

Statistical physics of liquid-crystalline polymers

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Usp. Fiz. Nauk **156**, 427–476 (November 1988)

The current status of the physics of liquid-crystalline polymers is reviewed. Major attention is paid to the theory of the nematic state of solutions and melts of polymers of varying architecture, and also of polyelectrolytes. The conditions for phase equilibrium in solutions and melts and the elastic properties of systems are studied, as well as light scattering in the region of a nematic phase transition and the dynamic properties of rigid-chain polymers.

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1. INTRODUCTION

The properties of matter in the liquid-crystalline (LC) state are intermediate between those of a liquid and of a crystalline solid. Like liquids, liquid crystals lack true, long-range translational order. At the same time, in a liquid-crystalline phase the molecules still maintain long-range orientational order. That is, like crystalline solids, liquid crystals are anisotropic.

As is well known, the tendency to formation of a liquid-crystalline phase is most marked for substances whose molecules have an elongated shape.¹⁻² In this case anisotropy can arise even from pure steric reasons—owing to the impossibility of arranging a sufficiently compact system of anisodiametric particles isotropically.

From this standpoint it is evident that rigid-chain macromolecules, i.e., macromolecules for which the length l of an effective segment of the chain (see Sec. 3.1) is much greater than the characteristic thickness d of the chain should easily form a liquid-crystalline phase. This is actually so; examples of macromolecules capable of forming liquid-crystalline phases of different types are any of the helical macromolecules (α -helical polypeptides, DNA macromolecules, etc.), aromatic polyamides, a number of cellulose esters, and certain polyisocyanates.³⁻⁵ The shape asymmetry parameter of such macromolecules (i.e., the ratio l/d) can be very large (for the first two examples mentioned above it can reach several hundreds).

In these cases, as a rule, an anisotropic phase is formed

not only in the pure polymeric substance (in the polymer melt), but also in a more or less concentrated solution of such macromolecules. Liquid-crystalline polymer melts are often called thermotropic polymeric liquid crystals (since for such substances the liquid-crystalline transition most naturally can be caused by a temperature change), while anisotropic polymer solutions are called lyotropic liquid crystals.

Both in the thermotropic and in the lyotropic case, a liquid-crystalline phase is formed in a system of sharply anisometric polymer molecules ($l \gg d$). Its properties must, of course, considerably differ from the properties of low-molecular-weight liquid crystals, for which the asymmetry parameter l/d is usually not so large. In particular, in the theoretical treatment of liquid-crystalline ordering in solutions and melts of rigid-chain polymers the most important problem is to find the asymptotic characteristics when $l/d \gg 1$. The existence of an additional large parameter leads to the possibility of a more complete theoretical study of rigid-chain polymers in the liquid-crystalline state as compared with low-molecular-weight liquid crystals.

Rigid-chain macromolecules are not the sole class of polymers capable of forming a liquid-crystalline phase. Such a phase can arise also in melts (more rarely in concentrated solutions) of copolymers containing both flexible and rigid (mesogenic) regions of the chain. The corresponding systems (especially the thermotropic ones) have been studied especially intensively experimentally.^{5,6} As a rule, the specifics of the equilibrium properties of such liquid crystals is expressed to a considerably smaller degree than for the case of rigid-chain macromolecules (since usually the asymmetry parameter of a mesogenic group is not so large). However, from the standpoint of dynamic properties these systems remain highly distinctive objects that combine the features of polymers and liquid crystals.

On the whole, it is precisely the combination of the characteristic properties of macromolecular systems with the features of low-molecular-weight liquid crystals that gives rise to the specifics of liquid-crystalline polymers and sustains the fundamental interest in studying them. It is also essential that biopolymers, which play an important role in the functioning of biological systems, often form ordered structures of a liquid-crystalline type.

The remarkable properties of polymeric LC dictate their varied practical applications: liquid-crystalline polymer solutions are used as the basis for producing high-strength fibers; mixtures of polymers capable of liquid-crystalline ordering with traditional film-forming flexible-chain polymers are used to create strengthened films (self-reinforced plastics). Films of liquid-crystalline polymers can be used as selective optical filters; optical elements based on liquid-crystalline polymer films are promising for use in recording systems and long-term information storage.

In polymer systems crystalline ordering of all three known types can occur: nematic, cholesteric, and smectic.¹ The simplest of them is nematic order, which is characterized by chains of the rigid-chain macromolecules (or long axes of mesogenic groups) having a preferential orientation along a certain axis, while long-range translational order in the arrangement of the molecules and links is completely absent here. In this review we shall mainly take up the studies on the theory of nematic order in polymer systems, since

the fundamental tenets of the theory of polymeric cholesterics and smectics have as yet not been sufficiently developed.

2. NEMATIC ORDER IN AN ATHERMAL SOLUTION OF LONG RIGID RODS

In this section we shall treat one of the simplest systems in which an isotropic phase-nematic transition can occur.

2.1. The Onsager theory and its modifications

The first molecular theory of nematic ordering was proposed by Onsager⁷ for a solution of cylindrical, long, rigid rods of length L and diameter d ($L \gg d$). In polymer language this system is a model for a system of extreme rigid-chain macromolecules whose flexibility is so insignificant that it cannot be manifested in the length L . In Ref. 7 Onsager treated the case of an athermal solution, in which only repulsive forces act among the rods, owing to their mutual impenetrability, and liquid-crystalline order arises from purely steric causes.

The basic steps of the Onsager method consist in the following. Let N rods lie in the volume V so that their concentration is $c = N/V$, while the volume fraction of rods in the solution is $\varphi = \pi c L d^2/4$. Let us introduce the orientational distribution function $f(\mathbf{n})$ of the rods: $c f(\mathbf{n}) d\Omega_{\mathbf{n}}$ is the number of rods per unit volume with directions lying within the bounds of the small solid angle $\Delta\Omega_{\mathbf{n}}$ about the direction \mathbf{n} . Evidently in the isotropic state we have $f(\mathbf{n}) = \text{const} = \frac{1}{4}\pi$. In a liquid-crystalline phase $f(\mathbf{n})$ is a function with a maximum on the anisotropy axis.

The Onsager approximation consists in writing the free energy of the solution of rods as a functional of f in the form

$$F = N\mathbf{T} \left[\ln c + \int f(\mathbf{n}) \ln (4\pi f(\mathbf{n})) d\Omega_{\mathbf{n}} + \frac{1}{2} c \int \int f(\mathbf{n}_1) f(\mathbf{n}_2) B(\gamma) d\Omega_{\mathbf{n}_1} d\Omega_{\mathbf{n}_2} \right]. \quad (2.1)$$

The first term in Eq. (2.1) amounts to the free energy of translational motion of the rods; the second term describes the losses of orientational entropy owing to liquid-crystalline order; the third term is the free energy of interaction of the rods in the second virial approximation. In this last term $B(\gamma)$ is the second virial coefficient of interaction of rods whose long axes, specified by the unit vectors \mathbf{n}_1 and \mathbf{n}_2 , form the angle γ . When only steric interactions of the rods are present⁷ we have

$$B(\gamma) = 2L^2d \sin \gamma. \quad (2.2)$$

Thus the fundamental approximation of the Onsager method is that the interaction of the rods is taken into account in the second virial approximation. Hence this method is applicable only at a low enough concentration of the solution of rods. Very simple estimates of the virial coefficients of steric interaction of the rods—the second virial coefficient is $B \sim L^2d$ and the third is $C \sim L^3d^3 \ln(L/d)^8$ —show that the second virial approximation ($cB \gg c^2C$) is valid under the condition $c \ll 1/Ld^2$ or $\varphi \ll 1$. We shall see below that in the limit $L \gg d$ a liquid-crystalline transition in the solution of rods occurs precisely at $\varphi \ll 1$. Therefore, for studying this transition and the properties of the anisotropic phase that arises in the limit $L \gg d$ (which is of greatest interest from the standpoint of application to rigid-chain molecules), the On-

sager method is exact.^{9,10}

The next step in the Onsager method is to find the equilibrium distribution function $f(\mathbf{n})$ by minimizing (2.1). Direct minimization yields an integral equation that can be solved only numerically (see Ref. 11). Therefore an approximate variational method was used in Ref. 7 with the trial function

$$f(\mathbf{n}) = \text{const} \cdot \text{ch}(\alpha \cos \theta), \quad \int f(\mathbf{n}) d\Omega_{\mathbf{n}} = 1. \quad (2.3)$$

Here θ is the angle between the vector \mathbf{n} and the direction of the anisotropy axis, while α is the variational parameter. One must substitute the trial function of (2.3) into Eq. (2.1) and minimize it with respect to α . The found minima correspond to possible phases (isotropic and liquid-crystalline). One can study the transition between these phases by the usual method by equating the pressures $\Pi = (c^2/N)\partial F/\partial c$ and chemical potentials $\mu = (F + c\partial F/\partial c)/N$ of the two phases.

As a result it turned out that⁷:

a) the orientational ordering in the solution of long rigid rods is a first-order phase transition that occurs at low concentrations of the rods in solution ($\varphi \sim d/L \ll 1$) at which the second virial approximation is still applicable:

b) when $\varphi < \varphi_i$ the solution is isotropic, when $\varphi > \varphi_a$ it is anisotropic, and when $\varphi_i < \varphi < \varphi_a$ the solution separates into isotropic and anisotropic phases, where we have

$$\varphi_i = \frac{3.34d}{L}, \quad \varphi_a = \frac{4.49d}{L}, \quad w \equiv \frac{\varphi_a}{\varphi_i} - 1 = 0.34; \quad (2.4)$$

c) the order parameter $s = \langle 3 \cos^2 \theta - 1 \rangle / 2$ (the averaging is performed by using the equilibrium function $f(\mathbf{n})$) at the point of appearance of the liquid-crystalline phase (i.e., when $\varphi = \varphi_a$) equals

$$s_0 = 0.84. \quad (2.5)$$

We stress that the only fundamental physical restriction of the Onsager method involves the second virial approximation, i. e., the condition $\varphi \ll 1$. The use of the variational procedure is simply a method of simplifying the calculation. The integral equation that arises upon exact minimization of the functional of (2.1) can be solved numerically to a high degree of accuracy; this has been done in Refs. 11 and 12. As a result it was found that

$$\varphi_i = \frac{3.290d}{L}, \quad \varphi_a = \frac{4.223d}{L}, \quad s_0 = 0.796. \quad (2.6)$$

This shows that using the variational method leads to a very small error ($\sim 5\%$) in determining the characteristics of the liquid-crystalline transition.

Thus the Onsager method that we have presented is applicable at low concentrations of the solution of rods: $\varphi \ll 1$. Many publications^{8,12-16} have been devoted to attempts to generalize this method to the case of high concentrations ($\varphi \sim 1$). The approach of Parsons¹³ is distinguished by the greatest simplicity and generality from the standpoint of application to solutions of rigid-chain macromolecules. The essence of this approach consists in the following. We can associate the internal energy of the system of rods with the pair correlation function $g(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2)$ of two rods having the orientations \mathbf{n}_1 and \mathbf{n}_2 (\mathbf{r} is the vector joining their centers):

$$U = \frac{N^2}{2V} \int f(\mathbf{n}_1) f(\mathbf{n}_2) g(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2) \Phi(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2) d^3r d\Omega_{\mathbf{n}_1} d\Omega_{\mathbf{n}_2}. \quad (2.7)$$

Here $\Phi(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2)$ is the energy of pairwise interaction of the rods. In the case in which the interaction is determined only by the shape of the rods, it can be represented in the form

$$\Phi(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2) = \Phi\left(\frac{r}{\sigma}\right), \quad (2.8)$$

Here $\delta = \delta(\mathbf{n}_1, \mathbf{n}_2, \mathbf{r}/r)$ is the minimum distance to which rods having the given orientations can approach. The central approximation¹³ consists in writing the function g in the same form:

$$g(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2) = g\left(\frac{r}{\sigma}; \varphi\right). \quad (2.9)$$

The approximation (2.9) is exact at low concentrations of the solution; at higher concentrations it is essentially an approximation of the mean-field type, which separates the translational degrees of freedom from the orientational. If we adopt the approximation (2.9), then we can write the free energy of steric interaction of the rods F_{ster} in the form¹³ (cf. the last term in Eq. (2.1)):

$$F_{\text{ster}} = NTJ(\varphi) \cdot \frac{2}{\pi d^2 L} \int f(\mathbf{n}_1) f(\mathbf{n}_2) B(\gamma) d\Omega_{\mathbf{n}_1} d\Omega_{\mathbf{n}_2}, \quad (2.10)$$

$$J(\varphi) = \int_0^\varphi g(1; \varphi) d\varphi. \quad (2.11)$$

At low concentrations of the solution of rods ($\varphi \ll 1$) we have $g(1; \varphi) \approx 1$. Therefore we have $J(\varphi) \approx \varphi$, and Eq. (2.10) reduces to the third term in Eq. (2.1).

The generality of Eq. (2.10) consists in the fact that it describes the results of many other studies^{12,14-16} that have posed the problem of calculating the free energy in a concentrated solution of rigid rods (for more details see Ref. 17). This formula is used below in analyzing nematic ordering in a solution of rigid-chain macromolecules in the presence of attractive forces. At the present stage it is only worth emphasizing that the Onsager method can be generalized in systematic fashion for describing solutions of any arbitrary concentration.

2.2. The lattice theory of Flory

Another approach to solving the problem of liquid-crystalline ordering in a solution of rigid rods was developed by Flory.¹⁸

We present below a modified variant¹⁹ of Flory's theory that enables avoiding certain undesirable artifacts of the original approach.¹⁸ Each rod is treated as a sequence of cells of a cubic lattice (Fig. 1a) whose number x plays the role of the parameter L/d . To describe inclined rods, Flory used a family of y shorter segments with x/y cells in each (Fig. 1b). If the origin of a rod lies at the zero point, then the coordinates of its end—in the (y_1, y_2) plane perpendicular to the supposed axis of ordering are

$$y_1 = x \sin \theta \cdot \cos \varphi, \quad y_2 = x \sin \theta \cdot \sin \varphi. \quad (2.12)$$

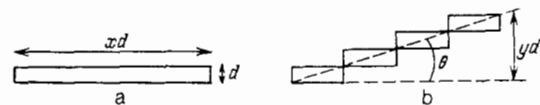


FIG. 1. Arrangement of rods on a lattice in the theory of Flory. a—Rod oriented along the axis of ordering. b—Inclined rod.

Here θ and φ are the spherical angles that fix the direction of the rod (\mathbf{n}). The number of segments into which we must divide the chosen rod is

$$|y_1| + |y_2| = x \sin \theta (|\cos \varphi| + |\sin \varphi|). \quad (2.13)$$

Upon averaging the right-hand side of Eq. (2.13) over the axially symmetric distribution $f(\mathbf{n})$, we obtain

$$y = \frac{4x}{\pi} \int \sin \theta f(\mathbf{n}) d\Omega_n. \quad (2.14)$$

Let n_2 rods of length x lie in a lattice containing n cells. The free energy of such an athermal system can be represented as the sum of two terms:

$$F = F_{\text{orient}} + F_{\text{comb}}.$$

Here

$$F_{\text{orient}} = n_2 T \int f(\mathbf{n}) \ln(4\pi f(\mathbf{n})) d\Omega_n \quad (2.15)$$

is the orientational component of the free energy, while we have

$$F_{\text{comb}} = -T \ln \mathcal{L}_{\text{comb}}. \quad (2.16)$$

Here $\mathcal{L}_{\text{comb}}$ is the number of ways of arranging on the lattice the set of rods having the given orientations. We can write the combinatorial factor in the form

$$\mathcal{L}_{\text{comb}} = (n_2!)^{-1} \prod_{j=1}^{n_2} v_j. \quad (2.17)$$

Here v_j is the number of ways in which one can arrange the j th rod under the condition that $j-1$ rods already lie in the lattice. Evidently v_{j+1}/n is the product of the probabilities that each of the cells that the $(j+1)$ th rod must cover is free. The probability p_1 that the first cell for each of the segments (see Fig. 1) is free is equal to the fraction of the cells free at the given instant, i.e.,

$$p_1 = \frac{n-jx}{n}. \quad (2.18)$$

On the other hand, the probability p_2 that the second, third, etc., cell of each segment is free must be calculated with the additional condition that the previous cell in the direction of the axis of ordering was also free. This implies that the cell under study cannot in principle be occupied by a second, third, etc., link of previously arranged segments, i.e.,

$$p_2 = \frac{n-jx}{n-jx+jy}. \quad (2.19)$$

We see that $p_2 > p_1$; within the framework of the lattice model that leads to liquid-crystalline ordering. Thus we have $v_{j+1} = np_1^y p_2^{x-y}$. Therefore we have

$$\mathcal{L}_{\text{comb}} = (n_1 + yn_2)! [n_1! n_2! n^{n_2(y-1)}]^{-1}. \quad (2.20)$$

Here $n_1 = n - n_2 x$ is the number of free cells (solvent molecules).

The free energy F_{comb} equals

$$F_{\text{comb}} = T \left\{ n_1 \ln(1-\varphi) + n_2 \ln \frac{\varphi}{x} + n_2(y-1) - (n_1 + yn_2) \ln \left[1 - \varphi \left(1 - \frac{y}{x} \right) \right] \right\}. \quad (2.21)$$

Here $\varphi = xn_2/n$ is the volume fraction of rods in the solution.

The expressions (2.16) and (2.21) fully determine the free energy of the system, and hence all its equilibrium properties. The liquid-crystalline phase transition in the system was studied in Ref. 19. The results for an athermal solution for $x = L/d \gg 1$ are:

$$\varphi_1 = \frac{7.89d}{L}, \quad \varphi_a = \frac{11.57d}{L}, \quad w = 0.47, \quad s_0 = 0.92. \quad (2.22)$$

Upon comparing the relationships of (2.22) with the asymptotically exact results (in the limit $L/d \gg 1$) of the Onsager theory of (2.4), we can conclude that, although the results of the lattice method are qualitatively correct as applied to the given problem, they differ quantitatively rather strongly from the exact values. Evidently this is a consequence of the many uncontrolled assumptions allowed in the presented derivation, as well as the artificial character of the lattice model.

We should also note that a number of other lattice theories of nematic ordering of rigid rods have been proposed besides the Flory theory,²⁰⁻²³ of which the best known are the approaches of Di Marzio²⁰ and Zwanzig.²¹ However, as applied to polymer problems, these approaches have not been used as widely as the Flory approach.

