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Theory of Liquid-Crystalline Ordering in Melts of Macromolecules with Stiff and Flexible Fragments in the Main Chain. 1

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ABSTRACT: A theory of orientational ordering in melts of polymers containing stiff and flexible fragments in the main chain is suggested. The theory is developed within the framework of a lattice model by means of a method which, by a generalization of the well-known procedure of Flory, enables us to take into account the induced ordering of flexible fragments in the anisotropic phase. For various values of the flexibility parameter of flexible fragments, f_0, the phase diagrams are constructed and the properties of the liquid-crystalline transition are investigated. It is shown that the straightening and stiffening of flexible fragments in the anisotropic phase may be quite substantial; the effect is particularly pronounced at $f_0 < 0.63$ when according to Flory ordering takes place in melts of polymers which include only a flexible component. For $f_0 > 0.63$ the possibility of an additional phase transition between two different nematic phases is predicted. It is concluded that accounting for the partial ordering of flexible fragments in the anisotropic phase is necessary in the theoretical treatment of thermotropic liquid-crystalline polymer systems.

1. Introduction

In recent years significant attention has been paid to experimental study of liquid-crystalline ordering of polymers containing stiff (mesogenic) and flexible fragments in the main chain.[1-4] However, theoretical works in this field are not numerous. One can mention only the detailed analysis of the coupling between the nematic ordering and the helix–coil transition in polypeptide solutions, which was performed in ref 5–7. (In these papers, helical parts of the chains were regarded as rigid rods and coil parts as flexible spacers.) At the same time, theoretical investigation of the properties of the liquid-crystalline transition in solutions and melts of copolymers with stiff and flexible fragments in the main chain was until recently apparently lacking.

Not until 1981 was, a paper published by Matheson and Flory[8] (see also ref 9) in which the liquid-crystalline transition in a solution of macromolecules containing rigid rods, freely rotating joints between the rods, and flexible fragments was considered on the basis of the well-known lattice method.[10,11] A flexible fragment is independent of the extent of orientational ordering in the solution. This assumption seems to be inconsistent, as it is evident that the self-consistent orientational field due to the liquid-crystalline order affects the flexible chain fragments as well as the rigid ones, leading to "straightening" and "stiffening" of the former. The ordering of flexible fragments, accompanying the formation of the liquid-crystalline phase, is also indicated by some of the experimental results.[12-14]

In this paper we consider (within the latter model of Flory) orientational ordering in melts of regular copolymers containing stiff and flexible fragments in the main chain, taking into account the fact that the properties of flexible fragments, as well as of rigid ones, are changed when liquid-crystalline order is established. It will be shown that rejection of the Matheson–Flory assumption leads to significant changes in certain specific features of the liquid-crystalline transition.

The case of polymer melts was chosen for the investigation in this paper (in contrast to ref 8, where main focus was on the study of orientational ordering in polymer solutions) because (a) this case is most interesting with respect to the application of the results to thermotropic liquid-crystalline polymeric systems and (b) it is for this case that Flory's lattice method should give the best results, while for the study of dilute liquid-crystalline polymeric solutions the method of Onsager[15] is more suitable.

Some preliminary data regarding the ordering of macromolecules with stiff and flexible fragments in solution and in the melt were discussed in ref 16.

For the sake of simplicity we confine the present work to athermal polymer melts only. In this case liquid-crystalline ordering occurs solely for steric reasons. Further, to simplify the calculations we assume that the repeating blocks of regular copolymers under consideration (see Figure 1) are separated by freely rotating junctions (for a detailed discussion on this point, see section 2). We believe that in the majority of cases this assumption does not lead to significant changes in qualitative effects. A theory in which repeating blocks are connected into the chain in a more realistic way is currently being developed and will be considered in a separate publication.

The paper is organized as follows. We first describe the model of the polymeric system under investigation (section 2). Then we examine the properties of liquid-crystalline transition in this system, based on the Matheson–Flory assumption that the degree of flexibility of flexible chain fragments is independent of orientational ordering (section 3). In section 4 we describe our method for calculation of the free energy of the liquid-crystalline phase, which takes into account the partial ordering of the flexible fragments. Finally, in section 5, we discuss the obtained results.

