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Liquid-Crystalline Ordering in Solutions of Semiflexible Macromolecules with Rotational-Isomeric Flexibility

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ABSTRACT: The orientational ordering in solutions of semiflexible macromolecules with rotational-isomeric flexibility is considered. It is shown that in this case the liquid-crystalline transition has many features essentially different from the corresponding features for persistence or freely jointed flexibility models: the isotropic phase becomes unstable at lower polymer concentrations and the appearing anisotropic phase is much more ordered and more concentrated; the width of the phase separation region is thus anomalously large. The transition properties depend essentially on the ratio of two flexibility parameters: the length of the usual Kuhn segment of the chain controlled by the rotational isomerism and the length of a *second* Kuhn segment (concept introduced in this paper) connected with a small persistent flexibility component, which is always present in real chains. The behavior of a solution of semiflexible rotational-isomeric chains in external orientational fields of dipole and quadrupole types is analyzed as well. It is shown that to suppress the phase transition, which takes place when the solution is concentrated, it is necessary to apply much stronger fields than for the persistence or freely jointed flexibility models. A phase transition can be induced by an external orientational field at practically any concentration of the initially isotropic solution. The susceptibility of the solution in zero dipole field, χ_0, in the case under consideration increases with the solution concentration in the anisotropic phase, c, according to the power law $\chi_0 \sim c^{5/2}$ (to be compared with the exponential increase for the persistence model and with practical independence of c for the freely jointed model).

1. Introduction

It is well-known that in sufficiently concentrated solutions of stiff-chain polymers an orientationally ordered phase can appear. In ref 1–5 the corresponding liquid-crystalline phase transition was studied in detail for the case of completely stiff macromolecules (long, absolutely rigid rods). Accounting for the partial flexibility of the chain of a stiff polymer naturally constitutes the next fundamental problem. This problem has been considered in recent papers by Flory and Matheson[6,7] and by Ronca and Yoon,[22–24] and in our papers.[8–11] From the theoretical point of view the simplest partially flexible chains are the so-called semiflexible macromolecules whose effective Kuhn segment length, l, is much smaller than the total contour chain length, L, but much larger then the width of the chain, d: $L \gg l \gg d$. The consideration of a solution of chains for which $L \sim l$ is much more complex.[11]

Semiflexible macromolecules can differ depending on the flexibility mechanism of a polymer chain. Simplest is the freely jointed model, where the chain can be represented as a sequence of freely jointed rigid rods of length l and diameter d (Figure 1). Orientational ordering in solutions of semiflexible freely jointed macromolecules was considered in 1978 independently in ref 6 and 8. It was shown that the properties of the liquid-crystalline transition are practically the same as in a solution of disconnected rigid rods of length l and diameter d.

It should be emphasized, however, that freely jointed chains are encountered very rarely in the real polymer world. The most common flexibility models are the persistence one (which is due to the gradual accumulation of the effect of small thermal vibrations of valence angles, bonds, etc.) and the rotational-isomeric one.[12] Persistent semiflexible chains can be represented as long, absolutely homogeneous elastic filaments of width d and a Kuhn segment length l (Figure 2). The liquid-crystalline transition in a solution of semiflexible persistent chains was considered in ref 10; it was shown that it takes place at significantly higher polymer concentrations and that the order parameter at the transition point is much smaller than for a solution of freely jointed chains with the same parameters d and l. Thus, the results of ref 10 permit us to conclude that the conditions for orientational ordering in solutions of semiflexible polymers depend in an essential way on the mechanism of the chain flexibility.

It is consequently important to analyze the liquid-crystalline transition in solutions of semiflexible chains with other flexibility models (differing from the freely jointed and persistence ones) and, primarily, with the widely used rotational-isomeric flexibility model. This is precisely the aim of the present paper.

It is noteworthy that the majority of known polymers able to form a liquid-crystalline phase in solution (helical polypeptides, aromatic polyamides[13]) exhibit a persistence flexibility mechanism. At the same time, there is no fundamental reason why liquid-crystalline solutions of rotational-isomeric semiflexible macromolecules should not exist. Taking into account the recent intensive increase of the number of papers on the synthesis of new classes of stiff-chain polymers[14] and the prevalence of the rota-

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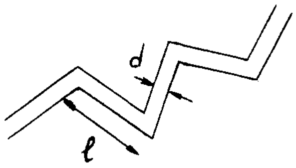
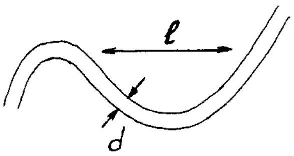


Figure 1.



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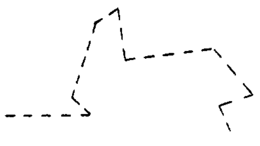

Figure 3.

tional-isomeric flexibility mechanism, we may expect in the very near future the appearance of systematic experimental investigations of liquid-crystalline solutions of semiflexible rotational-isomeric polymer chains. Such investigations would be very interesting, since, as shown in this paper, the liquid-crystalline transition in this case must have many specific features.

The plan of this paper is the following. In section 2 we describe models of polymer chains with a rotational-isomeric flexibility mechanism. Section 3 deals with the method of calculation and the results for the corresponding liquid-crystalline transitions. In section 4 we study the behavior of a solution of semiflexible rotational-isomeric chains in external orientational fields of dipole and quadrupole types (the corresponding problem for freely jointed and persistent macromolecules was solved in ref 15). Finally, in section 5 we discuss separately the behavior of the susceptibility of a solution of semiflexible rotational-isomeric macromolecules in an external field of the dipole type (compare with ref 16).

