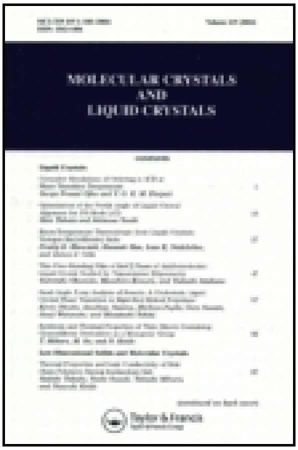

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

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Version of record first published: 24 Sep 2006.

To cite this article: T. A. Yurasova & A. N. Semenov (1991): Nematic Phase Transition in Systems of Polymer Chains with Mesogenic Groups, Molecular Crystals and Liquid Crystals, 199:1, 301-308

To link to this article: http://dx.doi.org/10.1080/00268949108030941

Mol. Cryst. Liq. Cryst., 1991, Vol. 199, pp. 301–308
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Printed in the United States of America

Nematic Phase Transition in Systems of Polymer Chains with Mesogenic Groups

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(Received July 27, 1990)

Nematic phase transition in melts of mesogenic macromolecules is studied. Each polymer chain is regarded as a sequence of rigid and flexible segments. Mean field approximation is used to calculate free energy of the system. Equilibrium temperature dependences of order parameters are obtained both for rigid and flexible fraction, and phase transition temperature is calculated. It is examined how lengths of different chain segments and values of anisotropic interaction between them can influence various properties of phase transition in the system. In a set of cases more often realized in experiments (when flexible segments are shorter or at least comparable with rigid ones) ordering of flexible component proves to be extremely weak in the vicinity of phase transition point. But there is a range of values of flexible spacer relative length and of anisotropic interaction between different segments when flexible fraction turns out to be even more ordered than rigid one in the vicinity of phase transition point.

Keywords: nematic transition; polymer melts

INTRODUCTION

Orientational ordering in polymer systems with mesogenic groups seems to be of quite interest, in particular, because this is just the problem of fair relevance to construction of new liquid-crystalline polymer materials.

Theoretical investigation of liquid-crystalline ordering in such systems[1-4] was carried out mainly using lattice models of the Flory type. Lattice models, however, have a somewhat restricted range of appliance.[5-7] Thus, to get a more detailed idea of liquid-crystalline ordering in systems of mesogenic chains, one should not confine oneself to the lattice model but has to use, in addition, some other theoretical methods.

One of them is the Maier-Saupe mean-field theory. It was initially proposed for systems of rigid rods but then developed to be valid also for flexible polymers.[8-11] Here we apply it to polymer chains of complicated structure, each chain composed of interchanging rigid and flexible segments (Figure 1). Anisotropic interaction between different chain segments is taken into account: we allow not only for rigid-rigid interaction but also for rigid-flexible and flexible-flexible ones.[10,11]

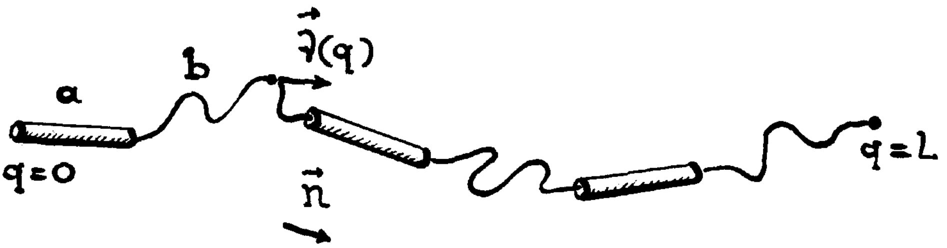

FIGURE 1 A polymer chain with rigid and flexible segments.