2. Model

Let us consider a system of polymer chains placed on a spatial lattice (a cubic one to be definite). Let each chain consist of identical alternating flexible and stiff fragments, occupying x' and x'' lattice sites, respectively. That part of either a flexible or a stiff fragment occupying one lattice site will be referred to as a chain link. Let N be the total number of flexible and stiff fragments in each chain. The manner in which the stiff fragments (rigid rods) are placed on the lattice is described in ref 11 and that of the flexible fragments in ref 10 (see also Figure 1). As in ref 10 we define the flexibility of flexible fragments in the absence of orientational ordering by the parameter f_0, which is the fraction of chain links in the bent conformation (with respect to the preceding unit). This parameter is related

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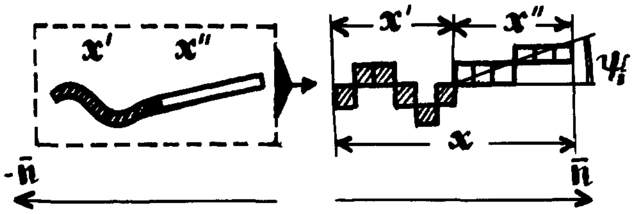


Figure 1. Repeating block of macromolecules in the model under consideration and the way of its arrangement on the lattice (for details see ref 10 and 11). This block is separated from the adjacent ones by freely rotating junctions.

to the additional energy ϵ per bend of a polymer chain by the formula[10]

$$f_0 = \frac{(z-2)\exp(-\epsilon/kT)}{1+(z-2)\exp(-\epsilon/kT)} \tag{1}$$

where z is the coordination number of the lattice (for the case of the cubic lattice under consideration, $z = 6$), k is the Boltzmann constant and T is temperature. At $\epsilon = 0$, $f_0 = 0.8$; an increase in ϵ, i.e., of the chain stiffness, corresponds to a decrease in f_0. We will assume that the lattice is densely filled with macromolecules (a polymer melt), i.e., that the total number of lattice sites is $n_0 = Nn_2(x' + x'')$, where n_2 is the total number of polymer chains in the system.

The mode adopted for conjugation of flexible and stiff fragments is worth a separate discussion. Let us assume that the probability that the chain is bent at the junction point of the end of a flexible fragment and the beginning of the stiff fragment is determined by the flexibility parameter of the flexible fragment. At the same time, let us assume that the last link of a stiff fragment and the initial link of the next flexible fragment are joined by an absolutely flexible freely rotating junction point, so that even in the limit $f_0 \rightarrow 0$ of negligible flexibility of "flexible" fragments the considered macromolecule becomes a sequence of freely jointed rods of length $x' + x''$, and not an absolutely rigid rod. This assumption leads to a significant simplification of the calculations; on the other hand, the only case excluded by this model corresponds to the situation in which the flexible fragments and the joints between the flexible and the stiff fragments are so rigid that macromolecules straighten as a whole and become by themselves similar to the rigid rods. This case is seldom found in real thermotropic liquid-crystalline polymeric systems.[5,12–14]

3. Orientational Ordering in the Matheson–Flory Approximation

In this section we examine the liquid-crystalline transition in the macromolecular melt described above, using the Matheson–Flory assumption[8] that the degree of flexibility of flexible chain fragments is always the same (characterized by the parameter f_0) irrespective of whether the system is or is not orientationally ordered. In ref 8 this question was not considered, since in that paper attention was principally paid to the study of liquid-crystalline ordering in polymer solutions.

The partition function Z of an athermal polymer melt in the case under consideration can be subdivided (as usually in the Flory method) into two factors, orientational and combinatorial (cf. ref 10 and 11):

$$Z = Z_{\text{orient}} Z_{\text{comb}} \tag{2}$$

The factor Z_{orient} describes the entropy of orientational ordering of stiff fragments (rods) and may approximately be written as[8]

$$Z_{\text{orient}} = y^{2Nn_2}; \qquad y = x''\langle \sin \psi_i \rangle \tag{3}$$

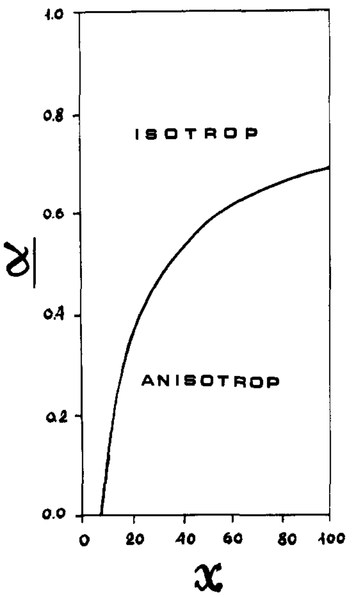


Figure 2. Phase diagram for athermal melt of macromolecules in the Matheson–Flory approximation.

