diagram might assume characteristics typical of those expected for two rodlike polymers.[17] In particular, the binodal for the isotropic phase would be extended to $v_3^* \sim 0.8$, and the composition range of biphasic solutions would be limited by a line below which a single anisotropic phase would occur. One could possibly treat such a diagram in terms of the Abe and Flory[17] theory of two rodlike polymers having axial ratios in the ratio 8:1, corresponding to the ratio of persistence lengths of PBA and X-500. Such a diagram is also expected[17] to show considerable inclination of tie lines with respect to the vertex-to-base line.

It will be interesting to explore in future work if these speculations can be put to a more stringent test in the case of pairs of mesogenic polymers exhibiting significant differences in their critical concentration before crystallization occurs. Also, quantitative determination of tie lines for systems involving PBA and a more flexible polymer than X-500 should be of interest, as well as a consideration of the possible role of actractive interactions between two polymers. The latter may occur for some special systems.

The above results and considerations should offer useful guidelines for the identification of conditions under which one could prepare technologically relevant composites based on these types of polymers.[22]

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Influence of External Field on the Liquid-Crystalline Ordering in Solutions of Stiff-Chain Macromolecules

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ABSTRACT: Using the Onsager method, we consider the influence of external fields of the dipole and quadrupole types on the liquid-crystalline ordering in solutions of completely stiff macromolecules (rigid rods), freely jointed semiflexible macromolecules (chains of freely jointed rods), and persistent semiflexible macromolecules. We construct the corresponding phase diagrams in the variables strength of the external field–concentration. A sufficiently strong orientational field of either type suppresses effectively the liquid-crystalline phase transition—this leads to the existence of the critical point on the phase diagrams. At the same time, when a sufficiently strong "disorientational" field of the quadrupole type is applied, the liquid-crystalline phase transition becomes of the second order. The realization of the phase transition induced by the field is generally possible, the case of the macromolecule with a persistent flexibility mechanism in the dipole field being most favorable for its observation.

1. Introduction

It is well-known that in sufficiently concentrated solutions of stiff-chain macromolecules the liquid-crystalline phase can appear.[1] Polymeric materials prepared from liquid-crystalline solutions have remarkable mechanical properties;[1,2] this is mainly due to high orientational order

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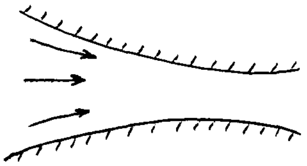

Figure 1. Hydrodynamic flow in a conical tube corresponding to the case of longitudinal shear.[3]

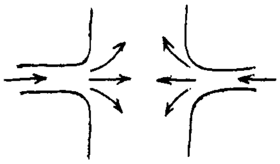

Figure 2. Realization of a "disorientational" quadrupole field in the central part of a volume in which fluid is pumped from two opposite directions.

in such solutions. The degree of orientational order can be increased if an initially ordered solution is placed in an external orientational field. This may be an external electric field, a magnetic field, or the effective field that appears when the solution is placed in an inhomogeneous hydrodynamic flow.

The aim of this paper is the theoretical consideration of the properties of the liquid-crystalline transition in solutions of stiff-chain polymers in the presence of an external field. The most important types of external orientational fields are the following: the dipole-type field, in which the potential energy of a straight-chain segment is proportional to $-\cos\theta$ (θ being the angle between the segment direction and the orientation axis), and the quadrupole-type field, in which the potential energy of a segment is proportional to $-\cos^2\theta$. The external magnetic (electric) field in the case when polymer chain segments have a constant magnetic (electric) moment directed along the chain is an example of the dipole-type field. The role of quadrupole-type field can be played either by the external magnetic (electric) field in the case when the macromolecular segments have zero dipole moments and nonzero uniaxial anisotropic susceptibilities or by the effective hydrodynamic field due to the inhomogeneous vortex-free "longitudinal shear" flow (see ref 3 and Figure 1). It is also noteworthy that if a stiff-chain macromolecule is introduced in some way inside a polymer network sample, the effective field acting on the segments of this macromolecule when the sample is uniaxially stretched is of the quadrupole type.