2.3. The problem of polydispersity

Up to now we have assumed that all the rods have the same length. This situation is characteristic of polymers of biological origin. However, most often polymer solutions prove to be polydisperse. That is, they contain macromolecules of differing molecular masses. The generalization of the theories presented in Secs. 2.1 and 2.2 to this general case presents no difficulties in principle. The effect of polydispersity on a nematic phase transition has been analyzed in a number of theoretical studies by using both the Onsager method²⁴⁻²⁸ and the Flory theory.²⁹⁻³² The fundamental qualitative results of these studies coincide. The effect of polydispersity is treated below with the example of a very simple (and very well studied) bidisperse system containing rods of two lengths L_1 and L_2 .

Let φ_1 and φ_2 be the volume fractions in the solution of rods of the first and second type, respectively, while $\varphi = \varphi_1 + \varphi_2$, and $q = L_2/L_1 > 1$:

$$z = \frac{\varphi_2}{\varphi}$$

is the weight fraction of the long rods;

$$\bar{L} = L_1(1-z) + L_2 z \quad (2.23)$$

is the weight-average length of the rods. Just as in the case of a monodisperse system, the nematic transition occurs at $\varphi \sim d/\bar{L}$. Therefore we can naturally use the reduced volume fraction ϑ :

$$\vartheta = \frac{\varphi \bar{L}}{d}. \quad (2.24)$$

The results obtained for this system by the Onsager method by a computer calculation²⁶ are shown in Figs. 2 and 3 for $q = L_2/L_1 = 2$ (analogous results have been obtained purely analytically²⁷; see also the review of Ref. 33). Figure 2 shows the phase diagram of the system. The curved lines surround the region of separation into two phases. In the monodisperse case $L_1 = L_2$ these curves would be converted into parallel straight lines: $\vartheta_1 = 3.29$, $\vartheta_a = 4.22$. We see that poly-

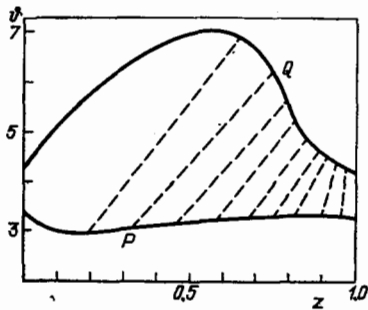


FIG. 2. Phase diagram of a solution of rods having the length ratio $L_2/L_1 = 2$. z is the weight fraction of the longer rods, ϑ is the reduced volume concentration of the solution. The curves surround the phase-separation region. The ends of the broken lines correspond to coexisting phases.

dispersity leads to a small decrease in the lower (isotropic) boundary of the separation region and simultaneously to a strong increase in its upper (anisotropic) boundary. Consequently the relative width of the separation region w substantially increases as compared with the monodisperse case (by a factor of 4.7 for $z = 0.5$ and $q = 2$).

The dotted lines in Fig. 2 join points that correspond to coexistent phases (e.g., the points P and Q). The volume fraction of the longer rods in the anisotropic phase (point Q) is considerably greater than in the isotropic phase (point P):

$$\frac{\varphi_{2a}}{\varphi_{2i}} = 3.7.$$

Thus the phase separation in the nematic transition is accompanied by a strong fractionation effect, which can be used to diminish the degree of polydispersity of a system. With increase in the parameter $q = L_2/L_1$, the ratio $\varphi_{2a}/\varphi_{2i}$ increases approximately according to an exponential law. That is, the fractionation effect is enhanced even further.

The dependence of the order parameters s_1 and s_2 (corresponding to the two types of rods) and of the mean order parameter

$$\bar{s} = (1 - z)s_1 + zs_2 \quad (2.25)$$

on the weight fraction z of the long rods at $\vartheta = \vartheta_a$ is shown in Fig. 3. We see that at $z \sim 0.5$ the mean order parameter is $\bar{s} \approx 0.92$, i.e., appreciably higher than in the monodisperse case ($s = 0.79$). We note also the substantial decrease in the order parameter of the shorter rods s_1 in the case in which the fraction of these rods is small (i.e., $z \rightarrow 1$).

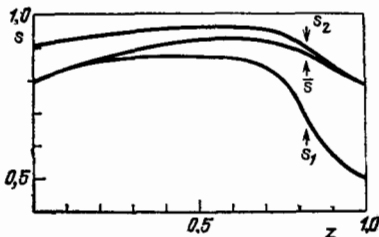


FIG. 3. Dependence of the orientational order parameters of the short (s_1) and long (s_2) rods and also that of the mean order parameter \bar{s} on the weight fraction z of the long rods.

2.4. Comparison of the continuum and lattice approaches

While staying within the framework of the lattice model one cannot completely eliminate various uncontrollable assumptions involving the relationship of the macromolecules with the previously defined space lattice. The artificiality of this relationship is evident even for the case of a solution of rigid rods. The lattice method faces even greater difficulties in trying to treat nematic ordering in solutions of rigid-chain macromolecules having partial flexibility. Here the presence of the fixed space lattice leads to substantial restrictions on the mechanism of flexibility of the polymer chain, many of which (e.g., the persistent mechanism most widespread for rigid chains) cannot be represented within the framework of the lattice model.

Therefore, apparently, precisely the continuum approach is most promising from the standpoint of studying liquid-crystalline order in polymeric systems. Within the framework of this approach one can also take account naturally of the presence of partial flexibility of a chain of arbitrary nature, of the influence of nonsteric interaction forces between the molecules, and of complications involving a high concentration of the solution of polymer chains (see below).

As regards the lattice model, it can be successfully applied to solve a number of concrete problems in those cases in which the continuum approach leads to too complicated calculations. Below we note a number of examples of this type. However, for drawing a complete picture of the existing trends and qualitative features of liquid-crystalline order in different polymer systems, the lattice method is absolutely insufficient.

3. ATHERMAL SOLUTIONS OF PARTIALLY FLEXIBLE POLYMERS

Having treated the problem of nematic ordering of a very simple system—an athermal solution of rigid rods—we now proceed to more realistic polymeric objects. The first circumstance that we must allow for in analyzing liquid-crystalline ordering in polymer solutions is that real rigid-chain macromolecules always have a certain finite flexibility.

Macromolecules differ in terms of the mechanism of flexibility of the polymer chain. The simplest mechanism of flexibility (from the standpoint of theoretical description) belongs to the freely linked chain, which amounts to a sequence of hinged rigid rods of length l and diameter d , with $l \gg d$ (Fig. 4a). The direction of each successive rod in the equilibrium state is random and does not depend on the direction of the previous ones. For this reason the mean-square distance between the ends of the chain $\langle R^2 \rangle$ equals

$$\langle R^2 \rangle_0 = Ll, \quad L \gg l. \quad (3.1)$$

Here L is the total contour length of the chain.

If the polymer chain has any other mechanism of flexibility (e.g., if the orientations of adjacent links are correlated), then Eq. (3.1) is satisfied, as before, but with a renormalized length l . In the general case this renormalized length is called the effective (Kuhn) segment of the polymer chain.

Most rigid-chain macromolecules are characterized, not by the freely linked, but by the so-called persistent mechanism of flexibility, in which the flexibility arises from the

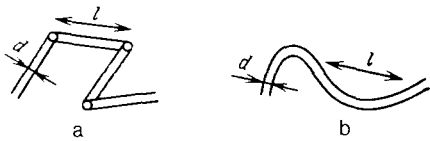


FIG. 4. a—Freely linked chain. b—Persistent chain.

accumulated effect of small oscillations in the valence angles. We can represent a persistent macromolecule in the form of a homogeneous cylindrical elastic filament of diameter d (Fig. 4b). The elasticity of the filament is such that it can be substantially bent only on scales of the order of l .

Depending on the relationship of the total contour length L of the macromolecule to the length l of the effective Kuhn segment, rigid-chain macromolecules can be referred to one of the three following fundamental classes: a) If the length of the Kuhn segment is so large that $l \gg L \gg d$, then we can neglect the flexibility of the polymer chain, and we arrive at the case of limiting rigid-chain macromolecules (rigid rods) treated above. b) If $L \gg l \gg d$, the rigid-chain macromolecule includes many Kuhn segments. From the global standpoint it stays in the state of a random coil. Such macromolecules are called semiflexible. c) Of course, intermediate cases are possible in which the contour length of the macromolecule and the length of the Kuhn segment are of the same order of magnitude: $L \sim l$. In real experiments this type of macromolecules is found rather often.

The transition of an athermal solution of partially flexible polymer chains to an anisotropic phase has been studied in a series of papers³⁴⁻³⁹ (see also the review of Ref. 33) by using the continuum approach (the Onsager approach). Below we shall present some fundamental results of these studies and briefly characterize the method by which these results were obtained.

3.1. Free energy

Let us start with the case of semiflexible macromolecules with $L \gg l \gg d$.³⁴⁻³⁷ By analogy with the treatment given in Sec. 2, we can conclude that the free energy of a solution of these macromolecules in the Onsager approximation must consist of the contribution F_{conf} describing the entropy losses upon orientational ordering and the free energy F_{ster} of steric interaction of the macromolecules in the second virial approximation (the translational free energy for long polymer chains is generally inessential^{36,37}).

To write the expression for F_{ster} we note that, since $l \gg d$ for semiflexible macromolecules, one can always divide the polymer chains into regions of length λ so that $d \ll \lambda \ll l$, and call these regions elementary links. In essence, the elementary links thus defined are long rigid rods. Therefore the second virial coefficient of interaction of two links having the orientations \mathbf{n}_1 and \mathbf{n}_2 is $B(\gamma) = 2Z\lambda^2 d |\sin \gamma|$ (cf. Eq. (2.2)). Upon allowing for this, we can write the expression for F_{ster} in the form (cf. the third term in Eq. (1.1)):

$$F_{\text{ster}} = \frac{1}{2} N \frac{L}{\lambda} T \cdot \frac{4}{\pi} \frac{\varphi^2}{\lambda d^2} \int f(\mathbf{n}_1) f(\mathbf{n}_2) \cdot 2\lambda^2 d |\sin \gamma| d\Omega_{\mathbf{n}_1} d\Omega_{\mathbf{n}_2} \quad (3.2)$$

(N is the total number of macromolecules in the solution, and $f(\mathbf{n})$ is the orientation distribution of the unit vectors \mathbf{n}

tangential to the chain.) This is because L/λ is the number of elementary links in the macromolecule, while $4\varphi/\pi\lambda d^2$ is their concentration in the solution. We see that, as should be so, the quantity λ in Eq. (3.2) drops out, so that finally we have³⁶

$$F_{\text{ster}} = NTL \cdot \frac{4\varphi}{\pi d} \int f(\mathbf{n}_1) f(\mathbf{n}_2) \sin \gamma d\Omega_{\mathbf{n}_1} d\Omega_{\mathbf{n}_2} \quad (3.3)$$

The method proposed in Refs. 36 and 37 of determining the entropy contribution F_{conf} is based on the idea that the dependence of the unit vector \mathbf{n} on the number of links can be treated as a realization of a discrete random walk of a point on the unit sphere (the number of the link plays the role of the time, while the position of the point of the sphere is fixed by the vector \mathbf{n}). The function $f(\mathbf{n})$ in this case amounts to a somehow normalized "concentration" of links at the "point" \mathbf{n} . Thus the problem of calculating the orientational entropy reduces to the following: to find for the described random walk the entropy corresponding to the given "concentration" distribution $f(\mathbf{n})$ of links (referred to the entropy of an isotropic distribution). In such a form this formulation is fully analogous to the formulation of the problem of calculating the conformational entropy of a polymer globule with a given distribution of the spatial concentration $n(\mathbf{r})$ of links, which was solved in the classical study of I. M. Lifshitz⁴⁰ (see also the reviews of Refs. 41, 42). The sole difference is that now the topic is the spatial distribution of links, rather than involving real three-dimensional space. Upon rewriting I. M. Lifshitz's result for this case, we obtain^{36,37} the following expression for semiflexible freely linked macromolecules (see Fig. 4a):

$$F_{\text{conf}} = NT \frac{L}{l} \int f(\mathbf{n}) \ln(4\pi f(\mathbf{n})) d\Omega_{\mathbf{n}}; \quad (3.4)$$

while for semiflexible persistent macromolecules we have (Fig. 4b):

$$F_{\text{conf}} = NT \frac{L}{l} \int \frac{(\nabla_{\mathbf{n}} f)^2}{4f} d\Omega_{\mathbf{n}}. \quad (3.5)$$

3.2. Nematic ordering in a solution of semiflexible chains

Equations (3.3)–(3.5) fully determine the free energy of a solution of semiflexible molecules for the models depicted in Fig. 4. In full analogy with the Onsager method (see Sec. 2), further calculations³⁴⁻³⁷ led to the following conclusions.

For the flexibility models being studied, the orientational ordering of the athermal solution has the character of a first-order phase transition and occurs at low concentrations of the polymer in solution. More exactly, when $\varphi < \varphi_i$ the solution is homogeneous and isotropic, when $\varphi > \varphi_a$ it is homogeneous and anisotropic, while when $\varphi_i < \varphi < \varphi_a$ it separates into isotropic and nematic phases, with $\varphi_i \sim \varphi_a \sim d/l \ll 1$.

The following characteristics of nematic ordering were obtained³⁴ for an athermal solution of freely linked semiflexible chains:

$$\varphi_i = \frac{3.25d}{l}, \quad \varphi_a = \frac{4.86d}{l}, \quad w = 0.50, \quad s_0 = 0.87. \quad (3.6)$$

On comparing the results of (3.6) with (2.4) and (2.5) we conclude that hinge linking of the rods in long chains leads only to quite insignificant changes in the characteristics of the isotropic phase-nematic transition: the region of phase separation is somewhat expanded, while the order param-

eter of the orientationally ordered phase that arises is slightly increased. Analogous conclusions were drawn⁴³ on the basis of analyzing results obtained by using the Flory lattice approach.

For an athermal solution of persistent semiflexible chains the characteristics of the liquid-crystalline transition proved to be the following³⁶:

$$\varphi_1 = \frac{10.48d}{l}, \quad \varphi_a = \frac{11.39d}{l}, \quad w = 0.09, \quad s_0 = 0.49. \quad (3.7)$$

We can easily see that orientational ordering in a solution of persistent chains occurs at substantially larger concentrations than in a solution of freely linked macromolecules (for the same d/l). Moreover, the relative concentration jump of the polymer at the transition, as well as the order parameter upon appearance of the liquid-crystalline phase, prove to be considerably smaller in this case. Analysis shows (see Ref. 36) that this arises from the fact that the entropy losses in the case of strong orientational ordering prove to be substantially larger for the persistent mechanism of flexibility than for the freely linked case. Comparing the results of (3.6) and (3.7), we can also draw the important conclusion that the character of the orientational ordering substantially depends, not only on the magnitude of the Kuhn segment, but also on the distribution of flexibility along the contour of the polymer chain.

Orientational ordering in solutions of polymer chains having certain other flexibility mechanisms has been studied in Refs. 37, 39, 44, and 45.

3.3. Dependence of the characteristics of the liquid-crystalline transition on the length of the macromolecules

Now let us proceed to analyze nematic ordering in solutions of partially flexible macromolecules with $L \sim l$. In this case the problem is substantially complicated as compared with the semiflexible limit treated above with $L \gg l$, since it turns out when $L \sim l$ that we cannot introduce a single distribution function $f(\mathbf{n})$ for all points of the polymer chain³⁸: the fact becomes essential that the degree of orientational ordering must depend on the position of the unit vector \mathbf{n} on the chain (e.g., the end links of the chain must generally be more disordered than the middle links). However, it has proved possible also for this case to apply the method of I. M. Lifshitz⁴⁰; the corresponding theory was developed in Ref. 38. Here we shall present the obtained results only for the persistent mechanism of flexibility, which is most often encountered for real rigid-chain polymers.

The following interpolation formulas were obtained³⁸ for the characteristics of the nematic transition in a solution of macromolecules with persistent flexibility for an arbitrary relation between L and l :

$$\frac{\varphi_1 l}{d} = \frac{3.34 + (11.3L/l) + (4.06L^2/l^2)}{1 + (0.387L/l) L/l}, \quad (3.8)$$

$$\ln w = - \frac{1.07 + (14.4L/l) + (84.1L^2/l^2)}{1 + (34.5L^2/l^2)}, \quad (3.9)$$

$$\ln s_0 = - \frac{0.166 + (3.56L/l) + (15.9L^2/l^2)}{1 + (22.5L^2/l^2)}. \quad (3.10)$$

Figure 5 shows the dependences of w and s_0 on L/l calculated by Eqs. (3.8)–(3.10). The order parameter reaches a minimum equal to $s_0 = 0.41$ at $L/l = 0.4$, while the relative width of the separation region has a minimum $w = 0.043$ at $L/l = 0.3$.

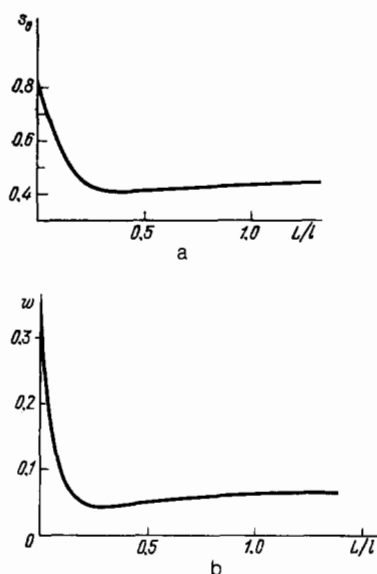


FIG. 5. a—Dependence of s_0 on L/l for a solution of long persistent chains.³⁸ b—Dependence of w on L/l for a solution of long persistent chains.³⁸

The fundamental conclusion that we can draw from analyzing the results presented in Fig. 5 is the following. Only very rigid or very short macromolecules behave like rigid rods. Even a small flexibility of the chain of persistent type (say, $L/l \sim 0.1$) suffices to make the properties of the liquid-crystalline transition closer to those obtained in the limit of semiflexible chains $L/l \gg 1$ than for the limit of absolutely rigid rods $L/l \ll 1$ (despite the fact that the geometric shape of the macromolecules is far closer to rodlike when $L/l \sim 0.1$). In particular, such high values of the order parameter at the point s_0 , as in the Onsager theory ($s_0 = 0.84$), are possible only for very rigid and not too long chains. Even when $L/l \sim 0.1$, the magnitude of s_0 proves to be substantially less (see Fig. 5a)—approximately of the same order as is obtained in the self-consistent-field theory of Maier and Saupe.¹

3.4. Conformations of polymer chains in the nematic phase

The dependence of the properties of a system on the flexibility mechanism of the polymer chains is manifested not only in the thermodynamic characteristics of the nematic phase transition, but also in the conformations of the semiflexible macromolecules in the liquid-crystalline phase.^{46,47}

A very important conformational characteristic is the mean square of the projection R_z of the segment joining the ends of the chain on the direction of the director (the z axis), $\langle R_z^2 \rangle$.

