Theory of Nematic Ordering in the Melts of Macromolecules with Different Flexibility Mechanisms

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ABSTRACT: On the basis of a general theoretic approach proposed in the previous paper by the authors, the liquid-crystalline ordering in the melts of macromolecules with different types of partial flexibility is studied. Both the forces of steric repulsion and those of the isotropic and anisotropic attraction between the macromolecules are taken into account. It is shown that (i) for all the systems studied a critical value of the chain anisodiametry parameter can be introduced, above which the polymer melt is always anisotropic and the isotropic–nematic transition cannot be observed, (ii) in the melts of persistent macromolecules, the temperature of nematic ordering, the order parameter, and the volume change at the transition point are significantly lower and the entropy change at the transition is somewhat lower than for the melts of rigid rods, semiflexible freely jointed polymers, or rotational-isomeric polymers with the same anisodiametry parameter, and (iii) with the increase of external pressure the region of stability of the nematic phase increases—pronounced effects can be obtained for pressures $\Pi \gtrsim 10$ atm.

1. Introduction

In a recent paper[1] we have proposed an approximate universal method, with the help of which it is possible to study in the framework of a unique approach the statistical mechanics of the nematic ordering in polymer solutions of arbitrary concentrations and melts. In this method both the forces of steric repulsion and those of the attraction between the macromolecules are taken into account; the method can be applied to polymers with arbitrary structure, an arbitrary flexibility mechanism, and an arbitrary relationship between the total chain length, L, and the length of the Kuhn segment, l. In ref 1 this method was applied to the consideration of the liquid-crystalline ordering in the solutions of stiff-chain macromolecules with limited flexibility at arbitrary solution concentrations and arbitrary temperatures (or solvent quality). In the present paper we will use this method for the study of the properties of the liquid-crystalline transition in the melts of macromolecules with different mechanisms of partial flexibility (i.e., thermotropic polymer liquid crystals).

Thermotropic polymer liquid crystals in systems of stiff macromolecules with partial flexibility have been studied recently in many experiments (see, for example, ref 2 and 3); some theoretical papers dealing with this topic have appeared as well.[4–8] The discussion of the methods of ref 4–8 and a comparison with the approach proposed in the present paper will be given below.

Since the method used in this article was developed in detail in ref 1, in the following section we will briefly describe the general approach of ref 1 and the results that we will use further. In section 3 we will consider these results from the point of view of the application for the study of the nematic ordering in the melts of polymer chains. Sections 4–6 contain the results of the calculations for the melts of macromolecules with different mechanisms of partial flexibility.

As in ref 1, we will consider the melts of the following types of macromolecules: (a) completely stiff macromolecules ($l \gg L$), i.e., long rigid rods of length L and diameter d (Figure 1a); (b) semiflexible macromolecules ($L \gg l$) with a freely jointed flexibility mechanism, i.e., long chains of freely jointed rigid segments of length l and diameter d (Figure 1b); (c) semiflexible macromolecules with a persistent (homogeneously distributed along the chain contour) flexibility mechanism (Figure 1c); (d) semiflexible macromolecules with a rotational-isomeric flexibility mechanism (Figure 1d), which consist of elementary subunits of length a and diameter d, the angle γ between the adjacent subunits being $\gamma_0 = 60°$ (with the probability $p << 1$; gauche conformation) or $\gamma = 0$ (with the probability $1 - p$; trans conformation) (cf. ref 9). The value of p depends on temperature: $p \sim \exp(-\Delta U/T)$, where ΔU is the energy difference between the trans and gauche conformations.

For all the macromolecules listed above we will consider the statistical mechanics of the nematic ordering in the melt. Thus, in the present paper we will study the liquid-crystalline transition only for the limiting cases of the melts of completely stiff ($L << l$) and semiflexible ($L \gg l$) macromolecules. The generalization of our method for the case of macromolecules with $L \sim l$, as well as for the case of copolmers including stiff and flexible fragments of the chain, does not give rise to any difficulties (cf. ref 10) and will be considered in subsequent publications.

