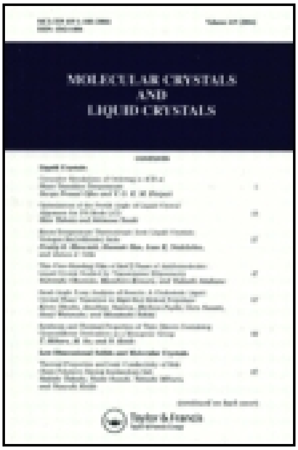

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Theory of Liquid-Crystalline Order in Solutions of Rigid-Chain Macromolecules. Effects of Intramolecular Heterogeneity

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Theory of Liquid-Crystalline Order in Solutions of Rigid-Chain Macromolecules. Effects of Intramolecular Heterogeneity

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Athermal solutions of long polymer chains consisting of two types of freely jointed segments differing in length are considered. Two regimes of the orientational ordering are possible. The regime when short segments are almost completely disordered is characterized by an abruptly narrow biphasic region. Under the regime when both long and short segments are apparently ordered the boundaries of the biphasic region coincide approximately with those of phase transition in solution of homopolymer with segments of weight-average length $\langle x \rangle$.

Keywords: Chain; segment; anisotropy; phase; transition; order

I INTRODUCTION

The molecules of typical mesogenes capable of forming the nematic-crystalline (LC) phase are known to contain stiff extended nuclei and flexible aliphatic parts.[1] The monomer units of polymers forming liquid crystals are characterized by the same type of chemical structure.[2] Consequently, a theoretical investigation of the formation of the LC state in systems with a predetermined distribution of intramolecular flexibility is topical.

The present paper deals with the thermodynamics of athermal solutions of long polymer chains consisting of two types of freely jointed segments differing in length. The main relationships of phase separation and the characteristics of an anisotropic solution are considered.

In an athermal solution, all interactions in system reduce to steric interactions between segments.[3,4] In contrast, in thermotropic systems to which the mesogenes of the type considered here mainly belong, the anisotropy of mutual attraction of mesogenic groups (Maier-Saupe molecular field[5]) also plays an important role. However, as has been shown in Reference 6, when the geometric anisotropy is very pronounced, it acquires the determining significance in the formation of the LC state.

This paper has the following sections. Section II contains the equations for the determination of the boundaries of phase separation obtained in the framework of the lattice model.[4,7–10] Section III considers typical phase diagrams for polymer solutions calculated on the basis of these equations.[10] The results make it possible to introduce the concept of two regimes of orientational order in anisotropic solutions of macromolecules containing segments of different lengths (Section IV), and to investigate the phase separations in these regimes (Sections V, VI).

II MODEL AND METHOD

Let each dissolved molecule contain n_x freely jointed cylindrical segments of the same diameter. The dimensionless length x is equal to the number of units in a segment or to the asymmetry parameter of the segment, i.e. the ratio of its length to diameter. The complete number of units in the macromolecule is $\Sigma_x xn_x$.

In order to describe the solution of macromolecules, the Flory lattice model[4] will be used, its later modifications[7–10] will be taken into account. A detailed calculation of free energy and the conditions of the phase equilibrium of the system considered has been reported in Reference 10. Here the results of Reference 10 will be briefly adduced.

A segment oriented by the angle Ψ to the axis of the nematic order retains the freedom of rotation with respect to this axis. The orientation with respect to the axis is determined by the value of y equal to the averaged projection of the segment on the plane normal to this axis (Figure 1).

$$y = \frac{4}{\pi} x \sin \Psi \tag{1}$$

The Flory lattice model assumes all possible orientations of segments with respect to the axis of the nematic order as a result of the division of segments into subparticles parallel to the axis (Figure 1). In an isotropic solution in which all orientations are equally probably, $\langle \sin \Psi \rangle = \pi/4$, and the mean value of y for a segment of length x is $y_x = x$.

The equilibrium values of y_x in an anisotropic solution are determined by the minimization of the free energy of the solution with respect to y. This gives the equation[7,10]

$$y_x = \frac{4}{\pi} x \frac{f_2(x)}{f_1(x)} \tag{2}$$

where

$$f_i(x) = \int_0^{\pi/2} \sin^i \Psi \exp(-\alpha_x \sin \Psi) \alpha\Psi, \tag{3}$$

$$\alpha_x = -\frac{4}{\pi} x \ln[1 - v_2(1 - \bar{y}/\bar{x})], \tag{4}$$

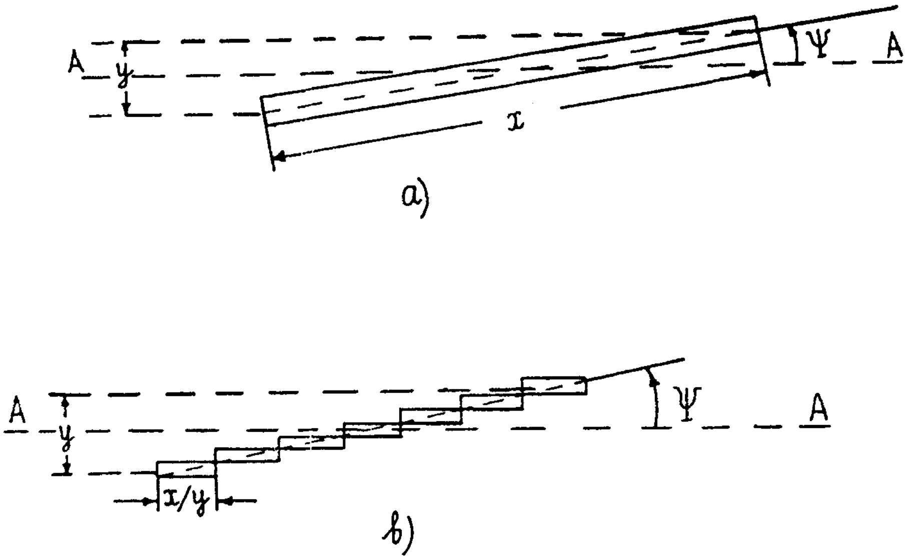

FIGURE 1 a) Segment oriented at angle Ψ to the axis of nematic order AA; b) Its representation as y subsegments, each parallel to the axis AA.

