Theory of isotropic–nematic phase transition in nematic block copolymers

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A model is suggested to treat nematic block copolymers with mesogenic groups in the main chains. It is based on a mean-field approach taking into account attractive interactions between chain segments, and allows the description of chains with varying flexibility (with somewhat flexible mesogens). The free energy is calculated; it yields the behaviour of the temperature-dependent nematic–isotropic phase transition in the system for various sets of parameters (concentration of the two components and constants of anisotropic interaction).

(Keywords: block copolymers; phase transition; nematic structure; modelling; anisotropy)

INTRODUCTION

Liquid-crystalline ordering in block copolymers was previously treated by many workers[1–7]. A system of polymer chains containing stiff mesogenic groups (*Figure 1a*) was considered by most of them using various lattice models[1–5]. It has been shown, however, that an alternative approach might be better for special kinds of structures (with mesogenic units having a weaker anisotropy of shape and stronger attractive interactions between chain segments)[6,7]; it is based on a mean-field approximation (of the Maier–Saupe type) and leads to somewhat different results for the systems in question.

On the other hand, there is experimental evidence that the properties of liquid-crystalline block copolymers can depend on the particular chemistry of the mesogenic groups (how stiff they actually are). For example, the dynamic experiments by Ungar *et al.*[8] give values of the nematic–isotropic phase transition temperature T_{NI} that increase with the heating rate, and this dependence is much more dramatic in the case of stiffer mesogenic groups.

In another set of experiments the reduction of the phase transition temperature is observed with increase in the concentration ϕ of flexible spacers[9]. The tendency of T_{NI} at $\phi \rightarrow 1$ might allow one to 'extract' nematic quality of the alkyl spacers using an appropriate model for the copolymer. The authors conclude that it suggests the presence of a virtual mesophase in polyethylene, which was previously theoretically predicted[10]. The shape of the $T_{NI}(\phi)$ dependence also proves to be sensitive to the particularities of the chain geometry and to the relative values of orientational interactions between the chain segments.

Therefore, a theoretical model is proposed below to describe some real chemical structures. Namely, we consider polymer chains of varying flexibility containing stiffer and less stiff units (*Figure 1b*), i.e. segments of the types 1 and 2. A mean-field approximation is used, and a path-integral technique is involved to obtain the free energy of the system. The equilibrium temperature dependence of order parameters is plotted. The phase transition temperature is found to be altered by the relative concentration of stiff and flexible fractions and by anisotropic interactions between the chain segments.

MODEL AND METHODS

Thus a melt of worm-like block copolymer chains of the sort shown in *Figure 1b* is treated here. Let q be the curvilinear coordinate along the chain; a tangent vector $\boldsymbol{t}(q)$ can be introduced at any point. Then, according to a mean-field approach[11], an elementary part of the chain, dq, feels the influence of a certain orientational field caused by all surrounding chain segments. The corresponding orientational energy dH, in general, would depend on the direction $\boldsymbol{t}$ of the given part dq and would

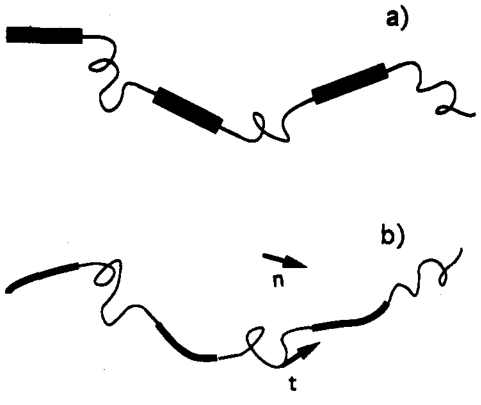

Figure 1 Block copolymer chains: (a) stiff mesogenic groups; (b) more flexible mesogens

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also be proportional to the average order parameter of the melt:

$$dH = -Vs(q)\eta\, dq$$
$$s(q) = P_2(\boldsymbol{n}, \boldsymbol{t}) = [3(\boldsymbol{n}.\boldsymbol{t})^2 - 1]/2 \qquad (1)$$
$$\eta = \langle P_2(\boldsymbol{n}.\boldsymbol{t})\rangle$$

(angle brackets mean the average taken over all directions of the chain segments and over all chains in the melt). Here $\boldsymbol{n}$ is the director, and V is a constant of attractive interactions.