Owing to the fluctuation theorem, we have⁴⁸

$$\langle R_z^2 \rangle = \chi_0 \langle R^2 \rangle_0. \quad (3.11)$$

Here $\langle R^2 \rangle_0 = Ll$ is the mean square of the distance between the ends of the chain in the isotropic phase (see (3.1)), and χ_0 is the susceptibility of the system to an external orienting field in which the energy of a region of the chain of length λ and orientation \mathbf{n} equals

$$\tilde{U}_{\text{ext}}(\mathbf{n}) = -uT \frac{\lambda}{l} n_z. \quad (3.12)$$

By definition the quantity χ_0 equals

$$\chi_0 = \frac{\partial \int n_z f(\mathbf{n}) d\Omega_{\mathbf{n}}}{\partial u} \quad \text{for } u = 0. \quad (3.13)$$

Below we treat specifically the susceptibility χ_0 as the quantity most convenient for calculations. In an isotropic phase, owing to symmetry, we have $\chi_0 \neq 0$. To find the susceptibility of the liquid-crystalline phase we must minimize the free energy of the solution of semiflexible macromolecules located in the external field of (3.12). The field contribution to the free energy equals

$$F_{\text{ext}} = N \frac{L}{\lambda} \int \tilde{U}_{\text{ext}}(\mathbf{n}) f(\mathbf{n}) d\Omega_{\mathbf{n}}. \quad (3.14)$$

Minimization under the additional normalization condition

$$\int f(\mathbf{n}) d\Omega_{\mathbf{n}} = 1 \quad (3.15)$$

yields the equation

$$\frac{l}{NTL} \frac{\delta F_{\text{conf}}}{\delta f(\mathbf{n})} + U_{\text{ster}}(\mathbf{n}) + U_{\text{ext}}(\mathbf{n}) = E, \quad (3.16)$$

where $E = \text{const}$. Also

$$U_{\text{ext}}(\mathbf{n}) = \frac{l}{NTL} \frac{\delta F_{\text{ext}}}{\delta f(\mathbf{n})} = -un_z \quad (3.17)$$

is the reduced external field;

$$U_{\text{ster}}(\mathbf{n}) = \frac{l}{NTL} \frac{\delta F_{\text{ster}}}{\delta f(\mathbf{n})} = \frac{i8lq}{\pi d} \int \sin \gamma_{\text{un}} f(\mathbf{n}') d\Omega_{\mathbf{n}'}. \quad (3.18)$$

is the reduced mean molecular field caused by steric interaction.

For freely linked macromolecules we can write Eq. (3.16) in the form

$$\ln f(\mathbf{n}) + U(\mathbf{n}) = E, \quad (3.19)$$

Here U is the effective field:

$$U(\mathbf{n}) = U_{\text{ext}}(\mathbf{n}) + U_{\text{ster}}(\mathbf{n}). \quad (3.20)$$

Let us consider a sufficiently concentrated nematic solution with $\varphi \gg \varphi_a$. Such a solution must be strongly anisotropic. Therefore the function $U_{\text{ster}}(\mathbf{n})$ must have two deep minima near the directions making the angles $\theta = 0$ and $\theta = \pi$ with the z axis. The equilibrium distribution function (in the absence of an external field) is

$$f_0(\mathbf{n}) = \text{const} \cdot \exp(-U_{\text{ster}}(\mathbf{n})).$$

This must have two sharp maxima near the directions $\theta = 0$ and $\theta = \pi$. Addition of a weak external field leads to a small increase in the amplitude of one maximum as compared with the other. The solution of Eq. (3.20) has the form

$$f(\mathbf{n}) = f_0(\mathbf{n}) \exp(un_z). \quad (3.21)$$

Upon substituting (3.21) into (3.13), we find that

$$\chi_0 = \frac{2s+1}{3}.$$

That is, $\chi_0 \rightarrow 1$ with increasing concentration of the solution (in the region $\varphi \gg \varphi_a$). Thus, in the nematic solution the freely linked chains are somewhat extended in the direction of the axis of orientational order. However, the magnitude of $\langle R_z^2 \rangle$ increases by a factor of no more than three as compared with its value in the isotropic phase.

If the flexibility of the macromolecules is of persistent type, then the behavior of the susceptibility proves to be

completely different. In this case it is convenient to use the substitution

$$f(\mathbf{n}) = \psi^2(\mathbf{n}). \quad (3.22)$$

Upon substituting (3.22) into (3.5), we obtain the expression

$$F_{\text{conf}} = \frac{NTL}{l} \int (\nabla_{\mathbf{n}} \psi)^2 d\Omega_{\mathbf{n}}. \quad (3.23)$$

In form this is analogous to the expression for the kinetic energy of a quantum-mechanical particle (a rotator). We can treat Eq. (3.15) as the normalization condition of the "wave function" $\psi(\mathbf{n})$. In this regard it is not remarkable that Eq. (3.16) acquires the form of the Schrödinger equation for the case under discussion:

$$-\nabla_{\mathbf{n}}^2 \psi(\mathbf{n}) + U\psi(\mathbf{n}) = E\psi(\mathbf{n}). \quad (3.24)$$

Here the potential $U = U(\mathbf{n})$ is determined by Eq. (3.20). The free-energy minimum corresponds to the ground state of the quantum-mechanical particle.

We can naturally treat the external field U_{ext} as a perturbation. The correction to the wave function of the ground state, $\delta\psi_0$, caused by this perturbation has the form

$$\delta\psi = \sum_{m=1}^{\infty} \frac{\langle m | \hat{U}_{\text{ext}} | 0 \rangle}{E_0 - E_m} \psi_m. \quad (3.25)$$

Here ψ_m and E_m are the normalized eigenfunctions and their corresponding eigenvalues of the unperturbed Eq. (3.24),

$$\langle m | \hat{U}_{\text{ext}} | 0 \rangle = \int \psi_m^* U_{\text{ext}} \psi_0 d\Omega_{\mathbf{n}}.$$

When $\varphi \gg \varphi_a$ the solution is strongly anisotropic, and as was noted above, the unperturbed potential $U_{\text{ster}}(\mathbf{n})$ consists of two deep potential wells. Here these wells are separated by a high potential barrier lying near the line $\theta = \pi/2$. As is known,⁴⁹ the spectrum of such a system has a doublet structure with an exponentially small magnitude of splitting. Therefore we can restrict the treatment in the summation of (3.25) to the first term alone. Let $\psi(\mathbf{n})$ be the normalized wave function of the ground state of one isolated well. Then we have⁴⁹:

$$\begin{aligned} \psi_0(\mathbf{n}) &= \frac{1}{\sqrt{2}} (\psi(\mathbf{n}) + \psi(-\mathbf{n})), \\ \psi_1(\mathbf{n}) &= \frac{1}{\sqrt{2}} (\psi(\mathbf{n}) - \psi(-\mathbf{n})), \end{aligned} \quad (3.26)$$

$$\Delta \equiv E_1 - E_0 = 2\psi \left(\frac{\partial \psi}{\partial \theta} \right)_{\theta=\pi/2}. \quad (3.27)$$

By using Eqs. (3.13), (3.22), and (3.25)–(3.27), we can easily find the susceptibility:

$$\chi_0 = \frac{2}{\Delta}. \quad (3.28)$$

To calculate the right-hand side of Eq. (3.27), we shall use the quasiclassical approximation

$$\psi = A (q \sin \theta)^{-1/2} \exp \left(- \int q(\theta) d\theta \right), \quad (3.29)$$

where

$$q(\theta) = (U_{\text{ster}}(\theta) - E)^{1/2};$$

A is the normalization constant. Upon substituting (3.29)

into (3.27) and (3.28), we finally find⁴⁷

$$\chi_0 \approx \vartheta^{-2/3} \exp(3.82 \vartheta^{1/2} - 7.1 \vartheta^{1/6}), \quad \vartheta \gg 1. \quad (3.30)$$

Here $\vartheta = \varphi l/d$. Thus, for the case of persistent macromolecules the susceptibility χ_0 , and hence also $\langle R_z^2 \rangle$, sharply increases according to an exponential law upon increasing the concentration of the nematic solution. In other words, the macromolecules are strongly stretched out along the director. This effect can be called (in a certain sense) the stiffening of persistent macromolecules in the liquid-crystalline state.

The physical meaning of the found differences between persistent and freely linked macromolecules consist in the following. In both cases the distribution function in the anisotropic state, $f(\mathbf{n})$, has two sharp maxima at $\theta = 0$ and $\theta = \pi$. The orientation of each segment of the freely linked chain belongs to one of these maxima with the same probability $\approx \frac{1}{2}$, independently of the orientation of adjacent segments. For persistent chains the situation differs: upon increasing the order (with increasing concentration) a change in the orientation of the chain to the opposite one requires ever larger expenditures of energy. Therefore the mean distance between adjacent jumps in orientation averaged over the chain increases very rapidly (exponentially). We can easily show that $\langle R_z^2 \rangle$ must be proportional to this mean distance.

We can generalize Eq. (3.28) to take account of the finite total contour length L of the persistent macromolecule¹⁷:

$$\chi_0 = \frac{2}{\Delta} \left\{ 1 - \left[1 - \exp\left(-\frac{L\Delta}{l}\right) \right] \left(\frac{L\Delta}{l}\right)^{-1} \right\}. \quad (3.31)$$

Thus, when $L\Delta/l \ll 1$ the susceptibility approaches the limiting value $\chi_0 = L/l$ that corresponds to the maximum possible magnitude attainable upon complete extension of the polymer chains along the z axis:

$$\langle R_z^2 \rangle = L^2.$$

Strong "stiffening" of polymer chains has also been predicted for certain other mechanisms of flexibility.³⁷ These results have been confirmed further in a set of recent studies.^{50,51}

3.5. Comparison with experiment

How we shall compare the theory presented in this section with the experimental data obtained for three of the best studied rigid-chain polymers—poly- γ -benzyl-L-glutamate (PBG), polyparaphenynterephthalamide (PPTP), and polyparabenzamide (PBA). All these polymers have a persistent mechanism of flexibility.

Let us start with a PBG solution. The volume fractions of the polymer in the coexisting isotropic and anisotropic phases (φ_i and φ_a) measured for a series of molar masses of PBG in dichloromethane (DCM) with addition of trifluoroacetic acid (TFA) are shown in Fig. 6 (from the data of Refs. 52 and 53). This same diagram shows the theoretical dependences (dotted lines) calculated by Eqs. (3.8)–(3.9). Here the following characteristics of PBG macromolecules known from the literature were used. The molecular mass per link is $M_0 = 219$, the molecular mass per unit length is $M_L = 150 \text{ \AA}^{-1}$,⁵⁴ the length of the effective segment is $l = 2000 \text{ \AA}$,⁵³ and the diameter is $d = 16 \text{ \AA}$.⁵⁴ We see that the

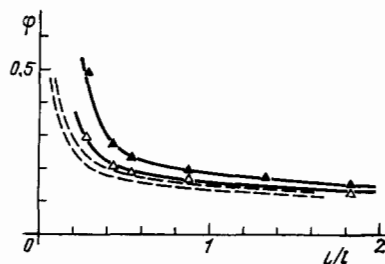


FIG. 6. Theoretical (broken lines) and experimental (solid lines) dependences of φ_i and φ_a on L/l for macromolecules of PBG.

theory, without using any adjustable parameters, conveys very well the character of the variation of the critical concentrations with increasing L . We can only note a relatively small (about 20%) decrease in the calculated data with respect to the measured data. Perhaps the reason for this involves the renormalization of the effective diameter (which determines the second virial coefficient) owing to the discreteness of the solvent. We note that the experimental width of the phase-separation region exceeds rather substantially the theoretical width in the region of low molecular masses. This deviation is explained apparently by the fact that the theory was constructed for monodisperse solutions, while in practice a scatter always exists in the molecular masses of the polymer. As is known (see Sec. 2.3), polydispersity leads to expansion of the region of phase separation, which should be especially noticeable in the case of short macromolecules, for which the critical concentration depends strongly on the length of the polymer chain.

The critical concentrations (φ_i) found by experiment for a solution of PBA in dimethylacetamide (DMA)⁵⁵ are shown in Fig. 7. The macromolecules of PBA have the following characteristics: $M_0 = 119$, $M_n = 18.3 \text{ \AA}^{-1}$, and $d = 5.5 \text{ \AA}$.⁵⁵ The experimental data for the length of the effective segment have a strong scatter. Hence we can naturally choose l as an adjustment parameter. The best agreement of the theory (see Fig. 7, dotted line) with experiment is attained for $l = 2000 \text{ \AA}$. We see from Fig. 7 that the theoretical values of the critical concentration φ_i are too low by about 10%. This can be explained by the same factors as for the solution of PBG.

We note that the order parameter s measured by infrared spectroscopy in the nematic phase considerably exceeds the value predicted by the theory (Sec. 3.3). Thus, for PBA in DMA at the phase-transition point we have $s_0 = 0.76$ ⁵⁵ (the molecular mass of the polymer is $M = 11,000$), whereas according to the theory $s_0 = 0.42$



FIG. 7. Theoretical (broken line) and experimental (solid line) dependences of φ_i on L/l for molecules of PBA.

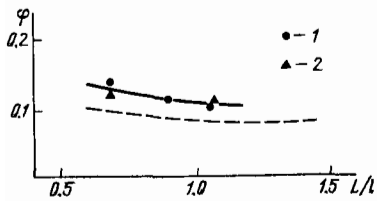


FIG. 8. Theoretical (broken line) and experimental dependences of φ , on L/l for macromolecules of PPTA. 1—data of Ref. 57; 2—data of Ref. 58.

(see Sec. 3.3). For PBG ($M = 55 \times 10^3$ to 450×10^3) in DCM + TFA, the order parameter at the transition point is even higher: $s_0 = 0.94$ to 0.98^{53} (according to the theory $s_0 \gtrsim 0.4$). The reasons for this difference are as follows. First, the polydispersity of real polymer solutions (whose degree was essentially not monitored in Refs. 56 and 53) leads not only to expansion of the phase-separation region, but also to an increase in the order parameter in the nematic phase (see Sec. 2.3). Second, real solutions are non-athermal. That is, effective attractive forces act among the macromolecules. This effect also leads to an appreciable elevation of the order parameter, especially when $L/l \gtrsim 1$ (see Sec. 4). We note parenthetically that, conversely, polydispersity is manifested most strongly when $L/l \lesssim 1$. Finally, a certain orienting action of the walls of the cell into which the polymer solution is placed is not ruled out.

The experimental results^{57,58} for the critical concentration of a solution of PPTA in 99% sulfuric acid are shown in Fig. 8. The characteristics of the macromolecules of PPTA are: $M_0 = 238$, $M_L = 18.5 \text{ \AA}^{-1}$, $d = 5.2 \text{ \AA}$,⁵⁸ and l is the adjustment parameter. The theoretical curve for $l = 800 \text{ \AA}$ is shown in Fig. 8 by the dotted line.

4. NEMATIC ORDERING IN NON-ATHERMAL POLYMER SOLUTIONS

Up to now we have discussed exclusively athermal polymer solutions. In this case the nematic ordering occurs at low concentrations of the rigid-chain polymer. In trying to allow for the influence of the attractive forces between the macromolecules on the properties of the liquid-crystalline transition a problem directly arises, involving the fact that the separated anisotropic phase can be very concentrated, and the second virial approximation of Onsager is inapplicable for describing it. This circumstance was manifested even in the first study on this topic,¹⁸ in which a phase diagram was constructed by the lattice method for nematic ordering in a solution of rigid rods in the presence of short-range attractive forces among them (the diagram constructed in Ref. 18 has qualitatively the same form as the phase diagram from Fig. 9a).

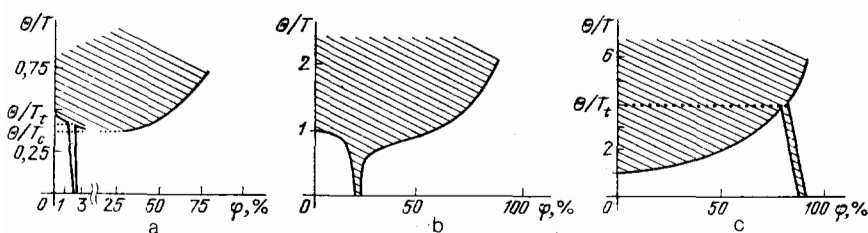


FIG. 9. Phase diagrams for nematic ordering in solutions of semiflexible persistent macromolecules with $l/d = 500$ (a), 50 (b), and 5 (c).⁶² The phase-separation is cross-hatched. The critical point in Fig. 9c corresponds to the intersection point of the line of the phase diagram with the coordinate axis.

A number of aspects of the role of attractive forces of the links in nematic ordering of a solution of rigid-chain polymers were refined in Refs. 59 and 61. However, these studies could not claim exhaustive solution of the problem, since the treatment in them was based to some degree on the lattice approach of Flory. Hence the most widespread mechanisms of partial flexibility of polymer chains remained outside the framework of the analysis (see Sec. 3).

This problem was first studied consistently by using the continuum approach in Ref. 62 (see also Refs. 63–65). We shall present below the fundamental ideas and results of this study for the cases of solutions of extreme rigid-chain ($L \ll l$) and semiflexible ($L \gg l$) macromolecules.

4.1. Free energy

To describe the properties of the nematic ordering in a polymer solution in the presence of attractive forces and to construct the corresponding phase diagrams, we must first of all generalize the expression (3.3) for the free energy F_{ster} of steric interaction of macromolecules to the region of high concentrations of the polymer in solution. To do this it was proposed⁶² to use the approach of Parsons (see Sec. 2), in which the quantity F_{ster} is defined by Eq. (2.10). Here as a reasonable approximation for the function $J(\varphi)$ in Eq. (2.10) it proved possible to use the simple relationship

$$J(\varphi) = -\ln(1 - \varphi) \quad (4.1)$$

(For details see Ref. 62). Thus we have (cf. Eqs. (2.10) and (3.3))

$$F_{\text{ster}} = \frac{4NTL}{\pi d} |\ln(1 - \varphi)| \int f(\mathbf{n}_1) f(\mathbf{n}_2) \sin \gamma \, d\Omega_{\mathbf{n}_1} \, d\Omega_{\mathbf{n}_2} \quad (4.2)$$

In the limit $\varphi \ll 1$, Eq. (4.2) reduces to Eq. (3.3), which is valid for a dilute solution. We should also note that this expression is essentially a continuum analog of Eq. (2.21), which was used in the lattice theory of Flory (see Ref. 62). Thus, Eq. (4.2), while retaining all the merits of the corresponding relationship in the Flory theory, is free from the defects of that theory caused by the reference to a preassigned space lattice.