Situations when the external field of the quadrupole type shows not an orientational but a "disorientational" effect (i.e., when the segment potential energy in this field is proportional to $+\cos^2\theta$) are also possible. The disorientational quadrupole field can be obtained with the help of hydrodynamic flows (Figure 2); a field of this type is acting on the macromolecule situated inside a uniaxially compressed polymer network sample.

In the present paper we consider the liquid-crystalline ordering in polymer solutions in the presence of the above-mentioned types of external fields.

It is well-known that stiff-chain macromolecules can be divided into two main classes:[4] completely stiff macromolecules, which can be represented as long rigid rods of length l and diameter d ($l \gg d$, Figure 3a), and semiflexibile macromolecules whose persistence length, $\tilde{l}$, is much smaller than the total contour chain length, L, but much larger than the width of the chain, d: $L \gg \tilde{l} \gg d$. Further, semiflexibile macromolecules can differ depending on the flexibility distribution along the chain contour; two extreme cases are (i) the chain consisting of freely jointed rigid rods of length $l = 2\tilde{l}$ and diameter d ($l \gg d$, Figure 3b) and (ii) the chain completely homogeneous along the contour-persistence chain (Figure 3c; $l = 2\tilde{l}$, the effective Kuhn segment).

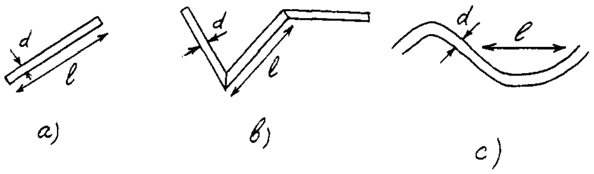

Figure 3. (a) Completely stiff macromolecule; (b) semiflexible freely jointed chain; (c) semiflexible persistent chain.

The liquid-crystalline ordering in solutions of long rigid rods in the absence of external fields was first considered in the classical paper by Onsager.[5] In ref 6 and 7 the Onsager method was generalized for solutions of semiflexible macromolecules with a freely jointed flexibility mechanism[6] and with a persistent flexibility mechanism.[7] It was shown that even in the absence of external fields the liquid-crystalline transition in solutions of semiflexible polymers differs essentially for cases b and c of Figure 3.[7,8]

In the present paper we analyze the influence of external fields on the liquid-crystalline ordering for the three qualitatively different models of stiff-chain macromolecules shown in Figure 3.

The liquid-crystalline transition in polymer solutions in the presence of an external field was first analyzed theoretically in ref 9 and 10 for the cases of rods and of freely jointed semiflexible chains in the quadrupole orientational field. In these papers Flory's lattice method was employed .[11] In ref 4 it was shown that even in the absence of external fields the calculations of ref 11 give quantitatively inaccurate expressions for the characteristics of the liquid-crystalline transition in the limit $l \gg d$ (for a detailed criticism of the Flory method, see ref 4). In ref 9 and 10 the application of the Flory method to the study of orientational ordering in the presence of an external field has led not only to quantitatively inaccurate results but also to qualitatively incorrect conclusions. For example, in ref 9 it was concluded that in the presence of an external orientational field (smaller than some critical field), the existence of the isotropic phase in dilute solution is possible—this result is, of course, physically meaningless.

In contrast to the Flory method, the method proposed by Onsager in ref 5, which is based on the second virial approximation, is physically well grounded (the validity of the second virial approximation is due to the small value of the polymer volume fraction in solution at which liquid-crystalline ordering takes place) and, moreover, asymptotically exact in the limit $l \gg d$.[4,12] Thus, following recent papers[4,5,8] we apply this method also in the present paper. The foundations of this method, which will be necessary for our consideration, are presented in the following section.