Actually, there are three different constants (V_{11}, V_{12} and V_{22}) in the case in question; they describe interactions between segments of the two different types (1–1, 1–2 and 2–2 interactions; see *Figure 1b*). Moreover, two different order parameters (η_1 and η_2) should be involved to characterize nematic ordering in the system (i.e. the order parameters for the stiffer and the less stiff fraction separately). Obviously, we introduce two different Kuhn lengths (l_1 and l_2) at the same time and the total segment lengths a and b of the more flexible and stiffer components. Based on equation (1) and including the elastic bending energy of a worm-like chain (proportional to $(\partial t/\partial q)^2$), one can get the following Hamiltonian for the ith chain segment:

$$H_{ik} = \int_{(i-1)(a+b)+\delta_{2k}a}^{i(a+b)-\delta_{1k}b} [-2Ts(q)g_k/3 + l_kT(\partial t/\partial q)^2]\, dq \qquad (2)$$

with

$$g_k = 3(V_{1k}a\eta_1 + V_{2k}b\eta_2)/[2(a+b)T]$$

$V_{12} = V_{21}$, T is temperature (in the units of energy), and $k=1$ or $k=2$ depending on the sort of segment under consideration.

If U is the total energy per chain, i.e.

$$U = \sum_i H_{ik}$$

then, quite similarly to ref. 12, the free energy of the system will be equal to:

$$F = -N\langle U\rangle/2 - NT\ln Z$$
$$= Nm(V_{11}a^2\eta_1^2 + 2V_{12}ab\eta_1\eta_2 + V_{22}b^2\eta_2^2)/(a+b) - NT\ln Z \qquad (3)$$

where N is the number of chains in a melt, $(2m)$ is the total number of segments in a chain, and

$$Z = \int d\boldsymbol{t}_1 \ldots d\boldsymbol{t}_{2m+1} \prod_{i=1}^{2m} G_1(\boldsymbol{t}_{i-1}, \boldsymbol{t}_i)G_2(\boldsymbol{t}_i, \boldsymbol{t}_{i+1}) \qquad (4)$$
$$G_k(\boldsymbol{t}_{i-1}, \boldsymbol{t}_i) = \int \exp(-H_{ik}/T)\, D\boldsymbol{t}_i(q)$$

with H_{ik} determined by equation (2). The G_k can be thought of as propagators for the tangent vector along a segment of type k.

Thus equation (3) could be used to calculate the free energy of the melt. In order to find the equilibrium state of the system, a set of minimizing equations:

$$\partial F/\partial\eta_1 = 0 \qquad \partial F/\partial\eta_2 = 0 \qquad (5)$$

should be solved. Regarding temperature as a parameter, we can find from here the equilibrium temperature dependence of η_1 and η_2.

It is possible to write an analytical formula for the free energy if we resort to the so-called spherical approximation[13]. It is based on the assumption that the magnitude of the tangent vector $\boldsymbol{t}$ can vary from point to point (i.e. it is not necessarily equal to unity); but the essential requirement is that its average value should still be equal to unity (the average is taken over all directions of a segment and then along the chain). It means that we allow for a finite rigidity of chain segments or, in other words, for a certain variation in their lengths. At this point we depart in our treatment of worm-like chains from Wang and Warner[14], who also consider mean-field coupling, but calculate the free energy using an eigenfunction expansion of (2).

This additional restriction for the tangent vector allows the path integrals (4) be reduced to the well known harmonic oscillator type. In this case the Hamiltonian H_{ik} given by equation (2) should be replaced by the modified Hamiltonian H_{ik} (refs. 6, 7):

$$H_{ik} = H_{ik} + \mu_k T \int [t^2(q) - 1]\, dq$$

where μ_k is a Lagrangean multiplier.

