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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):

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

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

$$\langle\cos^2\psi_j\rangle = h \qquad (2)$$

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

$$y = x''\langle\sin\psi_i\rangle \qquad (3)$$

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

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

In particular, this assumption was made by Marrucci and

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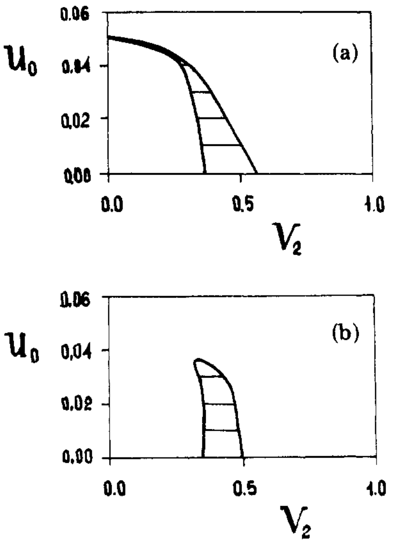

Figure 1. Phase diagrams for a solution of rigid rods with $x'' = 20$ subjected to external orientational quadrupole fields obtained with the use of the approximation of ref 8 (a) and via the procedure suggested in this paper (b).

Ciferri,[9] who examined the effect of an external orientational field on the liquid-crystalline ordering in a solution of long rigid rods.

A more detailed analysis reveals, however, that for the purposes of the present work Flory's 1956 approximation is inadequate. As was emphasized in ref 10, in this approximation the exact form of the orientational distribution function for the rods is substituted for a simplified one. In the case of a large order parameter in the anisotropic phase such a simplification does not significantly affect the final results (see ref 10). However, if the formation of an anisotropic phase with a small order parameter is possible, the description of this phase based on the 1956 approximation may produce substantial errors.

This fact becomes more evident if we consider the phase diagram for a solution of rigid rods subjected to an external field, the coordinates being intensity of the field, u_0, and volume fraction of polymer in the solution, V_2, that was obtained in ref 9 with the 1956 approximation (Figure 1a). The region to the left of the dashed region of phase separation corresponds to the isotropic phase; a homogeneous anisotropic phase is stable to the right of the dashed region. It can be seen that at $u_0 < (u_0)_{\mathrm{cr}}$ it is predicted that in a certain concentration range an *absolutely* isotropic phase (with $y = x''$) exists in spite of the presence of the external orientational field—a result lacking physical sense because a *finite* orientational field must deliberately induce a *finite* degree of anisotropy. This result was obtained because the application of a not too intensive external field to an initially isotropic phase produces an anisotropic phase with a small order parameter; the 1956 approximation is inadequate for its description, and it is necessary to take into account the exact form of the orientational distribution of rods.

In the paper by Flory and Ronca[10] it was shown that when the exact orientational distribution of rods is taken into account, the expression for Z_{orient} (i.e., eq 3 of ref 1) is significantly modified; for a solution of rigid rods of length x'' in the absence of an external field, it acquires the form

$$Z_{\mathrm{orient}} = [\sigma f_1 e^{ay}]^{Nn_2} \tag{5}$$

where

$$a = -\ln\,[1 - V_2(1 - y/x'')]$$

$$y = \frac{4}{\pi} x'' \langle \sin \psi_i \rangle$$

Here, V_2 is the volume fraction of rods in the solution

$$f_1 = \int_0^{\pi/2} \sin \psi \exp\left(-\frac{4}{\pi} a x'' \sin \psi\right) \mathrm{d}\psi \tag{6}$$

and σ is the normalization factor, of which the specific value is unimportant. In the presence of an external orientational field of quadrupole symmetry, the above formulas (5) and (6) should be modified in order to take into account the fact that the rods are subjected both to the self-consistent field proportional to $\langle \sin \psi_i \rangle$ and to the external field proportional to $-\langle \cos^2 \psi_i \rangle$. Thus these formulas take the forms

$$Z_{\mathrm{orient}} = \left[\sigma f_1 \exp\left(\frac{4}{\pi} a x'' \langle \sin \psi_i \rangle - u_0 x'' \langle \cos^2 \psi_i \rangle\right)\right]^{Nn_2} \tag{5'}$$