2. Free Energy of a Solution of Stiff-Chain Macromolecules

Let us consider a solution of completely stiff (Figure 3a), freely jointed semiflexible (Figure 3b), or persistent semiflexibile (Figure 3c) macromolecules. Below we use the term segment to denote all the macromolecule (rigid rod) (in the case of Figure 3a), the straight-chain segment between two junction points (in the case of Figure 3b), or the part of the chain whose length is equal to the length of the effective segment (in the case of Figure 3c). Let N be the total number of segments dissolved in the volume V, T the temperature, and $f(\vec{n})$ the orientational distribution function for the unit vectors, $\vec{n}$, tangential to the chain (in cases a and b of Figure 3, this function is, as a matter of fact, the orientational distribution function for the straight segments). In ref 5–7 it was shown that the free energy of a solution of stiff-chain polymers in the absence of external fields can be generally represented as a sum of three terms: $F = F_1 + F_2 + F_3$, where F_1 corresponds to the translational entropy of the motion of the macromolecules as a whole, F_2 describes the entropy of orientational ordering, and F_3 reresents the free energy of the interaction of segments in the second virial approximation. In ref 6 it was shown that the translational entropy should be taken into account only for completely stiff but not for semiflexible macromolecules; thus (here and below index A denotes a solution of rigid rods, index B corresponds to a solution of freely jointed semiflexible polymers, and index C is attributed to a solution of persistent semiflexible polymers)

$$F_1 = NT \ln (N/V) \qquad \text{(1A)}$$

$$F_1 = 0 \qquad \text{(1B,C)}$$

The contribution to the free energy due to the entropy of orientational ordering can be written in the form[7]

$$F_2 = NT\int f(\vec{n}) \ln (4\pi f(\vec{n}))\, \mathrm{d}\Omega_{\vec{n}} \qquad \text{(2A,B)}$$

$$F_2 = NT\int \frac{[\nabla f(\vec{n})]^2}{4f(\vec{n})}\, \mathrm{d}\Omega_{\vec{n}} \qquad \text{(2C)}$$

where $\mathrm{d}\Omega_{\vec{n}}$ is an element of spatial angle. As to the free energy of the interaction of segments (we shall assume throughout this paper that this interaction is purely steric, i.e., repulsive), we can use the results of ref 5–7, where it was shown that for all three cases in the second virial approximation

$$F_3 = T\frac{N^2l^2d}{V}\int |\sin \gamma| f(\vec{n})f(\vec{n}')\, \mathrm{d}\Omega_{\vec{n}}\, \mathrm{d}\Omega_{\vec{n}'} \qquad \text{(3A–C)}$$

where γ is the angle between vector $\vec{n}$ and $\vec{n}'$.

In the presence of an external field each straight segment with the orientation $\vec{n}$ acquires an additional potential energy $U(\vec{n})$; thus it is necessary to add a new term F_4 to the expression for the free energy:

$$F_4 = N\int U(\vec{n})f(\vec{n})\, \mathrm{d}\Omega_{\vec{n}} \qquad \text{(4A–C)}$$

[it is easy to understand that for a persistent chain, when the segments are not straight, eq 4 for the potential energy of the chain in an external field is still valid]. As already mentioned in the Introduction, we consider the two most important types of external fields: the dipole field, $U(\vec{n}) = -uT \cos \theta$, and the quadrupole field, $U(\vec{n}) = -(3/2)uT \cos^2 \theta$ (u being the dimensionless parameter of the field). In the latter case the values $u > 0$ correspond to the orientational field and the values $u < 0$ to the "disorientational" one.

Before proceeding to the study of the liquid-crystalline ordering in the presence of an external field, we first recall briefly the results obtained in ref 5–7 in the absence of a field. To find the equilibrium free energy and the equilibrium distribution function $f(\vec{n})$, it is necessary to minimize the functional F defined by eq 1–3 with respect to all possible functions $f(\vec{n})$. In ref 5–7 the approximate variational method was used for this purpose. The trial function was chosen in the form

$$f(\vec{n}) = \text{const} \times \cosh (\alpha \cos \theta) \qquad \text{(5)}$$

where α is the variational parameter and const is the normalization constant (normalization condition $\int f(\vec{n})\, \mathrm{d}\Omega_{\vec{n}} = 1$). Trial function 5 was substituted in the expression for the free energy, which was then minimized with respect to α; as a result possible phases and the conditions of equilibrium of these phases were found in a standard way.