Substituting this into the formula for the propagators, equation (4), we come to the following:

$$G_k(\boldsymbol{t}_i, \boldsymbol{t}_{i+1}) = \exp[(\mu_k - g_k/3)d_k] \prod_{\alpha=1}^{3}$$
$$\times \int \exp\left(-l_k \int [\omega_{k\alpha}^2\mu_{i\alpha}^2 + (\partial t_{i\alpha}/\partial q)^2]\, dq/2\right) Dt_{i\alpha}(q) \qquad (6)$$

with $\omega_{k\alpha}^2 = 2(\mu_k - \delta_{\alpha 3}g_k)/l_k$, $k=1,2$; $d_1 = a$, $d_2 = b$; and $\alpha = 1, 2, 3$ corresponding to x, y and z components of $\boldsymbol{t}$. These are already integrals, which can be calculated exactly[15]; the αth factor in the product is equal to:

$$\{\omega_{k\alpha}l_k/[2\pi\sinh(\omega_{k\alpha}d_k)]\}^{1/2}\exp\{-[\omega_{k\alpha}l_k/2\tanh(\omega_{k\alpha}d_k)]$$
$$\times [(t_{i,\alpha})^2 + (t_{i+1,\alpha})^2] + [\omega_{k\alpha}l_k/\sinh(\omega_{k\alpha}d_k)](t_{i,\alpha}t_{i+1,\alpha})\}$$

To evaluate the function Z given by equation (4), with the propagators (6), we transform to Cartesian coordinates. Finally, the second term in equation (3) can be written as:

$$\ln Z = 2m[(\mu_1 - g_1/3)a + (\mu_2 - g_2/3)b - (\omega_{1x} + \omega_{1z}/2)$$
$$\times a - (\omega_{2x} + \omega_{2z}/2)b] + (2m-1)[\ln(\omega_{1x}l_1)$$
$$+ \tfrac{1}{2}\ln(\omega_{1z}l_1) + \ln(\omega_{2x}l_2) + \tfrac{1}{2}\ln(\omega_{2z}l_2) - 2\ln(\omega_{1x}l_1$$
$$+ \omega_{2x}l_2) - \ln(\omega_{1z}l_1 + \omega_{2z}l_2)]$$

Equations (5) together with these below:

$$\partial F/\partial\mu_1 = 0 \qquad \partial F/\partial\mu_2 = 0 \qquad (7)$$

yield a set of four simultaneous equations with four variables (η_1, η_2, μ_1 and μ_2), which determine the equilibrium behaviour of the system. These equations are:

$$[1 - (2x_k)^{-1/2} - 0.5(2y_k)^{-1/2}]d_k/l_k + [(2m-1)/(2m)]$$
$$\times \{1/x_k - 1/(2y_k) - 2(x_k)^{-1/2}/[(x_1)^{1/2} + (x_2)^{1/2}]$$
$$-(y_k)^{-1/2}/[(y_1)^{1/2} + (y_2)^{1/2}]\} = 0 \qquad (8)$$
$$\{\eta_k + 0.5[1 - 1.5(2y_k)^{-1/2}]\}d_k/l_k - 0.375(y_k)^{-1/2}$$
$$\times [(2m-1)/(2m)][(y_1)^{-1/2} + (y_2)^{-1/2} - 0.5(y_k)^{-1/2}] = 0$$

where $k = 1, 2$, $y_k = (\mu_k - g_k/3)l_k$, $x_k = \mu_k l_k$ and g_k is defined in equations (2).

RESULTS AND DISCUSSION

The number of model parameters can be easily reduced to five namely $\beta_1 = V_{12}/V_{11}$, $\beta_2 = V_{22}/V_{11}$, a/b, l_2/l_1 and $\varepsilon = (2m-1)/2m$. Equations (8) have been treated numerically for various sets of parameters; some results are shown in *Figures 2–4*.

