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# Mean-field theory for the phase transitions of nematic polymers in a magnetic field: application to magnetic birefringence

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With the help of a theory which is based on functional integrals, we calculate the evolution, with temperature and degree of polymerization, of the orientational order parameter of thermotropic nematic polymers under a magnetic field. We compare our results with those obtained experimentally from magnetic birefringence measurements on polyesters. The validity of the application of the mean-field theory in the case of semiflexible liquid crystal polymers which consist of sequences of mesogenic units and flexible spacers is also discussed. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: mean-field theory; nematic polymers; magnetic birefringence)**

## INTRODUCTION

Semirigid polymers, in solution or in the melt, have received much attention through experimental[1–9] and theoretical[10–20] work in recent years. The study of the nematic–isotropic transition has been one of the most important goals. Although the influence of external fields has been studied theoretically for rigid-rod macromolecules, as, for example, in the case of elongational flow[21–23], some theoretical work has already been devoted to investigations on semirigid polymers[13,24–26].

As the temperature of the nematic–isotropic transition is reached, a number of physical properties exhibit divergences. Such pretransitional effects are shown by measurements of the intensity of the scattered light and of the electric- and magnetic-field-induced birefringence[27–30].

This paper deals with the influence of a magnetic field on the phase transition of a semi-rigid polymer, which is described here through the use of the elastic worm-like chain model, as previously reported[14]. We also give some comments and observations on the experimental work carried out on the magnetic birefringence of various polyesters.

## THEORY

The polymer is described as a worm-like chain, with a continuous space curve of contour length $L$ and a bending elastic constant $\kappa$. The chain stiffness is also defined by its persistence length, i.e. $q = \kappa/kT$. All lengths are given in monomer units, so that $L$ is equal to the degree of polymerization. Here we only consider the elastic intramolecular interactions between neighbouring segments. The elastic energy associated with the chain is given by the following[31]:

$$U_{\mathrm{el}} = \frac{\kappa}{2}\int_0^L \mathrm{d}s\left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 \tag{1}$$

with $\boldsymbol{r}$ being the tangent to the curve at a contour distance $s$ from the origin of the chain (*Figure 1*), where $|\boldsymbol{r}| = 1$.

The segments of the different chains themselves interact with each other, due to steric constraints and dispersion forces. Orientation-dependent interactions, due to the cylindrical symmetry of the polymer segments, are assumed to be predominant. The local orientation of a polymer segment (the orientation of $\boldsymbol{r}$ at $s$) with respect to the nematic axis (which is taken as the $z$-axis) is $\theta(s)$ (*Figure 1*). These interactions can induce the appearance of nematic order, and the order parameter per segment is then defined as follows:

$$S = \left\langle \frac{1}{L}\int_0^L \mathrm{d}s P_2[\cos\theta(s)] \right\rangle \tag{2}$$

with $\langle\ \rangle$ being the thermodynamic average over all the chain conformations, and $P_2[\cos\theta(s)]$ the usual second-order Legendre polynomial, i.e. $1/2[3\cos^2\theta(s) - 1]$.

The potential, at point $s$, due to the intermolecular interactions, is then given as follows:

$$v(s) = -uSP_2[\cos\theta(s)] \tag{3}$$

where $u$, the effective strength of the average orientational intersegement interaction, represents an average over the intermolecular distance.

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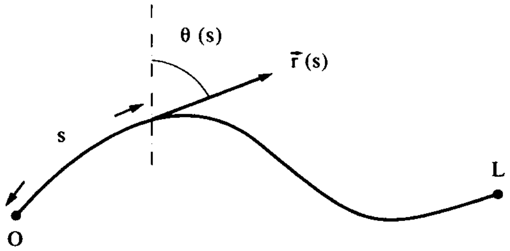


**Figure 1** Conformation of a worm-like polymer chain

Next, we consider a magnetic field $\boldsymbol{H}$, applied along the $z$-direction. A polymer segment will experience a torque, due to its magnetic anisotropy $\Delta\chi(=\chi_{\parallel}-\chi_{-})$, with $\chi_{\parallel}$ and $\chi_{\perp}$ being respectively the magnetic susceptibility, parallel and perpendicular to the backbone of the polymer. This torque tends to align the segments parallel to the magnetic field when $\Delta\chi$ is positive or perpendicular to the field when it is negative. For simplicity, we only consider positive values of $\Delta\chi$, i.e. the case, for example, of polymers containing benzene rings in the polymer chains, such as certain polyesters[32].

Therefore, the nematic axis, for a uniform phase, is parallel to $\boldsymbol{H}$. This external field introduces an increase in the potential at point $s$, which is given by the following expression:

$$-\tfrac{1}{3}\Delta\chi P_2[\cos\theta(s)]\boldsymbol{H}^2-\tfrac{1}{6}\bar{\chi}\boldsymbol{H}^2 \tag{4}$$

where $\bar{\chi}(=(2\chi_{\perp}+\chi_{\parallel})/3)$ is the average magnetic susceptibility[33], when $\boldsymbol{H}=0$. Let us take $v_{\mathrm{e}}=1/3\Delta\chi\boldsymbol{H}^2$, so that the orientation-dependent part of the potential due to the field $\boldsymbol{H}$ is $v_{\mathrm{e}}(s)=-v_{\mathrm{e}}P_2[\cos\theta(s)]$. Then, the total orientational energy for a polymer chain is given by the following:

$$\int_0^L \mathrm{d}s[v(s)+v_{\mathrm{e}}(s)].$$

Up until now, we have only considered a thermotropic polymer, in the melt. In the case of a lyotropic polymer in solution in an ideal solvent of spherical molecules, without any polymer–solvent interactions, all of the above remains valid if we replace $u$ by $uX$, with $X$ being the volume fraction of the polymer (keeping in mind, as mentioned above, that $u$ represents an average for the intermolecular distances). Mixtures with interacting solvents (e.g. liquid crystals) have been treated in other publications[29,34].