THE MODEL

The Method of Calculation

Let us consider a certain polymer chain in a melt and use a curvilinear coordinate q along the chain (Figure 1). Let $\vec{n}$ be a director showing a prevailing direction of segment orientation in the system and $\vec{v}\,(q)$ be a tangent vector for the chain at a point q; $|\vec{n}| = 1$. It is assumed that

$$\vec{v}(q)\,\big|_{q\,=\,(i\,-\,1)(a\,+\,b)} = \vec{v}(q)\,\big|_{q\,=\,ia\,+\,(i\,-\,1)b} \equiv \vec{v}_i \tag{1}$$

(here i is a number of a current chain unit made of one rigid segment of length a and of one flexible segment of length b, $i = 1, 2, \ldots, p$). Equation 1 means that $\vec{v}(q)$ varies continuously along the chain so that the chain contour curve is not broken anywhere.

We shall use two different averaged order parameters to describe an orientational order in rigid (η_1) and flexible (η_2) segments. They are

$$\eta_1 = \frac{1}{p}\left\langle \sum_{i=1}^{p} s_i \right\rangle, \; \eta_2 = \frac{1}{pb}\left\langle \sum_{i=1}^{p} \int_{ia+(i-1)b}^{i(a+b)} s(q)dq \right\rangle . \tag{2}$$

where

$$s(q) = \{3(\vec{v}(q), \vec{n})^2 - 1\}/2, \; s_i = \{3(\vec{v}_i, \vec{n})^2 - 1\}/2 \tag{3}$$

These parameters are averaged both over all macromolecules (this is marked with broken brackets) and over the total length of segments of the given sort along the chain.

Orientational order in the system as a whole is defined by parameter $\eta = (a\eta_1 + b\eta_2)/(a + b)$.

In accordance with Maier-Saupe approach, we assume that each elementary part dq of a chain is affected by a certain mean field. Energy of their interaction dH

depends, on the one hand, on the average order in the system and, on the other hand, on the orientation of the part dq itself:

$$dH_k = -\left(\frac{\beta_{1k} a \eta_1 + \beta_{2k} b \eta_2}{a + b}\right) s(q)\, dq + \frac{lT}{2}\left(\frac{\partial \vec{v}}{\partial q}\right)^2 dq, \qquad (4)$$

$$k = 1, 2$$

In fact, here are two different equations for two values of k since dq may belong either to a rigid segment of a chain ($k = 1$) or to a flexible one ($k = 2$). Kuhn segment length l is defined for one flexible segment, and temperature T is measured in energy units. Parameters β_{11}, β_{12} and β_{22} are used to take into account anisotropic interactions of three different types (i.e., rigid-rigid, rigid-flexible and flexible-flexible interactions; $\beta_{12} = \beta_{21}$). These parameters depend on chemical structure of macromolecules, on density of the system. The second term in Equation (4) corresponds to elastic bending energy of a flexible spacer.

Thus the energy of the ith chain unit consisting of one rigid and one flexible group is the following:

$$H_i = -\left(\frac{\beta_{11} a \eta_1 + \beta_{12} b \eta_2}{a + b}\right)\left(\frac{3(\vec{v}_i, \vec{n})^2 - 1}{2}\right) a + \int_{(i-1)b+ia}^{i(a+b)} \cdot \left\{ -\left(\frac{\beta_{12} a \eta_1 + \beta_{22} b \eta_2}{a + b}\right)\left(\frac{3(\vec{v}(q), \vec{n})^2 - 1}{2}\right) + lT\left(\frac{\partial \vec{v}}{\partial q}\right)^2 \right\} dq \qquad (5)$$

Now the average energy of a macromolecule, U, can be drawn: $U = \langle \Sigma_{i=1}^{p} H_i \rangle$. Then the free energy of the whole system containing N macromolecules will be the following:

$$F = -\frac{NU}{2} - NT \ln Z$$

$$= \frac{N(\beta_{11} a^2 \eta_1^2 + 2\beta_{12}\, ab\eta_1\eta_2 + \beta_{22} b^2 \eta_2^2)p}{2(a + b)} - NT \ln Z, \qquad (6)$$

$$Z = \int d\vec{v}_1 \ldots d\vec{v}_{p+1} \underbrace{\iint} \exp\left\{\left(-\sum_{i=1}^{p} H_i\right)\Big/ T\right\} D[\vec{v}_1(q)] \ldots D[\vec{v}_p(q)]. \qquad (7)$$

The free energy F should be known in order to treat nematic phase transition in the system.