It was shown (see ref 5–7) that for all three cases of Figure 3 the orientational ordering is the first-order phase transition, which occurs at polymer volume fractions in solution $\vartheta \sim d/l$. At $\vartheta < x_0^{(i)}d/l$ the solution is isotropic, at $\vartheta > x_0^{(a)}d/l$ it is anisotropic, and in the interval $x_0^{(i)}d/l < \vartheta < x_0^{(a)}d/l$ it separates into isotropic and the anisotropic phases. Numerical values for $x_0^{(i)}$ and $x_0^{(a)}$ are the following:

$$x_0^{(i)} = 3.34 \qquad x_0^{(a)} = 4.49 \qquad x_0^{(a)}/x_0^{(i)} - 1 = 0.34 \qquad \text{(6A)}$$

$$x_0^{(i)} = 3.25 \qquad x_0^{(a)} = 4.86 \qquad x_0^{(a)}/x_0^{(i)} - 1 = 0.50 \qquad \text{(6B)}$$

$$x_0^{(i)} = 10.48 \qquad x_0^{(a)} = 11.39 \qquad x_0^{(a)}/x_0^{(i)} - 1 = 0.087 \qquad \text{(6C)}$$

The order parameter $\eta = \langle 3 \cos^2 \theta - 1\rangle/2$ (averaging is performed with the use of the equilibrium distribution $f(\vec{n})$) in the anisotropic phase at the transition point was shown to be equal to

$$\eta = 0.84 \qquad \text{(7A)}$$

$$\eta = 0.87 \qquad \text{(7B)}$$

$$\eta = 0.49 \qquad \text{(7C)}$$

Analyzing eq 6 and 7, Khokhlov[6] and Khokhlov and Semenov[7] concluded that the liquid-crystalline ordering in a solution of freely jointed semiflexible macromolecules occurs practically in the same way as in the corresponding system of disconnected segments, whereas for the case of persistent semiflexible chains the liquid-crystalline transition takes place at significantly higher polymer concentrations in the solution and the order parameter at the transition point is much smaller than for solutions of rods or of chains of freely jointed rods with the same parameters l and d.

3. Liquid-Crystalline Ordering in the Presence of an External Field of the Dipole Type

In the presence of an external field of the dipole type $U(\vec{n}) = -uT \cos \theta$, the directions $\vec{n}$ and $-\vec{n}$ become nonequivalent, so that trial function 5 no longer reflects the symmetry of the problem. Thus, for minimization of the free energy of a solution in a field of the dipole type (eq 1–4), the trial function was chosen in the form

$$f(\vec{n}) = \text{const} \times \cosh (\alpha \cos \theta + s) \qquad \text{(8)}$$

where s is the second variational parameter. The appearance of this parameter is connected with the mentioned nonequivalence of the directions $\vec{n}$ and $-\vec{n}$ for a system in a dipole field, i.e., with the existence of the additional order parameter $\eta' = \langle \cos \theta\rangle$ (in addition to the usual order parameter $\eta = \langle 3 \cos^2 \theta - 1\rangle/2$).

The minimization of the free energy with trial function 8, as well as the calculation of the characteristics of the transitions between possible phases, is performed in this case in complete analogy with ref 5–7. Omitting the corresponding intermediate calculations [these calculations are rather lengthy, so that to reach final results a computer was used], we describe only the final results.

In Figures 4 and 5 we present the calculated phase diagrams for a polymer solution in an external field of the dipole type in variables u–x ($x = \vartheta d/l$ is the value proportional to the polymer volume fraction in solution) for the cases of rigid rods (Figure 4, curve A), long chains of

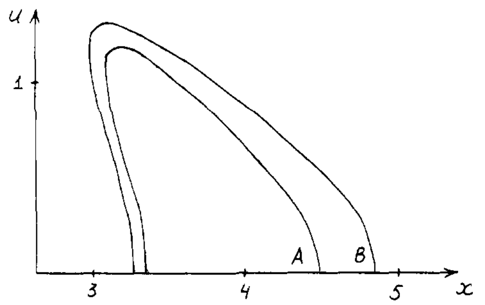

Figure 4. Phase diagrams for a solution of rigid rods (A) and of freely jointed chains of rods (B) in a dipole field.