## CALCULATIONS

In order to obtain the orientational order of the polymer chain in the presence of a magnetic field, we need to calculate thermodynamic averages for the polymer chain[14]. The expression for the Boltzmann factor associated with a polymer conformation is as follows:

$$\exp\left\{-\beta\left[\frac{\kappa}{2}\int_0^L \mathrm{d}s\left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2+\int_0^L \mathrm{d}s\left(v(s)-\frac{\langle v(s)\rangle}{2}+v_{\mathrm{e}}(s)\right)\right]\right\} \tag{5}$$

with $\langle v(s)\rangle=-uS^2, v_{\mathrm{e}}(s)$ is the contribution of the external field, and $\beta=1/\kappa_{\mathrm{B}}T$ ($\kappa_{\mathrm{B}}$ is the Boltzman constant). We introduce the statistical weight, $G(\boldsymbol{r},\boldsymbol{r}',L)$, which measures the probability of finding a polymer, with a given conformation and an orientation $\boldsymbol{r}$ at contour length $s=0$, and $\boldsymbol{r}'$ at $s=L$, which is given as follows:

$$G(\boldsymbol{r},\boldsymbol{r}'L)=\int d\{\mathrm{conf}\}\delta[\boldsymbol{r}(0)-\boldsymbol{r}]\delta[\boldsymbol{r}(L)-\boldsymbol{r}'] \times\exp\left\{-\beta\left[\frac{\kappa}{2}\int_0^L \mathrm{d}s\left(\frac{\partial\boldsymbol{r}}{\partial s}\right)^2 +\int_0^L \mathrm{d}s\left(v(s)-\frac{\langle v(s)\rangle}{2}+v_{\mathrm{e}}(s)\right)\right]\right\} \tag{6}$$

Thus, we can calculate the orientational order parameter through the following self-consistent equation:

$$S=\frac{1}{ZL}\int_0^L \mathrm{d}s \times\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\mathrm{d}\boldsymbol{r}''G(\boldsymbol{r},\boldsymbol{r}',s)P_2[\cos\theta(s)]G(\boldsymbol{r}'',\boldsymbol{r}',L-s) \tag{7}$$

with $Z=\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'G(\boldsymbol{r},\boldsymbol{r}',L)$ being the partition function of the polymer.

As mentioned before[14], $G(\boldsymbol{r},\boldsymbol{r}',L)$ is the solution of a differential equation, namely the following:

$$\left[\frac{\partial}{\partial L}-\frac{1}{2\beta\kappa}\Delta_{\boldsymbol{r}'}+\beta\left(v(s)-\frac{\langle v(s)\rangle}{2}+v_{\mathrm{e}}(s)\right)\right]G(\boldsymbol{r},\boldsymbol{r}',L) =\delta[\boldsymbol{r}(0)-\boldsymbol{r}']\delta(L) \tag{8}$$

and the problem is thus reduced to the calculation of eigenvalues and eigenvectors of a matrix system which was chosen to be of the order seven, so as to obtain sufficient precision.

Let $v_{\mathrm{e}T}(=v_{\mathrm{e}}/u)$ be the relative strength of the external field with regard to the intermolecular interactions. For each value of $v_{\mathrm{e}T}$, we calculate, self consistently, the value of $S$ for various temperatures. The system has almost always one solution: for rather low temperatures, $S>0$ corresponds to the nematic phase, for high temperatures, $S$ is very small but different from zero, and for the intermediate range of temperatures, these two solutions may co-exist with another one which corresponds to a maximum of the free energy.

For sufficiently small $v_{\mathrm{e}T}$ value, a first-order transition from a very low ordered phase to a higher ordered nematic one exists at a temperature $T_{\mathrm{c}}$ (*Figure 2*). We only calculate here a 'pseudo-transition' temperature[35] where the free energies are equal in the two phases and we neglect the biphasic domain. At the transition, the orientational order parameter jumps from a value $S_{\mathrm{c_i}}$ to a value $S_{\mathrm{c_n}}$.

For a critical value $v_{\mathrm{ec}}$ of the external field, $S_{\mathrm{c_i}}$ and $S_{\mathrm{c_n}}$ merge in a single solution, the transition is no more first-order in nature, and for greater values there is no longer a transition, with the order parameter exhibiting a smooth and increasing behaviour when the temperature is lowered (*Figure 2*). The corresponding $v_{\mathrm{erc}}(=v_{\mathrm{ec}}/u)$ value seems to be always ca. $10^{-2}$.

A plot of the transition temperature *versus* the external field shows a linear variation (*Figure 3*), with a $T_{\mathrm{c}}$ maximum deviation from $T_{\mathrm{c}}(v_{\mathrm{c}}=0)$ of some tens of degrees at $v_{\mathrm{ec}}$ (typically $\sim 20\,\mathrm{K}$). Thus the external field

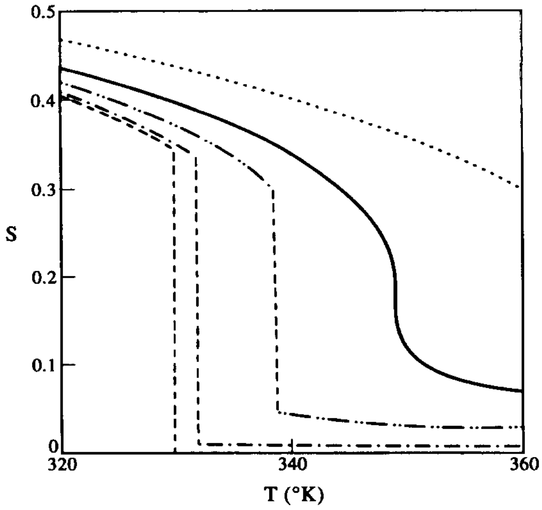


**Figure 2** Influence of the external field $v_{er}$ on the temperature variation of the order parameter $S$, obtained by the direct calculus method, with $L = 20, q = 10$ and $T_c(v_e = 0) = 330\,K$: (– – –) 0; (–·–·) $10^{-3}$; (– ··· ··) $4.5 \times 10^{-3}$; (——) $10^{-2}$; (· · ·) $2.4 \times 10^{-2}$