where ψ_i is the angle between the ith rod and the anisotropy axis, and the averaging is performed over all rods in the system. In the Matheson–Flory approximation it is easy to obtain the following expression for Z_{comb} (cf. ref 10 and 11):[17]

$$Z_{\text{comb}} = \frac{1}{n_2!} C_{Nx'n_2}^{f_0Nx'n_2} \Bigl(\prod_{j=1}^{n_2} \nu_j\Bigr) \exp\left(-f_0 N n_2 x' \frac{\epsilon}{kT}\right) \tag{4}$$

where $C_{Nx'n_2}^{f_0Nx'n_2}$ is the number of ways of choosing $f_0Nx'n_2$ elements from the total of $Nx'n_2$ elements, and ν_j is the number of ways of placing on the lattice the jth macromolecule with fixed bending points within the flexible fragments, provided $j - 1$ macromolecules are already arranged on the lattice:

$$\nu_j = \frac{[n_0 - N(x' + x'')(j-1)]^{(x'+x'')N}(z-2)^{Nf_0x'}}{[n_0 - N(x'' - y)(j-1)]^{(x''-y)N}{n_0}^{N(x'+y)-1}} \tag{5}$$

The procedure leading to eq 4 and 5 is entirely identical with that used in ref 8.

Taking into account eq 1–5, the free energy $\mathcal{F}_0$ of the athermal isotropic melt under consideration can be written as

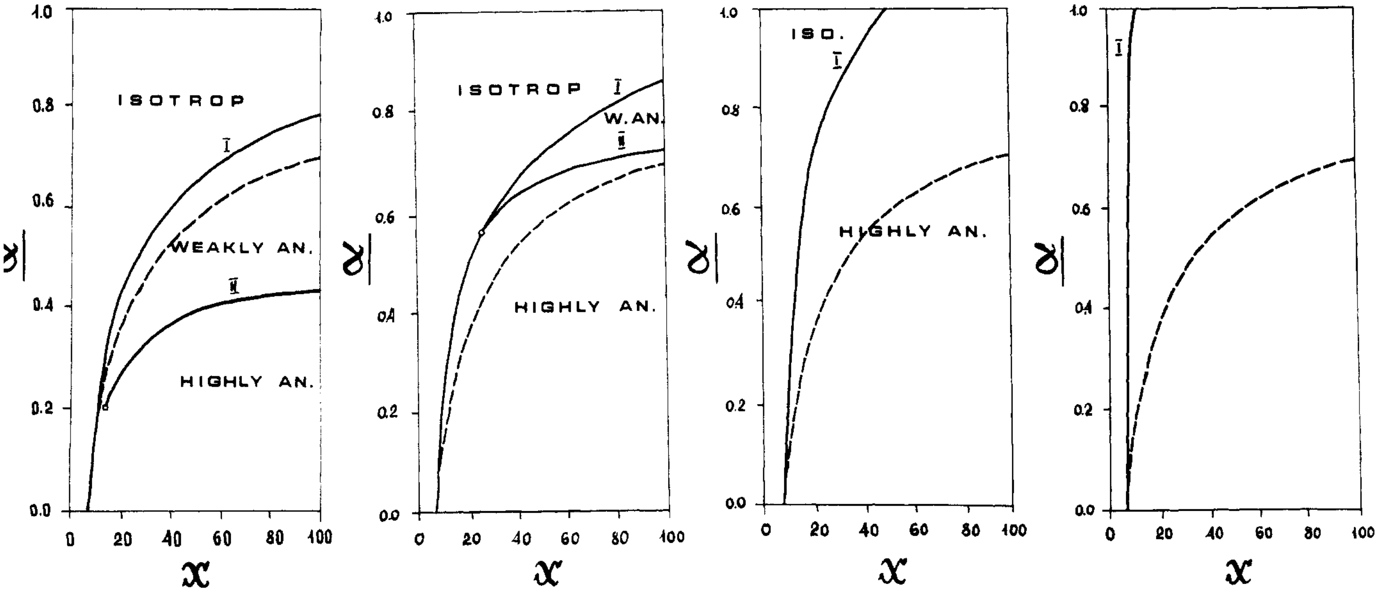
$$\begin{aligned} \mathcal{F}_0/kT = -\ln Z = \\ -n_2 \ln [N(x' + x'')] + Nn_2x' \ln (1 - f_0) - \\ n_2N(x' + y) \ln \left[\frac{x' + y}{x' + x''}\right] + Nn_2(x' + y - 2 \ln y) - n_2 \end{aligned} \tag{6}$$

The equilibrium value of the parameter y, which characterizes the extent of ordering of stiff fragments in the anisotropic phase, is determined, as usual,[8,11] from the condition of minimization of the free energy with respect to y ($\partial\mathcal{F}_0/\partial y = 0$):

$$\exp\left(-\frac{2}{y}\right) = \frac{y + x'}{x' + x''} \tag{7}$$

As regards the expression for the free energy of the isotropic phase, it can be obtained, as was already shown in ref 8, directly from eq 6 by substituting $y \rightarrow x''$.