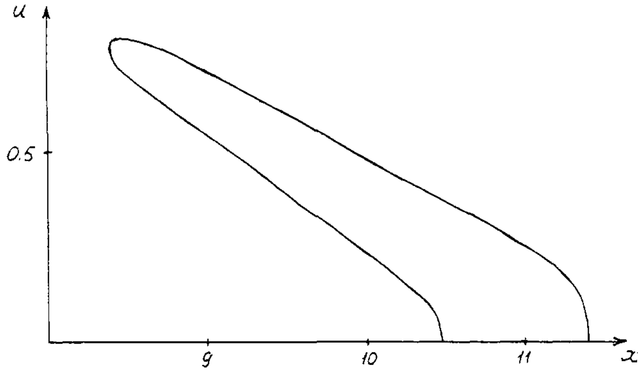

Figure 5. Phase diagram for a solution of persistent chains in a dipole field.

freely jointed rods (Figure 4, curve B), and persistent chains (Figure 5). The curves in Figures 4 and 5 are the boundaries of the phase separation regions. It can be seen that the phase diagrams for all three cases are qualitatively similar (with the exception that for the solution of persistent chains the phase separation region is very significantly shifted to the region of higher concentrations). In the presence of a sufficiently weak external field when polymer concentration in solution is increased, the system (in all the three cases) still undergoes a first-order phase transition. It should be emphasized that at $u \neq 0$ this is the transition between two anisotropic phases with different anisotropy degrees. As the strength of the external field, u, is increased, the phase separation region becomes more narrow and shifts to lower concentrations. Finally, at some critical value of the external orientational field, u_c, the intersegmental interaction that is responsible for the phase transition is effectively suppressed (due to the high value of the external field the segments are "sufficiently oriented" even in dilute solution, and there is no need for additional rearrangement (phase transition) when the concentration of the solution is increased), and the phase separation region disappears. Parameters of the critical point are the following:

$$u_c = 1.20 \quad x_c = 3.16 \quad \eta_c = 0.58 \quad \eta_c' = 0.64 \tag{9A}$$

$$u_c = 1.33 \quad x_c = 3.09 \quad \eta_c = 0.60 \quad \eta_c' = 0.68 \tag{9B}$$

$$u_c = 0.80 \quad x_c = 8.40 \quad \eta_c = 0.31 \quad \eta_c' = 0.56 \tag{9C}$$

(η_c and η_c' are the order parameters at the critical point). At all values of u up to the critical point, the order parameter η of the more ordered phase at the transition point for the persistent macromolecule is much smaller than for the other two cases.

Since the curves of Figures 4 and 5 shift to the left as u increases, in some concentration region a phase transition induced by the field can take place. The value x_m corresponding to the smallest x at which such a transition can occur (i.e., the x coordinate of the extreme left point of the phase separation region) is equal to

$$x_m = 3.08 \quad (x_0^{(i)} - x_m)/(x_0^{(a)} - x_0^{(i)}) = 0.23 \tag{10A}$$

$$x_m = 2.98 \quad (x_0^{(i)} - x_m)/(x_0^{(a)} - x_0^{(i)}) = 0.17 \tag{10B}$$

$$x_m = 8.38 \quad (x_0^{(i)} - x_m)/(x_0^{(a)} - x_0^{(i)}) = 2.31 \tag{10C}$$

From eq 10 and Figures 4 and 5 it can be seen that for cases A and B the phase transition can be induced by the field only over very narrow concentration regions, whereas for a solution of persistent chains this region is much broader. Thus, the phase transition in a solution of stiff-chain polymers induced by an external field of the dipole type, apparently, can be most easily realized for long chains with a persistent flexibility mechanism.

In Figure 4 the curve encircling the phase separation region for a solution of rods (curve A) lies entirely inside the curve for the chains of freely jointed rods (curve B). This is due to the fact that the free energy for case B differs from the free energy for case A only in one respect, namely, in the absence of the translational entropy term, which always favors disorientation, ie., opposes the orientational ordering. It is clear that the absence of a factor opposing the ordering must lead to a sharper phase transition, which is characterized by a greater bound of the order parameter and a broader phase separation region. This statement can be easily proved rigorously.