$$f_1 = \int_0^{\pi/2} \sin \psi \exp\left(-\frac{4}{\pi} a x'' \sin \psi + u_0 x'' \cos^2 \psi\right) \mathrm{d}\psi \tag{6'}$$

where

$$\langle \cos^2 \psi_i \rangle = \frac{1}{f_1} \int_0^{\pi/2} \cos^2 \psi \sin \psi \exp\left(-\frac{4}{\pi} a x'' \sin \psi + u_0 x'' \cos^2 \psi\right) \mathrm{d}\psi \tag{7}$$

$$\langle \sin \psi_i \rangle = \frac{1}{f_1} \int_0^{\pi/2} \sin^2 \psi \exp\left(-\frac{4}{\pi} a x'' \sin \psi + u_0 x'' \cos^2 \psi\right) \mathrm{d}\psi \tag{8}$$

Equation 7 defines, in particular, the free energy for the interaction of rods with the external field (see eq 1).

Formulas 5 and 6 were used in ref 10 to determine the exact conditions for the liquid-crystalline ordering in solutions of rigid rods in the absence of external fields, and it was shown that the deviations from the results obtained with the 1956 approximation are small. To illustrate the fact that the 1956 approximation is inadequate in the case when the external orientational field is applied, we show in Figure 1b a phase diagram calculated via formulas 5 and 6 for the liquid-crystalline transition in a solution of rigid rods in the variables u_0 and V_2 for $x'' = 20$. (Compare with the analogous phase diagram shown in Figure 1a, obtained in the 1956 approximation.) Concentrating a solution of rods at $u_0 < (u_0)_{\mathrm{cr}}$ results in the phase transition between two anisotropic phases; at $u_0 > (u_0)_{\mathrm{cr}}$ the rods are highly oriented even in the dilute solution and this phase transition is effectively suppressed; hence the value $u_0 = (u_0)_{\mathrm{cr}}$ corresponds to the critical point in the diagram. These conclusions are in full accord with the results of ref 2, obtained with the Onsager method, and they contradict Figure 1a and the data of ref 9, which were obtained with the 1956 Flory approximation.

For the sake of completeness let us present the results that are obtained by applying formulas 5 and 6 to the problem of liquid-crystalline ordering in a melt of rigid rods subjected to an external field. The phase diagram for this case in the variables u_0 and x'' is shown in Figure 2, and the dependence of the order parameter[13] of rods in the melt, S^{s}, on u_0 along the curve of the phase coexistence is presented in Figure 3. One may see that, in this case as well, there exists a critical point ($(u_0)_{\mathrm{cr}} = 0.127$; $(x'')_{\mathrm{cr}} = 5.25$) such that for $u_0 > (u_0)_{\mathrm{cr}}$ the properties of the melt

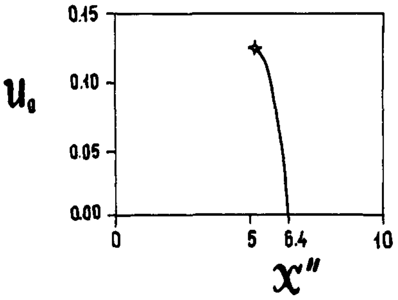

Figure 2. Phase diagram for a melt of rigid rods subjected to external orientational quadrupole fields. The asterisk marks the critical point.

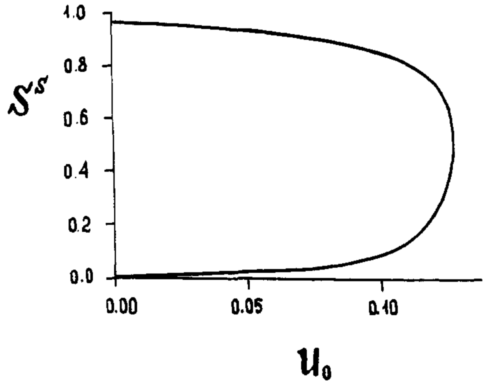

Figure 3. Dependence of the order parameter in a melt of rods on u_0 calculated along both sides of the coexistence curve.

are changed gradually with variation in x''.