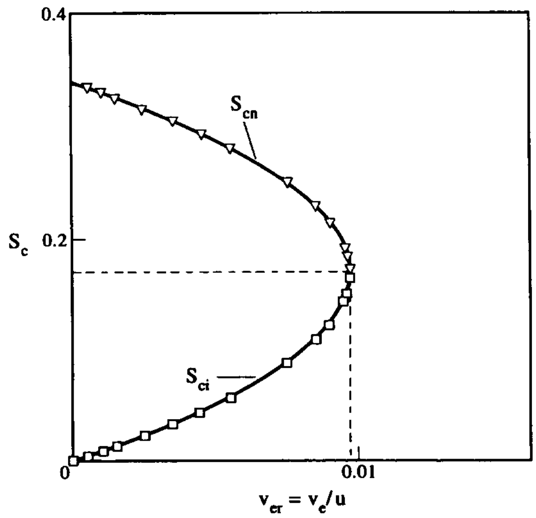


**Figure 4** Variation of the order parameters at the transition, in the isotropic ($S_{c_i}$, □) and anisotropic ($S_{c_n}$, ▽) phases, as a function of $v_{er}$; the parameters of the chain are the same as in *Figure 2*

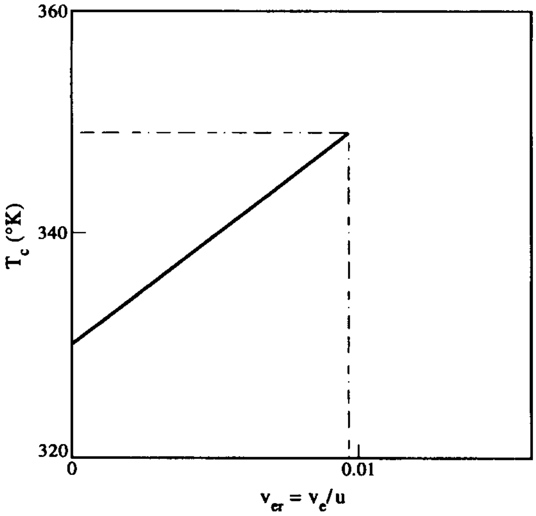


**Figure 3** Variation of the nematic–isotropic transition temperature $T_c$ with the external field $v_{er}$, from the direct calculus method; the polymer parameters are $L = 20$ and $q = 10$

induces some order in the isotropic phase and moves the transition point towards higher temperatures. We note that for $v_e < v_{ec}$, the greater $v_e$ is, then the lower is $S_{c_n}$ and the greater is $S_{c_i}$, until $v_e = v_{ec}$ where $S_{c_n} = S_{c_i} \sim S_c(v_e = 0)/2$ (*Figure 4*).

Calculations can also be done by using a Landau–de Gennes-type expansion of the free energy, as follows[25,26]:

$$\Delta F_e = F_e(S) - F_e(0)$$
$$= ES + A(T - T^*)S^2 - BS^3 + CS^4 \qquad (9)$$

The coefficients $E, A, B$ and $C$ are dependent on the external field, while $E, B$ and $C$, moreover, are also temperature dependent. They are determined by an expansion of the partition function given in the case of the previous calculus method. Thus, all of the expressions obtained previously for an elongational flow are derived in this present study, in the same manner, for a magnetic field.

We shall call this type of approach the LDG (Landau–de Gennes) method, and the first approach the direct calculus methods which, as a result, can be applied with an elongational flow.

Both methods give the same qualitative results: a linear variation of the transition temperature with the external field, a critical value of the external field $v_{ec}$, above which no transition still occurs, with only a smooth variation of the order parameter with the temperature, and for $v_e < v_{ec}$, a jump of the order parameter at the transition, from $S_{c_i}$ to $S_{c_n}$, with $S_{c_i}$ ($S_{c_n}$) being an increasing (decreasing) function of $v_e$. The direct method gives good precision but needs quite long numerical calculations, while the LDG method shows poor precision but uses simple analytical expressions.

In both methods, we need three polymer parameters. Two are clearly characteristics of the chain, namely the degree of polymerization, $L$, and the persistence length, $q$, estimated, for example, from intrinsic viscosity measurements[36–38], while the third one may be either the transition temperature without an external field $T_c(v_e = 0)$ or the effective strength of the orientational interaction $u$. If one chooses, as we have done, the first one, i.e. $T_c(v_e = 0)$ (easily determined experimentally), the two methods do not give the same value for $u$. Although the difference is only of the order of a few calories per mole, if one takes the value $u$ obtained from one method and uses it in the second method, this will introduce a great variation in $T_c(v_e = 0)$ ($\sim$ tens of degrees).

Let us rewrite the resulting expressions of the LDG method as follows:

$$T_c = T_c(v_e = 0)\left[1 + \left(\frac{2}{S_c(v_e = 0)}\right)\frac{v_e}{u}\right] \qquad (10)$$

$$S_{c_{i,n}} = \tfrac{1}{2} S_c(v_e = 0)[1 \mp (1 - \delta)^{1/2}] \mp (1 - \delta)^{1/2}\left(\frac{v_e}{u}\right) \qquad (11)$$

with $\delta = v_e/v_{ec} \leq 1$.