2. Models

In this paper we consider three polymer chain models with a rotationl-isomeric flexibility mechanism (models A, B, and C). We begin with the description of the most simple model, **model A** (Figure 3). In this model the polymer chain is represented as a sequence of subsegments (links) of length a, each link being able to take two qualitatively different conformations: the trans conformation (step forward) or the gauche conformation (bending). We assume the angle of bending to be arbitrary with equal probability (no fixation valence angle). The difference of this model from the freely jointed one (Figure 1) lies in the fact that the places of bending are not fixed: bending can take place at each step with some probability p. Of course, in order to have a stiff-chain polymer (i.e., a polymer able to form a liquid-crystalline phase in the solution), the value of p should be much less than unity; i.e., the trans conformation should be energetically much more favorable than the gauche conformation. The function $g(\bar{n},\bar{n}')$, the conditional probability that a link of the chain is oriented along the unit vector $\bar{n}$ provided the previous link is oriented along $\bar{n}'$, for this model has the form

$$g(\bar{n},\bar{n}') = (1-p)\delta(\bar{n}-\bar{n}') + p/4\pi; \qquad p \ll 1 \quad (1)$$

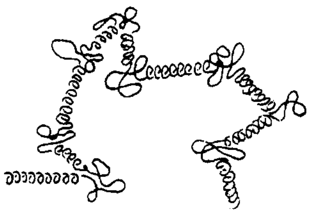

Figure 4.

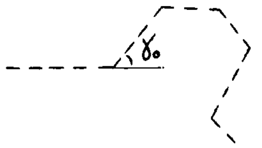

Figure 5.

It is noteworthy also that the value of p is connected with the length of the Kuhn segment of the chain, l, via the relation

$$l = a\frac{2-p}{p} \cong \frac{2a}{p} \quad (2)$$

Model A is, obviously, the simplest polymer chain model with a rotational-isomeric flexibility mechanism; it appears oversimplified from the point of view of real chains. However, this model is directly applicable to at least one class of macromolecules: helical chains at temperatures slightly below the helix–coil transition temperature, when small amounts of coil portions begin to appear among the helical parts of the chain (see Figure 4). In terms of model A these portions play the role of the bendings; their position on the chain, as well as the bending angle, is not fixed.

More closely reflecting real chains is **model B**, which differs from model A only in the fact that the valence angle connected with the bending, γ_0, is fixed (Figure 5). For this model

$$g(\bar{n},\bar{n}') = (1-p)\delta(\bar{n}-\bar{n}') + \frac{p}{2\pi \sin \gamma_0}\delta(\gamma - \gamma_0) \quad (3)$$

$$l = \frac{a(2-p(1-\cos\gamma_0))}{p(1-\cos\gamma_0)} \cong \frac{2a}{p(1-\cos\gamma_0)} \quad (4)$$

Model C. We show further that the properties of the liquid-crystalline transition in models A and B are determined by the presence of the δ-function $\delta(\bar{n}-\bar{n}')$ in expressions 1 and 3, i.e., by the fact that the part of the chain between two bends is strictly rectilinear. However, in reality this is not the case: due to small thermal vibrations in the trans conformation, parts of the chain between the bends always possess some small flexibility of persistent character. In model C we take into account both the fixation of the valence angle γ_0 and this small flexibility component. Thus this model is a further approximation to the properties of real chains.

In model C, due to the persistent flexibility the δ-function $\delta(\bar{n}-\bar{n}')$ in eq 3 transforms into a peak of finite width. The specific form of this peak is not essential, and to be definite we assume the Guassian form:

$$g(\bar{n},\bar{n}') = (1-p)\frac{l_2}{4\pi a}\exp\left(-\frac{l_2(\bar{n}-\bar{n}')^2}{4a}\right) + \frac{p}{2\pi \sin\gamma_0}\delta(\gamma-\gamma_0) \quad (5)$$

(Of course, thermal vibrations of the valence angle γ_0 will "broaden" the δ-function also in the second item of eq 5; however, accounting for this broadening has practically no effect on the properties of the liquid-crystalline transition.) The width of the peak at $\bar{n} = \bar{n}'$ in eq 5 is determined by the value of l_2, which has the meaning of the Kuhn segment length for a chain with forbidden gauche conformations—the flexibility of such a chain is persistent solely because of the small thermal vibrations of the chain in the trans conformation. The value of l_2 will be hereinafter referred to as the second Kuhn segment length (in contrast to the usual Kuhn segment of length l, which is controlled by the rotational isomerism).

We show below that the ratio of the lengths of the second and usual Kuhn segments, $\nu = l_2/l$, plays an important role in the properties of the liquid-crystalline transitions. For real chains $\nu \sim 10\text{–}100 \gg 1$.[12] Since the height of the potential barriers between the trans and gauche conformations usually correlates with the amplitude of thermal vibrations, it is possible to say (with some reservation) that the ratio ν is larger for polymers with low dynamic flexibility. It is also noteworthy that the rotational-isomeric approximation[12] is better for chains with large ν.

Below we assume in the majority of cases that the inequality $\nu \gg 1$ is fulfilled. In this case the length of the usual Kuhn segment, l, in model C is still determined by eq 4.

3. Liquid-Crystalline Transition in Solutions of Semiflexible Rotational-Isomeric Chains

We now calculate the properties of the liquid-crystalline transition in solutions of semiflexible chains with rotational-isomeric flexibility following the ideas of the Onsager method,[1] which has some advantages for stiff-chain polymers ($l >> d$) (see ref 5). For semiflexible chains ($L >> l$) the free energy of the solution per macromolecule in the framework of the Onsager method can be expressed as a sum of three terms: $F : F_1 + F_2 + F_3$, where $F_1 = T \ln \vartheta$ is the free energy of the translational motion of the macromolecule as a whole (T being the temperature and ϑ the polymer volume fraction in the solution); F_3 is the free energy of the interaction of the chain parts in the second virial approximation: in the presence solely of forces of steric repulsion (as will be assumed in the present paper) we have[5,10]

$$F_3 = \frac{4}{\pi} T \frac{L\vartheta}{d} \int |\sin \gamma_{\bar{n}\bar{n}'}| f(\bar{n}) f(\bar{n}')\, \mathrm{d}\Gamma\, \mathrm{d}\Gamma' \qquad (6)$$

Here, $f(\bar{n})$ is the orientational distribution function for the links, with the normalization condition $\int f(\bar{n})\, \mathrm{d}\Gamma = 1$, $\mathrm{d}\Gamma = \mathrm{d}\Omega/4\pi$, $\mathrm{d}\Omega$ is the element of the spatial angle, and $\gamma_{\bar{n}\bar{n}'}$ is the angle between the unit vectors $\bar{n}$ and $\bar{n}'$. As to the free energy F_2, it describes the orientational entropy of the chains (or, in terms of ref 22–24, the configurational free energy under the constraint of fixed orientational distribution function, $f(\bar{n})$). It is this term that depends on the specific flexibility model.[10]