Once the expressions for the free energy of the isotropic and anisotropic phases are obtained, the subsequent analysis of the liquid-crystalline transition can be performed in a standard way. One of the results of this analysis is given in Figure 2, which presents the phase



(a) (b) (c) (d)

Figure 3. Phase diagrams for the athermal melt obtained with regard for the induced ordering of flexible fragments are $f_0 = 0.8$ (a), $f_0 = 0.7$ (b), $f_0 = 0.6$ (c), and $f_0 = 0.4$ (d). The isotropic phase is stable to the left of the curves I. The dashed line shows the curve for the isotropic–nematic transition derived in the Matheson–Flory approximation.

diagram for the system considered in terms of variables α and x. (Here, $\alpha = x'/(x' + x'')$ is the fraction of flexible fragments in the chain and $x = x' + x''$ is the total length of the repeating block of the chain.) A liquid-crystalline nematic phase is thermodynamically stable in the region to the right of the curve in Figure 2. This curve intersects the $\alpha = 0$ axis at $x = 6.702$, which corresponds to Flory's result for the critical degree of asymmetry, above which a liquid-crystalline phase is formed in an athermal melt of rigid rods. When $x \to \infty$, $\alpha \to 1$, it is easy to check that in this limit the liquid-crystalline transition is similar to that in a dilute athermal solution of long rods. Thus, in the Matheson–Flory approximation the flexible chain component actually serves as a kind of a "diluent", in which the stiff fragments are situated (as in the solution). The phase diagram of Figure 2 appears to be independent of either N or f_0. The latter result (that the features of the liquid-crystalline transition are independent of the flexibility parameter f_0 of the flexible component) clearly reveals a limitation of the Matheson–Flory approximation.

4. Free Energy of the Liquid-Crystalline Phase with Regard for the Ordering of Flexible Fragments

Let us now discard the Matheson–Flory approximation; i.e., let us take into account the partial ordering of flexible fragments in the anisotropic phase. This ordering arises through the action of the self-consistent orientational field on the flexible chain fragments. Consequently, when describing these fragments it is necessary to discern not only the "bent" or "straight" conformation of each link, but the orientation of each link with respect to the anisotropy axis as well. The state of the flexible chain component will hence be characterized by the following three parameters (in contrast to the single parameter f_0 in the Matheson–Flory approximation): h, the fraction of links that are parallel to the ordering axis; f, the fraction of links in the bent conformation (in the anisotropic phase $f < f_0$ because of the "stiffening" effect of the self-consistent orientational field); and g, the fraction of links in the bent conformation that are parallel to the ordering axis (i.e., the fraction of links in a conformation corresponding to the bend from the direction perpendicular to the ordering axis onto the direction parallel to this axis).

The parameter h determines the number of links in the flexible fragments, for which it is necessary to take into account the effect of the increase in probability for a step along the ordering axis compared to that in the perpendicular direction—the same effect as reckoned for $(x'' - y)$ links of each stiff fragment in the Matheson–Flory approximation. For macromolecules of the type considered, this effect, first described in ref 11 for the case of absolutely rigid rods, consists of the following: in consecutive distribution of the links of the jth macromolecule in a lattice, the probability of finding the vacant site located in the direction of the ordering axis relative to the site occupied on the previous step is not equal to the volume fraction

$$[n_0 - N(x' + x'')(j - 1)]/n_0 \qquad (8)$$

of the vacant sites (as for the sites lying in the direction perpendicular to the ordering axis relative to that occupied on the previous step) but to the ratio

$$\frac{n_0 - N(x' + x'')(j - 1)}{n_0 - N(x'' - y + hx' - gx')(j - 1)} \qquad (9)$$

of the number of vacant sites to the total number of sites *minus* the number of sites which are occupied by the second, the third, etc. links in uninterrupted sequences of links that are paralleled to the ordering axis. Since the site in which we have placed the previous link was vacant, it is in principle impossible for these links to cover the next site along the ordering axis.