The application of equation (10) to the data obtained with the direct method shows very good agreement, with the error being less than $10^{-3}$ for $v_{er} \leq 10^{-3}$ and reaching

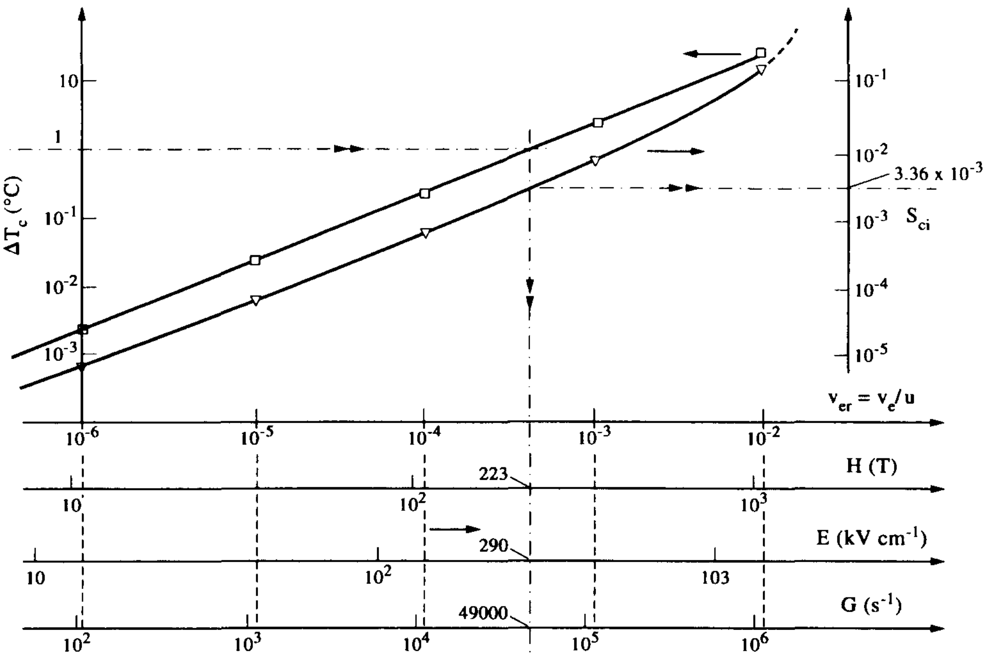


**Figure 5** Shift of the transition temperatures $T_c$ and order parameters in the paranematic phase $S_{c_i}$ (from the direct calculus method, with the molecular parameters $L = 14.6, q = 1$) as a function of the external field with various scales $(v_{er}, H, E, G)$; $u = 5.6458$ kcal mol$^{-1}$, $\Delta\chi = 0.99 \times 10^{-28}$ erg G$^{-2}$, $\Delta\epsilon = 10$, $f \sim 4 \times 10^{-8}$ g s$^{-1}$

$5 \times 10^{-2}$ at around $v_{er_c}$ (always below the practical experimental precision). Equations (11) are also good expressions for fitting the results of the direct method, with an error of ca. 5%.

Therefore, the expressions given by the LDG method seem to be good approximations for the direct calculus approach. By keeping this in mind, both the LDG and the direct calculus approaches will become complementary methods in our investigations. We can, for example, obtain the interaction parameter $u$ and the order parameter at the transition $S_c(v_e = 0)$, without an external field, by using the direct method (with the procedure given in refs 25 and 26). This allows us to obtain a good estimation of the modifications introduced by the application of an external field $v_e$, just with the help of equations (10) and (11). A better precision can be reached via the direct calculations, if necessary.

The maximum strength of the magnetic field which can be easily obtained for practical use is, at the present time, around 10 T and leads to $v_{e_r}$ values of ca. $10^{-6}$. Thus, by the use of such fields, we cannot hope to reach the critical point $v_{ec}$ and the shift of $T_c$ will be undetectable within the useful experimental precision. However, the application of such magnetic fields will induce an order parameter of $\sim 10^{-5}$ in the isotropic phase—the so-called 'paranematic' phase—and we shall see later that these calculations will be of some practical interest.

The usual values obtained for the strain rate of a flow field are 10 to 50 000 s$^{-1}$[13], so we can expect in the case of elongational flows, to have the strongest orientational effects.

The same procedure as given above can be used with an electric field (when there is no electrical conduction) by using $v_e = 1/3(\Delta\epsilon/4\pi)E^2$, with $\Delta\epsilon$ being the anisotropy of the dielectric permittivity and $E$ the strength of the electric field. Strong effects are also expected in this case.

A typical plot of the shift of the transition temperature $T_c$ and of the associated induced order parameter $S_{c_i}$, in the paranematic phase, is shown in *Figure 5*, as a function of the external field, expressed on a multiscale axis (the relative external field $v_{e\tau}$, with the corresponding magnetic ($H$), electric ($E$) and elongational flow ($G$) field strengths). We have taken the usual values of $\Delta\chi \sim 10^{-7}$ emu cgs g$^{-1}$ (refs 39 and 40), $\Delta\epsilon \sim 10$ (ref. 41), and a friction coefficient in dilute solutions of $\sim 10^{-8}$ g s$^{-1}$ (ref. 21) (the estimations for concentrated solutions or pure melt polymers being very difficult). We can see that a magnetic field of 10 $T$ is equivalent to an electric field of 10 kV cm$^{-1}$ (for a sample of 10 $\mu$m thickness, under 10 V) and to a strain rate of 100 s$^{-1}$. Thus, it seems that electrical and elongational flow fields will be easier to handle for practical interest. A shift of ca. 1 K in the transition temperature and an orientational order parameter of ca. $10^{-3}$ in the paranematic phase will, theoretically, be obtained for $H \sim 225$ T, $E \sim 300$ kV cm$^{-1}$ and $G \sim 50\,000$ s$^{-1}$.

## RESULTS AND DISCUSSION

Magnetic birefingence experiments allow the estimation of the orientational order of a nematic polymer in its paranematic phase, via the measurement of the anisotropy of the refractive index, $\Delta n = n_\parallel - n_\_$, with $n_\parallel$ and $n_\perp$ being the refractive index for light electric polarization, respectively, parallel and perpendicular to the nematic director **n** and $\boldsymbol{H}$. The parameter $\Delta n$ is used to calculate the Cotton-Mouton ($CM$) constant from the following:

$$\Delta n = CM\lambda\boldsymbol{H}^2 \qquad (12)$$

where $\lambda$ is the wavelength of light.