Some features of the phase transition are likely to depend on the total molecular weight M of polymer chains (or degree of polymerization). Evidently, $M \sim m$, and, as can be seen from equations (8), this dependence is entirely determined by the factor $\varepsilon = (2m-1)/2m$, which does not change noticeably if $m \gg 1$. Therefore, the influence of the molecular weight is fairly slight and would be better expressed for shorter chains (this conclusion agrees with experiments[8,9]).

In *Figure 2* two curves are compared. They are the temperature dependence of the order parameter η for a melt of worm-like uniform chains ($l_1 = l_2$, $a = b$ and $V_{11} = V_{12} = V_{22}$) and for a melt of block copolymer chains with slightly different segments ($l_2/l_1 = 0.9$). In the latter case the two order parameters can be hardly differentiated as they are nearly equal to each other, $\eta_1 \approx \eta_2$, because the difference in the segments' stiffness and in their interaction is not essential. But still certain changes in the behaviour of the system can be noticed: while some of the chain segments are getting stiffer (l_1 is increased), the order parameter at the phase transition point becomes somewhat higher; the transition temperature, however, slightly reduces. The values of interaction parameters, V, in this case are nearly the same.

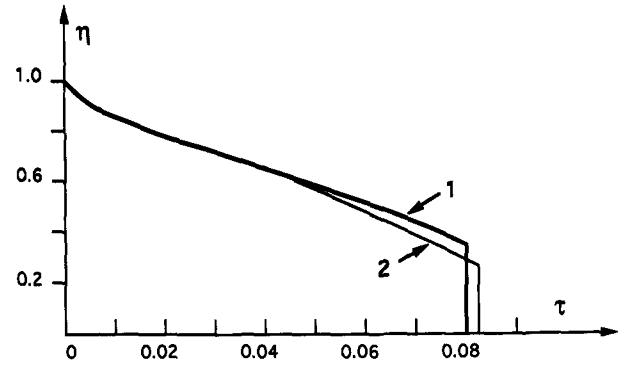

Figure 2 The temperature dependence of the order parameter η: curve 1, uniform flexible chain; curve 2, chain containing slightly different segments, $a/l_1 = b/l_2 = 10$, $l_2/l_1 = 0.9$, $V_{11} = 0.9\ V_{12}$, $V_{22} = V_{12}$; in this case $\eta_1 \approx \eta_2$

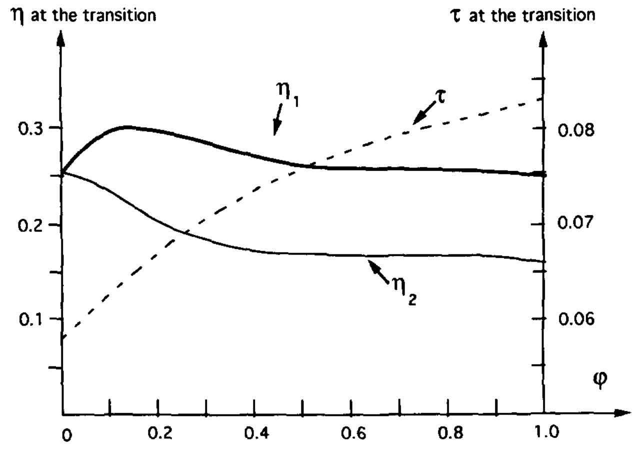

Figure 3 The phase transition values of the order parameters (η_{1t}, η_{2t}) and dimensionless temperature τ_t *versus* concentration ϕ of stiffer segments; $\phi = a/(a+b)$, $b/l_2 = 10$, $l_2/l_1 = 0.5$, $V_{11} = 0.8\ V_{12}$, $V_{12} = 0.9\ V_{22}$