Further, in the case being discussed we must add to the free energy the term F_{int} associated properly with the forces of intermolecular attraction. It was shown⁶² that in most cases one can write with good accuracy

$$F_{\text{int}} = -\frac{LN\varphi}{2d} (u_0 + u_a s^2). \quad (4.3)$$

Here u_0 and u_a are constants characterizing respectively the isotropic and anisotropic components of the attractive forces, and $s = \langle 3 \cos^2 \theta - 1 \rangle / 2$ is the order parameter. Expression (4.3) corresponds to the Maier-Saupe approximation in the theory of low-molecular-weight liquid crys-

tals. In order of magnitude we have $u_0, u_a \sim u(r_a/d)^3$ where u is the characteristic radius of the attractive forces (cf. Ref. 62). We can also rewrite Eq. (4.3) in the form

$$F_{\text{int}} = -\frac{LN\varphi\Theta}{d}(1 + \kappa s^2). \quad (4.4)$$

Here $\Theta = u_0/2$ is the theta temperature of the polymer solution (the temperature at which the osmotic second virial coefficient vanishes), while $\kappa = u_a/u_0$. As a rule, the anisotropic component of the attractive forces is substantially weaker than the isotropic component⁶⁶; in the concrete calculations of Ref. 62 it was assumed that $\kappa = 0.1$ as a reasonable estimate (it turned out that the properties of the liquid-crystalline transition depend only very weakly on κ . Therefore an exact specification of this quantity is inessential).

4.2. Phase diagrams

The formulas (3.4)–(3.5), (4.2), and (4.4) fully determine the free energy of a polymer solution of arbitrary concentration in the presence of attractive forces between the macromolecules. For a solution of persistent macromolecules the phase diagrams calculated by these formulas⁶² for the liquid-crystalline transition in the variables φ and Θ/T for several values of the asymmetry parameter l/d are shown in Fig. 9. For large l/d the phase diagram has the characteristic form shown in Fig. 9a. In the region of relatively high temperatures we have a narrow corridor of phase separation into isotropic and anisotropic phases lying in the dilute-solution region. Conversely, at low temperatures the region of phase separation is very broad, while an isotropic, practically fully dilute phase and a concentrated, strongly anisotropic phase coexist. These two regimes are separated by the interval between the triple-point temperature T_t and the critical temperature T_c ($T_c > T > T_t$), in which there are two regions of phase separation: between isotropic and anisotropic phases, and between two anisotropic phases having differing degrees of anisotropy. The temperatures T_t and T_c substantially exceed the Θ -temperature.

With decrease in the ratio l/d the interval between T_c and T_t becomes narrower and drops out when $(l/d)_{c_1} = 125$. When $l/d < 125$ there are no critical nor triple points on the diagram (see Fig. 9b), and one can speak only of the crossover temperature T_{cr} between the narrow high-temperature corridor of phase separation and the very broad low-temperature region of separation. The temperature T_{cr} decreases with decreasing l/d ; for $l/d_{c_2} \approx 50$, when these temperatures become lower than the Θ -point, the situation qualitatively changes again: now we have triple and critical points corresponding to an additional phase transition between two isotropic phases (see Fig. 9c). The concentration of one of these phases is extremely low. Hence the left-hand boundary of the separation region in Fig. 9c merges with the coordinate axis.

The phase diagrams of a solution of freely linked chains (or rigid rods) undergo a sequence of changes with decreasing ratio l/d analogous to that shown in Fig. 9. For a solution of freely-linked chains we have $(l/d)_{c_1} = 20$, $(l/d)_{c_2} = 6.8$; for a solution of rigid rods the corresponding values are $(L/d)_{c_1} = 15$, $(L/d)_{c_2} = 3.5$.

The dependence of the order parameter s of a nematic solution of persistent macromolecules at the transition point on the reduced temperature T/Θ is shown in Fig. 10 for l/d

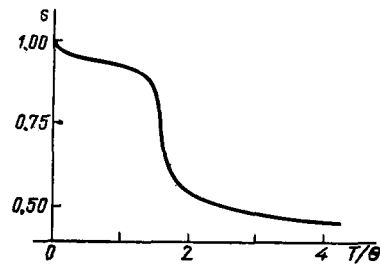


FIG. 10. Dependence of the order parameter s_0 of a nematic solution of persistent macromolecules ($l/d = 100$) on the reduced temperature T/Θ .

$d = 100$. We see that the attractive forces (temperature effects) affect the value of s very substantially when $T/\Theta \lesssim 2$.

For experimental verification of the phase diagrams shown in Fig. 9, one must use a rigid-chain polymer that forms a nematic phase in solution over a rather broad temperature interval. This condition is best satisfied by poly- γ -benzyl-L-glutamate (PBG). As is known, it possesses a persistent mechanism of flexibility. The experimental phase diagram of a solution of PBG (molecular mass $M = 310,000$) in dimethylformamide obtained in Refs. 67 and 68 is shown in Fig. 11 (curve 1). We see that this is phase diagram qualitatively resembles that shown in Fig. 9a (for large asymmetry parameters)¹¹; in particular, the fact of equilibrium coexistence of two anisotropic phases was carefully verified and proved in Ref. 69.

For a quantitative comparison of the data presented in Fig. 11 with the theory, we must first determine the Θ -temperature for the solution being discussed. Unfortunately, systematic measurements of the osmotic second virial coefficient of this system have not been performed. On the basis of the sparse data contained in Ref. 58, we can make only the rough estimate $\Theta \approx 110$ K. With the molecular mass $M = 310,000$, the PBG macromolecules have the parameters $L/d = 130$, $L/l = 1.0$. Therefore, as was shown in the previous section, we can consider them to good accuracy to be semiflexible. The phase diagram for semiflexible persistent macromolecules for $l/d = 130$ as constructed on the basis of the theory of Ref. 62 is shown in Fig. 11 (curve 2). The

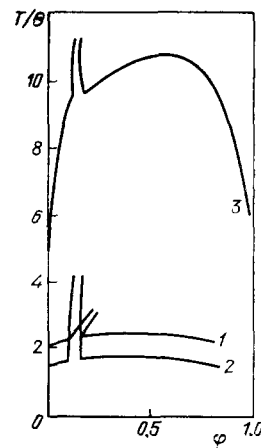


FIG. 11. Phase diagram of a solution of PBG in dimethylformamide ($M = 310,000$). 1—experiment^{67,68}; 2—theory⁶²; 3—theory¹⁸.

analogous phase diagram for rigid rods with asymmetry $L/d = 130$ according to the Flory theory¹⁸ is shown by curve 3 in the same diagram. We see that the Flory theory agrees considerably more poorly with the experimental data than the theory of Ref. 62. Apparently the quantitative differences of curves 1 and 2 involve the error in determining the Θ -temperature and also the fact that PBG molecules near the triple point have a strong tendency to aggregate.

4.3. Ordering of solutions of polyelectrolytes

Many rigid-chain polymers, including most polymers of biological origin (DNA, α -helical proteins) acquire charges in solution. The influence of the Coulomb interaction of the links of a polymer on the LC transition was first treated in Refs. 70 and 71 for the case of infinitely thin rods. However, the method used in these studies was not fully valid. The Onsager theory was systematically generalized to the case of a salt solution of charged rigid rods in Refs. 72 and 73 (see also the review of Ref. 33). Below we shall discuss the fundamental ideas and results of these studies.

The electrostatic interaction potential of two cylindrical rods (of length L and diameter d) charged with the linear density σ has the following form in the Debye-Hückel approximation⁴⁸:

$$U_{el} = \frac{\sigma^2}{\epsilon} \int \frac{\exp(-r(\lambda_1, \lambda_2)/r_D)}{r(\lambda_1, \lambda_2)} d\lambda_1 d\lambda_2. \quad (4.5)$$

Here $r(\lambda_1, \lambda_2)$ is the distance between the points having the coordinates λ_1 and λ_2 (Fig. 12), ϵ is the permittivity of the solvent, and the Debye radius is

$$r_D = \left(\frac{4\pi e^2}{\epsilon T} \sum_a z_a^2 n_a \right)^{-1/2} \quad (4.6)$$

In Eq. (4.6) n_a and $z_a e$ are respectively the mean concentration and the charge of the ion of type a (including the counterions). The approximation (4.5) is valid if $r_D \gg d$ and if the electrostatic potential φ_{el} throughout the region accessible to the ions satisfies the condition

$$\frac{e\varphi_{el}}{T} \ll 1.$$

In the case $L \gg r_D$ we can write the latter in the form (omitting the logarithmic factors)

$$\frac{\sigma e}{\epsilon T} \ll 1, \quad \frac{\sigma e r_D^2 L c}{\epsilon T} \ll 1. \quad (4.7)$$

Here c is the concentration of the rods.

The second virial coefficient of interaction of two rods whose axes (\mathbf{n}_1 and \mathbf{n}_2) form the angle γ equals

$$B(\gamma) = \int \left[1 - \exp\left(-\frac{U(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2)}{T}\right) \right] d^3r. \quad (4.8)$$

Here

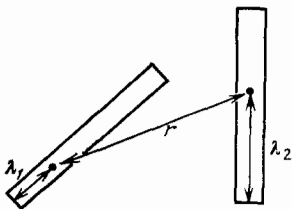


FIG. 12. Two interacting rods. The distance between the points with coordinates λ_1 and λ_2 is r .

$$U(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2) = U_{st} + U_{el}. \quad (4.9)$$

is the interaction potential of the rods, which is equal to the sum of the steric and electrostatic contributions; \mathbf{r} is the radius vector joining the centers of the rods. By analogy with (4.9) we can conveniently represent the coefficient $B(\gamma)$ in the form

$$B(\gamma) = B_{st}(\gamma) + B_{el}(\gamma).$$

The steric term B_{st} is determined by Eq. (2.2):

$$B_{st}(\gamma) = 2L^2 d \sin \gamma = 2L^3 p \sin \gamma. \quad (4.10)$$

Here we have $p \equiv d/L$. The contribution of the electrostatic interaction B_{el} depends on the magnitude of the dimensionless parameters

$$w = \frac{\sigma^2 r_D}{\epsilon T}, \quad q = \frac{r_D}{L}.$$

To calculate the free energy of the system we can use the second virial approximation (as is known, the condition for applicability of this approximation is satisfied in the region of a nematic transition if $L \gg r_D$). Upon substituting (4.8) into Eq. (2.1) and performing the usual minimization operation, we can find all the equilibrium characteristics of nematic ordering in the system. Let us study the results obtained in Ref. 72 for the most interesting case with $1 \gg q \gg p$. The most important qualitatively different situations are shown in the diagrams (Fig. 13) in the variables q and w .

When $w \ll p/q$ (region I in Fig. 13) the electrostatic interaction is insignificant: $B(\gamma) \approx B_{st}(\gamma)$. Hence the nematic ordering occurs just as is described in Sec. 2.1 (see Eqs. (2.4)–(2.5)):

$$\varphi_1 = 3.3p, \quad \frac{\varphi_a}{\varphi_1} - 1 = 0.3, \quad s_0 = 0.8. \quad (4.11)$$

When $p^{1/2} \gg w \gg p/q$ (region II in Fig. 13), the electrostatic interaction gives a contribution appreciable in magnitude, but effectively isotropic, to the second virial coefficient²¹: $B(\gamma) = B_{st}(\gamma) + wqL$.³ Consequently the region of phase separation is substantially narrowed, while the order parameter s_0 at the transition point is decreased (the isotropic term wqL ³ makes an unfavorable large concentration jump at the transition):

$$\varphi_1 = 3.6p, \quad \frac{\varphi_a}{\varphi_1} - 1 \sim \frac{wq}{p} \ll 1, \quad s_0 = 0.53. \quad (4.12)$$

In region III³⁾ ($q \gg w \gg p^{1/2}$) the anisotropic component

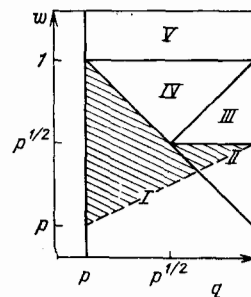


FIG. 13. Diagram of states of a solution of charged rigid rods in the variables $q = r_D/L$, $w = \delta^2 r_D / \epsilon T$ (on a log-log scale). I— $w \ll p/q$; II— $p^{1/2} \gg w \gg p/q$; III— $q \gg w \gg p^{1/2}$; IV— $1 \gg w \gg p/q$; V— $w \gg 1$. In the cross-hatched region a second orientational phase transition can occur.

of the electrostatic interaction effectively dominates over the contribution from steric forces:

$$B(\gamma) \approx B_{el}(\gamma) \approx wqL^3 \left[1 - \frac{w}{\sin(\gamma+q)} \right].$$

On the other hand, in this region the isotropic electrostatic term is still predominant. Therefore the concentration jump in the transition remains small:

$$\varphi_1 \sim \frac{p^2}{w^2} |\ln q|, \quad \frac{\varphi_a}{\varphi_1} - 1 \sim \frac{w}{q} \ll 1, \quad s_0 = 1 - \text{const} \cdot q^2. \quad (4.13)$$

We note that the order parameter s_0 in the nematic phase in the regime being discussed is very high (and independent of w , i.e., of the charge of the rods). The high value of s_0 is explained by the specific "hyperbolic" dependence of B_{el} on the angle γ .

When $l \gg w \gg p/q$, $w \gg q$ (region IV), the electrostatic interaction becomes substantially anisotropic:

$$B(\gamma) \approx B_{el}(\gamma) \approx wqL^3 \left[1 - \frac{w}{\sin(\gamma+w)} \right], \quad \gamma \gg w, \\ \approx qL^3 \sin \gamma \cdot \ln \frac{w}{\gamma}, \quad q \ln \frac{w}{\gamma} \ll \gamma \ll w.$$

This substantially expands the region of phase separation. The characteristics of the nematic transition in this regime are:

$$\varphi_1 \sim \frac{p^2}{wq} |\ln w|, \quad s_0 = 1 - \text{const} \cdot w^2; \\ \frac{\varphi_a}{\varphi_1} - 1 \sim \min \left[\frac{(w/q)^{1/2}}{\ln(w/q)}, |\ln w| \right] \gg 1. \quad (4.14)$$

In region V ($w \gg 1$), which corresponds to the most highly charged rods, the effect of the electrostatic interaction is reduced mainly to renormalizing the effective diameter of the rods:

$$B(\gamma) \approx B_{el}(\gamma) = qL^3 \sin \gamma \cdot \ln \frac{w}{\gamma}. \quad (4.15)$$

Equation (4.15) coincides with (4.10) to logarithmic accuracy with the renormalized value $\tilde{d} = r_D \ln w$. Therefore in the region that we are discussing we have

$$\varphi_1 = \frac{3.3p^2}{q \ln w}, \quad \frac{\varphi_a}{\varphi_1} - 1 = 0.3, \quad s_0 = 0.8. \quad (4.16)$$

In the regions $(pq)^{1/2} \ll w \ll p/q$, $(pq)^{1/2} \ll w \ll p^{1/2}$ (these regions are cross-hatched in Fig. 13) a second orientational transition occurs between two anisotropic phases upon increasing the concentration of the solution.

In Ref. 73 (see also Ref. 33) actually only the case of strongly charged rods was treated (regime V). These studies showed that the Coulomb interaction leads not only to renormalization of the diameter of the rods, but also to an additional weak (in the studied regime) effect. The authors called it the "twisting effect." The influence of this effect is characterized by the small parameter h , which equals $h = 1/\ln w$ to logarithmic accuracy. The results of detailed numerical analysis⁷³ of the dependence of the characteristics of the nematic transition on the parameter h can be represented in the form

$$\frac{\varphi_a}{\varphi_1} - 1 = 0.27 - 0.045h + 0.5h^2, \\ s_0 = 0.79 + 0.13h + 0.6h^2, \quad h \ll 0.3. \quad (4.17)$$

When $h = 0$ the formulas of (4.17) coincide with the corresponding formulas of (4.16) (apart from rounding errors). With decreasing charge on the rods (decreasing parameter w) the parameter h increases, causing an increase in the order parameter s_0 and a relative concentration jump at the transition. These trends fully correspond to what should occur in a transition from regime V to regime IV. Thus the results of Refs. 72 and 73 agree with one another.

Estimates of the characteristic parameters of the systems show that such highly charged polymers as DNA are usually described by regimes III-V. At the same time, the degree of charging of α -helical polypeptides can vary over a very broad range, so that it is possible to realize any of the discussed regimes. The wealth of qualitatively new types of LC ordering in solutions of rigid-chain polyelectrolytes renders their experimental study of great interest.

5. ORIENTATIONAL ORDERING OF POLYMER MELTS

Theoretical prediction of the thermodynamic properties of such dense systems as polymer melts involves considerable difficulties. Besides other factors, the fact plays a role that only not too rigid polymers can exist in the nematic state in the melt (for polymers of high rigidity of the chain the decomposition temperature proves to be lower than the melting point). Therefore the large parameter l/d cannot be used in fully. These difficulties have given rise to a considerable variety of theoretical approaches to the problem. Here one cannot single out any one of them that one could use to derive all the fundamental results.

In the studies discussed below mainly three approaches have been used, initiated by the studies of Onsager,⁷ Maier and Saupe,¹ and Flory.¹⁸

5.1. Melts of linear homopolymers

The formulas derived above for the different contributions to the free energy (3.4)–(3.5), (4.2), and (4.4) can also be used to analyze nematic ordering in thermotropic systems—melts of rigid-chain macromolecules with varying flexibility (if we understand φ to be the degree of packing of the polymer in the melt as compared with the maximally dense packing). This has been done in a recent study⁶³; in this section we shall briefly present some of the results of this study and compare them with the conclusions of other studies on the theory of polymeric nematics based on rigid-chain macromolecules.^{19,74–81}

We note first of all that in thermotropic solutions we must use as the external parameter not the concentration c of the polymer nor the volume fraction φ (as in solutions), but the pressure Π . The role of the external pressure has been studied in detail in Ref. 63, where it was shown that: a) from the standpoint of thermodynamics of liquid-crystalline ordering, the normal atmospheric pressure can be treated as a negligibly small quantity; b) at high enough external pressure $\Pi \approx 10^3$ atm we should expect a substantial increase in the region of stability of the nematic phase; c) as $\Pi \rightarrow \infty$ in melts of any particles that are anisodiametric to any degree and have a rigid steric core of interaction (in particular, in polymer melts), a liquid-crystalline phase should be observed.