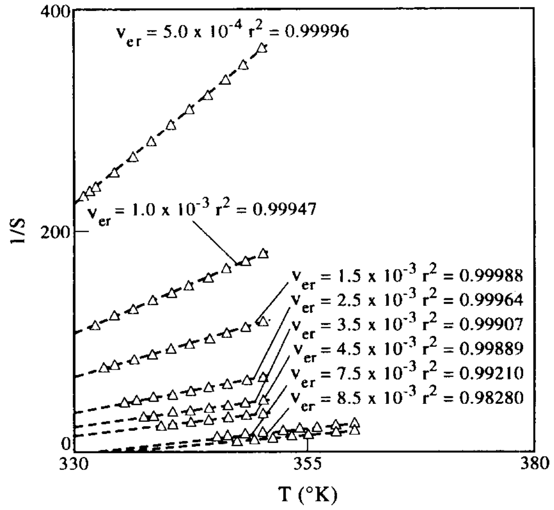


**Figure 6** Influence of the external field $\nu_{er}$ on the variation of $1/S$ with $T$, from the direct calculus method with the polymer parameters $L = 20$, and $q = 10$ $r^2$ are the linear regression coefficients of the curves

A plot of $1/CM$ *versus* the temperature $T$ shows a linear variation, as follows:

$$\frac{1}{CM} = A_2(T - T^*) \tag{13}$$

and gives the so called $T^*$ temperature, at the intersection on the $T$-axis by a linear extrapolation[42]; $T^*$ corresponds to the limit of metastability of the isotropic phase and $A_2$ is related to the second virial coefficient. For liquid crystal molecules, it is well known that $T^*$ is just a few degrees below the isotropic-to-nematic phase transition temperature $T_c$ while for nematic polymers, the difference $(T_c - T^*)$ is greater and lies around 20–30 K [42].

We shall use some of the theoretical results obtained previously to try to understand this phenomenon. It is known that $\Delta n$ can be related to the anisotropy of the dielectric susceptibility $\Delta\epsilon$, and we can write $\Delta\epsilon = (\epsilon_\| - \epsilon_\perp) = (\sqrt{\epsilon_\|} - \sqrt{\epsilon_\perp})(\sqrt{\epsilon_\|} + \sqrt{\epsilon_\perp})$. As a first approximation, we can then rewrite $\Delta\epsilon$ in the same way as that given for liquid crystal molecules[33], i.e. as $\Delta\epsilon \sim 2\Delta n\bar{n}$, with $\bar{n}$ being the average refractive index. In addition $\Delta\epsilon$ can be related to the orientational order parameter $S$, under the magnetic field, through $\Delta\epsilon = pS$. The quantity $p$ is a phenomenological parameter depending on the molecular characteristics of the monomer (electric polarizability, etc.) and of the chain (density of segments), which we will not describe here for reasons of simplicity, as it is of no real use for our present purpose.

Thus we have $\Delta n \sim \Delta\epsilon/2\bar{n} = pS/2\bar{n}$, and using equation (12), we obtain the following:

$$\frac{1}{CM} = \frac{\lambda H^2}{p} 2\bar{n} \frac{1}{S} \tag{14}$$

The order parameter $S$, under a given magnetic field $\boldsymbol{H}$ (or $v_e$), is thus proportional to the Cotton–Mouton constant.

As a consequence, the theory has to give a linear variation of $1/S$ *versus* $T$ over a wide range, which is found (*Figure 6*) for various values of the external field $v_e$. So, following equation (13), we can write the following:

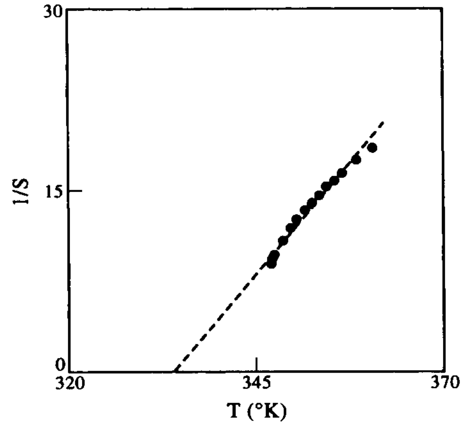


**Figure 7** Shape of the variation of $1/S$ with $T$ for $\nu_{er} = 8.5 \times 10^{-3}$, with the polymer parameters used in *Figure 2*

$$\frac{1}{S} = \alpha(T - T^*) \tag{15}$$

Thus, $\alpha$ is proportional to $A_2$ as follows:

$$\alpha = A_2 \frac{1}{2\lambda H^2} \frac{p}{\bar{n}} \tag{16}$$

We see that the lower is $v_e$, then the better is the linear fit. We also found (*Figure 7*) the same deviation near $T_c$ and the same general shape that is found for the experimental curves of $1/CM$ as a function of $T$, in both polymers and liquid crystal molecules[43] (the dotted line is only an approximation for both theory and experiment). We can then deduce $T^*$ from the plots of $1/S$ as a function of $T$ by a linear extrapolation, and a quite interesting observation can be made that, for polymers, $(T_c - T^*)$ is quite large and equal to ~ 35–40 K (so that $(T_c - T^*)/T_c \sim$ 10–12%).

We can now compare these last theoretical results with the experimental data obtained by Maret[42] for a series of aromatic polyesters (with mesogenic groups and flexible spacers in the mainchain), known as DDA-9, as well as for the two corresponding low molecular weight compounds PAA (para-azoxy-anisole) and 9-DDA-9 (see *Table 1*), which have been described elsewhere[30]. For each sample, the length $L$ and the experimental transition temperature are known. These values are reported in the first part of *Table 1*, together with the experimental results obtained by Maret[42] from magnetic birefringence measurements (with $\lambda = 6328$ Å). The maximum magnetic field used was $\boldsymbol{H} = 12\,T$, so we have used a value of $v_{er}$ of $10^{-6}$. The persistence length for such polyesters is nearly equal to 1.

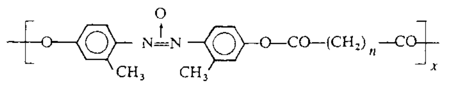
We have previously shown[44] that in the theoretical mean-field model (without an external field, $v_{er} = 0$), a knowledge of $L$ and $q$ determines, for each degree of polymerization, all of the characteristics of the isotropic–nematic phase transition: the orientational order parameter at the transition, $S_{c0}$, and the quantities $\kappa_B T_c/uL$ (or $\kappa_B/T_c/uq$) and $\kappa_B T^*/uL$ (or $\kappa_B T^*/uq$), etc. Therefore, from the experimental transition temperature $T_c$, we can determine the orientational interaction parameter $u$, and then $S_{c0}$ (*Table 1*, second part).