The parameter g, together with f, completely defines the number of chain links in bent conformations of various types: of all the Nn_2x' links of flexible fragments, $Nn_2x'g$ links correspond to the bend toward the ordering axis, just the same amount to the bend from this axis to the perpendicular direction, and $Nn_2x'(f - 2g)$ chain links to the bends in the plane perpendicular to the ordering axis. It is noteworthy that there are two ways for the first type of bends (two directions of the ordering axis), $(z - 2)$ ways for the second type of bends, and $(z - 4)$ ways for the third type of bends.

It is easy to obtain $\bar{\nu}_j$, the number of ways are arrangement on the lattice for the jth macromolecule with fixed *positions and types of bends* in the flexible fragments, provided $j - 1$ macromolecules are already placed on the lattice. For the chosen model it should be written in the following form (cf. eq 5, obtained in the Matheson–Flory approximation):

$$\bar{\nu}_j = \frac{[n_0 - N(x' + x'')(j - 1)]^{N(x'+x'')}[2(z - 2)]^{Ngx'}}{[n_0 - N(x'' - y + x'(h - g))(j - 1)]^{N(x''-y+x'(h-g))}} \times \frac{(z - 4)^{N(f-2g)x'}}{{n_0}^{N[x'(1-h+g)+y]-1}} \quad (10)$$

The partition function of the athermal melt can still be expressed in the forn (2), where the value of Z_{orient} is determined by eq 3. As regard the expression for Z_{comb}, it must now be written in the following form:

$$Z_{\text{comb}} = \frac{1}{n_2!} C_{hx'Nn_2}^{gx'Nn_2} C_{(1-h)x'Nn_2}^{(f-g)x'Nn_2} C_{(f-g)x'Nn_2}^{gx'Nn_2} \left(\prod_{j=1}^{n_2} \bar{\nu}_j\right) \times \exp\left(-\frac{fNn_2x'\epsilon}{kT}\right) \quad (11)$$

where the product of the three combinatorial factors C gives the number of ways for the links in the bent conformation to be distributed within the flexible fragments at fixed f, g, and h values. The first of these factors represents the number of ways to choose $gx'Nn_2$ first elements of the uninterrupted sequences of links parallel to the ordering axis from the total quantity $hx'Nn_2$ of such links. The second factor gives the number of ways for $(f - g)x'Nn_2$ first links of the rectilinear sequences of links between two chain bends lying in the plane perpendicular to the ordering axis to be chosen from the total quantity $(1 - h)\cdot x'Nn_2$ of such links. Finally, the third factor gives the number of ways available for $gx'Nn_2$ uninterrupted sequences of links parallel to the ordering axis to be distributed among $(f - g)x'Nn_2$ rectilinear sequences of links that are located in the plane perpendicular to the ordering axis.

With eq 2 and 3 and 10 and 11 are taken into account, the free energy of the anisotropic phase of an athermal melt of the macromolecules under consideration can be written as follows (cf. eq 6, obtained in the Matheson–Flory approximation):

$$\begin{aligned} \mathcal{F}_0/kT = {} & -n_2 \ln [N(x' + x'')] + Nn_2x'\Bigg\{-h \ln h - (1 - h) \ln (1 - h) + (f - 2g) \ln \left[\frac{f - 2g}{z - 4}\right] + g \ln \left[\frac{g^2}{2(z - 2)}\right] + \\ & (h - g) \ln (h - g) + (1 - f - h + g) \ln (1 - f - h + g) + \frac{f\epsilon}{kT}\Bigg\} - \\ & n_2N \ln y^2 - n_2 + n_2N(x'(1 - h + g) + y) - n_2N[y + x'(1 - h + g)] \ln \left[\frac{y + x'(1 - h + g)}{x' + x''}\right] \end{aligned} \quad (12)$$

This expression for $\mathcal{F}_0$ contains four parameters f, g, h, and y (instead of only the parameter y in eq 6; the equilibrium values of these parameters are to be determined from the minimization of the free energy with respect to them. Minimization results in the following equations:

$$f = \frac{2g \exp(\epsilon/kT) + (z - 4)(1 - h + g)}{\exp(\epsilon/kT) + (z - 4)} \quad (13)$$

$$\frac{y + x'(1 - h + g)}{x' + x''} = \frac{h(1 - f - h + g)}{(1 - h)(h - g)} \quad (14)$$

$$\frac{y + x'(1 - h + g)}{x' + x''} = \frac{(z - 4)g^2(1 - f - h + g)}{2(z - 2)(h - g)(f - 2g)^2} \quad (15)$$

$$\frac{y + x'(1 - h + g)}{x' + x''} = \exp(-2/y) \quad (16)$$

which, together with eq 12, completely define the free energy of the liquid-crystalline phase. As regards the free energy of the isotropic phase, it may still be obtained by substituting $y \rightarrow x''$ in eq 6.