2. Free Energy of Concentrated Solutions or Melts of Stiff-Chain Polymers

Let us consider a solution or melt of one of the objects shown in Figure 1. Below we will use the term "segment" to denote all the macromolecule, rigid rod in the case of Figure 1a, the straight-chain segment between two junction points in the case of Figure 1b, or the part of the chain whose contour length is equal to the length of the Kuhn segment in the cases of Figure 1c,d. Let N be the total number of segments in the volume V, $c = N/V$, where T is the temperature and $f(\vec{n})$ the orientational distribution function for the unit vector, $\vec{n}$, tangential to the chain (in the cases of Figure 1a,b this function is, as a matter of fact, the orientational distribution function for the straight segments). Let us adopt the following normalization condition for $f(\vec{n})$: $\int f(\vec{n})\,d\Omega = 1$, $d\Omega$ being an element of spatial angle.

The free energy of the system under consideration in the mean-field approximation can be represented as a sum of four terms $F = F_1 + F_2 + F_3 + F_4$ (cf. ref 1), where the term F_1 corresponds to the entropy of the translational motion of the macromolecules as a whole, the term F_2 is due to the entropy of orientational ordering, F_3 is the free energy of steric interaction of the segments (i.e., of the segment repulsion due to their mutual impenetrability), and the term F_4 is connected with the forces of attraction between the segments. The terms F_1 and F_2 were calculated already in a series of papers[9–12] devoted to the liquid-crystalline ordering in the dilute solutions of macromolecules; they

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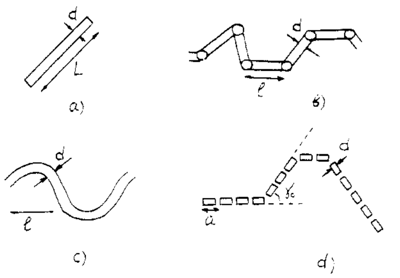

Figure 1. (a) Completely stiff macromolecule; (b) semiflexible freely jointed chain; (c) semiflexible persistent chain; (d) semiflexible rotational-isomeric chain.

remain unchanged for the case of a concentrated solution or melt

$$F_1^{\mathrm{A}} = NT \ln c, \qquad F_1^{\mathrm{B,C,D}} = 0 \tag{1}$$

$$F_2^{\mathrm{A,B}} = NT \int f(\vec{n}) \ln (4\pi f(\vec{n}))\, \mathrm{d}\Omega \tag{2}$$

$$F_2^{\mathrm{C}} = NT \int [\nabla f(\vec{n})]^2/4f(\vec{n})\, \mathrm{d}\Omega \tag{3}$$

$$F_2^{\mathrm{D}} = -NT(l/a) \int f(\vec{n}) \ln (\hat{g}\psi/\psi)\, \mathrm{d}\Omega \tag{4}$$

(in eq 1–4 the indices A, B, C, and D correspond to Figure 1, parts a, b, c, and d). In eq 4 the auxiliary function $\psi(\vec{n})$ is connected to $f(\vec{n})$ through the equation

$$\psi\hat{g}\psi = f(\vec{n})$$

$$\hat{g}\psi \equiv (1-p)\psi + (p/2\pi) \int \delta(\vec{n}\vec{n}' - \cos \gamma_0)\psi(\vec{n}')\, \mathrm{d}\Omega' \tag{5}$$

and the length of the Kuhn segment, l, is equal to

$$\frac{l}{a} = \frac{1}{p \sin^2 (\gamma_0/2)} - 1 = \frac{4}{p} - 1 \tag{6}$$

As to the free energy of the steric interaction of segments, F_3, it was found in ref 1 that for all the four cases shown in Figure 1 this term can be approximately represented in the form

$$F_3 = NTc_{\max}\tilde{l}^2 d \ln [(1 - c/c_{\max})^{-1}] \int |\sin \lambda| f(\vec{n}_1) f(\vec{n}_2)\, \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2 \tag{7}$$

where $\tilde{l} \equiv L$ for rigid rods and $\tilde{l} \equiv l$ for semiflexible chains, γ is the angle between the vectors $\vec{n}_1$ and $\vec{n}_2$, and $c_{\max}$ is the concentration corresponding to the maximally dense packing for the system of macromolecules. Equation 7 was obtained in ref 1 with the ideas developed by Parsons in ref 13 for the study of liquid-crystalline ordering in the system of long rigid rods. The form (7) for the free energy corresponds to the mean-field approximation separating the orientational and translational degrees of freedom. In the limit of a dilute solution, i.e., at $c \ll c_{\max}$, eq 7 coincides with the well-known formula for the free energy of steric interaction of segments in the second virial approximation (see ref 9–12). On the other hand, it was shown in ref 1 that in the case of sufficiently strong ordering eq 7 amounts to the expression for the steric part of the free energy, which is equivalent to that obtained in the lattice theory by Flory.[14] Thus, the expression (7) retaining all the advantages of the approximations of the virial method and of the Flory theory is free from their main shortcomings (which are connected with the possibility of considering only dilute solutions in the case of virial theory and with the existence of the predetermined spatial lattice in the case of the Flory theory; cf. ref 1 and 15).