3. Phase Diagrams for the Melt of Macromolecules with Stiff and Flexible Fragments in the Main Chain Subjected to an External Orientational Field

Let us now return to treating the problem formulated in the Introduction. It is evident that, no less than for the case of the solution of rigid rods that has been discussed in the previous section, the description of the melt of macromolecules with stiff and flexible fragments in the main chain subjected to an external orientational field is inadequately described with the 1956 Flory approximation, and it is necessary to take into account the exact form of the orientational distribution of the stiff fragments.

For the case under consideration the partition function Z_{orient}, corresponding to the orientational entropy of stiff fragments (rods), is still defined by eq 5′ and 6′ and eq 7 and 8 with the only difference that the expression for a is now the following:

$$a = -\ln \left[\frac{y + x'(1 - h + g)}{x' + x''} \right] \tag{9}$$

(cf. the last term of eq 12 of ref 1), in accordance with the fact that the self-consistent field is now induced not only by the stiff fragments but by the flexible fragments as well. To calculate the combinatorial contribution to the partition function, Z_{comb}, eq 11 of ref 1 is still valid. As regards the free energy (1) for the interaction of the macromolecules with the external field, it is given by eq 2 and 7. Thus the free energy of the melt of given macromolecules subjected to an external orientational field is now completely determined:

$$\mathcal{F} = -kT \ln Z_{\text{orient}} - kT \ln Z_{\text{comb}} + \Delta F \tag{10}$$

We will not give here the explicit bulky form of the expression for F.

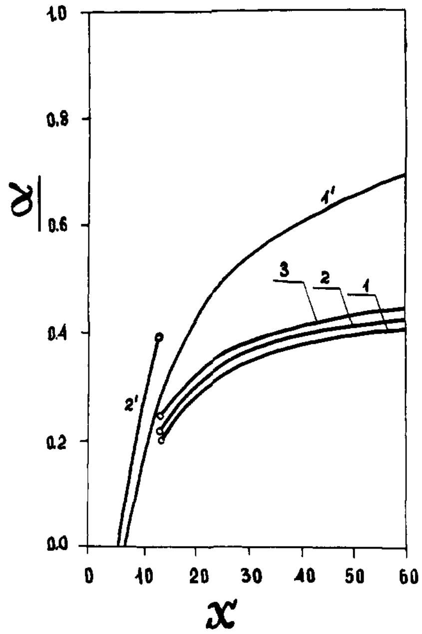

Figure 4. Phase diagrams for a melt of macromolecules with stiff and flexible fragments in the main chain for $f_0 = 0.8$ and various u_0 values: $u_0 = 0$ (curves 1 and 1′), $u_0 = 0.1$ (curves 2 and 2′), and $u_0 = 0.2$ (curve 3).

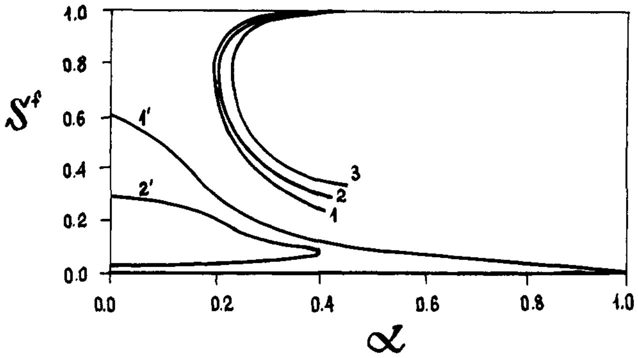

Figure 5. Dependences of order parameters of the flexible component S^f on α calculated along both sides of the coexistence curves shown in Figure 4.