The same calculations are also true when an external field is applied to the sample. Thus we can determine

**Table 1** Experimental results from ref. 42 and data obtained from the present theoretical study[a]

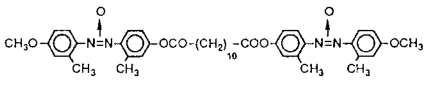
| | | PAA | 9-DDA-9 | DDA-9 | | | | | | | | PE7-3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | I[b] | L[b] | L[b] | 39[b] | II[b] | Sp4[b] | 52[b] | 41[b] | |
| From ref. 42 | $L$ | 1.0 | 1.0 | 2.5 | 9.1 | 9.1 | 13.3 | 14.6 | 21.5 | 32.7 | 44.2 | ? |
| | $T_c$ (K) | 404.7 | 372.0 | 349.4 | 408.8 | 408.5 | 409.0 | 416.8 | 386.7 | 428.1 | 419.6 | 404.0 |
| | $T^*$ (K) | 401.3 | 356.0 | 332.0 | 383.6 | 381.6 | 382.4 | 383.2 | 339.5 | 393.5 | 385.8 | 389.5 |
| | $A_2 \times 10^{-8}$ ($G^2$ cm $K^{-1}$) | 24.5 | 71.0 | 78.0 | 106.0 | 105.0 | 102.0 | 93.0 | 75.0 | 57.7 | 55.5 | 63.9 |
| | $H$ (cal mol$^{-1}$)[c] | 215.0 | 1042.0 | 1090.0 | 1660.0 | 1660.0 | 1670.0 | 1670.0 | 1670.0 | 1670.0 | 1670.0 | 442.0 |
| | $S_c$ | 0.37 | 0.61 | 0.70 | 0.69 | 0.69 | 0.70 | 0.74 | 0.84 | 0.91 | 0.94 | 0.45 |
| | $(T_c - T^*)$ (K) | 3.40 | 16.0 | 17.40 | 25.20 | 26.90 | 26.60 | 33.60 | 47.20 | 34.60 | 33.80 | 14.50 |
| | $(T_c - T^*)/T_c$ ($\times 10^2$) | 0.84 | 4.30 | 4.98 | 6.16 | 6.59 | 6.50 | 8.06 | 12.21 | 8.08 | 8.06 | 3.59 |
| From this work | $u/L$ (kcal mol$^{-1}$) | 3.6528 | – | 2.1472 | 0.6176 | 0.6172 | 0.4175 | 0.3866 | 0.2417 | 0.1749 | 0.1265 | – |
| $u_{er} = 0$ | $u$ (kcal mol$^{-1}$) | 3.6528 | – | 5.3681 | 5.6210 | 5.6169 | 5.5535 | 5.6458 | 5.1970 | 5.7208 | 5.5914 | – |
| | $S_{c_0}$ | 0.4289 | – | 0.3430 | 0.3509 | 0.3509 | 0.3526 | 0.3529 | 0.3540 | 0.3548 | 0.3552 | |
| | $T_c$ (K) | 404.7019[d] | – | 349.4020 | 408.8023 | 408.5023 | 409.0023 | 416.8024 | 386.7022 | 428.1024 | 419.602 | |
| | $S_{c_n}$ | 0.428[d] | – | 0.3430 | 0.3509 | 0.3509 | 0.3526 | 0.3529 | 0.3540 | 0.3548 | 0.3552 | |
| | $S_{c_i} \times 10^6$ | 9.90[d] | – | 8.3770 | 7.9822 | 7.9822 | 7.9363 | 0.9275 | 7.8988 | 7.8782 | 7.8680 | – |
| $u_{er} = 10^{-6}$ | $T^*$ (K) | 367.59[d] | – | 312.1466 | 363.2778 | 363.0252 | 363.2360 | 370.1149 | 343.2488 | 379.8844 | 372.288 | |
| | $(T_c - T^*)$ (K) | 37.11[d] | – | 37.26 | 45.52 | 45.48 | 45.77 | 46.89 | 43.45 | 48.22 | 47.31 | – |
| | $(T_c - T^*)/T_c$ | 9.17 | – | 10.66 | 11.14 | 11.13 | 11.19 | 11.20 | 11.24 | 11.26 | 11.28 | – |
| | $\alpha \times 10^6$ ($K^{-1}$) | 2720.0[d] | – | 3204.5535 | 2751.9310 | 2754.7705 | 2753.2015 | 2701.8822 | 2913.5036 | 2632.4688 | 2686.2415 | |

[a] The molecular structures of the aromatic polyesters are the following:

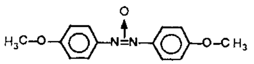


with $n = 10$ for DDA-9 and $n = 7$ for PE7-3, and for the two low molecular weight liquid crystals it is:

9-DDA-9:



PAA:



[b] Apellations 1 to 41 refer to the degree of polymerization, $X$ = L of the polyesters