The free energy F_3 determined by eq 7 depends essentially on the maximal segment packing concentration $c_{\max}$. It is obvious that $c_{\max} \sim 1/d^2\tilde{l}$. In the present paper we will assume, to be definite, that

$$c_{\max} = (4/\pi)(1/d^2\tilde{l}) \tag{8}$$

The choice of any other numerical coefficient of the order of unity in eq 8 does not lead to the change of the qualitative conclusions of the present study.

The free energy F_4 corresponding to the forces of attraction can be written in the usual mean-field form (cf. ref 1)

$$F_4 = -(\pi/4)\tilde{l}^2 dNc(w_0 + w_{\mathrm{a}}\eta^2) \tag{9}$$

where w_0 is the characteristic value of the attraction energy between monomeric units, the ratio w_{a}/w_0 describes the anisotropy of the attraction forces, $\eta = \langle P_2(\vec{n}\vec{n}_0)\rangle \equiv \int f(\vec{n})P_2(\vec{n}\vec{n}_0)\, \mathrm{d}\Omega$ is the order parameter defined in a usual way, $P_2(\vec{n}\vec{n}_0)$ is the second Legendre polynomial, and $\vec{n}_0$ is the direction of the anisotropy axis. As a rule, the anisotropic part of the attraction is much smaller than the isotropic part;[16,17] following ref 1, we will use in specific calculations the value $w_{\mathrm{a}}/w_0 = 0.1$ as a reasonable estimation. In ref 1 it was noted that although eq 9 is exactly valid only for the case when the characteristic radius of the attractive forces, r_{a}, is much larger than the characteristic width of the chains, d, it can be applied in the general case $r_{\mathrm{a}} \sim d$, as well, if we want to develop an approximate theory describing the main qualitative effects.

Equations 1–9 determine completely the free energy of a polymer system (either solution or melt). With this expression for the free energy, which is valid for solutions of arbitrary concentrations and melts at arbitrary temperatures for an arbitrary chain length and flexibility mechanism, it is possible to perform the most effective comparison of the results that are obtained in different particular cases and to obtain the general picture of available tendencies and qualitative specific features of the liquid-crystalline transition.

3. Thermodynamic Properties of Melts of Stiff-Chain Macromolecules

In order to find the equilibrium free energy of a system at a given segment concentration c, it is necessary to minimize the expression $F = F_1 + F_2 + F_3 + F_4$ given by eq 1–9 with respect to all possible orientational distribution functions $f(\vec{n})$. Following ref 1 and 9–12, we will use for this purpose an approximate variational method. For the cases shown in Figure 1a–c, the trial function was chosen in the form (cf. ref 12)

$$f(\vec{n}) = \mathrm{const} \exp(-\alpha \cos^2 \varphi) \tag{10}$$

where φ is the angle between the vector $\vec{n}$ and the orientation axis, α is the variational parameter, and const is the normalizing constant. For the case of Figure 1d it is convenient to represent in the form (10) not the function $f(\vec{n})$ itself but the auxiliary function $\psi(\vec{n})$ (see eq 5). As a result of the minimization we will determine possible phases (minima of the free energy) and the free energy of these phases $F = F(N,T,c)$.

Of course, in the consideration of the liquid-crystalline ordering in polymer melts one should use as an external parameter not the segment concentration c but the pressure Π. Let us estimate the effect of external pressure on the properties of the liquid-crystalline transition. From eq 1–9 we can obtain for the isotropic melt of macromolecules

$$\Pi = -\partial F/\partial V = \varkappa cT + \frac{\pi}{4}\tilde{l}^2 dc^2\left(\frac{T}{1 - c/c_{\max}} - w_0\right) \tag{11}$$

where $\varkappa = 1$ for rigid rods and $\varkappa = 0$ for semiflexible chains.