In ref 10 it was shown that the problem of calculating the orientational entropy (i.e., of the term F_2) is analogous to that of the conformational entropy for the macromolecule in an external attractive potential field, which was solved by Lifshitz.[17,18] It turns out[10] that for semiflexible chains ($L >> l$) the formulas of ref 17 can be directly applied after obvious changes in notation:

$$F_2 = -T \frac{L}{a} \int f(\bar{n}) \ln \frac{\hat{g}\psi}{\psi}\, \mathrm{d}\Gamma \qquad (7)$$

where $\psi(\bar{n})$ is the additional function connected with $f(\bar{n})$ by the relation

$$\psi \hat{g} \psi = f(\bar{n}) \qquad (8)$$

$$\hat{g}\psi = \int g(\bar{n},\bar{n}')\psi(\bar{n}')\, \mathrm{d}\Gamma' \qquad (9)$$

and a is the length of an elementary subsegment (link) in models A, B, and C.

The functions $g(\bar{n},\bar{n}')$ in models A, B, and C are determined by eq 1, 3, and 5. Since we are considering only sufficiently stiff chains ($l >> d$), in all three cases the operator $\hat{g}$ is close to the unit operator. We can use this fact by expanding the logarithm in eq 7; in eq 8 we can then write in the main order that $\hat{g}\psi \cong \psi$ (compare with ref 10). As a result the following expressions for F_2 (per chain) can be obtained:

$$F_2^{\mathrm{A}} = 2T \frac{L}{l} \left[1 - \left(\int f^{1/2}(\bar{n})\, \mathrm{d}\Gamma\right)^2\right] \qquad (10\mathrm{a})$$

$$F_2^{\mathrm{B}} = \frac{2TL}{l(1 - \cos \gamma_0)} \left[1 - \frac{2}{\sin \gamma_0} \int f^{1/2}(\bar{n}) f^{1/2}(\bar{n}') \delta(\gamma - \gamma_0)\, \mathrm{d}\Gamma\, \mathrm{d}\Gamma'\right] \qquad (10\mathrm{b})$$

$$F_2^{\mathrm{C}} = F_2^{\mathrm{B}} + T \frac{L}{l_2} \int \frac{[\nabla f(\bar{n})]^2}{4f(\bar{n})}\, \mathrm{d}\Gamma, \qquad \nu \gg 1 \quad (10\mathrm{c})$$

In eq 10 the value of $p << 1$ is already expressed in terms of the Kuhn segment length, l, using eq 2 (model A) and eq 4 (models B and C). Equations 10a–c are exact in the stiff-chain limit $l >> d$, which we are considering in this paper. For flexible chains ($l \sim d$) the more general expression (7) should be used.

Thus, the free energy F for the cases under consideration is defined by eq 6 and 10. To find the equilibrium orientational distribution for the chain links the value of F should be minimized with respect to all possible functions $f(\bar{n})$. Let us choose a trial function in the form (compare with ref 10)

$$f(\bar{n}) = \frac{2}{1 + \dfrac{\sinh (2\alpha)}{2\alpha}} \cosh^2 (\alpha \cos \theta) \qquad (11)$$

where α is the variational parameter and θ is the angle between the vector $\bar{n}$ and the ordering axis. Substituting the function (11) in eq 6 and 10, evaluating the corresponding integrals, and minimizing the free energy $F = F_1 + F_2 + F_3$, we find in the usual way the possible phases and the conditions for their equilibrium (compare with ref 5). Let us proceed directly to the results obtained.

Model A. Even in this simplest model the minimization of the free energy has led to unexpected results. It is found that, independently of the value of the solution concentration, a minimum of F at finite nonzero values of α does not exist. At low concentrations, most favorable is the minimum corresponding to $\alpha = 0$ (isotropic phase); with increase in concentration another minimum corresponding to $\alpha = \infty$ (absolutely order phase) becomes deeper. Thus, in this model the liquid-crystalline ordering is an abrupt transition between the isotropic and absolutely ordered phase, without any intermediate states. Polymer volume fractions in the isotropic and anisotropic phase coexisting in the solution, ϑ_{i} and ϑ_{a}, for model A are equal to

$$\vartheta_{\mathrm{i}} = d/l; \qquad \vartheta_{\mathrm{a}} = Ld/3l^2 \qquad (12)$$

When the length of the macromolecules, L, is so large that the value of ϑ_{a} calculated according to eq 12 turns out to be $\gtrsim 1$, the Onsager method cannot be used and instead of the second equality (12) we should write $\vartheta_{\mathrm{a}} \sim 1$. Thus, liquid-crystalline ordering in model A begins at signifi-

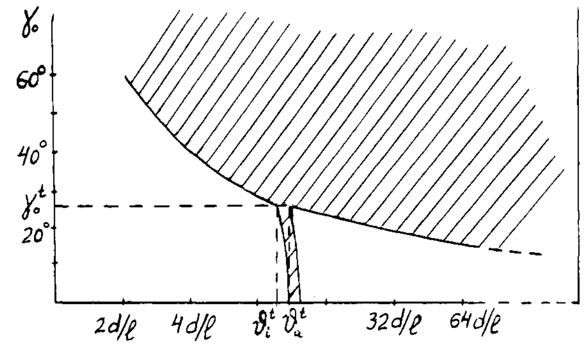

Figure 6. Phase diagram for the liquid-crystalline transition in model B in variables γ_0 and ϑ. The phase separation region is shaded.

cantly lower polymer concentrations than for the freely jointed ($\vartheta_i = 3.25d/l$) or persistence ($\vartheta_i = 10.48d/l$) models[10] and is characterized by a much wider phase separation region (in the anisotropic phase usually $\vartheta_a \sim 1$) and by practically absolute order in the anisotropic phase.[25]

The physical meaning of the results obtained can be easily understood if we take into account the fact that according to eq 10a the loss in orientational entropy even for the case of absolute ordering ($\alpha \to \infty$ or $f(\vec{n}) \to 4\pi\delta(\vec{n})$) remains finite. (It should be recalled that for the case of freely jointed or persistence flexibility models, $F_2 \to \infty$ at $\alpha \to \infty$.[8,10]) It is for this reason that the state $\alpha = \infty$ can "compete" with the other states, and, beginning with some finite polymer concentration, the gain in the interaction free energy F_3 in this state becomes larger than the corresponding loss in F_2. Obviously, the finiteness of F_2 at $\alpha \to \infty$ is connected with the presence of the δ-function $\delta(\vec{n} - \vec{n}')$ in eq 1.