[c] Transition enthalpy

[d] Estimated from $\lim q \rightarrow \infty$ in the model

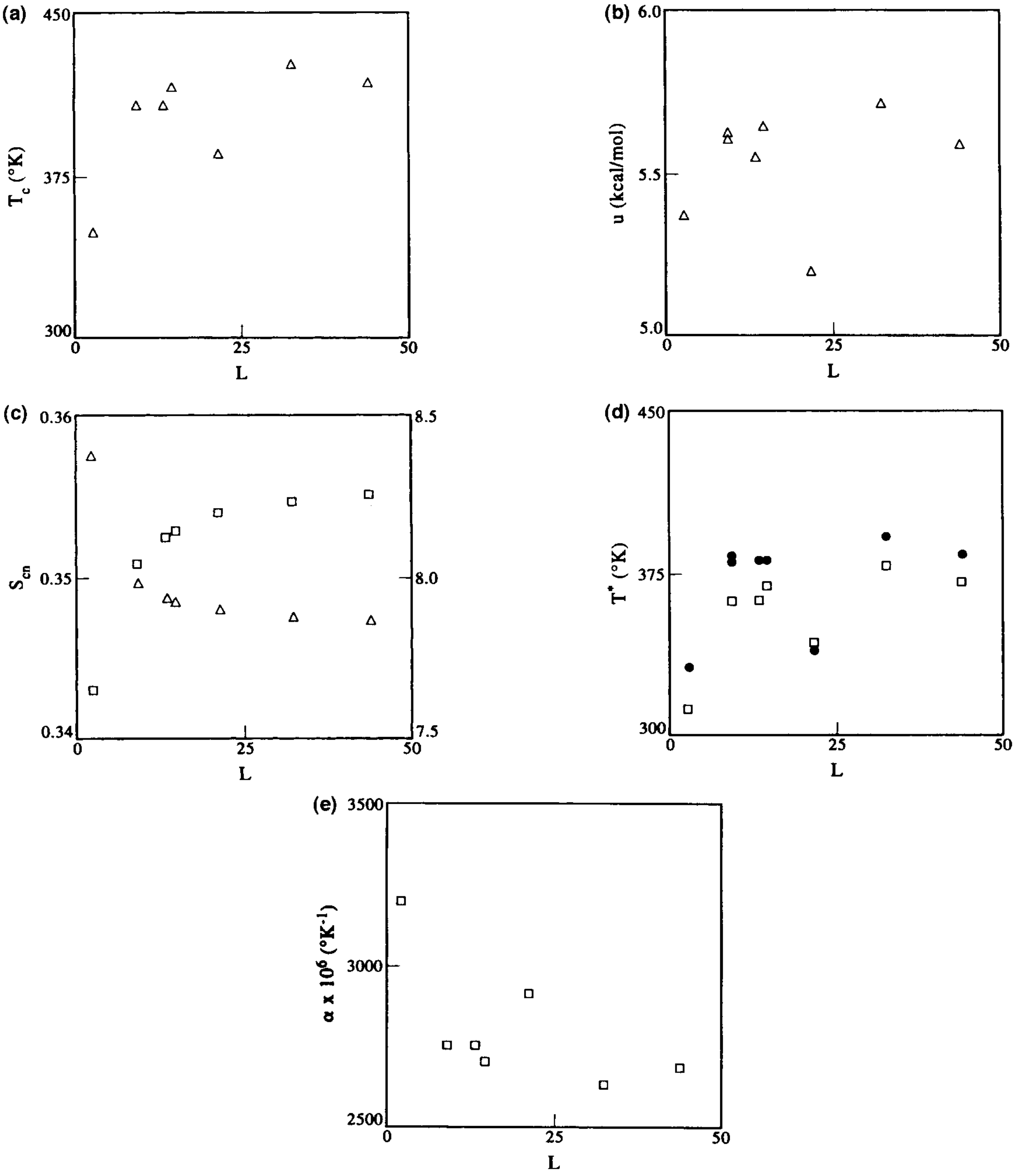


**Figure 8** Influence of the degree of polymerization $L$, for various samples of DDA-9 (ref. 42) with $q = 1$ and $v_{er} = 10^{-6}$, on: (a) the transition temperature $T_c$; (b) the interaction parameter $u$; (c) the order parameters at the transition, $S_{c_n}$ (anisotropic) (□) and $S_{c_i}$ (isotropic) (△); (d) the $T^*$ temperature, calculated (□) and experimental (●) values; (e) the slope $\alpha$ of the curve $1/S(T)$

theoretically, for an external magnetic field $v_{er}(= 10^{-6})$, the related quantities $S_{c_n}$, $S_{c_i}$, $T_c$ and $T^*$, and $\alpha$ (*Table 1*, third part).

Calculations show, for all of the $L$ values of the various samples, that we have the following (equations (10) and (11)):

$$T_c \simeq T_c(v_e = 0); S_{c_n} \sim S_c(v_e = 0) \sim 0.35;$$

$$S_{c_i} \sim 8 \times 10^{-6}; (T_c - T^*) \sim 35\text{–}45\,\mathrm{K}$$

We must give special attention to the value of the order parameter at the transition in the nematic phase, $S_{c_n}$. The mean field theory gives ~ 0.35, while values of ~ 0.70–0.88 have been deduced from nuclear magnetic resonance (n.m.r.) spectroscopic measurements[45]. The agreement is rather poor, but this discrepancy could have several origins. The worm-like model is perhaps not able to correctly describe such a polyester, which has a rather discontinuous structure, i.e. a rigid mesogenic entity followed by a flexible one, and so on, and could, moreover, exhibit 'hairpins' (folding of the chain) for the longer chains[46,47]. Steric repulsions, which may stabilize the liquid crystalline phase[48], are not included in the present model. Furthermore, it was shown that the increase of order in the chain length is caused by an increase of the biaxial character of the orientational order parameter[49,50,52]. In addition, due to sample polydispersity, a selective partitioning of chain lengths in the isotropic–nematic biphase occurs and leads to a heterogeneous molecular morphology in the pure nematic phase, with regions segregated both by chain length and level of orientated order[51].