Thus the influence of nonzero external pressure on the thermodynamic properties of the isotropic melt becomes essential only at

$$\Pi \gtrsim \tilde{l}^2 d c_{\max}{}^2 T \sim T/d^3 \qquad (12)$$

The same estimation is valid also for the nematic melt. For the characteristic values $T = 300$ K, $d = 5$ Å, inequality (12) gives $\Pi \gtrsim 10^3$ atm. Consequently, normal atmospheric pressure should be regarded as negligibly small from the point of view of the thermodynamics of liquid-crystalline ordering.

Thus we will perform all the calculations below under the assumption that the external pressure is minimal. Due to the presence of the translational entropy term F_1 for the case of rigid rods we cannot adopt simply that $\Pi = 0$, because in this case the condensed phase cannot exist at equilibrium. Consistent procedure should include the assumption that the condensed phase coexists with the dilute gaseous isotropic phase ("saturated vapor" phase of rods), whose free energy is also determined by the formula of the preceding section. Concentrations of rods in the condensed and dilute phases can be determined, as usual, by equating pressures and chemical potentials of rods in both phases. On the other hand, for the cases of long semiflexible chains shown in Figure 1b–d the term F_1 is equal to zero (see eq 1) and the equilibrium polymer concentration in the condensed phase can be determined consistently from the condition $\Pi = 0$. For both cases (rods and semiflexible chains) the point of the liquid-crystalline transition can be identified from the condition that the pressures and chemical potentials in the isotropic and anisotropic melt are equal.

Before proceeding to the results for the liquid-crystalline ordering in thermotropic polymer systems obtained with the procedure described above, we make two preliminary remarks.

First, at high enough external pressure $\Pi \gtrsim 10^3$ atm the steric interaction energy term F_3 (eq 7) can become very large (due to the increase of polymer concentration, c, which can become close to $c_{\max}$). This fact promotes the occurrence of the liquid-crystalline ordering. Thus, the general conclusion is that the higher the external pressure, the larger the region of stability of the liquid-crystalline phase (however, to obtain nonnegligible effects rather high pressures $\Pi \gtrsim 10^3$ atm are needed).

Second, it can be seen from our expression for the free energy (eqs 1–9) that at any (even rather small) value of the chain stiffness parameter $\tilde{l}/d$ the steric interaction energy term F_3 (eq 7) can be made as large as we want at a sufficiently high external pressure Π. Thus this term, which favors the liquid-crystalline ordering, will become the dominant contribution to the free energy. Consequently, our theory seems to predict that in the melt of any polymer the formation of the liquid-crystalline phase should be possible under high enough pressure. This conclusion, at first sight, seems rather strange from the general point of view and from the point of view of available experimental data; furthermore, it is in contradiction to the theory of Flory and Ronca.[14]

However, we think that this conclusion is really valid for the macromolecules with absolutely rigid steric interactions—in this case at high enough values of external pressure (i.e., at c close enough to $c_{\max}$) the anisotropic phase should appear at least from packing considerations. On the other hand, for real systems at these superhigh pressures, one should necessarily bear in mind that the forces of steric repulsion are not completely rigid—this fact was not taken into account in the above considerations and it weakens the tendency for liquid-crystalline ordering.

As to the theory of Flory and Ronca,[14] it is worthwhile to recall that according to this theory the athermal thermotropic melt of rods with $L/d < 6.4$ should be isotropic even at maximally dense packing. The comparison of this result with the above considerations allows us to emphasize the difference in our approach and the lattice model approach. First, in our method maximally dense packing corresponds to $\Pi \rightarrow \infty$, and in this case the isotropic phase cannot be realized. Second, in our approach the athermal system (without any attraction of rods) can exist in the condensed state only under high enough external pressure; on the other hand, the value of this pressure completely disappears from the lattice theory.[14]

In the following sections we will present the results obtained with our approach described above for the properties of the liquid-crystalline transition in thermotropic polymer melts under minimal external pressure for the case $w_a/w_0 = 0.1$. All the intermediate calculations will be omitted throughout.