So, first of all, the statistical integral Z of a macromolecule is to be found. Then, minimizing free energy over order parameters η_1 and η_2:

$$\partial F/\partial \eta_1 = 0, \qquad \partial F/\partial \eta_2 = 0, \qquad (8)$$

one might examine equilibrium properties of the melt.

The spherical approximation is used below to simplify the calculation and to derive free energy $F(\eta_1, \eta_2, T)$ as an explicit function of temperature and order parameters (see References 8 and 12).

Mathematically it means that not a tangent vector itself is assumed to be equal to one, but only its ensemble average value is. For the considered system it appears more convenient to require that the average value of a tangent vector is taken both over statistical ensemble and over chain length. To achieve more accuracy, we take the average over length of rigid segments and of flexible segments separately. Thus, we come to the conditional extremum problem which can be solved based on the Lagrange method of indefinite factors. Used in our case, the method leads to the modified value $\tilde{H}_1$ of the Hamiltonian involved in (Equations 6 and 7) for free energy. It should be the following:

$$\tilde{H}_i = H_i + \mu_1 T(\vec{v}_i^2 - 1) + \mu_2 T \int_{(i-1)b+ia}^{i(a+b)} (\vec{v}^2(q) - 1)\, dq \tag{9}$$

Here μ_1 and μ_2 are the Lagrange factors that should be found from equations:

$$\partial F/\partial\mu_1 = 0, \qquad \partial F/\partial\mu_2 = 0. \tag{10}$$

The set of Equations (10) in common with Equations (8) completely determines the equilibrium phase transition from nematic liquid crystal to isotropic melt.

RESULTS

Statistical integral (7) can be written in the following form:

$$Z = \int d\vec{v}_1 \ldots d\vec{v}_{p+1} \prod_{i=1}^{p} K(\vec{v}_i, \vec{v}_{i+1}), \tag{11}$$

where

$$K(\vec{v}_i, \vec{v}_{i+1}) = \underbrace{\iint}\, \exp\,(-\tilde{H}_i/T) D[\vec{v}_i(q)], \tag{12}$$

and $\tilde{H}_i$ is defined by Equation (9). Owing to the spherical approximation the integral[12] can be reduced to the well-known functional integral for the harmonic oscillator[12] and so can be calculated exactly. As a result, we get

$$Z = (\mu_1 a \sqrt{(\mu_1 - x_1)a})^{-p} \exp\left\{p\left[\left(\mu_1 - \frac{x_1}{3}\right)a + \left(\mu_2 - \frac{x_2}{3}\right)b - \frac{b}{\sqrt{2l}}\left(\sqrt{\mu_2 - x_2} - 2\sqrt{2\mu_2}\right)\right]\right\},\ x_j = \frac{3(\beta_{2j} b\eta_2 + \beta_{1j} a\eta_1)}{2(a+b)T}, \quad j = 1, 2. \tag{13}$$