Finally, it is noteworthy that in the case of the dipole-type field, the values of u whose moduli are equal but whose signs are opposite are physically equivalent; this is the reason that the phase diagrams in Figures 4 and 5 are not continued to the region $u < 0$. The fact that the boundaries of the phase separation region intercept the x axis at right angles is also connected with the symmetry with respect to the transformation $u \rightarrow -u$.

4. Liquid-Crystalline Ordering in the Presence of an External Orientational Field of the Quadrupole Type ($u > 0$)

The external orientational field of quadrupole symmetry $U(\vec{n}) = -(3/2)uT \cos^2 \theta$ $(u > 0)$ does not lead to nonequivalence of the directions $\vec{n}$ and $-\vec{n}$; thus in this case trial function 5 can be used for the minimization of the free energy. As in the previous section, we present the final results, omitting the intermediate calculations.

Phase diagrams for a polymer solution in an external orientational field of the quadrupole type ($u > 0$) in the variables u–x are shown in Figures 6 and 7 (upper half-planes). The qualitative form of these diagrams coincide with the ones described in the previous section with the exception that the boundaries of the phase separation region now intercept the x axis at finite slopes (this is connected with the nonequivalence of the fields u and $-u$). Parameters of the critical point are the following:

$$u_c = 0.40 \quad x_c = 3.22 \quad \eta_c = 0.61 \tag{11A}$$

$$u_c = 0.49 \quad x_c = 3.13 \quad \eta_c = 0.63 \tag{11B}$$

$$u_c = 0.17 \quad x_c = 10.15 \quad \eta_c = 0.25 \tag{11C}$$

The value of x_m (smallest x at which the phase transition induced by the field can take place) is equal to

$$x_m = 3.14 \quad (x_0^{(i)} - x_m)/(x_0^{(a)} - x_0^{(i)}) = 0.17 \tag{12A}$$

$$x_m = 3.03 \quad (x_0^{(i)} - x_m)/(x_0^{(a)} - x_0^{(i)}) = 0.14 \tag{12B}$$

$$x_m = 10.08 \quad (x_0^{(i)} - x_m)/(x_0^{(a)} - x_0^{(i)}) = 0.44 \tag{12C}$$

It can be seen that for the persistent macromolecule the

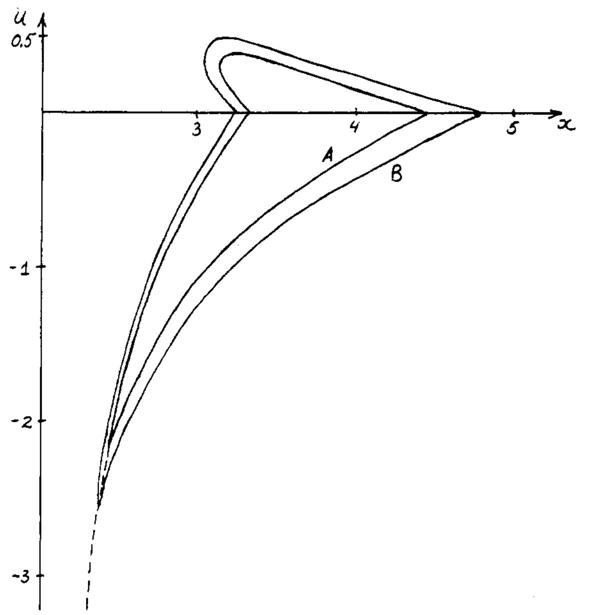

Figure 6. Phase diagrams for a solution of rigid rods (A) and of freely jointed chains of rods (B) in a quadrupole field.