4. Nematic Ordering in Melts of Rigid Rods and Freely Jointed Chains

In this section we will consider the results for the melts of rods and semiflexible freely jointed chains. Phase diagrams for these two systems (in variables $T/w_0 - \lambda \equiv \tilde{l}/d$) calculated with our expression for the free energy are shown in Figure 2a,b. In the framework of our theory the regions of stability of the three phases can be located—isotropic and anisotropic melt and the gaseous phase (at high temperatures). The reason both transition-temperature curves tend to zero at $\lambda \rightarrow 0$ is connected with the definition of w_0—see eq 9. Let us concentrate our attention primarily on the properties of the nematic–isotropic transition. From Figure 2a,b it can be seen, first of all, that the liquid-crystalline ordering can take place only in the case where the asymmetry parameter of the macromolecule, λ, is smaller than some definite critical value λ_c. For rigid rods $\lambda_c = 3.5$ (compare with the analogous value 6.4 in the theory of Flory and Ronca[14]), for semiflexible freely jointed chains $\lambda_c = 7$. At $\lambda > \lambda_c$ the melt at equilibrium is always (at any temperature) orientationally ordered. This result is quite understandable since the polymer melt is a rather dense condensed system and if the chain stiffness is high enough the liquid-crystalline ordering should take place already as a result of the anisotropy of steric interaction alone.

From Figure 2a,b it can be seen also that the temperatures of nematic ordering for melts of semiflexible freely jointed chains are always somewhat higher than for melts of rigid rods with the same asymmetry parameter λ. However, this difference is not very pronounced.

The dependence of the order parameter at the point of the liquid-crystalline transition, η, on λ is shown in Figure 3a (at $\lambda < 3.5$ curve A for the melt of rigid rods practically coincides with the curve B for the melt of semiflexible freely jointed chains). The value of η changes with increase in λ from $\eta = 0.43$ to $\eta = 0.94$ (for rigid rods) and from $\eta = 0.43$ to $\eta = 0.98$ (for semiflexible freely jointed chains).

The results for the entropy change per segment at the transition point are shown in Figure 4a and those for volume change in Figure 5a. Volume change at the transition seems to be too high from the experimental point of view; however, in the presence of even a small persistent component of flexibility (which is always the case in real situations) the volume change decreases significantly (see the following section).

Of course, the results presented in Figures 2–5 can be applied only at physically reasonable values of the chain stiffness parameter $\lambda = \tilde{l}/d$: at least the inequality $\lambda >$

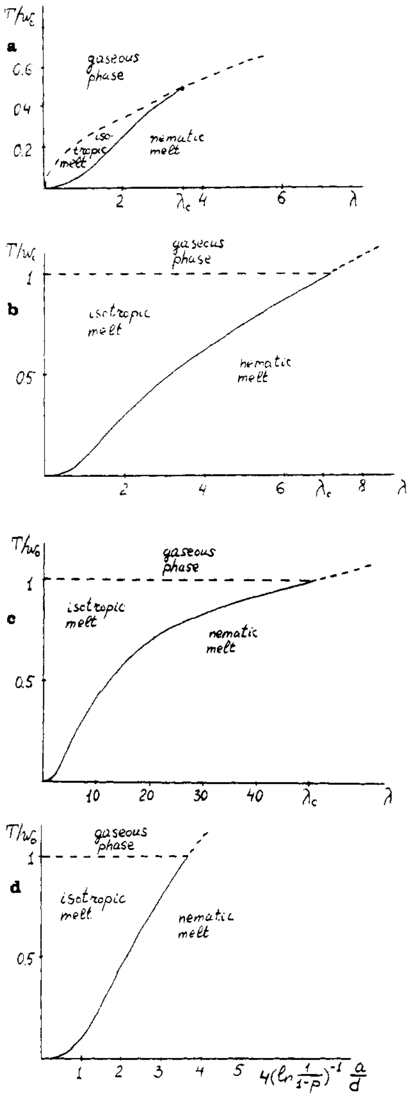

Figure 2. Phase diagrams for melts of rigid rods (a), semiflexible freely jointed (b), persistent (c), and rotational-isomeric (d) chains under minimal external pressure at $w_a/w_0 = 0.1$. Solid lines indicate isotropic–nematic transition and dotted lines indicate the high-temperature limit of the stability of the condensed phase.

1 should be fulfilled. However, in Figures 2–5 the results that can be formally obtained with our theory in the region $\lambda < 1$ are shown as well for the sake of completeness. In the formal limit $\lambda \rightarrow 0$ the steric interaction energy term F_3 is not essential and the liquid-crystalline ordering is solely due to the anisotropic attraction. Thus in this limit our theory for rigid rods coincides with the usual Maier–Saupe theory:[18] in this case the volume change at the transition point is equal to zero, $\eta = 0.43$, $\Delta S/N = 0.41$ (if we neglect the dependence of w_a on T). As it can be seen from Figures 2a–5a, Maier–Saupe results are exact only at rather small unphysical values of the parameter λ. In the most interesting region $\lambda > 1$ the influence of anisotropic attraction (the second term in eq 9) on the liquid-crystalline ordering is small; the nematic–isotropic transition is mainly due to the anisotropy of steric interactions.