It should be noted that liquid-crystalline ordering in solutions of semiflexible chains with formation of an absolutely ordered phase was discussed in ref 19 in the framework of the lattice model (where the flexibility mechanism is similar to the rotational-isomeric one). However, the fact that it is the absolutely ordered phase that is most favorable among all the anisotropic phases was not proved in ref 19.

Model B. Consideration of this model, which is closer to real chains with rotational-isomeric flexibility, is interesting also because in the limit $\gamma_0 \to 0$ it must transform into the persistence model; thus at least for small γ_0 the anomalous transition analogous to that for model A should not take place for this model.

The calculated phase diagram for model B in the variables γ_0 and ϑ (at fixed l) is shown in Figure 6. It can be seen that at sufficiently large values of γ_0 ($\gamma_0 > \gamma_0^t = 26.3°$) the transition is similar to that in model A: it is characterized by an anomalously wide phase separation region and by absolute order in the anisotropic phase. The boundary of the region of stability of the isotropic phase at $\gamma > \gamma_0^t$ corresponds to

$$\vartheta_i = \frac{1}{2\Gamma^2}\frac{d}{l} \tag{13}$$

where $\Gamma = \sin(\gamma_0/2)$.

When the solution is concentrated at $\gamma < \gamma_0^t$, at first an ordinary liquid-crystalline transition (close to that for the persistence model,[10] with a narrow separation region and a moderate order parameter at the transition point) takes place, and only upon further increase in concentration can a second transition with the formation of an absolutely ordered phase be observed. At such γ_0 the homogeneous isotropic phase is stable at

$$\vartheta < \vartheta_i = (10.29 - 11.5\Gamma^2)\frac{d}{l} \tag{14}$$

and the boundaries of stability of the homogeneous anisotropic phase with finite order parameters are defined by the relations

$$\vartheta_a' = (11.06 - 10.5\Gamma^2)\frac{d}{l};\qquad \vartheta_a'' = \frac{0.122}{\Gamma^3}(1 + 1.3\Gamma^2)\frac{d}{l} \tag{15}$$

(In eq 14 and 15 the first two terms of the expansion in powers of Γ^2 are taken into account.) The two regimes described above are separated by a triple point (see Figure 6) with the parameters

$$\gamma_0^t = 26.3°;\qquad \vartheta_i^t = 9.69\frac{d}{l};\qquad \vartheta_a^t = 10.51\frac{d}{l} \tag{16}$$

For real chains the angles γ_0 are usually larger than 26°. Thus in these cases the liquid-crystalline transition must occur in an anomalous way (as in model A). The physical reason for this remains the same as for model A.

Model C. For this model the calculations are rather long. Thus we have performed them only for the case $\gamma_0 = 60°$, but this is quite sufficient to make all the important qualitative conclusions. We list first the analytical results, which can be obtained in the most important limit $\nu \gg 1$. The boundaries of the phase separation region ϑ_i and ϑ_a for this case are given by the formulas

$$\vartheta_i = 2\frac{d}{l};\qquad \vartheta_a = 1.66\nu^{1/5}\frac{d}{l} \tag{17}$$

The relative width of the phase separation region, $w = \vartheta_a/\vartheta_i - 1$, at $\nu >> 1$, is thus equal to

$$w = \vartheta_a/\vartheta_i - 1 = 0.83\nu^{1/5} \tag{18}$$

The order parameter $\eta = \langle(3\cos^2\theta - 1)/2\rangle$ in the anisotropic phase at the transition point is defined by

$$\eta = 1 - 2.04/\nu^{4/5} \tag{19}$$

The results (17)–(19) allow one to draw the following conclusions. At $\nu = l_2/l >> 1$ the liquid-crystalline transition in model C retains anomalous features: the homogeneous isotropic phase becomes unstable at lower polymer concentrations, and the appearing anisotropic phase is much more concentrated and more ordered than for the freely jointed or persistence models with the same parameters d and l. However, the additional large parameter in eq 17–19 is not the number of Kuhn segments in the macromolecule L/l (as in models A and B), but the ratio of the lengths of the second and usual Kuhn segments, ν. Taking into account that $\nu \sim$ 10–100 and that the value of ν enters in some relations with a rather small power (see, for example, eq 17 and 18), it can be concluded that in the presence of the small flexibility component of persistent character the anomalous features of the transition in solutions of chains with rotational-isomeric flexibility are not so pronounced as for models A and B (nevertheless, these features remain essential).

The physical meaning of the results (17)–(19) is rather obvious: at $\nu >> 1$ until the characteristic angle connected with the ordering is larger than the characteristic width of the "broadened δ-function" in eq 5, the loss in orientational entropy defined by eq 10c behaves almost as in model B. At further ordering, however, the persistent flexibility component begins to play an essential role and the loss in entropy increases considerably—as for the persistence model (see ref 10). In particular, at $\alpha \to \infty$,

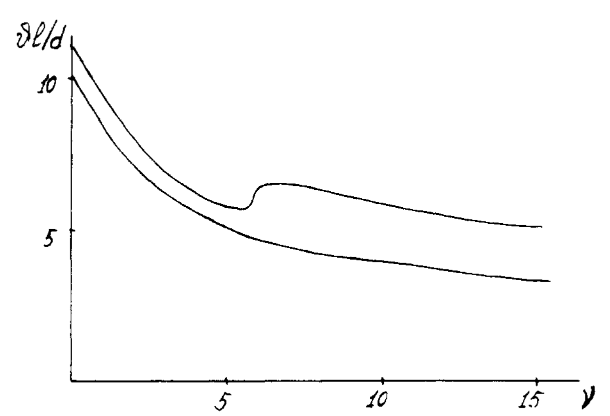

Figure 7. Dependence of $\vartheta_i l/d$ and $\vartheta_a l/d$ on ν in model C without fixation of the valence angle (the assumption of varying valence angle, as in model A, was introduced here to simplify the calculations).