Having obtained the free energy F, we may now construct the phase diagram in the standard way. Only two remarks concerning this procedure are noteworthy. First, at $u_0 \neq 0$ all phases that might exist in the system must be anisotropic, and all the phase transitions are thus the transitions between two anisotropic phases with different degrees of anisotropy. Second, when performing the specific calculations, it is often convenient to use the so-called asymptotic approximation introduced in ref 10, which is valid when $[(4/\pi)a + u_0]x'' \gg 1$, i.e., when the degree of anisotroy is not very small. This approximation simplifies some of the calculations significantly. Of course, the asymptotic approximation cannot be used to describe an anisotropic phase with small anisotropy; in these cases the exact expression for F must be considered.

Let us now proceed to the analysis of the phase diagrams obtained.

Figure 4 presents the spectrum of phase diagrams in the variables α and x for the case of maximum possible flexibility $f_0 = 0.8$ and various u_0 values: $u_0 = 0$ (curves 1 and 1′), $u_0 = 0.1$ (curves 2 and 2′), and $u_0 = 0.2$ (curve 3). Figure 5 represents the order parameters S^f of the coexisting phases as functions of α, the dependences having been calculated along the corresponding phase equilibrium curves. Analogous results for $f_0 = 0.7$ are presented in

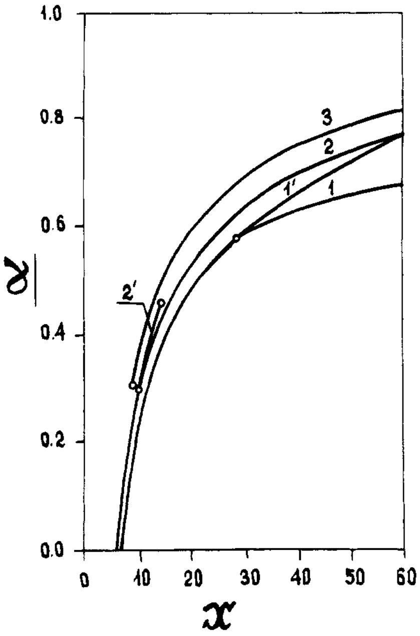

Figure 6. Phase diagrams for a melt of macromolecules with stiff and flexible fragments in the main chain for $f_0 = 0.7$ and various u_0 values: $u_0 = 0$ (curves 1 and 1′), $u_0 = 0.1$ (curves 2 and 2′), and $u_0 = 0.2$ (curve 3).

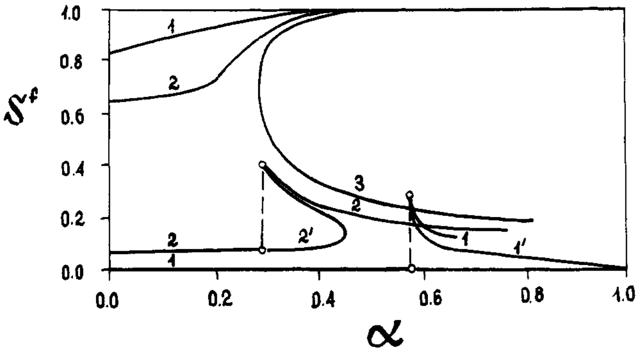

Figure 7. Dependences of order parameters of the flexible component S^f on α calculated along both sides of the coexistence curves shown in Figure 6.

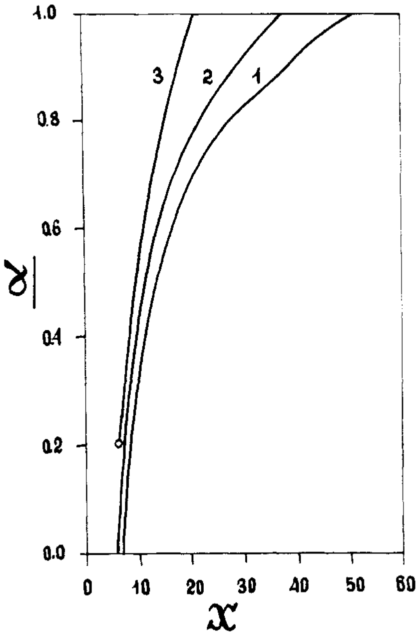

Figure 8. Phase diagrams for a melt of macromolecules with stiff and flexible fragments in the main chain for $f_0 = 0.6$ and various u_0 values: $u_0 = 0$ (curve 1), $u_0 = 0.1$ (curve 2), and $u_0 = 0.2$ (curve 3).