5. Liquid-Crystalline Transition with Regard for the Ordering of Flexible Fragments

Comparing the free energies of the isotropic and anisotropic phases, we obtain the conditions for the orientational ordering in the system under study. Making use of eq 13–16 we can then determine the main properties of the liquid-crystalline phase. The corresponding calculations, though tedious, are of no basic difficulty. Hence we will proceed directly to the results obtained.

Figure 3 presents the calculated phase diagrams for the liquid-crystalline transition for $f_0 = 0.8$ (Figure 3a), $f_0 = 0.7$ (Figure 3b), $f_0 = 0.6$ (Figure 3c), and $f_0 = 0.4$ (Figure 3d) obtained with regard for the partial ordering of flexible fragments. For an easy comparison, the dashed line in the figures corresponds to the coexistence curve for the isotropic and anisotropic phases obtained in the Matheson–Flory approximation (this curve is independent of f_0). It can be seen, first of all, that now the conditions for the liquid-crystalline ordering do depend on the value of f_0, as should be expected from the physical sense of the problem. It may then be noted that allowing for the ordering of the flexible fragments leads to a significant increase of the stability region for the anisotropic phase (curves I for the equilibrium of the isotropic and anisotropic phases are shifted to the left), which is the greater the lower is the value of f_0.

Let us examine in more detail the case $f_0 = 0.8$ (the maximum possible flexibility of flexible fragments, $\epsilon = 0$). The phase diagram corresponding to this case is shown in Figure 3a; it can be seen that, besides curve I of the coexistence between the isotropic and anisotropic phases, an additional curve II is present, describing the transition between two different anisotropic phases. These two phases will be subsequently called the "highly anisotropic" one (stable at lower α) and the "weakly anisotropic" one (stable at higher α). Curve II starts at a critical point with coordinates $\alpha_{\text{cr}} = 0.2$, $x_{\text{cr}} = 14.1$ (see Figure 3a). Thus at $f_0 = 0.8$ (as well as at any $f_0 > 0.63$) additional orientational ordering occurring via a phase transition is possible within the anisotropic phase.

The physical meaning of this rather unexpected result, which was impossible to obtain within the limits of the Matheson–Flory approximation, becomes clearer after examination of Figure 4, which presents the dependence on α of the order parameters S^{s} and S^{f} of the stiff and flexible fragments[18]

$$S^{\text{s}} = \frac{1}{2}\left[\frac{3(x'')^2}{(x'')^2 + 2y^2} - 1\right], \qquad S^{\text{f}} = \frac{3h - 1}{2} \quad (17)$$

in the anisotropic phase at the point of its equilibrium coexistence with the isotropic phase (for $f_0 = 0.8$). It is seen that when the value of α is sufficiently small, the degree of ordering of the flexible component in the anisotropic

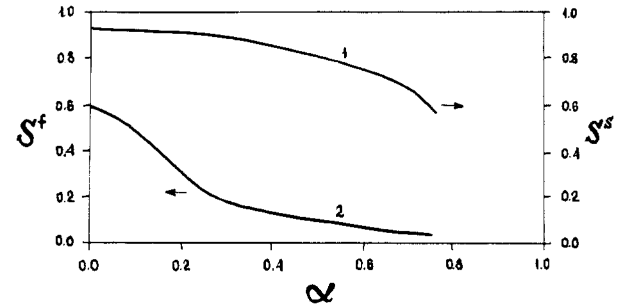


Figure 4. Order parameters S^s (1) and S^f (2) in the liquid-crystalline phase calculated along the coexistence curve I in Figure 3a (f_0 = 0.8).

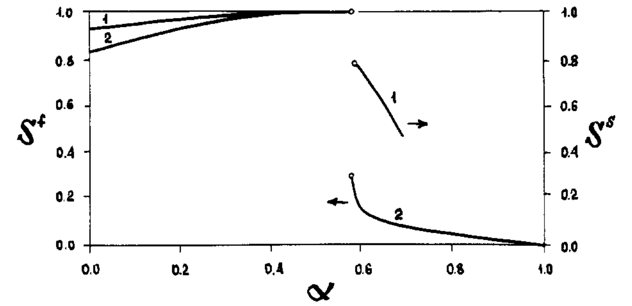


Figure 5. Order parameters S^s (1) and S^f (2) in the liquid-crystalline phase calculated along the coexistence curve I in Figure 3b (f_0 = 0.7).

phase can become quite significant.