We can illustrate what we have said with the example of such a flexible-chain polymer as polyethylene. Figure 14 shows the phase diagram of polyethylene in the variables of

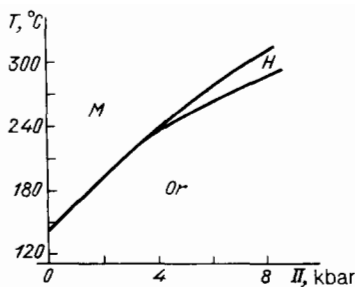


FIG. 14. Phase diagram of polyethylene in the variables pressure Π and temperature T .⁸² M—melt; H—hexagonal phase; Or—orthorhombic crystalline phase.

the pressure Π and temperature T .⁸² At high temperatures polyethylene exists in the state of a melt (M) with the symmetry of an ordinary isotropic liquid. At low temperatures the crystalline state with orthorhombic symmetry (Or) is thermodynamically stable. At atmosphere pressure a first-order transition occurs directly from the M to the Or phase with decreasing temperature. Yet if the external pressure is high enough ($\Pi > 4 \times 10^3$ atm), an intermediate state arises of liquid-crystalline type—the so-called hexagonal (H) phase. This state is characterized by long-range orientational order and absence of strict order in the packing of the polymer chains (conformational disorder). As we see from Fig. 14, the region of stability of the liquid-crystalline H phase substantially expands, while the M–H transition temperature increases with increasing pressure.

Figure 15a shows the phase diagram calculated⁶³ for a melt of long persistent chains in the variables T/θ and l/d for $\kappa = 0.1$ under the assumption of minimal (or atmospheric) external pressure. Analogous diagrams are obtained for melts of rigid rods, and also for semiflexible molecules with other mechanisms of flexibility. We see that, within the framework of the given theory, we can describe three phases— isotropic and anisotropic melts, and also a gaslike phase (at high temperatures). Of course, primarily the curve describing the coexistence of the isotropic and nematic melt has physical meaning. We see that nematic ordering can occur

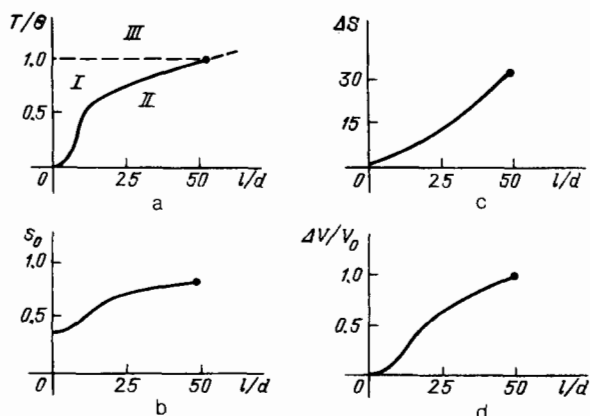


FIG. 15. a—Phase diagram of a melt of long persistent chains (I— isotropic melt, II—nematic melt, III—high-temperature gaseous phase). b—d—Dependences of the order parameter at the nematic ordering point (b), entropy of transition per effective segment (c), and relative volume change in the transition (d) on the parameter l/d in a melt of long persistent chains.⁶³

only if the asymmetry parameter l/d is smaller than the critical value $(l/d)_c \approx 50$. When $l/d > (l/d)_c$ the melt in the equilibrium state is always a nematic (at any temperatures). This result becomes quite understandable if we take account of the fact that a polymer melt is a condensed system. Therefore, if the rigidity of the chain is high enough, liquid-crystalline ordering in it must occur as a consequence of the anisotropy of the steric interactions alone. The critical value $(l/d)_c$ depends on the mechanism of flexibility of the chain. Thus, for example, for freely linked flexibility it turned out⁶³ that $(l/d)_c \approx 7$, while for a melt of rigid rods $(L/d)_c \approx 3.5$. We can compare the latter result with the prediction obtained on the basis of the lattice approach in the study of Flory and Ronca¹⁹ that a nematic phase must arise when $L/d > 6.4$ in a melt of rigid rods (even in an athermal one, without allowing for anisotropy of attractive forces).

Figure 15 shows also other characteristics of the nematic ordering in a melt of persistent chains (as a function of the asymmetry parameter l/d): the order parameter s_0 at the transition point (Fig. 15b), the entropy of the transition per effective segment ΔS (Fig. 15c), and the relative volume change in the transition $\Delta V/V_0$ (Fig. 15d). For melts of rigid rods and freely linked chains all these characteristics take on larger values. However, even a small component of flexibility of persistent character suffices to make the quantities s_0 , ΔS , and $\Delta V/V_0$ close to the values characteristic of persistent chains (see Ref. 63).

Of course, the results shown in Fig. 15 are applicable only for physically reasonable values of the asymmetry parameter l/d : as a minimum, we must have $l/d \gtrsim 1$. Nevertheless the curves in Fig. 15 have been extended down to $l/d = 0$. The formal limit $l/d \rightarrow 0$ within the framework of the model corresponds to the situation in which the steric interactions (the term F_{ster}) are inessential, and liquid-crystalline ordering occurs only because of anisotropy of the attractive forces (theory of the Maier-Sauper type). Liquid-crystalline ordering has also been treated in this limit in Refs. 74 and 75, whose results are close to those obtained in Ref. 63 (for $l/d = 0$). We see from Fig. 15, however, that these results are exact to any extent only at small values of l/d , while in the most interesting region $l/d \gg 1$ the steric interactions always dominate and the anisotropy of the attractive forces is always a secondary factor.

We note some additional conclusions of Refs. 74 and 75 that essentially should not depend qualitatively on whether one takes account of the steric forces or not. It was found that the order parameter at the transition point s_0 depends on the length of the persistent macromolecules L as follows. When $L \ll l$ the order parameter is $s_0 = 0.43$ (the Maier-Sauper result¹); with increasing L the value of s_0 declines to reach a minimum $s_0 = 0.34$ when $L \lesssim l$; then s_0 slightly increases to the value $s_0 = 0.36$ characteristic of very long macromolecules (compare this variation of $s_0(L)$ with the analogous variation for a polymer solution shown in Fig. 5a).

Also the conformations of the macromolecules were studied in Refs. 74 and 75. In the nematic phase the macromolecules are stretched along the axis of ordering (the z axis). The degree of extension can be characterized by the parameter

$$y = \frac{\langle R_z^2 \rangle}{\langle R^2 \rangle} \quad (5.1)$$

Here R_x and R_y are the projections of the vector joining the ends of the polymer chain. The magnitude of this parameter (at the transition point) depends on the length of the macromolecules: $y_0 = 3.25$ when $L \ll l$; as L increases the value of y_0 first declines slightly to the value $y_0 = 2.77$, and then increases substantially, reaching $y_0 = 14.4$ in the limit of very long persistent chains ($L \gg l$). With decreasing temperature of the nematic melt (in the case $L \gg l$) the polymer chains "unfold" further: the value of y rapidly increases exponentially (cf. the analogous conclusion for solutions with increase in concentration).

References 76 and 77 (see also Ref. 78) have essentially treated the same problem (and by the same method) as Refs. 74 and 75, and obtained similar results. It was found erroneously in Ref. 79 that nematic ordering in a melt of long persistent macromolecules is a second-order phase transition (the error was made in deriving an expansion of the Landau-De Gennes type).

Nematic ordering in a melt of semiflexible persistent macromolecules has also been treated in Refs. 80 and 81 by using the Flory lattice approach.¹⁹

5.2. Melts of copolymers with mesogenic groups in the main chain

As was noted in Sec. 1, an important class of macromolecules capable of LC ordering consists of copolymers containing rigid and flexible fragments. The rigid (mesogenic) fragments (of length L and diameter d) can be included either in the linear chain (Fig. 16a) or in side branches (Fig. 16b).

Let us study melts of linear copolymers (Fig. 16a). The conditions of existence of a nematic phase in such melts were first analyzed by using the Flory lattice method.^{44,83} These studies employed the assumption that the flexible component of the chain does not become ordered in the nematic melt. As was shown in Ref. 84 (see also Refs. 85–87), this assumption is incorrect. References 84–87 studied nematic ordering allowing for the stiffening of the flexible fragments of the chain by using a generalization of the lattice method.

Figure 17 shows the phase diagram calculated in Ref. 85 of an athermal melt in the variables L/d and α (α is the volume fraction of the flexible component) for the case of maximum flexibility of the flexible component, $l/d = 1.5$ (l is the length of the effective segment of the flexible regions). The region to the left of curve 1 corresponds to the isotropic melt, and that to the right to the nematic melt. In addition to curve 1, which corresponds to the isotropic phase-nematic transition, curve 2 is marked in the phase diagram, corresponding to a transition between two nematic phases—weakly anisotropic (stable at smaller anisodiametry param-

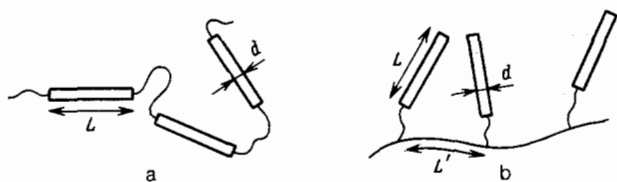


FIG. 16. Linear (a) and comblike (b) copolymers containing rigid and flexible fragments of the chain.

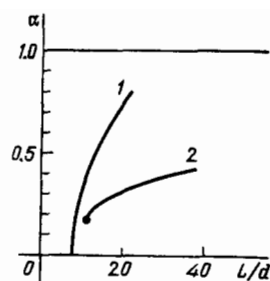


FIG. 17. Phase diagram of an athermal melt of linear copolymers for $l/d = 1.5$. L/d —anisodiametry parameter of the rigid fragment, α —volume fraction of the flexible component. Curve 1 corresponds to transition from the isotropic to the nematic phase; 2—transition between two anisotropic phases.⁸⁵

eters of the mesogenic regions, L/d) and strongly anisotropic (stable at larger L/d). The curve of transition 2 ends at a critical point with coordinates $(L/d)_c = 10$, $\alpha_c = 0.2$.

As was shown in Ref. 85, the physical meaning of the second transition is that the presence of the flexible component of the chain in the copolymers depicted in Fig. 16a can give rise to two opposing tendencies. For small α the flexible fragments are so strongly oriented in the liquid-crystalline transition that they play in the anisotropic phase the role of a "stiffener" rather than a "plasticizer" by effectively increasing the degree of asymmetry of the macromolecule. Conversely, for large α the flexible component of the chain is only weakly ordered in the liquid-crystalline transition and plays the more natural role of a "plasticizer" in the anisotropic phase (or of a "diluent"). The former tendency facilitates the formation of a strongly anisotropic phase, and the latter makes the weakly anisotropic phase more favorable. Yet the presence of both tendencies leads to the possible existence of an additional transition between the two phases.

Upon decrease in the flexibility of the flexible fragments of the chain (i.e., upon increase in the ratio l/d), the region of stability of the weakly anisotropic phase narrows and is shifted toward larger α .

The ordering of the flexible fragments of the chain in nematic thermotropic liquid crystals based on the macromolecules shown in Fig. 16a can be considerable (especially in the strongly anisotropic phase). This conclusion, which stems from the theoretical treatment, is also confirmed by a number of the experimental data.⁸⁸

5.3. Melts of comblike polymers

Nematic ordering in melts of comblike polymers with rigid fragments in the side chains (see Fig. 16b) has been analyzed in Refs. 89–91. In Ref. 91 a mean-field method of the Meier-Saupe type was used, with account taken only of the interaction of the mesogenic fragments. As was shown in this study, the orientational properties of the system substantially depend on the length L' of the fragment of the main chain between adjacent branches (the length of the spacer linking the mesogenic group with the main chain is assumed very small). When $L' \gg l$ (l is the effective segment of the main chain), LC ordering occurs just as in the corresponding low-molecular-weight system. In particular, the order parameter at the transition point is $s_0 = 0.43$. Upon increasing the density of the side branches (i.e., increasing l/l'

L'), the order parameter at the transition point (which characterizes the orientation of the mesogenic groups) declines monotonically. We note parenthetically that, for polymers with mesogenic groups in the main chain the order parameter s_0 either increases, or very slightly decreases upon decreasing the length of the flexible fragments L' . Thus the order parameter for comblike polymers proves to be always smaller than for their linear analogs. This conclusion agrees with the experimental data,^{6,92,93} and also with the theoretical results obtained by using the Flory lattice method.^{89,90}

A typical conformation of a comblike macromolecule in the nematic phase (for not too great a density of branching) is shown in Fig. 18a: the mesogenic groups are preferentially oriented along the direction u (along the "easy axis"), whereas the main chains lie mainly in the "easy plane" perpendicular to the axis of anisotropy. Thus the main chains do not form a cluster extended along the axis of anisotropy (as in the case of linear homopolymers), but a flattened cluster: the parameter $y = \langle R_z^2 \rangle / \langle R_x^2 \rangle$ (see Eq. (5.1)) must be smaller than unity. The experimental neutron-scattering data⁹⁴ confirm this conclusion: for a nematic melt of polymethacrylate we find $y = 0.82$.

At a sufficiently large density of side branches, $l/L' > (l/L')_c$, the order parameter s_0 at the isotropic melt-nematic transition point becomes negative. In this case the main chains are oriented along the director, while conversely the mesogenic groups lie preferentially in the "easy plane" (Fig. 18b). The phase diagram of the system in the variables l/L' and T obtained in Ref. 91 is shown schematically in Fig. 19 (I is the isotropic phase, phase N_+ corresponds to Fig. 18a; N_- to Fig. 18b; and N_2 is a biaxial phase intermediate between N_+ and N_-). The appearance of phase N_- is caused by the fact that the orientations of adjacent mesogenic groups in dense comblike macromolecules are strongly intercorrelated (owing to the condition of local orthogonality of the main chain and the mesogenic group). The critical value of the density found in Ref. 91 for a persistent chain is

$$\left(\frac{l}{L'}\right)_c = 18. \quad (5.2)$$

A phase of the N_- type was also obtained in Refs. 89 and 90. However, the cause of the ordering of the mesogenic groups in the "easy plane" here is completely different and involves the steric orientational interaction of the main chains (which was completely ignored in Ref. 91). Evidently both discussed factors operate in a real situation, while taking account of their joint action leads to a considerable decrease in the critical value of the density of branching as compared with the result of (5.2). This offers grounds for

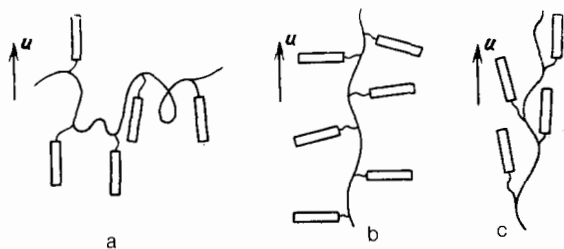


FIG. 18. Possible types of nematic ordering for comblike polymers. a—uniaxial ordering of the rigid fragments (phase N_+). b—Ordering of the rigid fragments in the easy plane (phase N_-). c—Strongly ordered state.

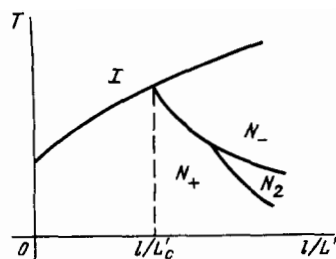


FIG. 19. Phase diagram of a melt of comblike macromolecules in the variables l/L' (effective density of side branches)—temperature.⁹¹ I— isotropic phase, N_+ —phase of "easy-axis" type, N_- —phase of "easy-plane" type, N_2 —biaxial phase.

hoping that a phase of the N_- type will be found experimentally.

Returning to the conformational properties of nematic melts, we note in closing that in the depths of an N_+ phase (i.e., far from the I- N_+ transition line) the state of the main chains can alter. Here the orienting action of the mesogenic groups can become so strong that the main chains will leave the "easy plane" and be oriented preferentially along the "easy" axis of anisotropy (Fig. 18c).⁹⁰

6. "NEMATIC" ORDERING IN THE PRESENCE OF AN EXTERNAL ORIENTING FIELD

The study of the behavior of polymeric systems capable of liquid-crystalline ordering in an external orienting field is of both fundamental and great practical interest, since the external field can serve for enhancing the degree of orientational order. In a number of cases this substantially improves the physicomechanical properties of materials based on a given polymer system.

In Refs. 95–97 the influence of an external orienting field on solutions of rigid-chain macromolecules was analyzed within the framework of the Onsager method. If $TU(\mathbf{n})$ is the potential energy acquired by a rectilinear region of a semiflexible molecule in the external field, while its length equals that of the effective segment having the orientation \mathbf{n} (in the case of a solution of rigid rods, a rod with the corresponding orientation), then we must add the following term to the free energy of the solution of these macromolecules, which is defined by Eqs. (3.3)–(3.5):

$$F_{\text{ext}} = NT \frac{L}{l} \int U(\mathbf{n}) f(\mathbf{n}) d\Omega_{\mathbf{n}} \quad (6.1)$$

(In the case of a solution of rigid rods we should omit the factor L/l in front of the integral). Then we should minimize the free energy in the usual way.

Let us distinguish the following fundamental types of orienting fields: a field of dipole type

$$U(\mathbf{n}) = -u \cos \theta \quad (6.2)$$

(θ is the angle between the vector \mathbf{n} and the axis of anisotropy), and a field of quadrupole type

$$U(\mathbf{n}) = -\frac{3}{2} u \cos^2 \theta. \quad (6.3)$$

For example, a dipole field can be an external magnetic (or electric) field in the case in which the links of the macromolecule have a constant magnetic (or electric) dipole moment directed along the chain. If the constant dipole moment is

zero, but the links possess an anisotropy of susceptibility, then these same fields can play the role of quadrupole fields. Here we must distinguish an orienting quadrupole field ($u > 0$) corresponding to a positive anisotropy of susceptibility (when the susceptibility in the direction along the chain is greater than in the transverse direction) and a "disorienting" field ($u < 0$) corresponding to a negative anisotropy. An external quadrupole field can also be caused by a laminar hydrodynamic flow of the "transverse shear" type.⁹⁸ Figure 20 shows flows corresponding to an orienting (a) and a "disorienting" (b) quadrupole field.

We shall present below some results of Refs. 95–97. Figure 21 shows phase diagrams of solutions of rigid rods (a) and long persistent chains (b) in an external dipole-type field.

We see that the phase diagrams for both cases are qualitatively similar (apart from the fact that the region of phase separation for the solution of persistent chains is strongly shifted toward higher concentrations). In the presence of a weak enough external field in a concentrated solution, as before, a first-order phase transition occurs in the system. However, it is important to stress that when $u \neq 0$ this is a transition between two anisotropic phases with differing degrees of anisotropy. With increasing u the region of phase separation narrows and is shifted toward lower concentrations. Finally, at a certain critical value of the external orienting field the interaction among the links responsible for the phase transition is effectively suppressed (the segments prove to be "sufficiently" oriented by the external field, even in the dilute solution, and they have no need to be rearranged in addition by phase transition upon concentrating the solution). Then the phase-separation region disappears. We note also that, since the curves in Fig. 21 are shifted to the left with increasing u , in a certain concentration range a field-induced phase transition can occur. This concentration region is much broader for persistent macromolecules than for rigid rods.