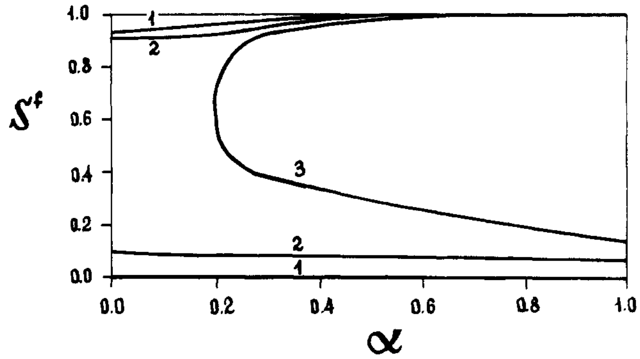

Figure 9. Dependences of order parameters of the flexible component S^f on α calculated along both sides of the coexistence curves shown in Figure 8.

Figures 6 and 7, and those for $f_0 = 0.6$ are shown in Figures 8 and 9.

Examination of Figures 4–9 permits the following conclusions. Let us first consider the case $f_0 > 0.63$. In this case, as shown in ref 1, at $u_0 = 0$ the phase diagram includes two types of phase equilibrium curves: equilibrium of isotropic and anisotropic phases (curves 1′ in Figures 4 and 6) and equilibrium between two anisotropic phases (curves 1 in Figures 4 and 6). When the external field is applied, a new critical point appears in the phase diagram (see curves 2′ in Figures 4 and 6, point A). A u_0 increases, this critical point "slides down" the phase equilibrium curve (of type 2′), "absorbing" it. Finally, at $(u_0)_{cr} = 0.127$ the critical point reaches the value $\alpha = 0$, which corresponds to a melt of rods, and the phase equilibrium curve of type 2′ vanishes. The physical interpretation for the effect of the appearance of a critical point on the phase coexistence curve is just the same as for the solution of rods (see previous section and ref 2); the basis of this effect is the fact that at $u_0 \neq 0$ the principle difference between the two coexisting phases disappears.

Curves 1 in Figure 4 and 6, describing at $u_0 = 0$ the coexistence of two anisotropic phases, are transformed on application of the field in a less pronounced way (see curves 2 and 3 in Figures 4 and 6). The major change in these curves with growth of u_0 consists of a gradual shift to higher α, which corresponds to the physically natural increase of the region of stability of the highly anisotropic phase with the increase in the intensity of the imposed orientational field.

At $f_0 < 0.63$ and $u_0 = 0$ the phase diagram exhibits only one equilibrium curve between the isotropic and highly anisotropic phases (Figure 8, curve 1). For $u_0 < (u_0)_{cr} = 0.127$ this curve is just shifted, increasing the area corresponding to the highly anisotropic phase (Figure 8, curve 2). At $u_0 > (u_0)_{cr}$ a critical point emerges on this curve at small α (Figure 8, curve 3). When the value of u_0 is further increased, this point shifts to higher α values, "absorbing" the phase equilibrium curve. Thus, at sufficiently high u_0 values, the phase diagrams appear to be qualitatively similar for all flexibility parameters f_0 (see Figures 4, 6 and 8, curves 3).

4. Orientational Ordering of the Melts of Flexible-Chain Polymers Induced by Uniaxial Elongation

A melt of long-chain flexible macromolecules, corresponding to $\alpha = 1$ and $x = \infty$, constitutes an important particular case of the consideration of this paper.[14] The calculations of the previous section, rewritten for this case,

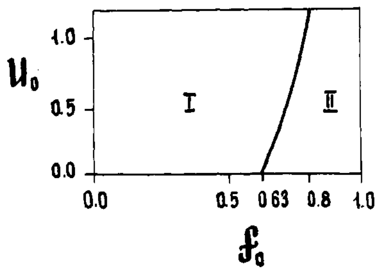

Figure 10. Phase diagram for a melt of flexible long-chain macromolecules subjected to external orientational field: (I) absolutely ordered phase; (II) the phase with a finite degree of anisotropy.

give the solution (within the framework of the lattice model) of the problem of orientational ordering of such melts under the influence of external orientational quadrupole fields (or under uniaxial elongation). This problem was discussed in the literature (see, for example, ref 11) in regard to the problem of orientational crystallization.