This means that, generally speaking, the presence of the flexible chain component in the macromolecules under consideration can produce two opposite tendencies. At small values of α, after the liquid-crystalline transition takes place, flexible fragments become so strongly oriented that in the anisotropic phase they play the stiffening (not softening!) role, because they increase effectively the degree of asymmetry of the macromolecules.[19] On the contrary, at higher values of α the flexible component is only slightly ordered in the course of the liquid-crystalline transition and plays in the anisotropic phase a more natural softening (plasticizing) role. The first tendency favors the formation of a highly anisotropic phase, while the second one promotes the formation of a weakly anisotropic phase; it is the presence of both tendencies that leads to the possibility of the additional phase transition between the two phases.

When the value of f_0 decreases, the stability region of the weakly anisotropic phase diminishes and is shifted toward larger values of α (see the phase diagram in Figure 3b for f_0 = 0.7). Beginning from $(f_0)_{cr}^1 \cong 0.745$ the critical point in the phase diagram transforms into a triple point (cf. Figure 3a,b). For $f_0 < (f_0)_{cr}^1$ the type of the dependence of the order parameters S^s and S^f on α along the coexistence curve of the isotropic and anisotropic phases is also altered (see Figure 5, which demonstrates these dependences for the case f_0 = 0.7). At such f_0 values, the order parameters in the highly anisotropic phase increase with an increase in α, so that in the vicinity of the triple point (at f_0 = 0.7, α_t = 0.576) this phase becomes practically completely ordered already at the curve of coexistence with the isotropic phase. The dependence of the order parameters on α along the coexistence curve for the isotropic and weakly anisotropic phases is the opposite (as is seen from Figure 5). On passing through the triple point the curves shown in Figure 5 undergo large discrete changes.

When the value of f_0 becomes lower than the critical value $(f_0)_{cr}^2 \cong 0.63$, the region of stability of the weakly anisotropic phase vanishes. The value $(f_0)_{cr}^2$ = 0.63 coincides with that obtained by Flory in ref 8, where it was shown that at $f_0 < 0.63$ the liquid-crystalline ordering must take place even in the melt of polymer chains that consist of only a flexible component (i.e., for α = 1). In full accord with this result the calculated curves of equilibrium between the isotropic and anisotropic phases at $f_0 < 0.63$ (in this case only the highly anisotropic phase exists) reach the α = 1 value at some finite values of x (see parts c and d of Figure 3, corresponding to f_0 = 0.6 and 0.4). If for f_0 = 0.6 and 0.4 we attempt to plot dependences similar to that in Figures 4 and 5, it will appear that S^s and S^f are close to unity practically everywhere in the liquid-crystalline phase; i.e., at these f_0 values (as well as at any $f_0 < 0.63$) both flexible and stiff fragments in the anisotropic phase are very strongly ordered. This effect is most pronounced at f_0 = 0.4 (Figure 3d); in this case the induced stiffening of the flexible component appears to be so essential that at any α the macromolecule in the anisotropic phase behaves as a sequence of freely jointed practically rigid rods of the length $x = x' + x''$ so that the coexistence curve for the isotropic and anisotropic phases is almost parallel to the α axis (see Figure 3d). Thus for $f_0 < 0.63$ the flexible component always plays a stiffening role.

Considering on the whole the results obtained, we can conclude that the application of the method developed in the present work, which takes into account the induced ordering of the flexible component, allows prediction of many effects which could not be contemplated in the simple Matheson–Flory approximation. For a sufficiently comprehensive comparison with experimental results the theory needs certain further developments. First of all, anisotropic attractive forces should be taken into account together with the steric interactions. However, even at the present stage some of the predictions suggested by the theory (concerning the extent of stiffening of the flexible chain fragments in the anisotropic phase, the possibility for equilibrium coexistence of the two different anisotropic phases, the values of order parameters at the transition points, etc.) are worth experimental exploration.

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(17) In this paper only liquid-crystalline melts of long-chain macromolecules ($N(x' + x'') \gg 1$) will be considered; hence we will neglect end effects in the subsequent formalae.