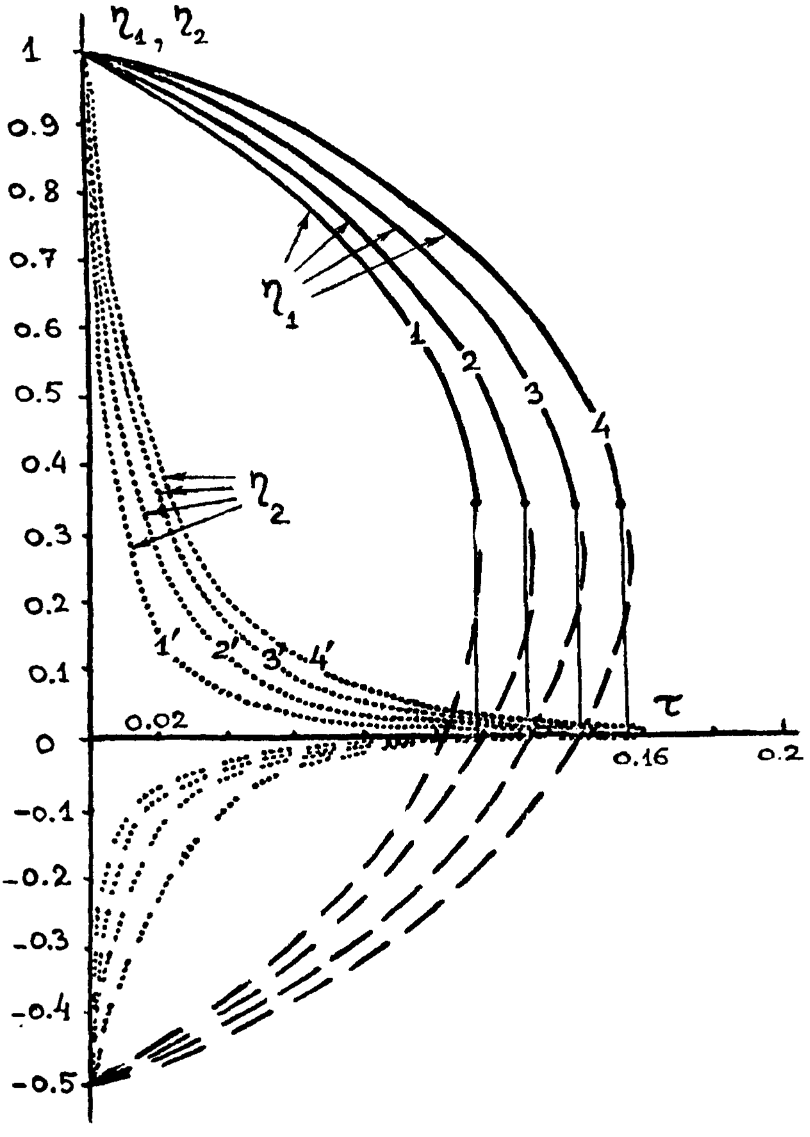

FIGURE 2 Temperature dependence of order parameters η_1 (for rigid fraction - lines 1–4) and η_2 (for flexible fraction - lines 1′–4′); $\tau \equiv T/(3\beta_{11}l)$; $a/l = 10$; $b/l = 100$; $V_2 = 0.1$, and V_1 is equal to 0.3 (curve 1), 0.5 (curve 2), 0.7 (curve 3) and 0.9 (curve 4). Here and below lines with blanks represent metastable states of the system.

Substituting this to Equations (7), and minimizing free energy over η_1,η_2, μ_1 and μ_2, one would obtain the set of equations for variables η_1 and η_2:

$$\frac{a\eta_1 + b\eta_2}{a + b} = \frac{\tau l}{a}\frac{9\eta_1}{(2\eta_1 + 1)(1 - \eta_1)}, \qquad (14)$$