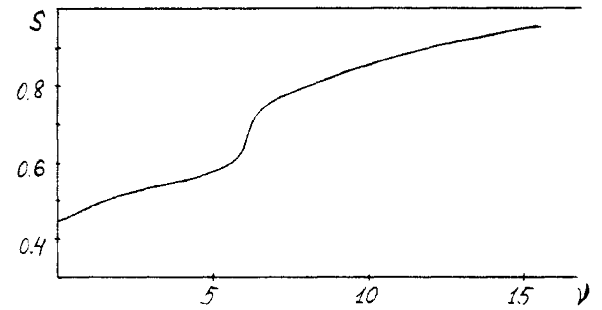

Figure 8. Dependence of the order parameter η at the liquid-crystalline transition point on ν in model C without fixation of the valence angle.

$F_2 \sim \alpha \to \infty$. Thus it is clear that for this model the transition properties should be intermediate between those of model B and the persistence model.

It should be noted that the values of ν for real polymer chains are usually not very large and that the asymptotic limit $\nu >> 1$ may be reached rather slowly. Thus, along with the analytical study of the liquid-crystalline ordering in model C for the limit $\nu >> 1$, it is interesting also to perform the corresponding numerical calculation at $\nu \sim 1$. The results of this calculation, presented in Figures 7 and 8, illustrate the changes of the properties of the liquid-crystalline transition when passing from the case $\nu << 1$ of pure persistent flexibility to the case $\nu >> 1$, which is described for $\gamma_0 = 60°$ by eq 17–19. It is noteworthy that there is steep variation of ϑ_i, ϑ_a, and η near $\nu \cong 5.75$. This steep variation is due to numerical causes and is not connected with the additional phase transition in the system. The asymptotic dependences of the type (17)–(19) are still not fully reached for the values of ν shown in Figures 7 and 8.

4. Liquid-Crystalline Solutions of Semiflexible Rotational-Isomeric Chains in an External Orientational Field

As in ref 15 we will consider two types of external orientational fields: a field of dipole type, in which the potential energy, $U(\bar{n})$, of a chain link (of length a) is equal to

$$U(\bar{n}) = -uT\frac{a}{l}\cos\theta \qquad (20)$$

Here, θ is the angle between the link direction and the orientation axis, and u is the dimensionless field parameter normalized in such a way that the potential energy of a straight chain segment of length l is described by the same formula $U(\bar{n}) = -uT\cos\theta$, as in ref 15. The other field is of quadrupole type, in which

$$U(\bar{n}) = -\frac{3}{2}uT\frac{a}{l}\cos^2\theta \qquad (21)$$

An external electric (magnetic) field in the case when the links have a constant electric (magnetic) moment directed along the chain is an example of the dipole-type field. The role of a quadrupole-type field can be played either by an external electric (magnetic) field in the case when the links have zero dipole moments or by an effective hydrodynamic field due to inhomogeneous "longitudinal shear" flow.[15]

In the presence of an external field, $U(\bar{n})$, it is necessary to add a new term

$$F_4 = \frac{L}{a}\int U(\bar{n})f(\bar{n})\,d\Gamma \qquad (22)$$

to the free energy of the solution per macromolecule; thus in order to study the properties of the liquid-crystalline transition in an external field, the free energy $F = F_1 + F_2 + F_3 + F_4$ (see eq 6, 10, and 22) should be minimized with respect to all possible functions $f(\bar{n})$.

We show further that the phase diagram in the variables u and x ($x \equiv \vartheta l/d$) for the liquid-crystalline transition in solutions of semiflexible macromolecules with rotational-isomeric flexibility in the presence of external fields described by eq 20 or 21 has the qualitative form shown in Figure 9, the critical point being located in the region of strong fields $u_c >> 1$ (in contrast to the cases considered in ref 15, for which $u_c \sim 1$). Thus it is most interesting to study the properties of the liquid-crystalline transition for models A, B, and C, on the one hand, in weak ($u << 1$) and, on the other hand, in strong ($u >> 1$) fields, since in these limiting cases one can hope to obtain not only numerical results but also analytical dependences. It is to these two limiting cases that we confine ourselves in the further discussion. As soon as at $u \sim 1$ the phase diagram in Figure 9 did not exhibit any peculiarities or characteristic points, the computer calculations designed to minimize the free energy for all values of u (as in ref 15) were not performed for the cases under study.

Although model C is closest to real chains with rotational-isomeric flexibility, from the systematic point of view it is convenient to begin with the consideration of models A and B (as in the previous section).

Model A. Let us first study the behavior of a solution of semiflexible chains for model A in an external quadrupole field.[21] As shown in the previous section, in the absence of the field we have for model A the liquid-crystalline transition between an isotropic and a highly concentrated, practically completely ordered phase. In the presence of the orientational field a transition between two anisotropic

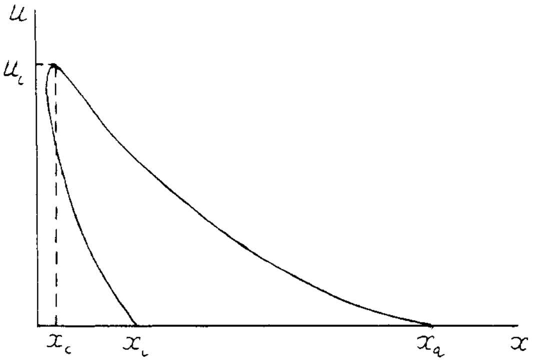

Figure 9. Qualitative form of the phase diagram for solutions of semiflexible macromolecules with rotational-isomeric flexibility in an external orientational field.

phases occurs; we call these phases simply phase I (low concentration, converting to the isotropic phase in the absence of a field) and phase II (highly concentrated, converting to the strongly anisotropic phase in the absence of a field). Phase II is always practically completely ordered; thus the free energy of this phase is equal to (see eq 21 and 22)

$$F_4^{\mathrm{II}} = -\frac{3}{2}uT\frac{L}{l} \tag{23}$$

The free energy F_4^{I} for phase I is determined, as usual, by eq 22.