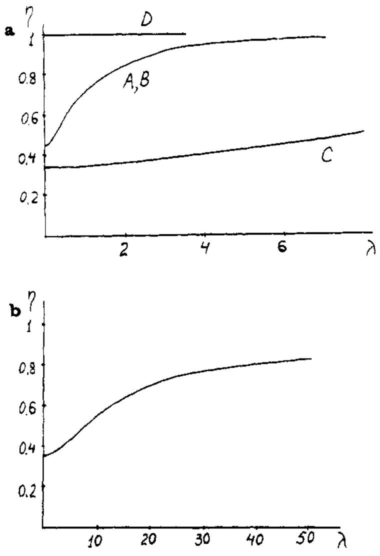

Figure 3. (a) Dependence of the order parameter at the nematic–isotropic transition point, η, on λ for melts of rigid rods (A), semiflexible freely jointed (B), persistent (C), and rotational-isomeric (D) chains. (b) Curve (C) plotted in another scale.

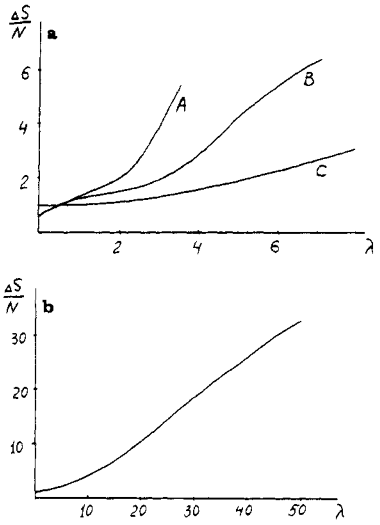

Figure 4. (a) Dependence of the entropy change per segment at the nematic–isotropic transition point, $\Delta S/N$, on λ for melts of rigid rods (A), semiflexible freely jointed (B), and persistent (C) chains. (b) Curve (C) plotted in another scale.

5. Nematic Ordering in Melts of Persistent Macromolecules

Now let us consider the results for melts of long persistent macromolecules with the Kuhn segment length l and diameter d (Figure 1c). The corresponding phase diagram is shown in Figure 2c, the order parameter at the isotropic–nematic transition point in Figure 3a,b, and the entropy and the volume change at the transition[24] in Figures 4a,b and 5a,b.

For this case the critical value of the parameter $\lambda = l/d$ turns out to be equal to $\lambda_c = 50$; i.e., it is much higher than for the freely jointed flexibility mechanism. Also the transition temperatures are much lower than for the melts of freely jointed macromolecules with the same values of λ (cf. Figure 2b,c). The order parameter at the transition point, η, increases with increase of λ from $\eta = 0.33$ (at $\lambda = 0$) to $\eta = 0.85$ (at $\lambda = 50$); i.e., the values of η for persistent macromolecules are also much lower than for their freely jointed counterparts: for example, at $\lambda = 5$ for persistent chains $\eta = 0.44$ and for freely jointed chains $\eta = 0.97$.

These results show that, as for the case of the ordering in solutions (see ref 12), it is much more difficult to obtain an orientationally ordered phase in melts of persistent macromolecules than in the corresponding melts of freely jointed chains.

It is essential also to note that for persistent macromolecules the entropy change at the transition is somewhat

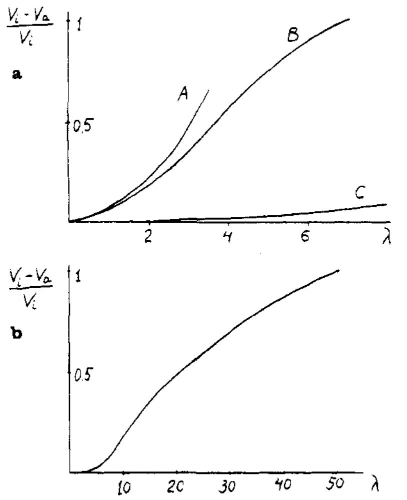

Figure 5. (a) Dependence of the relative volume change at the nematic–isotropic transition point, $(V_i - V_a)/V_i$ (V_i and V_a indicate volumes of isotropic and anisotropic melt, correspondingly, at the transition point) on λ for melts of rigid rods (A), semiflexible freely jointed (B), and persistent (C) chains. (b) Curve (C) plotted in another scale.

lower and the volume change is much lower than for the freely jointed chains with the same parameter λ. For example, at $\lambda = 5$ for persistent chains $(V_i - V_a)/V_i = 0.037$ and for freely jointed chains $(V_i - V_a)/V_i = 0.75$.