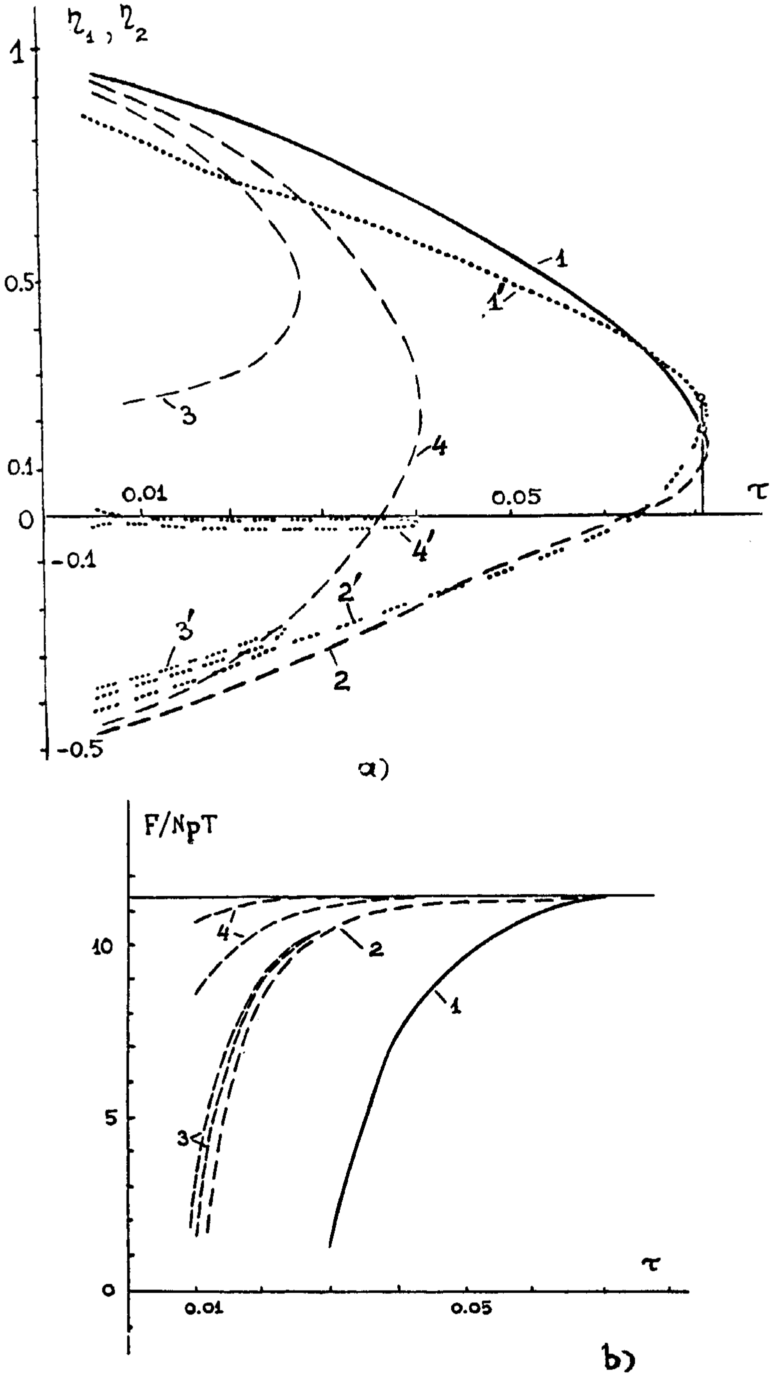

FIGURE 3 Temperature dependence (a) of order parameters η_1 (curves 1–4) and η_2 (curves 1′–4′); (b) of free energy divided by total number of segments and by temperature $F/(NpT)$. Curves 2–4, 2′–4′ correspond to metastable states of the system with higher values of F than for the state 1/1′; $a/l = 2$, $b/l = 10$, $V_1 = 0.1$, $V_2 = 1$.