Phase diagrams of polymer solutions in an external field of quadrupole type are shown in Fig. 22. The influence of an orienting field of this type (for $u > 0$) leads fundamentally to the same qualitative effects as for the just discussed case of a dipole field. On the other hand, the action of a "disorienting" quadrupole field ($u < 0$) requires separate discussion.

In the isotropic phase a weak field of this type induces an anisotropy of the "easy-plane" type. Here the distribution remains symmetrical with respect to the field direction. Yet the action of a quadrupole field with $u < 0$, however weak, on the anisotropic phase leads to instability of the state having a symmetrical distribution. As a result the direction of the director will lie in the "easy plane." That is, it will be perpendicular to the field direction. Thus, when $u < 0$ a transition

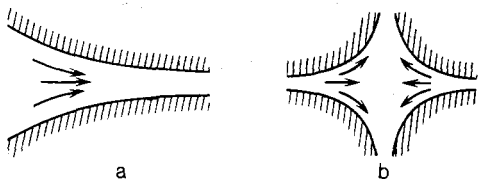


FIG. 20. Hydrodynamic flows corresponding to an orienting (a) and "disorienting" (b) quadrupole field.

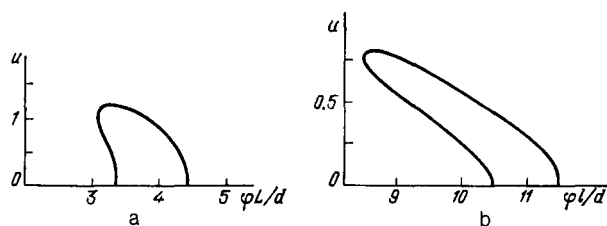


FIG. 21. Phase diagrams (in the variables of concentration and field) of solutions of rigid rods (a) and long persistent chains (b) in an external dipole-type field.

occurs between states of differing symmetry. Therefore this must necessarily be a phase transition. In a weak enough field this is a first-order phase transition, while with increasing $|u|$ the region of phase separation becomes appreciably narrowed (see Fig. 22, lower half-plane).

In a strong "disorienting" field the transition between the low- and high-concentration states of the solution becomes a second-order phase transition (dotted line in Fig. 22). As $u \rightarrow -\infty$ this transition occurs at

$$\varphi^* = \frac{3\pi^2}{16} \frac{d}{L} \quad (6.4)$$

for a solution of rigid rods and at

$$\varphi^* = \frac{3\pi^2}{8} \frac{d}{l} \quad (6.5)$$

for a solution of persistent macromolecules. The line of the second-order phase transitions joins the boundaries of the phase-separation region at a tricritical point. We see from Fig. 22 that the region in which a phase transition can be induced by a quadrupole-type "disorienting" field is considerably broader than the corresponding region for an orienting field ($u > 0$). This region is especially broad for a solution of persistent macromolecules.

As was shown in Ref. 99 by the Flory lattice method, effective suppression of the isotropic phase-nematic transition in an external orienting field and the presence of a critical point on the corresponding phase-equilibrium curves are also characteristic of melts of copolymers having rigid and flexible fragments in the main chain (see Fig. 16a).

In Ref. 99 an exact treatment was conducted (within the framework of the lattice model) of the problem of ordering of melts of flexible-chain polymers upon applying an ex-

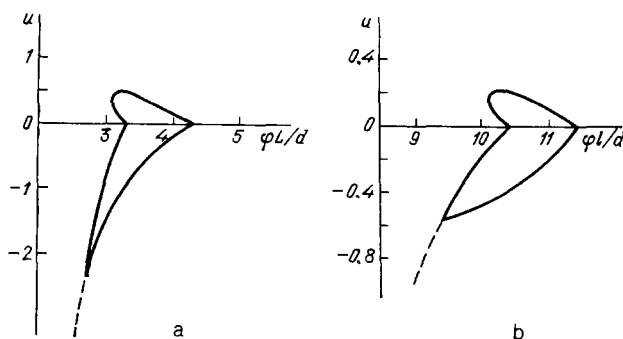


FIG. 22. Phase diagrams of solutions of rigid rods (a) and semiflexible persistent chains (b) in an external quadrupole-type field. The orienting field corresponds to the half-plane $u > 0$, and the "disorienting" field to $u < 0$.

ternal field of the type of (6.3) to them (e.g., during uniaxial stretch of the melt). The fundamental conclusion of Ref. 99 is that a strong enough external field (tensile) of this type induces in the melt a phase transition to a strongly ordered state with unfolded chains. Thus we obtain a justification for certain assumptions of the theory of orientational crystallization.¹⁰⁰

7. ELASTIC MODULI OF A POLYMERIC LIQUID CRYSTAL

According to the phenomenological theory,¹ the distorted state of a nematic with a weakly inhomogeneous field of the director $\mathbf{u}(\mathbf{r})$ corresponds to the additional free energy

$$F_d = \frac{1}{2} \int \{K_1 (\text{div } \mathbf{u})^2 + K_2 (\mathbf{u} \text{ rot } \mathbf{u})^2 + K_3 [\mathbf{u} \text{ rot } \mathbf{u}]^2\} d^3r. \quad (7.1)$$

Here K_1 is the splay elastic modulus, K_2 is the twist modulus, and K_3 is the bend modulus (Fig. 23). The relationship among these moduli determines the texture and many other macroscopic properties of nematics.

7.1. Solution of rigid rods

The elastic moduli of an athermal solution of long rigid rods were calculated in Refs. 101–104. These studies employed the Onsager method (see Sec. 2.1) generalized to the case of an inhomogeneous system. In this case we must write the free energy of steric interaction (the last term on the right-hand side of Eq. 2.1) in the form

$$F_{\text{ster}} = \frac{Tc^2}{2} \int f(\mathbf{n}, \mathbf{r}) f(\mathbf{n}', \mathbf{r}') B(\mathbf{n}, \mathbf{n}'; \mathbf{r} - \mathbf{r}') \times d\Omega_{\mathbf{n}} d\Omega_{\mathbf{n}'} d^3r d^3r'. \quad (7.2)$$

Here $f(\mathbf{n}, \mathbf{r})$ is the density of the orientational distribution of the rods, which depends on the spatial position \mathbf{r} of the center of mass of the rod; the function $B(\mathbf{n}, \mathbf{n}'; \mathbf{r} - \mathbf{r}')$ equals unity if the rods (\mathbf{n}, \mathbf{r}) and $(\mathbf{n}', \mathbf{r}')$ overlap, and zero in the opposite case. The generalization of the rest of the terms of the free energy is trivial. The final result is¹⁰³:

$$K_i = \frac{TcL^2}{24} \int L_i(\mathbf{n}) \frac{(\nabla_{\mathbf{n}} f_0(\mathbf{n}))^2}{f_0(\mathbf{n})} d\Omega_{\mathbf{n}} \quad (i=1, 2, 3). \quad (7.3)$$

Here $f_0(\mathbf{n})$ is the equilibrium distribution function in the undistorted state, and we have

$$L_1(\mathbf{n}) = \frac{3}{4}, \quad L_2(\mathbf{n}) = \frac{1}{4}, \quad L_3(\mathbf{n}) = \cos^2 \theta \quad (7.4)$$

(Here θ is the angle between \mathbf{n} and the director \mathbf{u}). Thus a solution of rods always satisfies the relationship

$$K_2 = \frac{K_1}{3}. \quad (7.5)$$

For the highly ordered state (order parameter $s \rightarrow 1$), the elastic moduli of the solution are asymptotically equal to:

$$K_1 = \frac{TL\varphi}{\pi d^2}, \quad K_2 = \frac{K_1}{3}, \quad K_3 = \frac{K_1}{1-s}. \quad (7.6)$$

The bend modulus K_3 is substantially larger than the rest of the moduli. This arises from the fact that rods that are oriented in the highly ordered solution specifically in the longitudinal direction cannot bend.

The influence of the electrostatic interaction of the rods on the elastic moduli of a nematic solution was studied in

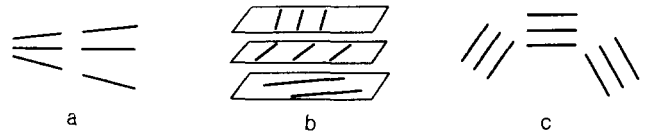


FIG. 23. Schematic diagram of splay (a), twist (b), and bend (c) deformations for a solution of rigid rods.

Ref. 105 for the case of strongly charged macromolecules (see Sec. 4.3). It turned out that electrostatic repulsion leads to a small decrease in moduli K_1 and K_2 (Eq. (7.5) remains in force). The relative change in the elastic moduli is approximately proportional to the small parameter $h \approx 1/\ln w$ (see Sec. 4.3). The variation of the longitudinal bending modulus K_3 is more complex in character. At low concentrations of the solution (near the concentrations of the LC transition) the modulus K_3 decreases slightly with increasing h . At higher concentrations K_3 increases appreciably with increasing h .

7.2. Partially flexible macromolecules

The elastic moduli of the melt of very long persistent macromolecules have been studied in Ref. 106; a solution of persistent (and freely linked) chains of arbitrary length in Ref. 103 (see also Ref. 104). We present below the theoretical method and fundamental results obtained for a solution of persistent chains in Ref. 103. We shall write the orientational distribution function of regions of the macromolecules, which depends both on the spatial position of the region \mathbf{r} and on its position along the chain λ ($0 < \lambda < L$) in the following form (cf. Eq. (3.22)):

$$f(\mathbf{n}, \mathbf{r}, \lambda) = \psi(\mathbf{n}, \mathbf{r}, \lambda) \psi(-\mathbf{n}, \mathbf{r}, L - \lambda). \quad (7.7)$$

The auxiliary function ψ satisfies the equation (cf. (3.24)):

$$l \frac{\partial \psi}{\partial \lambda} = \nabla_{\mathbf{n}}^2 \psi - U_{\text{ster}} \psi - \ln \frac{\partial \psi}{\partial \mathbf{r}}. \quad (7.8)$$

Here the mean molecular field $U_{\text{ster}} = U_{\text{ster}}(\mathbf{n}, \mathbf{r})$ is determined by analogy with Eq. (3.18). For a weakly deformed state of a nematic the function ψ has the form

$$\psi(\mathbf{n}, \mathbf{r}, \lambda) = \psi_0(\mathbf{n}\mathbf{u}; \lambda) + \frac{\partial u_{\alpha}}{\partial r_{\alpha}} \sigma_{\alpha\beta}(\mathbf{n}, \mathbf{u}, \lambda). \quad (7.9)$$

Here $\mathbf{u} = \mathbf{u}(\mathbf{r})$. The elastic moduli can be expressed in terms of ψ_0 and $\delta_{\alpha\beta}$:

$$K_i = -2Tlc \int_0^L d\lambda \int d\Omega_{\mathbf{n}} n_i n_i \sigma_{i1} \frac{\partial \psi_0(n_3; \lambda)}{\partial n_3} \times (i=1, 2, 3). \quad (7.10)$$

Here c is the concentration of the macromolecules, and n_1 , n_2 , and n_3 are the Cartesian components of the vector \mathbf{n} (axis 3 is chosen along the director \mathbf{u}).

The elastic moduli of a solution of long ($L \gg l$) persistent macromolecules in the case of low orientational order are equal to

$$K_1 \approx K_3 = \frac{50}{14\pi} Tl\varphi \frac{s^2}{d^2}, \quad K_2 \approx \frac{K_1}{10}, \quad s \ll 1. \quad (7.11)$$

The twist modulus K_2 has the smallest value (just as for a solution of rigid rods).

In the opposite limiting case ($s \rightarrow 1$) the values of the elastic moduli are¹⁰³:

$$K_2 = \frac{(1-s)Tl\varphi}{3\pi d^2}, \quad K_3 = \frac{2sTl\varphi}{\pi d^2},$$

$$K_1 \approx \frac{T}{4d} \vartheta^{4/3} \exp(3.82\vartheta^{1/2} - 7.1\vartheta^{1/6}). \quad (7.12)$$

Here $\vartheta = \varphi l/d \gg 1$. As before, the twist modulus K_2 is the smallest. As $s \rightarrow 1$ the bend modulus K_3 approaches a constant value, which is determined simply by the bending rigidity of the polymer chains themselves. We note that the ratio K_3/K_2 for a solution of persistent macromolecules is approximately twofold larger than for a solution of rigid rods. As Eq. (7.12) implies, the splay modulus K_1 increases exponentially rapidly with increasing concentration of the solution. The reason for the increase is that the polymer chains must form folds (Fig. 24a) to create a divergence of the field of the director, while their appearance in a strongly ordered nematic solution involves large energy expenditures.

Upon decrease of the length L of the persistent macromolecules, the splay modulus decreases according to the law

$$K_1(L) = K_1(\infty) \{1 - [1 - \exp(-z)] z^{-1}\}. \quad (7.13)$$

Here $z = TcL^2/2K_1(\infty)$. When $L \gg L_c = (K_1(\infty)/cT)^{1/2}$, the modulus is $K_1(L) \approx K_1(\infty)$. When $L \sim L_c$ the $K_1(L)$ becomes linear:

$$K_1(L) = \frac{Tl\varphi}{\pi d^2}, \quad z \ll 1. \quad (7.14)$$

We note that Eq. (7.14) coincides with the corresponding formula (7.6) for a solution of rigid rods. Thus the transition from a regime of flexible macromolecules to a regime of rigid rods for the modulus K_1 occurs at $L \sim L_c = (K_1(\infty)/cT)^{1/2} \gg l$, i.e., in the region of very long macromolecules. The reason for this becomes understandable if we bear in mind the fact that, in a strongly ordered solution, persistent macromolecules are strongly stiffened (see Sec. 3.4), and that the length L_c equals in order of magnitude the "stiffened" effective segment. As regards the moduli K_2 and K_3 , they smoothly go from the asymptotic $L/l \gg 1$ to $L/l \ll 1$ in the region $L \sim l$.

Recently several first experimental studies have appeared, devoted to measuring the elastic moduli of polymeric nematics.^{107,108} Their results agree with the relationships (7.6), (7.11)–(7.13). However, the existing data do not yet suffice for an exhaustive test of them.

8. ELASTIC LIGHT SCATTERING IN POLYMER SOLUTIONS IN THE REGION OF A LIQUID-CRYSTALLINE TRANSITION

Light scattering (along with x-ray and neutron scattering) is an important source of information, both on the properties of low-molecular-weight liquid crystals,¹ and on the conformations of macromolecules in polymer systems.⁹⁸

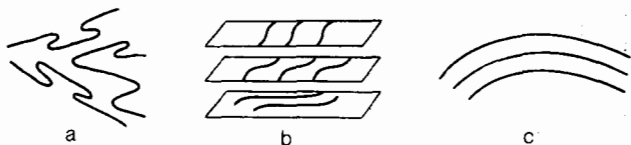


FIG. 24. Splay (a), twist (b), and bend (c) deformations in a solution of long persistent chains.

This method is especially useful in studying the isotropic polymer solution-nematic transition.⁵⁸ Light scattering in athermal solutions of rigid-chain polymers has been studied theoretically in Ref. 109 (see also Ref. 17). Below (in Secs. 8.2 and 8.3) we present briefly the results of these studies. Section 8.1 will treat certain general tenets of the theory of light scattering that will be necessary for the further treatment (see Ref. 110)

8.1. The connection between the intensity of light scattering and the generalized susceptibility

Let the following electromagnetic wave be incident on the system:

$$E = E_0 e \exp(i\omega t - ikr).$$

Its polarization is given by the unit vector e . The differential cross section in the direction \mathbf{k}' (\mathbf{k}' is the wave vector of the scattered wave) with the polarization e' is¹¹⁰

$$\sigma = \left(\frac{\omega}{c}\right)^4 e'_\alpha e'_\beta e_\alpha e_\beta \int \langle \kappa_{\alpha\alpha'}(\mathbf{r}) \kappa_{\beta\beta'}(\mathbf{r}') \rangle_c \times \exp[-iq(\mathbf{r} - \mathbf{r}')] d^3 r d^3 r'. \quad (8.1)$$

Here $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ is the wave scattering vector; $\kappa_{\alpha\beta}(\mathbf{r})$ is the permittivity tensor of the medium.

Now let us study concretely a solution of rigid-chain macromolecules, which can be considered locally to be continuous dielectric cylinders. Let κ_{\parallel} be the dielectric susceptibility permittivity per unit volume) of these cylinders in a direction parallel to their axis; κ_{\perp} is the permittivity in the perpendicular direction; κ_s is the dielectric susceptibility of the (isotropic) solvent. If the mean volume concentration of the polymer φ is small, then the susceptibility tensor of the solution has the form (see Ref. 110, Eq. (9.7)):

$$\kappa_{\alpha\beta}(\mathbf{r}) = \kappa_s \delta_{\alpha\beta} + \int \left(A \delta_{\alpha\beta} + B \frac{3n_\alpha n_\beta - \delta_{\alpha\beta}}{2} \right) \varphi(\mathbf{r}, \mathbf{n}) d\Omega_{\mathbf{n}}. \quad (8.2)$$

Here $\varphi(\mathbf{r}, \mathbf{n})$ is the local volume concentration at the point \mathbf{r} of the polymer chains oriented in the direction \mathbf{n} ; and we have

$$A = \frac{\kappa_{\parallel} + 2\zeta\kappa_{\perp}}{3} - \kappa_s, \quad B = \frac{2(\kappa_{\parallel} - \zeta\kappa_{\perp})}{3},$$

$$\zeta = \frac{2(1 + 4\pi\kappa_s)}{2 + 4\pi(\kappa_s + \kappa_{\perp})}. \quad (8.3)$$

Upon substituting (8.2) into (8.1), we find the cross section of excess scattering (as compared with the pure solvent) per unit volume; $h = \sigma_{exc}/V$:

$$h = \left(\frac{\omega}{c}\right)^4 e'_\alpha e'_\beta e_\alpha e_\beta (A^2 D(\mathbf{q}) \delta_{\alpha\alpha'} \delta_{\beta\beta'} + B^2 Q_{\alpha\alpha'\beta\beta'}(\mathbf{q})). \quad (8.4)$$

Here we have

$$D(\mathbf{q}) = \int \langle \varphi(\mathbf{r}) \varphi(0) \rangle_c e^{-i\mathbf{q}\mathbf{r}} d^3 r, \quad (8.5)$$

$$Q_{\alpha\alpha'\beta\beta'}(\mathbf{q}) = \int \langle Q_{\alpha\alpha'}(\mathbf{r}) Q_{\beta\beta'}(0) \rangle_c e^{-i\mathbf{q}\mathbf{r}} d^3 r. \quad (8.6)$$

In Eqs. (8.5)–(8.6)

$$\varphi(\mathbf{r}) = \int \varphi(\mathbf{r}, \mathbf{n}) d\Omega_{\mathbf{n}}$$

is the local volume concentration at the point \mathbf{r} , and

$$Q_{\alpha\beta}(\mathbf{r}) = \int \frac{3n_{\alpha}n_{\beta} - \delta_{\alpha\beta}}{2} \varphi(\mathbf{r}, \mathbf{n}) d\Omega_{\mathbf{n}}$$

is the tensor of the orientational-order parameters. The first term in the parentheses of Eq. (8.4) corresponds to scattering by fluctuations of the polymer concentration, and the second one to scattering by fluctuations of the anisotropy.