In ref 10 it was shown that for the case of the nematic–isotropic transition in dilute polymer solutions even a small persistent flexibility component in otherwise rodlike or freely jointed macromolecules leads to significant changes in the transition properties. In many cases these properties become closer to the semiflexible persistent limit than to the rodlike or freely jointed limit (cf. ref 10). We think that this conclusion is valid for the case of polymer melts as well. And since real polymer chains always have some small persistent flexibility component, it is the results presented in this section that should be regarded as most characteristic from the point of view of real thermotropic polymer liquid crystals.

As already mentioned, the formal limit $\lambda \rightarrow 0$ corresponds to the situation when the liquid-cystalline ordering is solely due to the anisotropic attraction of segments and the anisotropy of the forces of steric repulsion is not essential. This situation in melts of persistent macromolecules was considered recently also in ref 6. For the order parameter at the transition point, η, the authors of ref 6 have obtained

$$\eta = 0.356 \tag{13}$$

In ref 6 the exact minimization of the free energy was performed; thus the comparison of eq 13 with our result $\eta|_{\lambda=0} = 0.33$ allows us to estimate the accuracy of the variational method used in the present paper—the corresponding error appears to be smaller than 10%.

In ref 7 the same problem as in ref 6 was considered, and the results obtained are similar to those of ref 6 (although exact comparison is impossible due to the fact that the results of ref 7 are shown on shallow-scale plots). Besides that, the authors of ref 7 have published one more paper[8] devoted to the same topic. The analysis of the properties of the liquid-crystalline transition in ref 8 is based on the Landau–de Gennes expansion of the free energy in the powers of the order parameter. However, the coefficients in this expansion were found by an unsound method (for more details see ref 19), so the results of ref 8 are erroneous.

An attempt to consider the problem of nematic ordering in melts of semiflexible persistent macromolecules was undertaken by Ronca and Yoon[4,5] in the framework of the lattice approach by Flory.[14] Ronca and Yoon have introduced a finite cutoff length L_c, such that π/L_c represents the maximum curvature allowed for a persistent chain. The authors of ref 4 and 5 believe that by this way they can describe more accurately the flexibility mechanism, which is characteristic for real chains. We will not discuss here whether the introduction of an additional parameter L_c is indeed reasonable. We note only that in the limit $L_c \rightarrow 0$ the model by Ronca and Yoon transforms into the traditional persistent model. If we consider the results of ref 4 in this limit, we will obtain the general consclusion coinciding with that formulated above: also in the lattice model for the orientational ordering in the system of persistent macromolecules we need much stiffer chains and the order parameter at the transition point is lower than in the case of rodlike or freely jointed macromolecules. However, we emphasize once more that in our opinion the lattice model approach to the problem of thermotropic polymer liquid crystals in the form used in ref 4 and 5 has many shortcomings (for example, the impossibility of accounting for the effects of the external pressure, for the volume change at the transition, etc.).

6. Nematic Ordering in Melts of Macromolecules with a Rotational-Isomeric Flexibility Mechanism

One of the main specific features of the liquid-crystalline ordering in solutions of rotational-isomeric macromolecules (see Figure 1d) obtained in ref 9 was connected with the fact that at the transition point the completely ordered phase is formed. Analysis shows that this feature remains for the case of the melt as well.

The flexibility of rotational-isomeric macromolecules is characterized not only by the parameter l/d but also by the probability of bending at each step, p (there is no direct connection between these parameters; see eq 6). If the value of p is not close to unity (which is practically always the case), we have found that the liquid-crystalline phase in the melt of rotational-isomeric macromolecules is always completely ordered ($\eta = 1$), the transition temperature being determined implicitly by the simple analytical relation

$$1 + 0.1\frac{w_0}{T} + \ln\frac{w_0}{T} = \frac{d}{a}\ln\frac{1}{1-p} \tag{14}$$

A complete phase diagram for this case is shown in Figure 2d. It can be seen that the transition temperature defined by eq 14 is the highest in comparison with all the cases considered above. Thus the melt of macromolecules with a pure rotational-isomeric flexibility mechanism can be most easily transformed into the nematic phase. It can be shown also that the volume change at the transition is equal to

$$(V_i - V_a)/V_i = T/w_0 \tag{15}$$

As to the entropy change at the transition, its value depends essentially on the specific form of the dependence $p(T)$.