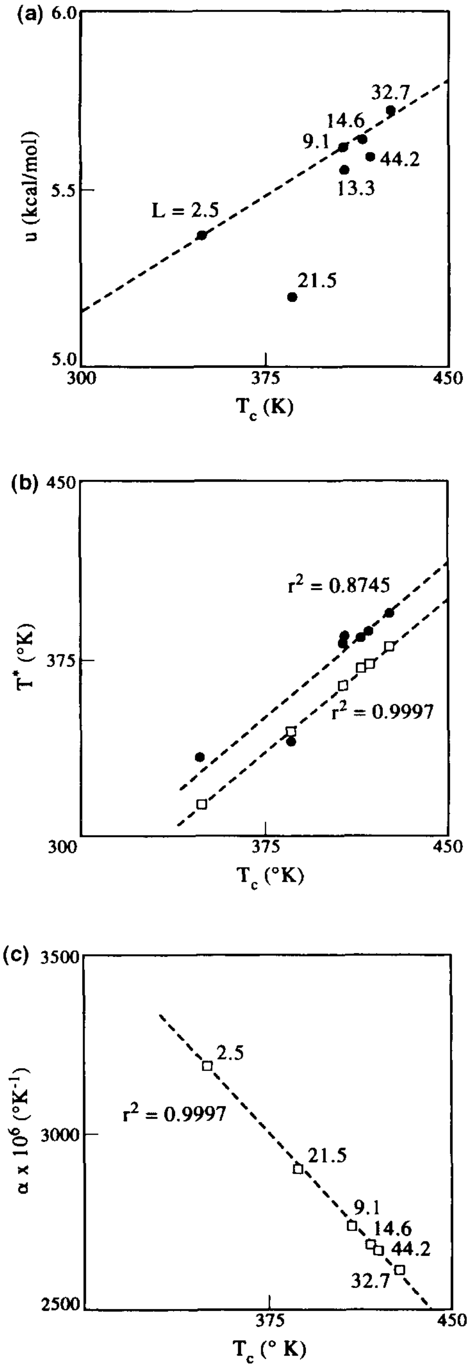


**Figure 9** Influence of the transition temperature $T_c$ for the samples and parameters given in *Figure 8*, on: (a) the interaction parameter $u$; (b) the $T^*$ temperatures, calculated (□) and experimental (●) values; (c) the slope $\alpha$ of the plot of $1/S$

We also note that there exists an incoherent point ($L = 21.5$) for the quantities $T_c$ and as a consequence, for $u$, $T^*$, and $\alpha$. These were determined (as for all of the samples) by using the experimental data with, certainly for that particular molecular weight, an overestimated value of the chain length ($L$ should be ca. 7). On the other hand, $S_c$, $S_{c_n}$ and $S_{c_i}$, which were calculated only by using $L$ (and $q = 1$) show continuous variations with $L$.

*Figure 8* illustrates the influence of the degree of polymerization $L$ on various quantities, namely the experimental transition temperature $T_c$, the calculated effective strength of the orientational interaction $u$, deduced (for $v_{er} = 0$) with the help of the mean-field approach, the theoretical orientational order parameters (under a relative field $v_{er} = 10^{-6}$) $S_{c_n}$ and $S_{c_i}$, the experimental and theoretical (as determined from the direct calculus method, by using the calculated $u$ values) $T^*$ values, and finally, the theoretical values of $\alpha$ for the slopes of the curves $1/S(T)$.

The usual[53] strong increase of $T_c$ at low values of $L$, followed by a rapid saturation, is observed (screening effect). The experimental values of $T^*$ are reported in *Figure 8d*. The theoretical $T^*$ temperature is lower than the experimental one, with quite a systematic deviation of ~10 to 20 K; the variation with $L$ is the same for both curves.

All of the curves of *Figures 8a*, *8b*, and *8d* have the same shape (an increasing function of $L$, with a saturation plateau at high values of $L$) while $\alpha$ in *Figure 8e* has a reversed evolution. This suggested a plot of $u$, $T^*$ and $\alpha$ as a function of $T_c$, shown in *Figures 9a–c*. A fairly good linear dependence with $T_c$ is found for $T^*$ and $\alpha$, with a better fit for the theoretical, when compared with the experimental $T^*$ values. The systematic deviation in $T^*$, mentioned above, is clearly seen in *Figure 9b*. A linear variation of $u$ with $T_c$ also appears for most of the points of *Figure 9a*, although some points are clearly out of alignment: $u$ seems to be weakly dependent on $L$.

It is found that $S_{c_n}$ displays a smooth and increasing variation with $L$ (*Figure 8c*), with its values falling in a short range of variation ($0.34 < S_{c_n} < 0.36$), with no obvious sensible dependence on the fluctuations of $T_c$ with $L$ (shown in *Figure 8a*), as mentioned above.

Now it will be useful to know the theoretical predictions when a magnetic field is applied to small liquid crystal SMLC molecule. For the reason previously developed[54], we can use the present model (in addition, another mean-field theory for liquid crystals[55]) until the limit of conventional SMLC liquid crystals, with $L = 1$ and $q \to \infty$ (for practical use, $q \sim 1000$). The application to PAA, with $T_c(v_c = 0) = 404.7$ K, $L = 1$ and $q = 1000$, leads to $S_{c_i} = 9.9 \times 10^{-6}$ and $T^* = 367.59$ K, so that $(T_c - T^*) \sim 37$ K ($(T_c - T^*)/T_c \sim 10\%$).

The deviation between experiments and theory is here, for low molecular weight liquid crystals, greater than 30 K. Therefore, we are tempted to conclude that the mean-field approximation, in the paranematic phase, seems to be a better approximation for nematic polymers than for small molecule liquid crystals. In the case of polymers, the dynamics of the reorientational rearrangements is slower than for small molecules, due to the chain elasticity; thus, the fluctuations could not easily develop through the phase and hence relax more rapidly. In contrast, for liquid crystals, as has been pointed out by numerous authors[32,56], the transition is more of a second-order type, with the development of very-long-range correlations.

## CONCLUSIONS

The first part of this study complements our previous work on elongational flow[25,26]. Two methods, namely the LDG expansion and the direct calculus approach, can be applied in the case of external fields, such as magnetic and elongational flow fields.

We have also shown that despite the strength of experimentally accessible magnetic fields being too low to induce any detectable shift of the transition temperature, the external field induces a weak order in the isotropic phase which, in turn, leads to predictable experimental magnetic birefringence measurements.

Another type of external field, which is of great technological interest, is the electric field. Therefore, numerous experimental reports on liquid crystals[57,58], and more recently on polymers[59,60], have appeared in the literature. In the latter case, this present model can also be used, but it is necessary to take account of electrical conduction (essentially, for high fields), which will rapidly induce electrodynamic instabilities (convection, etc.)[60–64].

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