $\bar{P}_1$ at high temperature is no longer zero because the external field induces polymer order. The perturbative approach is also applicable to describe the critical behaviour.

After some algebra we obtain the dielectric susceptibility of the polymers χ above the transition

$$\chi = \left(\frac{\partial P}{\partial E}\right)_{E \to 0}$$

$$= \frac{\mu^2}{bd^2}\left\{\frac{\tilde{T}^2}{|\tilde{T}^2 - \tilde{T}_c^2|} - 1\right\} \cong \frac{\mu^2}{2bd^2}\frac{T}{|T - T_c|} \tag{20}$$

and below the transition

$$\chi \simeq \frac{\mu^2}{4bd^2} \frac{T}{|T - T_c|},\tag{21}$$

where P is the polarization and d the sectional dimension. The exponent for χ is -1, the classical exponent as expected from mean field theory. The ratio of the Curie constants above and below $\tilde{T}_c$ is 2 which is confirmed by the numerical calculation.

4. Giant dielectric response

We predict a giant dielectric response. The polarization vector $\mathbf{P}$ is given, generally, by

$$\mathbf{P} = \chi \cdot \mathbf{E} + \chi^{(2)} : \mathbf{EE} + \chi^{(3)} : \mathbf{EEE}\tag{22}$$

where χ, $\chi^{(2)}$, $\chi^{(3)}$ are the linear and non-linear dielectric susceptibilities, respectively. In addition, the gradient of the electric field may contribute to the polarization, but it is not important in our case.

For the low molecular mass liquid crystals, the dielectric response χ_m is

$$\chi_m = \frac{1}{3} \frac{d\mu^2}{kT d^2 \varepsilon_0}.\tag{23}$$

For the nematic polymer, Gunn and Warner [14] predicted the linear polarization susceptibility χ_{np} to be given by

$$\chi_{np} = \frac{L\mu^2}{kT d^2 \varepsilon_0}$$

$$= 3\chi_m \left(\frac{L}{d}\right),\tag{24}$$

which is greater than χ_m by a factor of $3L/d$, the degree of polymerization. In polar nematic polymers, the polymers in the same domain respond as a whole and thus the linear susceptibility χ_{pp} is predicted to be

$$\chi_{pp} = n\frac{1}{3} \frac{L\mu^2}{kT d^2 \varepsilon_0}$$

$$= \chi_m \left(\frac{L}{d}\right) n.\tag{25}$$

It is even greater by a factor of the average number n of molecules in a domain. Accordingly, the non-linear dielectric response of the polar nematic polymers is also larger. A concomitant hysteresis of polarization versus applied electric field is also expected.

5. General systems: polar and nematic interactions

Based on the method and results for systems with either the potential of $P_1(\cos\theta)$ or $P_2(\cos\theta)$, we consider the more general case with both dipole and quadrupole interactions. Here

$$U_{dq} = -\int_0^L [b\bar{P}_1 P_1(\cos\theta) + a\bar{P}_2 P_2(\cos\theta)]\, ds.\tag{26}$$
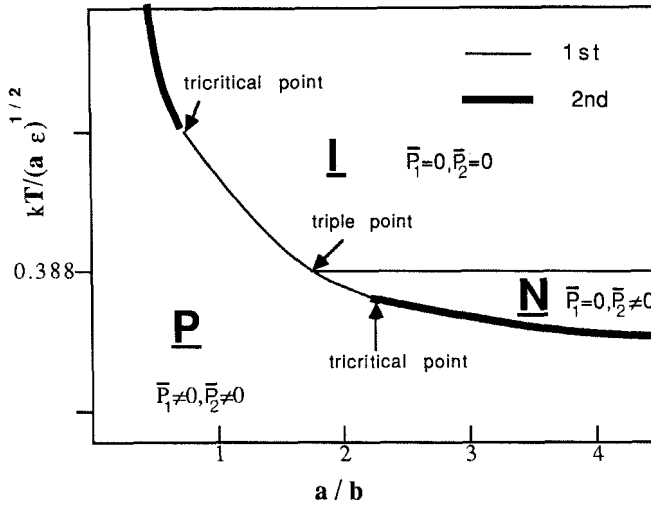
Figure 3.   The phase diagram for a general liquid crystal polymer system.

The $\bar{P}_1$ and $\bar{P}_2$ are the polar and the conventional nematic order parameters respectively, defined in the usual manner.

In the isotropic liquid state, $\bar{P}_1 = \bar{P}_2 = 0$; the usual non-polar nematics have $\bar{P}_1 = 0$, and $\bar{P}_2 \neq 0$; the polar nematic phase has both $\bar{P}_1$ and $\bar{P}_2$ not equal to zero. Krieger and James [16] have studied the phase diagram for molecular crystals with the potential

$$U = bP_1(\cos\theta) + aP_2(\cos\theta).\tag{27}$$

Later Ypma and Vertogen [10] examined the effect of permanent dipoles on the nematic–isotropic phase transition by assuming a similar potential. Their phase diagram is analogous to that in the mean field approximation [16]. Leung and Lin [17] suggested the same form of interaction for bowlic liquid crystals and then obtained a similar phase diagram. The sign of the dipolar coupling constant, b, determines whether the ferroelectric (minus sign) or antiferroelectric state (plus sign) appears. A similar phase diagram has also been obtained by Palffy-Muhoray et al. [13] by means of the Laudau–de Gennes theory. In analogy to those in the molecular crystals and the low molar mass liquid crystals we predict a phase diagram for the main chain polymer system with the interaction of equation (26). It is depicted in figure 3 where the ordinate is the ratio of quadrupolar to dipolar coupling constant, a/b, and the abscissa is the reduced temperature $kT/(a\varepsilon)^{-1}$. The scaling is a basic difference with the case of low molar mass materials and indicates that the contribution of the polymer stiffness plays an important role as does the nematic part.

It has been shown that the nematic phase does not exist if the quadrupolar coupling constant a is small, and the transition from the nematic to the isotropic phase is essentially independent of the dipolar coupling constant b, as for example at $kT/(a\varepsilon)^{1/2} = 0.388$. When b is small the dipolar interaction serves as an external field applied to the nematic polymers and it then makes the nematic–isotropic transition temperature shift slightly in a manner analogous to that in the low molar mass liquid crystals [9] or main chain nematic polymers [15]. The transition between the polar nematic phase and the isotropic phase is second order when the dipolar interaction dominates, i.e. a/b is small. As a/b increases the quadrupolar interaction becomes comparable with the dipolar

interaction, and then the transition becomes first order via a tricritical point. On further increase of a/b, a triple point appears where the isotropic, the polar and the nematic phases co-exist. Thereafter the nematic phase appears between the isotropic and the polar nematic phase. The transition from polar to nematic phase starts being first order. After a tricritical point this transition develops to second order because the quadrupolar interaction becomes significant. The temperature range of the nematic phase widens and finally the polar nematic phase would be shadowed by a glass transition. This is then the case of the conventional nematic limit.

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