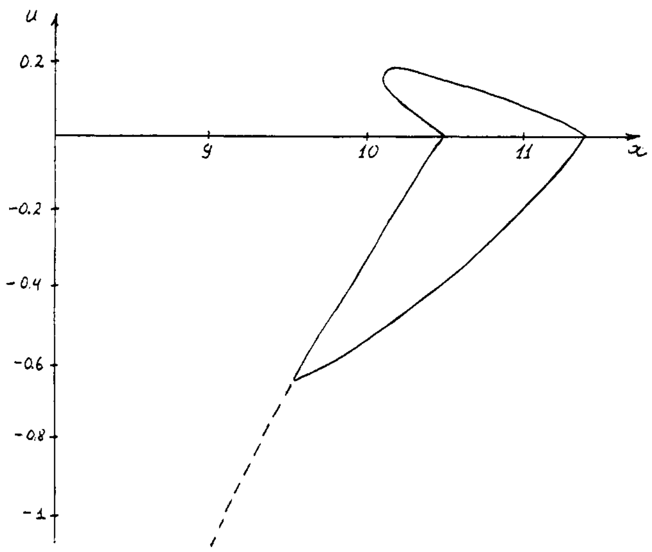

Figure 7. Phase diagram for a solution of persistent chains in a quadrupole field.

concentration region between the points x_m and $x_0^{(i)}$ is in this case significantly narrower than in the case of the dipole field. Thus, apparently, the most favorable possibilites for observing the phase transition induced by an orientational field exist for a solution of chains with a persistent flexibility mechanism in the dipole field.

5. Liquid-Crystalline Ordering in the Presence of an External "Disorientational" Field of the Quadrupole Type ($u < 0$)

We now consider a polymer solution in the external field $U(\vec{n}) = -(3/2)uT\cos^2\theta$ at $u < 0$ (Figures 6 and 7, lower half-planes). The action of the weak field leads to different effects for the isotropic and anisotropic phases. In the isotropic phase this field induces the anisotropy of the type "easy plane" with a symmetric distribution of rods with respect to the orientation axis. In this case, instead of trial function 5, which does not reflect the symmetry of the problem, for the calculation of the free energy it is convenient to use the function

$$f(\vec{n}) = \text{const} \times \exp(-\beta\cos^2\theta) \tag{13}$$

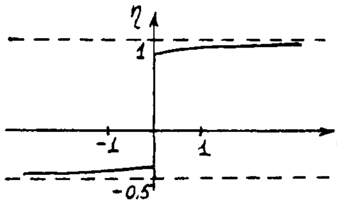

Figure 8. Dependence of the order parameter η or u at $x = 5$ for a quadrupole field (case A).

where β is the variational parameter.

As to the anisotropic phase, even the action of an infinitely weak quadrupole disorientational field induces in this phase an instability of the state with a symmetric distribution of rods with respect to the orientation axis.[13] As a result, at $|u| \ll 1$ the general structure of the nematic phase remains practically the same as in the absence of the field, but the director of this phase is always oriented in the "easy plane"; i.e., it becomes perpendicular to the orientation axis.

Consequently, the x axis of the phase diagrams of Figures 6 and 7 at $x > x_0^{(a)}$ is the line of the first-order phase transition, which occurs when we pass from the region $u > 0$ to the region $u < 0$. This transition is accompanied by the essential structural rearrangement in the system with the change in symmetry and with the significant bound of the order parameter η (see Figure 8).

Obviously, in the presence of the quadrupole field with $u < 0$ the distribution function $f(\vec{n})$ in sufficiently dilute solution is always symmetric with respect to the anisotropy axis, whereas in sufficiently concentrated solution it is always asymmetric. Thus, at any field the transition between these two states of the solution of different symmetry induced by the increase in concentration must be the phase transition. It is easy to understand (at least from continuity considerations) that in a sufficiently weak field ($|u| \ll 1$), this transition remains the first-order phase transition (as at $u = 0$). We have found the boundaries of the phase separation region for this case (Figures 6 and 7, $u < 0$, $|u| \ll 1$) by assigning the state of the symmetric "dilute" phase by trial function 13 and the state of the "asymmetric" concentrated phase by trial function 5, with the angle θ counted off from the orientation of the director of the nematic phase (in our case the director is oriented in the "easy plane"). For the case under consideration ($u < 0$, $|u| \ll 1$), it can be seen from Figures 6 and 7 that as the value of u increases, the phase separation region becomes noticeably narrower.