If we have a melt of flexible-chain polymers, it is obvious that as soon as it is subjected to even infinitely small strain it becomes anisotropic. What requires elucidation, however, is whether the degree of anisotropy increases gradually at subsequent elongations or whether at some critical value of the applied stress there should be a stepwise rise (i.e., a strain-induced phase transition).

The reported procedure[11] for the solution of this problem consists of the following. Elongation of an isolated polymeric chain and its resultant stiffening are considered. It is suggested that when the parameter f for an isolated strained chain equals $(f_0)_{cr}{}^2 = 0.63$, a stepwise phase transition will occur in a melt of chains with the corresponding elongation, leading to the formation of a highly anisotropic phase. In the preceding paper[1] we have demonstrated, however, that cooperative interaction of different chains, their induced stiffening, etc. are important for the occurrence of the liquid-crystalline phase transition in polymer melts. Obviously, these effects cannot be taken into account when considering the strain of an isolated macromolecule.

The calculations according to the method of this paper give the exact solution (within the lattice method of Flory) for the problem under consideration. It turns out that at any flexibility of the chain a phase transition induced by an external field is possible, the combined action of the external field and of the cooperative chain-stiffening effect resulting in the formation of an absolutely ordered phase (at $x = \infty$) with $f = 0$, $h = 1$, and $g = 0$. Figure 10 gives the dependence on f_0 of the external field intensity, u_0, at which this transition occurs. It can be seen that even for chains of extreme flexibility ($f_0 = 0.8$) the corresponding transition is possible and takes place at $u_0 \simeq 1.1$. At $f_0 < 0.63$ the chain, according to ref 12, spontaneously (at $u_0 = 0$) acquires an absolutely ordered state.

Figures 11 and 12 represent the dependences of the parameters f and h on f_0 in the phase with a finite degree of anisotropy at the point of its equilibrium with the completely ordered phase. It can be seen that the induced stiffening of flexible chains at this point may be quite substantial. It is also noteworthy that at the transition point the equality $f = \text{const} = 0.63$ is not valid; i.e., the assumption of ref 11 is inaccurate.

Summing up, it should be emphasized, however, that from the qualitative point of view the results of this section coincide with the results of ref 11. The advantages of the treatment suggested here are, on the one hand, its accuracy (within the method of Flory) and, on the other hand, the fact that the existence of the additional phase transition in the melts of flexible-chain polymers under strain is rigorously proved (but not postulated as in ref 11).

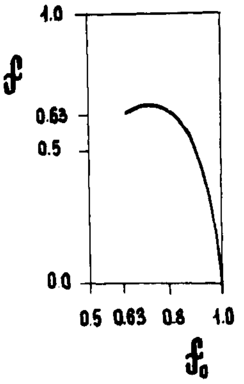

Figure 11. Dependence $f(f_0)$ in the phase with a finite degree of anisotropy along the curve of its equilibrium with an absolutely ordered phase.

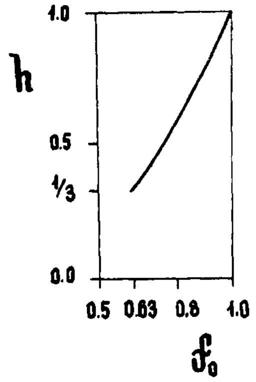

Figure 12. Dependence $h(f_0)$ in the phase with a finite degree of anisotropy along the curve of its equilibrium with an absolutely ordered phase.

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(13) To determine the order parameter S^* the simplified eq (17) of ref 1 was used.

(14) It may be noted that for $\alpha = 1$ and $x = \infty$ we do not need to assume that polymer chains contain rather unphysical freely rotating junctions between the repeating blocks (cf. part 1), since in this case we have only one infinitely long flexible fragment of the chain. The flexibilities of all links of this fragment are identical.