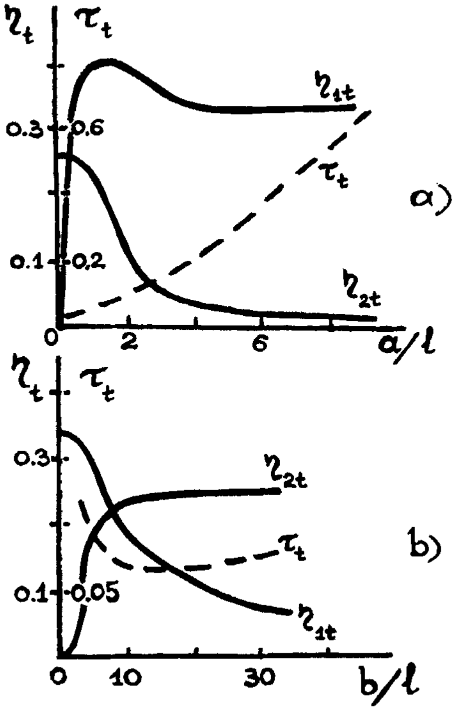

FIGURE 4 Order parameters η_{1t} (curve 1), η_{2t} (curve 2) and dimensionless temperature τ_t (curve 3) at the phase transition point versus relative length of a rigid segment a/l (a) and of a flexible spacer b/l (b); a) $b/l = 10$, $V_1 = V_2 = 0.5$; b) $a/l = 2$; $V_1 = 0.1$, $V_2 = 1$.

$$\frac{V_1 a\eta_1 + V_2 b\eta_2}{a + b} = \tau \frac{27\eta_2}{4(2\eta_2 + 1)^2(1 - \eta_2^2)}. \tag{15}$$

Here $V_1 \equiv \beta_{12}/\beta_{11}$, $V_2 \equiv \beta_{22}/\beta_{11}$, and $\tau \equiv T/(3\beta_{11}l)$ is a dimensionless temperature. This set of equations allows us to find out temperature dependences of order parameters η_1 and η_2. It has been solved numerically for various values of (a/l), (b/l), V_1 and V_2. Some curves are shown in Figure 2.

In some cases, two or three different solutions of Equations (14)–(15) have been found. They are presented in Figure 3 (curve 1, 1′, 2, 3). Values of free energy calculated and plotted in Figure 3b enable us to infer that solutions 1′, 2 and 3 correspond to metastable states of the system.

The values of order parameters η_{1t} and η_{2t} at the phase transition point has been derived from the following condition: $(F - F_0)|\eta_{1t}, \eta_{2t} = 0$, F_0 is the free energy of the system in a completely isotropic state. The phase transition temperature T_t has been calculated as well (Figure 4).

DISCUSSION

Examination and comparison of all the results may yield the following information.

To begin with, as rigid segments of chains become longer the possible temperature range of anisotropic phase appears wider. In most cases, a flexible fraction proves to be almost entirely disordered in the vicinity of phase transition point (Figure 2); the value of η_{1t} is greater than η_{2t} by a factor of 10^1-10^2. However, Figure 4b shows there is such a range of values of structure parameters (a/l, b/l) and anisotropic interaction parameters (V_1, V_2) that flexible fraction appears to be even more ordered than rigid one in the vicinity of phase transition point: $\eta_{1t} < \eta_{2t}$. This may happen when flexible spacers are much longer than rigid groups ($a << b$) and, besides, rigid-flexible interaction is quite weak ($V_1 << 1$) in comparison with those of rigid-rigid and flexible-flexible type ($V_2 \sim 1$). Two latter requirements mean that rigid groups do not practically interact with flexible segments, and, hence, ordering of rigid fraction is mainly determined by rigid-rigid attraction. But due to low concentration of rigid groups ($a << b$) the energy of their mutual attraction is low as well. This explains inequality $\eta_{1t} < \eta_{2t}$ in the given case.

It is worth noting that these results differ, to some extent, from predictions of the Flory theory.[1-3] As far as the lattice model is applied to the system, a flexible fraction turns out to be quite ordered just in the case when flexible spacers are much shorter than rigid rods. Such a discrepancy is due to the fact that steric interactions regarded in the lattice model were neglected in our treatment. Thus our conclusions and those drawn from the lattice model should be referred to different types of polymer systems. The model proposed above is valid for such polymer chains that various chain segments do not display a fairly strong anisotropy of their shape.

The suggested method is available even for $b << l$, since our results in this limiting case are in accordance with those reported in Reference 12 for rigid rods.

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