Let us first consider a weak field $u << 1$. In this case calculations by the Onsager method can be performed in the standard way, and for the boundaries of the phase separation region we obtain the following results (compare with eq 12):

$$\begin{aligned} x_{\mathrm{i}} &\equiv \vartheta_{\mathrm{i}}\frac{l}{d} = 1 - \frac{u}{2}; \\ x_{\mathrm{a}} &\equiv \vartheta_{\mathrm{a}}\frac{l}{d} = \frac{L}{3l}(1-u), \qquad u << 1 \end{aligned} \tag{24}$$

It can be seen that the application of an external field $u << 1$ shifts the phase separation region to lower concentrations and makes this region narrower.

Now let us consider a strong field $u >> 1$. In this case it is convenient to choose the trial function for the analysis of phase I in the form

$$f(\vec{n}) = \mathrm{const}/(1 + \alpha^2 \sin^2\theta)^2 \tag{25}$$

instead of the form (11), where α is the variational parameter, because the distribution (25) coincides with the exact distribution for the case when the free energy of interaction of macromolecules with the external quadrupole field is much larger than the free energy of interaction between the macromolecules. As a result of calculations using the Onsager method with the trial function (25), we obtain the following results for the boundaries of the phase separation region at $u >> 1$:

$$\begin{aligned} x_{\mathrm{i}} &= 0.53u \exp\left(-\frac{3}{4}u\right); \\ x_{\mathrm{a}} &= 0.51\frac{L}{l}u^2 \exp\left(-\frac{9}{4}u\right), \qquad u >> 1 \end{aligned} \tag{26}$$

Thus in the strong field the transition concentrations and the relative width of the phase separation region exponentially decrease with the increase of the field strength. The results (26) yield the parameters of the critical point:

$$\begin{gathered} u_{\mathrm{c}} = 0.67 \ln\frac{L}{l} >> 1; \\ x_{\mathrm{c}} = 0.44\left(\frac{\ln(L/l)}{L/l}\right)^{1/2} << 1; \qquad \eta_{\mathrm{c}} = 1 - \frac{6.8l}{L} \end{gathered} \tag{27}$$

Since the critical concentration is very small ($x_{\mathrm{c}} \sim (l/L)^{1/2} << 1$) the phase transition can be induced by the external quadrupole field at practically any concentration of the initially isotropic solution.

As already mentioned, the qualitative form of the phase diagram in the variables u and x for this case is shown in Figure 9.

Let us now consider a solution of semiflexible chains (model A) in an external dipole field.[20] The most important difference of this case from the case of the quadrupole field lies in the fact that in the region of weak fields, $u << 1$, two qualitatively different regimes of behavior of the strongly anisotropic phase (phase II) are possible. At $u << l/L$ the external field is too weak to orient all the links in phase II at the angle $\theta = 0$, as at $u = 0$ the links have the orientations $\theta = 0$ and $\theta = \pi$ with practically equal probability. This means that

$$F_4^{\mathrm{II}} = -\frac{1}{2}\left(\frac{L}{l}u\right)^2 T, \qquad u << l/L \tag{28}$$

If $u >> l/L$, all the links in phase II are oriented at the angle $\theta = 0$ to the anisotropy axis; thus (compare with eq 23)

$$F_4^{\mathrm{II}} = -\frac{L}{l}uT, \qquad u >> l/L \tag{29}$$

The difference of eq 28 and 29 leads finally to the difference in the expressions for x_{i} and x_{a} at $u << l/L$ and $u >> l/L$:

$$\begin{aligned} x_{\mathrm{i}} &= 1 - \frac{1}{4}\frac{L}{l}u^2; \\ x_{\mathrm{a}} &= \frac{L}{3l}\left(1 - \frac{L}{2l}u^2\right), \qquad u << l/L \end{aligned} \tag{30}$$

$$\begin{aligned} x_{\mathrm{i}} &= 1 - \frac{1}{2}u; \\ x_{\mathrm{a}} &= \frac{L}{3l}(1-u), \qquad l/L << u << 1 \end{aligned} \tag{31}$$

(Compare eq 31 and 24.) Thus, although $\partial x_{\mathrm{i}}/\partial u|_{u=0} = \partial x_{\mathrm{a}}/\partial u|_{r=0} = 0$ (as should be true in the dipole field, since in such a field the values u and $-u$ are physically equivalent), already at $u \sim l/L$ $\partial x_{\mathrm{i}}/\partial u \sim \partial x_{\mathrm{a}}/\partial u \sim 1$. In other words, in the limit $L/l \to \infty$ the phase separation curves intersect the x axis of the u–x phase diagram at finite slopes.

For the analysis of phase I in a strong field $u >> 1$ we choose a trial function in the form

$$f(\vec{n}) = \mathrm{const}/(1 + 2\alpha^2(1 - \cos\theta))^2 \tag{32}$$

where α is the variational parameter. (The reasons for this form are the same as for eq 25.) As a result of the calculations with the trial function (32) we have

$$\begin{aligned} x_{\mathrm{i}} &= 0.176u \exp(-u/2); \\ x_{\mathrm{a}} &= 0.056\frac{L}{l}u^2 \exp(-3u/2), \qquad u >> 1 \end{aligned} \tag{33}$$

The parameters of the critical point are

$$\begin{gathered} u_{\mathrm{c}} = \ln\frac{L}{l}; \qquad x_{\mathrm{c}} = 0.31\left(\frac{\ln(L/l)}{L/l}\right)^{1/2}; \\ \eta_{\mathrm{c}}' = 1 - \frac{4.48l}{L}; \qquad \eta_{\mathrm{c}} = 1 - \frac{13.4l}{L} \end{gathered} \tag{34}$$

Here, $\eta' = \langle\cos\theta\rangle$ is an additional order parameter, appearing in the dipole field. Comparing eq 33 and 34 with eq 26 and 27, we conclude that the phase diagrams for the liquid-crystalline transition in solutions of semiflexible chains described by model A are qualitatively similar for the fields of dipole and quadrupole types (with the exception of the behavior at $u << l/L$). The qualitative form of the phase diagram for the case under consideration coincides, consequently, with that shown in Figure 9.