8.2. Small-angle light scattering in isotropic solutions

If the scattering wave vector is small ($ql \ll 1$), then we can neglect the dependence of D and $Q_{\alpha\alpha'\beta\beta'}$ on \mathbf{q} in Eq. (8.4). We can easily express the coefficients $D(0)$ and $Q_{\alpha\alpha'\beta\beta'}(0)$ in terms of the equilibrium characteristics of the homogeneous solution. The result for an athermal solution of persistent macromolecules of arbitrary length L has the form

$$D(0) = \frac{\pi d^3}{4} \frac{\varphi}{2\varphi + (d/L)},$$

$$Q_{\alpha\alpha'\beta\beta'}(0) = \frac{\pi d^3}{10} \left(\frac{\varphi^*}{\varphi} - 1 \right)^{-1} \times \left[\frac{3}{2} (\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \delta_{\alpha\beta'}\delta_{\alpha'\beta}) - \delta_{\alpha\alpha'}\delta_{\beta\beta'} \right]. \quad (8.7)$$

Here

$$\varphi^* = \frac{12d}{l} \left\{ 1 - \left[1 - \exp\left(-\frac{6L}{l}\right) \right] \left(\frac{6L}{l} \right)^{-1} \right\}^{-1} \quad (8.8)$$

is the volume concentration of the polymer at which the solution loses stability with respect to anisotropy fluctuations.³⁸

Let us study the scattering of vertically polarized light in the horizontal plane. The scattered light has two components: vertical (V) and horizontal (H). Upon substituting (8.7) into (8.4), we find the differential cross section for the vertical component

$$h_V = \left(\frac{\omega}{c} \right)^4 d^3 \varphi \frac{\pi}{5} \left[\frac{5}{4} \frac{A^2}{2\varphi + (d/L)} + \frac{B^2}{\varphi^* - \varphi} \right] \quad (8.9)$$

and the degree of depolarization of the scattered light

$$\Delta \equiv \frac{h_H}{h_V} = 3 \left[4 + \frac{5A^2}{B^2} \frac{\varphi^* - \varphi}{2\varphi + (d/L)} \right]^{-1}. \quad (8.10)$$

In an extremely dilute solution, $\varphi \ll \varphi^*$, the scattering by density fluctuations predominates (the first term in the square brackets in Eq. (8.9); we assume that $A \gtrsim B$). If $L \ll l$, i.e., the macromolecules are rigid rods, then (when $\varphi \ll \varphi^*$) the cross section h_V is proportional to the length L of the macromolecule and to the concentration of the solution, while the degree of depolarization Δ is almost independent of these parameters. In the opposite limiting case ($L \gg l$) the degree of depolarization (when $d/L \ll \varphi \ll \varphi^*$) equals

$$\Delta = \frac{l\varphi B^2}{4(A^2 d)}.$$

Thus, in a dilute solution of semiflexible persistent macromolecules the degree of depolarization is proportional to the concentration.

As the concentration of the solution approaches the critical value ($\varphi \rightarrow \varphi^*$), scattering by anisotropy fluctuations comes to predominate. Here the degree of depolarization increases to its maximum value $\Delta = \frac{3}{2}$ (in a narrow region near $\varphi = \varphi^*$ Eq. (8.10) loses applicability; in this region an additional increase or decrease of Δ can occur; see below).

8.3. Light scattering in an athermal solution of semiflexible persistent macromolecules: general case

Light scattering in a solution of long persistent macromolecules ($L \gg l$) was studied in the general case (in which the vector \mathbf{q} does not approach zero) in Ref. 109. While omitting the rather unwieldy intermediate calculations, we shall proceed directly to presenting the results most important from the physical standpoint.

Let us study the scattering of vertically polarized light in the horizontal plane when $\varphi \approx \varphi^*$. It turns out that the applicability of (8.9)–(8.10) in the neighborhood of the critical point is limited by the strengthened inequality

$$l^2 q^2 \ll \frac{\varphi^* - \varphi}{\varphi^*}. \quad (8.11)$$

If the inequality opposite to (8.11) is satisfied, but on the other hand the quantity lq is still small,

$$\frac{\varphi^* - \varphi}{\varphi^*} \ll l^2 q^2 \ll 1, \quad (8.12)$$

then the following expressions for the cross section and the degree of depolarization hold:

$$h_V = \left(\frac{\omega}{c} \right)^4 B^2 \frac{\pi}{5} d^3 \frac{243.6}{l^2 q^2}, \quad (8.13)$$

$$\Delta \equiv \frac{h_H}{h_V} = \frac{39}{800} (11 - 9 \cos \theta) = 0.536 - 0.439 \cos \theta. \quad (8.14)$$

Here θ is the angle between the wave vectors of the incident and scattered waves. Upon considering Eqs. (8.10) and (8.14), we conclude that, if φ is not too close to φ^* , then the degree of depolarization does not depend on the scattering angle θ and monotonically increases with increasing φ to the value $\Delta \approx 0.75$; conversely, in the region $(\varphi^* - \varphi)/\varphi^* \lesssim l^2 q^2$ a substantial dependence of Δ on θ appears, with $\Delta < 0.75$ for $\theta < 119^\circ$. Thus, when $\theta < 119^\circ$, $lq \ll 1$, the $\Delta(\varphi)$ relationship must have a maximum.

In the general case in which the quantity lq is not small, the scattering characteristics can be found only by using a computer. The $\Delta(\varphi)$ relationships obtained as a result (in Ref. 109) for different values of lq are shown in Fig. 25.

The experimental studies^{58,111,112} investigated light scattering in solutions of poly- γ -benzyl- L -glutamate (PBG) and poly- p -phenylterephthalamide (PPTA) in the region of the LC transition. The $h_V(\varphi)$ relationships found in these studies (for $\theta = 90^\circ$) are compared with the theoretically calculated values¹⁰⁹ in Fig. 26 (the parameter A/B is an adjustment parameter).

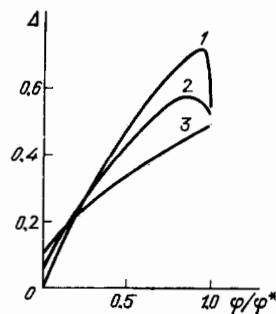


FIG. 25. Dependence of the degree of depolarization Δ (scattering angle $\theta = 90^\circ$) on the volume concentration φ of the polymer.¹⁰⁹ $A/B = 1$, $lq \rightarrow 0$ (curve 1); $lq = 3$ (2); $lq = 8$ (3).

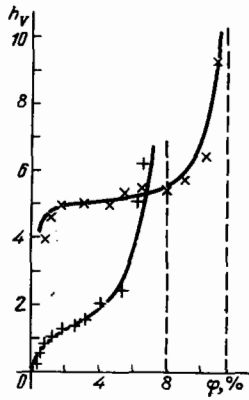


FIG. 26. Differential excess scattering cross sections h_v as functions of the concentration φ of the polymer (scattering angle $\theta = 90^\circ$) for a solution of PBG in DMF (+) and PPTA in sulfuric acid (x).⁵⁸ Solid curves—theoretical for $A/B = 1.3$, $lq = 3.25$, $\varphi^* = 0.08$, and for $A/B = 6$, $lq = 0.7$, $\varphi^* = 0.115$.

When $\varphi > \varphi^*$ the isotropic state is unstable and the solution must be liquid-crystalline. The light scattering by the nematic liquid crystal is described by the phenomenological theory,¹ whose condition of applicability (in the given case) has the form $ql \ll 1$. The differential scattering cross section per unit volume is¹

$$h = \left(\frac{3B\varphi}{2}\right)^2 \left(\frac{\omega}{c}\right)^4 T \sum_{\alpha=1,2} (e_\alpha e'_\alpha + e_3 e'_3)^2 \times [(K_3 - K_\alpha)(\mathbf{qu})^2 + K_\alpha]^{-1}. \quad (8.15)$$

Here \mathbf{u} is the director, K_1 , K_2 , and K_3 are the elastic moduli (see Sec. 7); e_1 , e_2 , and e_3 are the projections of the polarization vector (axis 3 is parallel to \mathbf{u} , axis 2 is perpendicular to the vectors \mathbf{u} and \mathbf{q}). If $\varphi \approx \varphi^*$, then the equilibrium order parameter s of the LC solution of persistent macromolecules is rather small (see Sec. 3.8). Therefore we can use Eqs. (7.11) to calculate the elastic moduli. Upon substituting (7.11) into (8.15) and averaging over all possible orientations of the director \mathbf{u} , we find for $\varphi \approx \varphi^*$:

$$h_v \approx \left(\frac{\omega}{c}\right)^4 B^2 \frac{\pi}{5} d^3 \frac{74.00}{l^2 q^2}, \quad (8.16)$$

$$\Delta \equiv \frac{h_H}{h_v} = 0.608 - 0.323 \cos \theta. \quad (8.17)$$

Comparing Eqs. (8.16) and (8.13) we conclude that, if the transition of the solution to the LC state occurs by spinodal decomposition at $\varphi = \varphi^*$, then at the transition point the scattering cross section h_v decreases by approximately a factor of three.

9. DYNAMICS OF CONCENTRATED SOLUTIONS OF RIGID-CHAIN POLYMERS

Up to now we have been discussing the equilibrium properties of liquid-crystalline polymer solutions and melts. The study of the dynamic (rheological, relaxational, etc.) properties of these systems is just as interesting as it is complex, and has begun relatively recently (the first theoretical study in this field appeared in 1975¹¹³).

In recent time only the theory of the hydrodynamic properties of concentrated solutions of extremely rigid-

chain macromolecules in an isotropic phase has been worked out in sufficient detail. Its foundations were laid in a series of studies by Doi and Edwards.¹¹³⁻¹¹⁶ Below we examine first the fundamental ideas and results of these studies, and then present the later results pertaining to the dynamics of nematic polymer solutions.

9.1. Isotropic solution of extremely rigid rods

Let N long rigid rods of length L and diameter d , $L \gg d$, be dissolved in the volume V . If the concentration of the solution $c = N/V$ is much smaller than a quantity of the order of L^{-3} , then spheres of diameter L circumscribed around the rods will not overlap, and the Brownian movement of the rods occurs independently (Fig. 27a). On the other hand, when $c \gtrsim 1/L^2 d$, nematic ordering arises in the solution of rods (see Sec. 2 and Fig. 27c). In this section we shall treat the dynamic properties of the solution in the intermediate region (Fig. 27b):

$$L^{-3} \ll c \ll L^{-2} d^{-1}. \quad (9.1)$$

Here, on the one hand, the solution is isotropic, and on the other hand, the motion of individual rods is strongly affected by the rods surrounding them. Such a treatment is necessary also for the subsequent analysis of the dynamics of a nematic solution, which will be conducted in the next section.

Since rigid-chain macromolecules (rods) cannot pass through one another without breaking the chain, substantial restrictions are imposed on the possible motions of rods in solution in the concentration region of (9.1). Reference 113 proposed modeling these restrictions by using the concept of an effective tube of radius a created by the neighboring rods in which the given macromolecule exists at each instant of time (see Fig. 27b). Here the macromolecule can move freely along the axis of the tube, while its mobility in the perpendicular direction is suppressed by the presence of the neighboring rods.

It was proposed¹¹³ to estimate the radius a of the tube from the following considerations. Since inside the tube the rod must move practically freely, other rods must be absent in the volume of the tube. The mean value of the maximum radius of the cylindrical region around a given rod that does not intersect other rods can be easily determined for the case of an isotropic solution from geometrical considerations. It turned out that

$$a = \frac{2}{\pi c L^2}. \quad (9.2)$$

In the concentration region of (9.1) we have $d \ll a \ll L$.

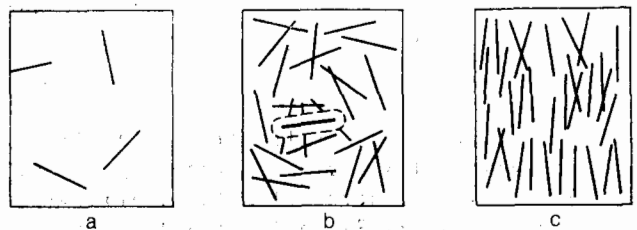


FIG. 27. Dilute (a), semidilute isotropic (b), and semidilute nematic (c) solutions of long rigid rods. The effective tube for one of the rods is shown in the semidilute isotropic solution.

Let us estimate the influence of the tube on the diffusional motion of the rod. As is known (see Refs. 117 and 118), in a dilute solution ($c \ll L^{-3}$; see Fig. 27a) the Brownian movement of the rod is determined by three diffusion coefficients—longitudinal translational (D_{\parallel}), transverse translational (D_{\perp}), and rotational ($D_r^{(0)}$), with

$$D_{\parallel} \equiv D = \frac{T \ln(L/d)}{2\pi\eta_s L}, \quad D_{\perp} = \frac{D}{2}, \quad D_r^{(0)} = \frac{6D}{L^2}. \quad (9.3)$$

Here η_s is the viscosity of the solvent. Here the overall translational diffusion coefficient equals

$$D_t^{(0)} = \langle \cos^2 \theta \rangle D_{\parallel} + \langle \sin^2 \theta \rangle D_{\perp} = \frac{2D}{3}. \quad (9.4)$$

Here θ is the angle between the axis of the rod and a certain chosen axis; in an isotropic solution we have $\langle \cos^2 \theta \rangle = \frac{1}{3}$, $\langle \sin^2 \theta \rangle = \frac{2}{3}$.

The presence of the tube hinders both the rotational and the translational motion of the rod. As regards the translational diffusion coefficient D_t , as before we can write Eq. (9.4) for it. However, here we must set $D_{\perp} = 0$ (owing to the presence of the tube). Hence we have

$$D_t = \frac{D}{3} = \frac{D_t^{(0)}}{2}. \quad (9.5)$$

The restrictions on the rotational motion of the rod are more substantial. Evidently, during the time τ_0 of existence in the original tube the orientation of the rod cannot escape the limits of the small solid angle $\Delta\Omega \sim (\Delta\theta)^2 \sim (a/L)^2$. Since the only possibility of leaving the tube involves diffusion along its axis, τ_0 is the time in which the rod is displaced diffusively along the axis of the tube to a distance of the order of L :

$$\tau_0 \sim \frac{L^2}{D}. \quad (9.6)$$

We can consider the Brownian movement of the orientation vector \mathbf{n} to be a random walk (in orientation space). Here, in the time τ_0 the mean-square displacement $(\Delta\theta)^2 \sim (a/L)^2$ occurs, and the displacements in different time intervals τ_0 are uncorrelated. Hence we have the following expression for the rotational diffusion coefficient D_r :

$$D_r \sim \frac{(\Delta\theta)^2}{\tau_0} \sim \left(\frac{a}{L}\right)^2 \frac{D}{L^2} \sim \frac{D_t^{(0)}}{(cL^3)^2}. \quad (9.7)$$

We see that, when $cL^3 \gg 1$, the rotation of the macromolecules is substantially hindered: $D_r \ll D_r^{(0)}$. We note also the very strong power-function dependence of the coefficient D_r on L : apart from logarithmic factors we have $D_r \propto L^{-9}$.

The maximum rotational relaxation time in the solution of rods, in agreement with Eq. (9.7), is

$$\tau_{\max} \sim D_r^{-1} \sim (cL^3)^2 (D_r^{(0)})^{-1}. \quad (9.8)$$

Hence we can find the linear viscosity η of the solution in a stationary shear flow. Actually, according to the common scaling relation (see Refs. 98, 119), we have

$$\eta \sim \tau_{\max} G. \quad (9.9)$$

Here G is the elastic modulus of the system (for small times $t < \tau_{\max}$ for which the flow of the solution does not succeed in developing); $G \sim cT$ (cf. Refs. 119, 120). Therefore, apart from logarithmic factors, Eqs. (9.3) and (9.9) imply that

$$\eta \sim \eta_s (cL^3)^3 \gg \eta_s. \quad (9.10)$$

Thus the viscosity of a concentrated solution of rigid rods

considerably exceeds the basic viscosity of the solvent and increases proportionally to the cube of the concentration of the solution.

The tube concept has also been applied for studying the more subtle rheological characteristics of an isotropic solution of extremely rigid-chain macromolecules (rigid rods) (see Refs. 114, 115, and 121). A generalization of the theory presented above to take account of a certain flexibility of the macromolecules has been performed in Refs. 122–125. A discussion of some discrepancies between theory and experiment, as well as of attempts to remove them, are contained in Refs. 126–129.

9.2. Phenomenological description of the dynamics of nematic liquids

The rheological properties of nematic liquids are well described by the linear phenomenological theory of Leslie, Ericksen, and Parodi (see Ref. 1). The viscous stress tensor in the flow of an incompressible liquid in this theory has the form

$$\begin{aligned} \sigma_{\alpha\beta} = & \alpha_1 u_\alpha u_\beta A_{\gamma\delta} u_\gamma u_\delta + \alpha_4 A_{\alpha\beta} + \alpha_5 A_{\alpha\gamma} u_\beta u_\gamma \\ & + \alpha_6 A_{\beta\gamma} u_\gamma u_\alpha + \alpha_2 N_\alpha u_\beta + \alpha_3 N_\beta u_\alpha. \end{aligned} \quad (9.11)$$

Here

$$A_{\alpha\beta} = \frac{1}{2} (v_{\alpha,\beta} + v_{\beta,\alpha}) \quad (9.12)$$

is the asymmetric component of the rate of deformation of the liquid (v_α is the hydrodynamic velocity field); u_α director of the nematic,

$$N_\alpha = \dot{u}_\alpha - \frac{1}{2} (v_{\alpha,\beta} - v_{\beta,\alpha}) u_\beta \quad (9.13)$$

is the rate of rotation of the director with respect to the liquid; $\alpha_1, \dots, \alpha_6$ are the six viscosity coefficients (Leslie coefficients), which are connected by the one Parodi relationship, which stems from the Onsager principle:

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5. \quad (9.14)$$

In the classical experiments of Miesowicz (see Ref. 1) the viscosity was measured in a stationary Couette flow (Fig. 28), in which the director of the nematic was oriented by a weak external field along a certain axis. The Miesowicz viscosities are connected to the Leslie coefficients (the axis 1 is chosen along the axis of flow, 2 along the velocity gradient, and 3 perpendicular to the first two; see Fig. 28):

$$\eta_1 = \frac{1}{2} (\alpha_3 + \alpha_4 + \alpha_6), \quad \eta_2 = \frac{1}{2} (\alpha_4 + \alpha_5 - \alpha_2), \quad \eta_3 = \frac{\alpha_4}{2}. \quad (9.15)$$

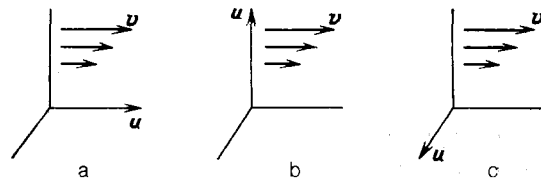


FIG. 28. Mutual orientation of the flow direction \mathbf{v} and the director \mathbf{u} of the nematic phase in experiments to determine the Miesowicz viscosities η_1 (a), η_2 (b), and η_3 (c).