It turns out that this narrowing leads finally to the change in character of the transition between the "dilute" and "concentrated" phases: in a sufficiently strong field this phase transition becomes second order (dotted lines in Figures 6 and 7). In order to prove this fact, we have considered, first of all, the solution in a very strong quadrupole field: $u \rightarrow -\infty$. In such a field all rods are oriented in the "easy plane" so that the problem reduces to the two-dimensional one (from the point of view of the orientational degrees of freedom). Performing for the two-dimensional problem the calculations that are analogous to the classical calculations by Onsager,[5] one can obtain that in this case the isotropic–nematic transition is actually the second-order phase transition that takes place for cases A and B at $x = 3\pi^2/16 \simeq 1.85$ (see also ref 14) and for case C at $x = 3\pi^2/8 \simeq 3.7$.

From this fact and the continuity requirement, it follows that the transition under consideration is the second-order phase transition not only in the limit $u \rightarrow -\infty$ but in a sufficiently strong quadrupole field ($|u| \gg 1$) as well. In

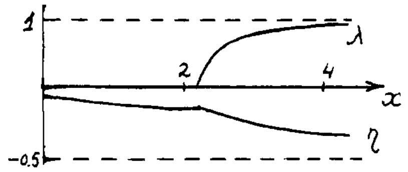

Figure 9. Dependence of the order parameters λ and η on x at $u = -4$ for a quadrupole field (case A). At the transition point the dependence $\eta(x)$ changes slope.

the case $|u| \gg 1$ the transition was analyzed with the trial function

$$f(\vec{n}) = \text{const} \times \exp(-\beta \cos^2 \theta)[1 + 2s_1 \cos 2\varphi + 2s_2 \cos 4\varphi] \tag{14}$$

where β, s_1, and s_2 are the variational parameters. The obtained curves, which determine the dependence of the concentration at the transition point on u, are shown in Figures 6 and 7 (dashed lines, $|u| \gg 1$). The order parameter corresponding to the second-order phase transition under consideration is $\lambda = \langle \sin^2 \theta \cos 2\varphi \rangle$. At the transition point, λ has a characteristic square root singularity, while η, which plays in this case a secondary role, behaves in a less singular manner (see Figure 9).

As usual, the line of the second-order phase transition meets the line of the first-order phase transition at the so-called tricritical point,[15] which in this case is situated at $|u| \sim 1$. For cases A and B consideration of the region $|u| \sim 1$ can be performed with rather good accuracy ($\sim$ 5%) simply by matching the asymptotic relations obtained at $|u| \ll 1$ and $|u| \gg 1$. As to the solution of persistent chains (case C), to ensure good accuracy it is necessary to consider additional the vicinity of the tricritical point with the help of the trial function

$$f(\vec{n}) = \text{const} \times \left[1 + \frac{r}{2}(3 \cos^2 \theta - 1) + \frac{3s}{2} \sin^2 \theta \cos 2\varphi\right]^2 \tag{15}$$

with the variational parameters r and s and only after this, to match the solution obtained at $u \sim u_t$ (in the vicinity of the tricritical point) with the asymptotic solutions at $|u| \ll 1$ and $|u| \gg 1$. In this case the accuracy for the curves on the phase diagram at $|u| \sim 1$ in case C (Figure 7) is also of the order of 5%. The parameters of the tricritical point turn out to be the following:

$$u_t = -2.2 \quad x_t = 2.4 \quad \eta_t = -0.37 \tag{16A}$$

$$u_t = -2.7 \quad x_t = 2.3 \quad \eta_t = -0.39 \tag{16B}$$

$$u_t = -0.65 \quad x_t = 9.5 \quad \eta_t = -0.11 \tag{16C}$$

(η_t is the order parameter η at the tricritical point). In cases A and B the phase equilibrium curves for the first-order phase transition meet at the tricritical point at a very small angle (of the order of 1°), whereas in case C this angle has no special smallness. The region in which the phase transition can be induced by the disorientational quadrupole field is in all cases much broader than the corresponding region for the orientational field.

Unfortunately, systematic experimental studies of the influence of external fields on the properties of the liquid-crystalline transition in solutions of stiff-chain polymers are unknown to the authors. Such studies for polymer chains with different flexibility mechanisms could provide experimental verification of the theoretical conclusions of this paper.

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