Model B. Now let us assume that the flexibility of polymer chains is described by model B. To be definite we present all the results for the valence angle $\gamma_0 = 60°$. We begin with consideration of the solution behavior in a field of quadrupole type. The study of the case of a weak field $u << 1$ is qualitatively completely analogous to that performed above for model A; the results for x_i and x_a are the following:

$$x_i = 2(1 - u/4); \qquad x_a = \frac{4L}{3l}(1 - u/2), \qquad u << 1 \tag{35}$$

In performing the analysis of the solution behavior in a strong field $u >> 1$, the only nontrivial question is the choice of the trial function $f(\bar{n})$ for phase I. It is clear that in model B this function must include two contributions: the main one, localized near the anisotropy axis, and a small addition, localized near the directions forming the angle $\gamma_0 = 60°$ with this axis. Thus, let us choose $f(\bar{n})$ in the form

$$f(\bar{n}) = f'(\bar{n}) + f'(-\bar{n}) \tag{36}$$

$$f'(\bar{n}) = \text{const}\left[\exp(-\alpha^2\theta^2) + \frac{\beta^2}{\alpha(3\pi)^{1/2}}\exp(-\alpha^2(\theta - \pi/3)^2)\right] \tag{37}$$

where α and β are the variational parameters. The values of x_i and x_a obtained as a result of the calculations with this trial function are

$$x_i = \frac{1.94}{u}; \qquad x_a = 4.1\frac{L}{l}\frac{1}{u^4}, \qquad u >> 1 \tag{38}$$

Thus, the transition concentration and the relative width of the phase separation region decrease in a strong field according to power laws (compare with the exponential decrease for model A). The parameters of the critical point are

$$u_c = 1.29\left(\frac{L}{l}\right)^{1/3} >> 1; \qquad x_c = 1.51\left(\frac{l}{L}\right)^{1/3} << 1; \qquad \eta_c = 1 - 9.3\left(\frac{l}{L}\right)^{4/3} \tag{39}$$

The small values of the critical concentration (i.e., of the values of x_c) indicate that, as for model A, the liquid-crystalline transition can be induced by the external field practically at any concentration of the initially isotropic solution.

Now we list the results obtained for a solution of model B polymer chains in the dipole field. These results do not require any additional comments:

$$x_i = 2(1 - Lu^2/8l); \qquad x_a = (4L/3l)(1 - Lu^2/4l), \qquad u << l/L \tag{40a}$$

$$x_i = 2(1 - u/4); \qquad x_a = (4L/3l)(1 - u/2), \quad l/L << u << 1 \tag{40b}$$

$$x_i = 4.35/u; \qquad x_a = 140L/lu^4, \qquad u >> 1 \tag{40c}$$

$$u_c = 3.18(L/l)^{1/3}; \qquad x_c = 1.37(l/L)^{1/3}; \qquad \eta_c' = 1 - 3.8(L/l)^{-4/3}; \qquad \eta_c = 1 - 11.3(L/l)^{-4/3} \tag{40d}$$

Model C. Finally, let us consider the most realistic model, model C, of rotational-isomeric chain flexibility with a small persistent component. Let us assume that $\gamma_0 = 60°$ and $\nu >> 1$. From the systematic point of view the study of this case is completely analogous to the corresponding study for model B.

For the solution in a quadrupole field we obtain

$$x_i = 2(1 - u/4); \qquad x_a = (4\pi\nu)^{1/5}(1 - 3u/10), \qquad u << 1 \tag{41a}$$

$$x_i = 1.94/u; \qquad x_a = (4\pi\nu)^{1/5}(1.96/u^{12/5}), \qquad u >> 1 \tag{41b}$$

$$u_c = 1.45\nu^{1/7}; \qquad x_c = 1.34\nu^{-1/7}; \qquad \eta_c = 1 - 5.8\nu^{-4/7} \tag{41c}$$

In the case of a dipole field:

$$x_i = 2(1 - 0.098\nu u^2); \qquad x_a = (4\pi\nu)^{1/5}(1 - 0.12\nu u^2), \qquad u << 1/\nu \tag{42a}$$

$$x_i = 2(1 - u/4); \qquad x_a = (4\pi\nu)^{1/5}(1 - 3u/10), \qquad 1/\nu << u << 1 \tag{42b}$$

$$x_i = 4.35/u; \qquad x_a = (4\pi\nu)^{1/5}(16.3/u^{12/5}), \qquad u >> 1 \tag{42c}$$

$$u_c = 3.69\nu^{1/7}; \qquad x_c = 1.18\nu^{-1/7}; \qquad \eta_c' = 1 - 2.08\nu^{-4/7}; \qquad \eta_c = 1 - 6.25\nu^{-4/7} \tag{42d}$$

The results (41) and (42) are most characteristic for real semiflexible macromolecules with rotational-isomeric flexibility mechanism, since it is in model C that this mechanism can be described most fully. Comparing eq 41 and 42 with the corresponding results obtained in ref 15 for freely jointed and persistence flexibility mechanisms, two specific features of the behavior of solutions of semiflexible macromolecules with rotational-isomeric flexibility mechanism in external orientational fields are worthy of note. First of all, in such solutions one needs much stronger fields to reach the critical point than for solutions of persistent of freely jointed macromolecules (this is connected with the fact that for rotational-isomeric flexibility the liquid-crystalline transition is most abrupt and pronounced and, consequently, we need a very strong orientational field to suppress this transition). Second, the critical concentration in such solutions is always essentially lower than the transition concentration in the absence of a field (whereas for other flexibility mechanisms these two concentrations are of the same order of magnitude). Thus for chains with rotational-isomeric flexibility mechanism the phase transition induced by the field can be observed over the widest concentration region.