The Leslie coefficients and Miesowicz viscosities were first calculated for nematic solutions of extremely rigid-chain macromolecules (rigid rods) in Refs. 116 and 130. However, here an ungrounded assumption was made, which led to erroneous results. A correct analysis of the problem was made in Ref. 131 (see also Refs. 132 and 133). We present below the fundamental results of all these studies.

9.3. Nematic solution of rigid rods

Let us study a solution of rodlike macromolecules having a very great chain rigidity. The rotational Brownian movement of these macromolecules (rods) under the action of an external orienting field $U_{\text{ext}}(\mathbf{n})$ and an (external) hydrodynamic flux is described by a diffusion equation of the form^{131,132}

$$\frac{\partial f}{\partial t} = D_r (\nabla_{\mathbf{n}}^2 f + \nabla_{\mathbf{n}} (f \nabla_{\mathbf{n}} U)) - \nabla_{\mathbf{n}} (\dot{\mathbf{n}} f). \quad (9.16)$$

Here $f = f(\mathbf{n})$ is the density of the orientational distribution of the rods, $U = U_{\text{ext}}(\mathbf{n}) + U_{\text{ster}}(\mathbf{n})$ is the effective orienting field acting on the rods, and D_r is the rotational diffusion coefficient of the rods, which is equal¹³⁴ (cf. Eq. (9.7)) to

$$D_r = \text{const} \cdot D_r^{(0)} \left[c L^3 \int f(\mathbf{n}) f(\mathbf{n}') \sin \gamma_{\mathbf{nn}'} d\Omega_{\mathbf{n}} d\Omega_{\mathbf{n}'} \right]^{-2}. \quad (9.17)$$

Here const is a numerical factor. The molecular field $U_{\text{ster}}(\mathbf{n})$ is equal (cf. Eq. (3.18)) to:

$$U_{\text{ster}}(\mathbf{n}) = \frac{8L\varphi}{\pi d} \int \sin \gamma_{\mathbf{nn}'} f(\mathbf{n}') d\Omega_{\mathbf{n}'}. \quad (9.18)$$

Here $\varphi = \pi c L d^2 / 4$ is the volume concentration of the polymer. The last term on the right-hand side of (9.16) arises from the hydrodynamic flow, and $\dot{\mathbf{n}}$ is the rate of variation of the orientation of the rods under the action of this flow:

$$n_{\alpha} = v_{\alpha, \beta} n_{\beta} - n_{\alpha} v_{\beta, \gamma} n_{\beta} n_{\gamma}. \quad (9.19)$$

The microscopical expression for the stress tensor of the solution has the form¹³⁰

$$\sigma_{\alpha\beta} = 3cT \left\langle n_{\alpha} n_{\beta} - \frac{\delta_{\alpha\beta}}{3} \right\rangle + c \left\langle n_{\beta} \frac{\partial U}{\partial n_{\alpha}} \right\rangle. \quad (9.20)$$

Here the averaging is performed by using the distribution function found from Eq. (9.16). If $U_{\text{ext}} = 0$, then the tensor of (9.20) is always symmetric.

The Leslie coefficients calculated on the basis of Eqs. (9.16)–(9.20) equal^{131,133}:

$$\alpha_i = \frac{cT}{2D_r} \tilde{\alpha}_i \quad (i = 1, \dots, 6). \quad (9.21)$$

Here the dimensionless quantities $\tilde{\alpha}_i$ are determined by the relationships

$$\begin{aligned} \tilde{\alpha}_1 &= -2r, & \tilde{\alpha}_2 &= -2(s + \Gamma), & \tilde{\alpha}_3 &= 2\Gamma, \\ \tilde{\alpha}_4 &= \frac{2(7 - 5s - 2r)}{35}, & \tilde{\alpha}_5 &= \frac{2(5s + 2r)}{7}, & \tilde{\alpha}_6 &= \frac{4(r - s)}{7}. \end{aligned} \quad (9.22)$$

Here

$$s = \int P_2(\cos \theta) f_0(\mathbf{n}) d\Omega_{\mathbf{n}}, \quad r = \int P_4(\cos \theta) f_0(\mathbf{n}) d\Omega_{\mathbf{n}} \quad (9.23)$$

are the equilibrium order parameters (θ is the angle between the director \mathbf{u} and the orientation of the rod \mathbf{n}), and we have

$$\Gamma = \frac{1}{2} \int \sin^2 \theta f_0(\mathbf{n}) \frac{\partial \Phi}{\partial \theta} d\Omega_{\mathbf{n}}. \quad (9.24)$$

The function $\Phi(\theta)$ satisfies the equation

$$\frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Phi}{\partial \theta} \right) - \Phi (\sin \theta)^{-1} = \sin \theta \frac{\partial U_0}{\partial \theta} \left(\frac{\partial \Phi}{\partial \theta} - 1 \right). \quad (9.25)$$

Here the molecular field $U_0(\mathbf{n}) = U_0(\theta)$ is determined by Eq. (9.18) with the equilibrium distribution function $f = f_0(\mathbf{n})$.

The dependences of the reduced Miesowicz viscosities on the concentration of the nematic solution calculated by Eqs. (9.15), (9.21)–(9.25) are shown in Fig. 29 on a log-log scale. We see that the three viscosities of the LC solution substantially differ in magnitude, with the greatest viscosity η_2 increasing, but the smallest one η_1 rapidly decreasing with increasing concentration. Figure 29 shows also the experimental values of the reduced viscosities of solutions of polyparabenzamide (PBA) in dimethylacetamide.¹³⁵ In the case of the isotropic solution we can speak of qualitative agreement of experiment and theory (curve 0). However the experimental data for the anisotropic solution do not agree with any of the theoretical curves. The reason for this is that the orientation of the director in the experiment was essentially uncontrolled (although apparently the experimental situation is closest of all to that depicted in Fig. 28a). Another reason is that the theoretical dependences are calculated for a homogeneous nematic solution, whereas actually the solution in the neighborhood of the point $c = c^*$ undoubtedly separates into two phases. That is, experimentally the viscosity not of a homogeneous solution, but of a dispersion of one phase in another was measured.¹³⁶

As is known, in a steady-state shear flow (Couette flow) the director of the nematic liquid is oriented (in the absence of external fields) at the Leslie angle θ_L to the flow direction,¹ with

$$\text{tg}^2 \theta_L = \frac{\alpha_3}{\alpha_2}. \quad (9.26)$$

The dependences of the ratio α_3/α_2 on the order parameter s calculated by Eqs. (9.21)–(9.25) is shown in Fig. 30 (curve 1). When $s \geq s_1 = 0.53$ the ratio α_3/α_2 is negative. This means that steady-state Couette flow of an LC solution of

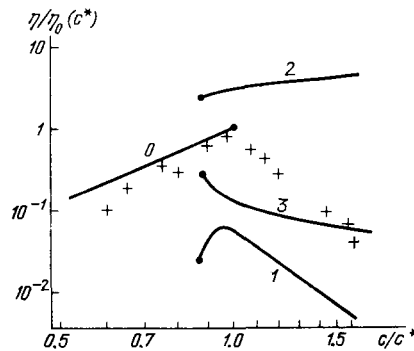


FIG. 29. Dependence of the viscosity of an isotropic solution (curve 0) and the Miesowicz viscosities of a nematic solution (curves 1, 2, and 3, respectively) on the reduced concentration c/c^* of the polymer. c^* is the concentration at which the isotropic state loses stability; "+"—experimental data.¹

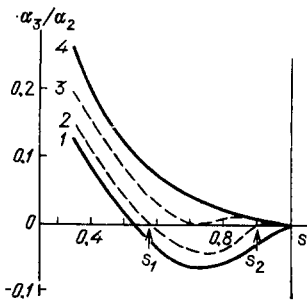


FIG. 30. Dependence of the ratio α_3/α_2 on the order parameter s for a nematic solution of persistent macromolecules of length L .¹³⁸ 1: $L \rightarrow 0^{131}$; 2: $L < L_c$; 3: $L = L_c$; 4: $L \rightarrow \infty$.

extremely rigid rods (for which $s \gtrsim 0.8 > s_1$; see Sec. 2) is unstable (more exactly, it loses stability already at very low shear velocities).^{131,137}

In the experiment of Miesowicz^{1,2} the steady-state shear flow can be replaced with an oscillating one (with the frequency ω). The dependence of the Miesowicz viscosities on the frequency was found theoretically in the form of an expansion in the small parameter $\varepsilon = 1 - s$.¹³¹ The result is:

$$\begin{aligned} \tilde{\alpha}_1 &= -2 \left(1 - \frac{5\varepsilon}{3} - \frac{10\varepsilon/3}{2-i\Omega} \right), & \tilde{\alpha}_2 &= -2 \left(1 - \frac{2\varepsilon}{3} \right), \\ \tilde{\alpha}_3 &= \frac{2\varepsilon}{3}, & \tilde{\alpha}_4 &= \frac{4\varepsilon/3}{2-i\Omega}, \end{aligned} \quad (9.27)$$

$$\begin{aligned} \tilde{\alpha}_5 &= 2 \left(1 - \frac{4\varepsilon}{3} - \frac{2\varepsilon/3}{2-i\Omega} \right), & \tilde{\alpha}_6 &= -\frac{2\varepsilon}{3} \left(1 + \frac{2}{2-i\Omega} \right), \\ \tilde{\eta}_1 &= \frac{cT\varepsilon^2}{9D_r} \left(1 - \frac{2}{1-i\Omega} + \frac{14}{3-i\Omega} \right), \\ \tilde{\eta}_2 &= \frac{cT}{D_r} (1 - \varepsilon), & \tilde{\eta}_3 &= \frac{cT\varepsilon/3D_r}{2-i\Omega}. \end{aligned} \quad (9.28)$$

Here $\Omega = 3\omega/3D_r$ is the reduced frequency. We note that the Parodi relationship (9.14) is fulfilled at all frequencies. The characteristic frequencies correspond to $\Omega \sim 1$, i.e.,

$$\omega \sim \frac{3D_r}{\varepsilon}.$$

For real solutions of rodlike macromolecules these frequencies are of the order of tens of hertz to kilohertz.

9.4. Nematic solution of semiflexible persistent chains

The dynamic properties of nematic solutions of polymer chains with a finite flexibility have been studied theoretically in considerably less detail than in the case of absolutely rigid rods. We present below some first results obtained along this line for a solution of very long persistent macromolecules ($L \gg l$).¹³⁸

Just as in the case of rigid rods (see the preceding section), the macromolecules surrounding a given one in a nematic solution create an effective tube for it (Fig. 31). One can show (see Ref. 125) that the characteristic radius a of this tube is much smaller than the length l of the effective segment ($a \ll l$) if $l \gg d$, i.e., if the macromolecules are rigid-chain ones. Consequently, the only large-scale motion of a given macromolecule with respect to its neighbors is crawling (reptation) along the tube (i.e., actually along its intrinsic contour). We note that a reptational dynamic theory was originally formulated for concentrated solutions (and

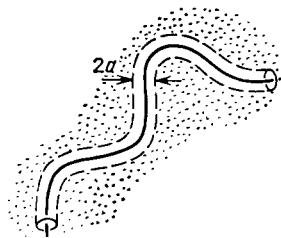


FIG. 31. The prohibition against intersection of a given macromolecule (shown by the solid line) with the surrounding chains (shown by dots) is modeled by an effective tube of radius a (dotted line), in which the given molecule lies.

melts) of flexible-chain polymers in Refs. 139 and 140.

Let us study a solution in which an external orienting field $U_{\text{ext}}(\mathbf{n})$ acts on the macromolecules (see Sec. 6), while the solution exists under conditions of steady-state flow with the velocity-gradient tensor $v_{\alpha\beta}$. Let $f(\mathbf{n}, \lambda, t)$ be the orientational distribution function of the unit vector \mathbf{n} tangent to the axis of the macromolecule (λ is the running coordinate along the polymer chain, $0 \leq \lambda \leq L$). The function f satisfies the following "reptational" kinetic equation¹³⁸:

$$\frac{\partial f}{\partial t} = D^* \frac{\partial^2 f}{\partial \lambda^2} + G. \quad (9.29)$$

Here D^* is the effective diffusion coefficient of the chain "along" the tube, and $G = G(\mathbf{n}, t)$ is the rate of variation of the distribution function caused by inhomogeneous flow:

$$G = -\nabla_{\mathbf{n}}(\dot{\mathbf{n}}f) + fv_{\alpha\beta} \left(n_{\alpha}n_{\beta} - \int f(\mathbf{n}') n'_{\alpha}n'_{\beta} d\Omega_{\mathbf{n}'} \right). \quad (9.30)$$

Here

$$f = f(\mathbf{n}, t) = L^{-1} \int_0^L f(\mathbf{n}, \lambda, t) d\lambda \quad (9.31)$$

is the distribution function averaged over the chain; the velocity $\dot{\mathbf{n}}$ is defined by Eq. (9.19). The effective boundary conditions for Eq. (9.29) have the form

$$f(\mathbf{n}, 0, t) = f(\mathbf{n}, L, t) = f_{\text{eq}}(\mathbf{n}, t). \quad (9.32)$$

Here the equilibrium distribution function f_{eq} is determined by Eq. (3.16), in which $U_{\text{ster}}(\mathbf{n})$ is the mean molecular field corresponding to the averaged function $f(\mathbf{n}, t)$ at the given instant of time t .

By analyzing the system of equations (9.29)–(9.32), we can find all the relaxational properties of the polymer solution. In particular, we can find the Leslie coefficients α_2 and α_3 , which have not only a "viscosity," but also a "relaxation" meaning.¹ The result is¹³⁸:

$$\begin{aligned} \alpha_2 &= \kappa \int_{-1}^1 f_0(z) [2zU'_0(z) - z^2(1-z^2)U''_0(z)] dz, \\ \alpha_3 &= \kappa \int_{-1}^1 f_0(z) (1-z^2)^2 U''_0(z) dz. \end{aligned} \quad (9.33)$$

Here $\kappa = TcL^3/48lD^*$, $z = \mathbf{n} \cdot \mathbf{u}$ (\mathbf{u} is the director), f_0 is the equilibrium orientational distribution function in the absence of external fields, and U_0 is the corresponding equilibrium molecular field.

The dependence of the ratio α_3/α_2 on the (equilibrium) orientational order parameter s of the nematic solution is shown in Fig. 30 (curve 4). Upon consideration Eq. (9.26), we find that in the LC phase at the transition point (i.e., when $s = 0.49$; see Sec. 3.2) the stationary Leslie angle is $\theta_L = 20^\circ$. As the order parameter increases (with increasing concentration of the solution), the value of θ_L substantially decreases, $\theta_L \rightarrow 0$ as $s \rightarrow 1$.

Thus the ratio of Leslie coefficients α_3/α_2 for semiflexible persistent macromolecules is always positive. This result qualitatively differs from that obtained in Sec. 9.3 for a solution of extremely rigid-chain macromolecules. The transition from the case $L \gg l$ (semiflexible macromolecules) to $L \ll l$ (rigid rods) occurs as shown in Fig. 30 (dotted lines): when $L < L_c$ the ratio α_3/α_2 becomes negative (and hence steady-state Couette flow loses stability) in some narrow region of values of the order parameter; with decreasing parameter L/l this region ($s_1 < s < s_2$) gradually expands.¹⁵⁸

10. CONCLUSION. OTHER PROBLEMS OF THE STATISTICAL PHYSICS OF LIQUID-CRYSTALLINE ORDERING IN POLYMER SYSTEMS

Despite the fact that the theory of liquid-crystalline polymers has begun to develop rapidly relatively recently, the number of studies in this field is already very considerable, and we have had no opportunity to take up many of them above. In this section we shall present a brief list of some of these studies.

The tendency to orientational ordering that rigid-chain polymers manifest must have an effect not only in solutions and melts, but also in intramolecular collapse, or the random coil-globule transition. In this case the different segments of a single macromolecule that have approached spatially must become locally ordered in orientation. Although the globule as a whole can be isotropic here, we must consider it liquid-crystalline in its local properties. Such a globule has been called an "intramolecular liquid crystal"; Refs. 10, 141–146 have been devoted to the theoretical study of the corresponding problems.

An interesting connection exists between helix-random coil transitions and nematic ordering of a polymer solution: as a rule the helical regions can be treated as rigid rods, and when their concentration is sufficient, the solution must transform to an anisotropic phase. In turn, the latter must give rise to a jump in the degree of helix formation. These problems have been studied in Refs. 147–153.

The theory of the cholesteric mesophase in polymer systems has been treated in Refs. 154–158, and approaches to the theoretical analysis of the structure of polymeric smectics have been indicated in Refs. 159–161. However, the theory of polymeric, cholesterics and smectics has been developed far less than for nematics.

It is of great interest to study liquid-crystalline elastomers. We note in this regard a recent theoretical study¹⁶² that examined nematic ordering in gels under the action of mechanical stress.

In closing we emphasize that, although many problems of the theory of liquid-crystalline ordering in polymer systems have already been solved, as a whole this field at present still exists in its initial stage of development. Among the most current directions of further study (for details see Ref. 163) are: the rheology of thermotropic polymeric liquid

crystals, the theory of liquid-crystalline elastomers, the statistical physics of the surface in liquid-crystalline polymers, the theory of smectic ordering in polymer systems, and the dynamics of phase transitions in liquid-crystalline polymers.

¹The deviation of the high-temperature corridor from the vertical toward higher concentrations involves the fact that actually the effective segment l is not constant, but depends on the temperature approximately according to the law $l \propto T^{-1/2}$. Therefore the ratio d/l (which determines the order of magnitude of the volume concentration at the transition) increases with increasing temperature. However, the theoretical phase diagrams are constructed for a constant value of l .

²Hereinafter we omit the numerical coefficients of w .

³This region was not distinguished in Ref. 72.

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Translated by M. V. King