It should be emphasized that, as for the case of a polymer solution,[9] the absolutely ordered phase in a polymer melt can be formed only for a purely rotational-isomeric flexibility mechanism. In the presence of even a small component of flexibility of the persistent type (which is always the case for real chains) properties of the nematic ordering, apparently, are changed very significantly and become closer to those for the melts of semiflexible persistent macromolecules (see previous section); in particular, the degree of orientational order in the anisotropic phase in this case should not be absolute.

Quantitatively the contribution of the persistent flexibility mechanism is determined by the value of the second effective segment, l_2, introduced in ref 9. The results of this section are valid only if $l_2/l \gg 1$. However, we do not assert at all that this is the case for real polymers. On the contrary, we think that the persistent component of flexibility is very essential for the properties of nematic ordering in the melts of polymers with rotational-isomeric flexibility. More accurate estimations are not yet possible because of the absence of experimental information on the values of l_2.

7. Conclusion

Thus, we have considered the properties of liquid-crystalline ordering in the melts of semiflexible macromolecules with different types of partial flexibility (and also in the melts of rigid rods). It was shown that each type of macromolecules has its own very pronounced specific properties of the transition to the anisotropic state.

The main conclusions can be summarized as follows:

(i) For each of the four systems considered (Figure 1a–d), it is possible to introduce a critical degree of chain stiffness ratio $\lambda = \bar{l}/d = \lambda_c$ in such a way that at $\lambda > \lambda_c$ polymer melt at equilibrium is always anisotropic. The value of λ_c depends on the flexibility mechanism.

(ii) Properties of the nematic–isotropic transition in melts of persistent macromolecules differ very essentially from the corresponding properties in other systems considered. For this case the temperature of nematic ordering, the order parameter, and the volume change at the transition point are significantly lower and the entropy change at the transition is somewhat lower than for the melts of rigid rods, semiflexible freely jointed, or rotational-isomeric polymers with the same anisodiametry parameter λ.

(iii) Even a small component of persistent flexibility in melts of rigid rods, semiflexible freely jointed, and rotational-isomeric macromolecules can change essentially the properties of the liquid-crystalline transition.

(iv) In the majority of cases nematic ordering in polymer melts is mainly due to the anisotropy of steric interaction. Anisotropy of attraction forces plays in these cases a secondary role.

(v) With the increase of external pressure the region of stability of nematic phase increases. Pronounced effects can be obtained for pressures $\Pi \gtrsim 10^3$ atm.

The degree of universality of the consideration of the present paper is rather high: from all the parameters characterizing polymer structure only the degree of chain stiffness (parameter λ) and the flexibility mechanism were important for us. We believe that with the help of our theory we were able to understand main tendencies and qualitative peculiarities of the nematic ordering in melts of polymers of different types. However, in order to be able to describe quantitatively experimental data, it is necessary, of course, to take into account more delicate details of macromolecular structure.

In particular, we think that it is very important to define more accurately the potential of repulsive forces between macromolecules, taking into account the fact that these forces are not absolutely rigid. There are indirect reasons to believe that in this case some of our results for melts of rigid rods and semiflexible freely jointed chains will change considerably; in particular the volume change at the transition (curves A and B in Figure 5) will become much smaller.

For specific polymers it is necessary also to take into account explicitly the inhomogeneity of polymer chain on a microscopic scale, the presence of massive side groups, etc. In principle, in the framework of our approach such modifications can be introduced without serious difficulties.

Our theory can be also easily modified to describe thermotropic liquid-crystalline melts of copolymers, including stiff and flexible fragments of the chain. For this case a lattice approach was developed recently,[20-23] and many interesting features of the nematic ordering in these systems were predicted. It is thus worthwhile to apply to this problem the much more universal and powerful method developed in ref 1 and in the present paper. The corresponding study is now in progress, and the results will be published elsewhere.

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(24) In the calculation of ΔS we assumed that the value of the Kuhn segment for persistent macromolecules is inversely proportional to temperature: $l = \mathrm{const}/T$.