(18) Equation 17 for S^s does not correspond to the common definition of the order parameter: $S^s = \langle (3 \cos^2 \theta - 1)/2 \rangle$, where θ is the angle between the direction of the rod and the ordering

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axis. At the same time, in the isotropic phase $S^s = 0$, in the absolutely ordered phase $S^s = 1$, and when the ordering is partial $0 < S^s < 1$. Consequently the S^s values from eq 17 characterize the extent of ordering of flexible fragments as well.

(19) It must be borne in mind that in the chosen macromolecular model the repeating blocks of a polymeric chain (of length $x = x' + x''$) are freely jointed together, so that even at extreme stiffening of the flexible component, the length of a rigid fragment does not exceed x.

Theory of Liquid-Crystalline Ordering in Melts of Macromolecules with Stiff and Flexible Fragments in the Main Chain. 2. Effect of External Orientational Fields

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ABSTRACT: The theory of orientational ordering in polymer melts containing stiff and flexible fragments in the main chain, as proposed in the preceding paper, is generalized for the case of the presence of an orientational external field of quadrupole symmetry. It is demonstrated that in this case Flory's "1956 approximation" is not applicable, and it is necessary to take into account the exact form of the orientational distribution function for the stiff fragments (rods), using the method proposed in the recent work of Flory and Ronca. Phase diagrams for different strengths of external field and for different values of the flexibility parameter of flexible fragments are constructed. It is shown that an additional critical point appears in the phase diagrams when the field is applied. The problem of orientational ordering induced by uniaxial elongation of melts of flexible-chain polymers is also considered. It is shown that such ordering, at a certain critical value of the applied stress, is always accompanied by a phase transition to a highly oriented absolutely ordered (in the framework of the lattice model) phase.

1. Introduction

In the preceding paper[1] we have developed, on the basis of a modified lattice method of Flory, the theory of orientational ordering in melts of polymers containing stiff and flexible fragments in the main chain. The structure of the phases formed and the character of corresponding phase transitions may vary significantly when an external orientational field is applied to the melt. Such fields may arise from uniaxial elongation of polymer melts due to the application of external electric or magnetic fields or due to certain types of flows of polymer melts (see ref 2 and 3). The aim of the present work is the study of the phase diagram for a melt of macromolecules with stiff and flexible fragments in the main chain in the presence of an external orientational field of quadrupole symmetry, i.e., of a field in which the potential energy of a rectilinear chain fragment is proportional to $-\cos^2\theta$, where θ is the angle between the direction of this fragment and the orientation axis. The effective field which appears with uniaxial strain of the melt represents the simplest example of a quadrupole field; a field of this type is also produced when nonpolar polymeric chains are subjected to an electric (or magnetic) field or in hydrodynamic "longitudinal shear" flow (see ref 2 and 3).

Experimental study of the effect of external orientational fields on the properties of thermotropic liquid-crystalline polymers containing mesogenic groups in the main chain has not so far been very intensive (see, however, ref 4–7). However, the present great interest in this class of polymers suggests that such studies will soon be carried out, providing the possibiity for experimental verification of the theoretical predictions of this paper.

Let us accept for the melt of macromolecules under consideration the same model and the same notation that was used in the preceding paper.[1] When an external orientational quadrupole field is applied, the additional term ΔF should be added to the free energy of the melt, $\mathcal{F}_0$ (see eq 12 or ref 1):

$$\Delta\mathcal{F}_0/kT = -u_0 N n_2 (x'\langle\cos^2\psi_j\rangle + x''\langle\cos^2\psi_i\rangle) \tag{1}$$

where the averaging is performed over all angles ψ_j between the links of the flexible component and the orientation axis (for the first term) and over all angles ψ_i between the stiff fragments (rods) and the orientation axis (for the second term). The dimensionless parameter u_0 defines the intensity of the applied external field (or the elongation of the sample).

As in the proposed model the links of the flexible component can acquire only three orientations, it is quite easy to see that

$$\langle\cos^2\psi_j\rangle = h \tag{2}$$

The rods may acquire a variety of different orientations, depending on the value of the y parameter. Hence the calculation of $\langle\cos^2\psi_i\rangle$ presents a more difficult problem, which is treated in the following section.

2. Free Energy of a System of Rigid Rods Subjected to an External Orientational Field

In Flory's approximation of 1956,[8] which was used in the preceding paper,[1] the equilibrium factor of disorientation is defined as

$$y = x''\langle\sin\psi_i\rangle \tag{3}$$

(see eq 3 of ref 1). Thus within the limits of this approximation

$$\langle\cos^2\psi_i\rangle = 1 - (y/x'')^2 \tag{4}$$

In particular, this assumption was made by Marrucci and

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