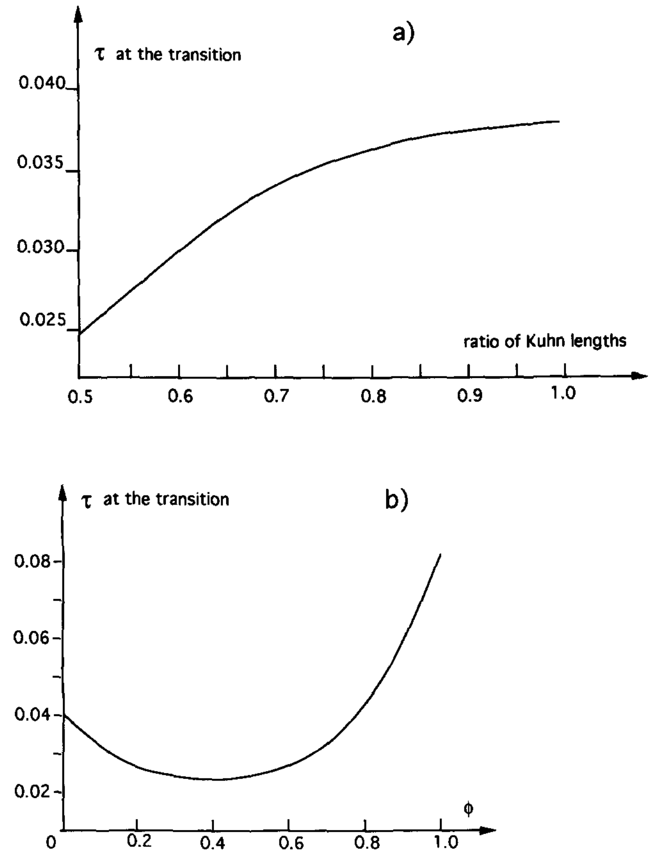

Figure 4 The phase transition temperature τ_t depending on: (a) the ratio l_2/l_1 of the block copolymer Kuhn lengths, $a/l_2 = 20$; (b) the fraction of stiffer segments $\phi = a/(a+b)$; $l_2/l_1 = 0.5$. For both curves $b/l_2 = 20$, $V_{11} = V_{22}$ and $V_{12} = 0$

In *Figure 3* the values of order parameters and of dimensionless temperature $\tau = T/(3V_{11}l_1)$ at the transition are plotted *versus* the concentration of stiffer groups. The ratio of the Kuhn lengths is now equal to 0.5. It can be seen that transition temperature τ_t increases with the concentration of the stiffer fraction, whereas both order parameters η_1 and η_2 slightly decrease and then become nearly constant for higher values of φ. In this case attractive interactions between the stiffer groups are slightly less than those between the more flexible segments: $V_{11} \leqslant V_{22}$.

Figure 4a shows that dependence of the phase transition temperature on the ratio l_2/l_1 is sharper for lower values of this ratio (i.e. in the case when segments of the two sorts are of essentially different stiffness).

It could be interesting to look at the effect of coupling. If the mutual interaction, modelled by V_{12} and coupled to the Kuhn segment lengths via their geometric mean $(l_1 l_2)^{1/2}$, is lower than the effective self-interactions $V_{11}l_1$ and $V_{22}l_2$, then at intermediate concentrations, when 1–2 interactions are significant, we may expect to observe a minimum in the transition temperature. This appears in *Figure 4b*. Both *Figures 4a* and *4b* describe the limiting case when the segments of the two different sorts do not interact at all ($V_{12}=0$). This means that nematic ordering of the flexible fraction would be only caused by binding of the segments combined together in polymer chains (and not by their orientational interactions with mesogens). The less the l_2/l_1 ratio, the more noticeable this effect can be. These results are confirmed by experiments[9].

CONCLUSIONS

The suggested approach allows the study of a nematic–isotropic phase transition in main-chain copolymers admitting a certain flexibility of mesogenic groups. Therefore, it can be relevant to a variety of real chemical structures. The equilibrium properties of the system are determined by a set of five independent parameters; this gives the possibility to describe in a number of different ways the system's behaviour observed in experiments.

The phase transition temperature T_{NI} proves to be sharply dependent on the coupling constant V_{12} (i.e. on the interaction between spacers and mesogens) and also on the relative flexibility of stiffer groups (l_2/l_1). The possibility of minima in the dependence of T_{NI} on the spacers' concentration ϕ is shown; this is explained by influence of coupling.

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