The qualitative form of the phase diagram in the variables u and x for model C coincides with one shown in Figure 9. However, because of the presence of the persistent flexibility component the specific features of the transition emphasized above are for this model not so pronounced as for models A and B.

5. Susceptibility of a Solution of Semiflexible Rotational-Isomeric Macromolecules in an External Orientational Field of Dipole Type

In this section we consider separately one of the important characteristics of a solution of semiflexible chains with rotational-isomeric flexibility mechanism, namely, the susceptibility of such a solution in a zero external orientational field of the dipole type

$$\chi_0 \equiv \partial\eta'/\partial u|_{u=0} \tag{43}$$

as well as the value of the mean-square end-to-end distance $\langle R^2 \rangle$ for macromolecules in the solution, which is closely connected to χ_0 (this connection is due to the fact that according to the fluctuation theorem[20]

$$\chi_0 = \langle R_z^2 \rangle / \langle R^2 \rangle_0 \tag{44}$$

where $\langle R_z^2 \rangle$ is the average square of the projection of the end-to-end distance vector on the orientation azis and $\langle R^2 \rangle_0 \sim Nl^2$ is the unperturbed mean-square end-to-end distance). In ref 16 it was shown that the concentration dependence of χ_0 and $\langle R^2 \rangle$ in the liquid-crystalline phase for a solution of semiflexible macromolecules with freely jointed and persistence flexibility mechanisms is completely different: for the freely jointed flexibility model the values of χ_0 and $\langle R^2 \rangle$ are practically independent of the solution concentration, *c*, in the anisotropic phase, while for the persistence flexibility model they increase exponentially with *c*. It was proposed (see ref 16) that the experimental data on the concentration dependence of χ_0 or $\langle R^2 \rangle$ in the anisotropic phase can thus be used to discriminate between different flexibility mechanisms of polymer chains. When this is the case, it is important also to study the dependences $\chi_0(c)$ and $\langle R^2 \rangle(c)$ for solutions of chains with rotational-isomeric flexibility mechanism. This is our aim in this section.

We consider the most realistic model, model C, of rotational-isomeric polymer chain with $\gamma_0 = 60°$ and $\nu >> 1$. For this model the free energy of a solution of semiflexible macromolecules in an external dipole field is determined by eq 6, 10c, and 20. The exact minimization of this free energy, with the additional normalization condition $\int f(\bar{n})\, \mathrm{d}\Gamma = 1$, leads to the following integrodifferential equation (compare with eq A.1 of ref 16)

$$4T\psi(\bar{n}) - 8T \int \delta(\cos\gamma - \cos\gamma_0)\psi(\bar{n}')\, \mathrm{d}\Gamma' - \frac{T}{\nu}\nabla^2\psi + U_{\mathrm{eff}}\psi = E\psi \quad (45)$$

where $\psi(\bar{n}) = [f(\bar{n})]^{1/2}$, $E = \lambda T$,

$$U_{\mathrm{eff}}(\bar{n}) = U_{\mathrm{ext}} + U_{\mathrm{self}} = -uT\cos\theta + 2T\vartheta\frac{l}{d}\int f(\bar{n}')|\sin\gamma_{\bar{n}\bar{n}'}|\, \mathrm{d}\Gamma' \quad (46)$$

where λ is an indeterminate multiplier. Although eq 46 is more complex than eq A.1 of ref 16, obtained for the case of persistent flexibility, its structure is in principle similar and thus it can be analyzed in complete analogy with ref 16. Omitting all the intermediate calculations, we list here only the final result for the dependence $\chi_0(x)$ in model C at $x >> 1$:

$$\chi_0 = 0.22x^{5/2}\nu^{1/2} \quad (47)$$

At the transition point, i.e., at $x = \vartheta_{\mathrm{a}} l/d$ (see eq 14), $\chi_0 = 0.78\nu >> 1$. Thus, in model C the susceptibility χ_0 increases with concentration in the anisotropic phase according to the power law $\chi_0 \sim x^{5/2} \sim \vartheta^{5/2}$ (compare with the exponential increase for the persistent flexibility mechanism).

Using eq 44 we conclude that the mean-square end-to-end distance, $\langle R^2 \rangle$, in the strongly anisotropic phase also increases with concentration according to the same law (since in this phase $\langle R^2 \rangle \sim \langle R_z^2 \rangle$). The physical reason for this increase is the same as in ref 16: the essential "stiffening" of the rotational-isomeric chain in the liquid-crystalline solution. The degree of this stiffening can be characterized by the value $l^* = \langle R^2 \rangle / L$, which can be naturally called the "stiffness length" of the chain. Since in the anisotropic phase $\langle R^2 \rangle \sim \langle R_z^2 \rangle$ and $\langle R^2 \rangle_0 \sim Ll$, it follows from eq 44 that

$$l^* = \chi_0 l \quad (48)$$

It is interesting to note, in particular, that for model C at the transition point $l^* = 0.78\nu l = 0.78l_2$; i.e., the "stiffness length" of the chain is of the order of the second Kuhn length.

Thus, the susceptibility χ_0 of liquid-crystalline solutions of semiflexible chains, as well as the macromolecular dimensions in the anisotropic phase, should be either practically independent of the solution concentration (freely jointed flexibility) or rapidly increase with concentration, following an exponential (persistent flexibility) or power (rotational-isomeric flexibility) law. Direct experiments to check these predictions have not yet been performed. However, in the computer experiment of ref 21 the effect of the essential expanding of the rotational-isomeric polymer chain with increase of concentration of the anisotropic phase was indeed observed. The dependence $\langle R^2 \rangle(x)$ found in ref 21 is very sharp; however, there are insufficient data to check the prediction $\langle R^2 \rangle \sim x^{5/2}$.

The above consideration shows that the study of the properties of the liquid-crystalline transition and of the appearing anisotropic phase in solutions of semiflexible polymers offers information on the flexibility mechanism of the chain, on the values of the usual and second Kuhn segments (in the case of the rotational-isomeric flexibility), etc. Thus the use of the theory developed in ref 8–11, 15, and 16 and in the present paper in the analysis of experimental data on orientational ordering in macromolecular solutions—for "classical" as well as for recently synthesized stiff-chain polymer—would be very interesting.

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