v_2 is the volume fraction of the dissolved polymer and $\bar{x} = \Sigma_x x n_x / \Sigma_x n_x$ and $\bar{y} = \Sigma_x y_x n_x / \Sigma_x n_x$ are the number-average values of the length and the parameter of segment orientation.

It is noteworthy that Equations (2)–(4) are valid for any solution of rodlike particles regardless of their inclusion in the chain as freely jointed segments.

The next step of a standard procedure for the determination of equilibrium between the phases is the calculation and the equating of chemical potential of each component (molecules of the solvent and the solute) in the isotropic and anisotropic phases. As a result, a system of equations for determination of phase boundaries is obtained

$$\begin{cases} \ln\left(\dfrac{1 - v_2'}{1 - v_2}\right) = \ln[1 - v_2'(1 - \bar{y}/\bar{x})] - \dfrac{\sum_x n_x \ln f_1(x)}{\sum_x x n_x} \\[2ex] \ln\left(\dfrac{1 - v_2'}{1 - v_2}\right) = v_2 - v_2' \cdot \dfrac{\bar{y}}{\bar{x}} + \ln[1 - v_2'(1 - \bar{y}/\bar{x})] \end{cases} \qquad (5)$$

where v_2 and v_2' are the volume fractions of solute at the boundary (anisotropic phase is shaded). Equations (5) are written for a solution of long chain molecules, i.e. at $\Sigma_x n_x >> 1$.

III TERNARY DIAGRAMS

Figures 2 and 3 show the results[10] (see also Reference 12) of numerical calculations of phase separation and the parameters of orientational order at anisotropic boundary carried out according to Equations (2)–(5). The case is considered in which each chain contains two types of segments: n_a of length x_a and n_b of length x_b.

The results are shown in Figure 2 in the form of ternary diagrams. In the diagram, the set of the states of solution with a certain chemical composition (predetermined n_a and n_b values) corresponds to a straight line starting from the apex and dividing the base in the ratio $x_b n_b : x_a n_a = v_b : v_a$. The displacement along the straight line from the apex to the base is the increase in solution concentration $v_2 = v_a + v_b$. The left-hand side of the triangle corresponds to a solution of chains consisting of segments $x_a (n_b = v_b = 0)$, and the right-hand side corresponds to that consisting of $x_b (n_a = v_a = 0)$. For comparison, the broken lines in Figure 2 show the phase diagrams for solutions of rodlike molecules of length x_a and x_b.[11]

It is clear from Figure 2 that ternary diagrams for solutions of a mixture of rods and for those of polymer molecules in which rods of different lengths are included in a single chain as segments, differ greatly. In the case of solutions of mixtures, a broad two-phase region occupies a considerable part of the diagram. The coexisting solutions are enriched with one of the components: isotropic and anisotropic solutions are enriched with short and long rods, respectively. In this case in the narrow range of the existence of the anisotropic phase, we have $y_a \simeq y_b$.[11]

If the heterogeneity is of the intra- and not of the intermolecular character, the redistribution of segments between the phases is impossible. As it has been shown in Reference 10, in this case the character of ternary diagrams is determined by ratio of x_a, x_b and $x_{\min}$ where $x_{\min}$ is the minimum value of the length of the mesogenic rod capable of forming the anisotropic phase in an athermal system. The Flory lattice model gives the value of $x_{\min} \simeq 6.7$.[7]

Figures 2a and 2b (solid lines) show the diagrams for typical limiting cases: a) $x_a > x_{\min} > x_b$ and b) $x_a > x_b > x_{\min}$ at $x_b/x_a > 0.2$. In the case a) only long segments are mesogenic and in case b) both long and short segments are mesogenic. It is clear that the diagrams in Figures 2a and 2b differ greatly: the width of the two-phase region in Figure 2b is approximately constant and that in Figure 2a becomes abruptly narrow and disappears virtually completely. The diagram in Figure 2c (solid line) refers to the intermediate case c): $x_a > x_b > x_{\min}$ at $x_b/x_a <$ 0.2 and, excluding the dashed region, may be represented as a combination of Figure 2a (the left-hand part of Figure 2c) and Figure 2b (the right-hand part of Figure 2c).

The different types of orientational order of anisotropic solutions near the boundary of phase separation (Figure 3a–c) are associated with characters of phase transitions in polymer solutions with different compositions (Figure 2a–c). In case a) only long mesogenic segments are markedly oriented at the boundary of the anisotropic phase (Figure 3a). For these segments we have $y_a < x_a$. Short segments near the boundary are virtually unoriented: $y_b \simeq x_b < y_a$.

In case b) an approximate equality $y_a \simeq y_b$ (Figure 3b) is valid along the entire boundary of the anisotropic solution. The intermediate case c) may be represented

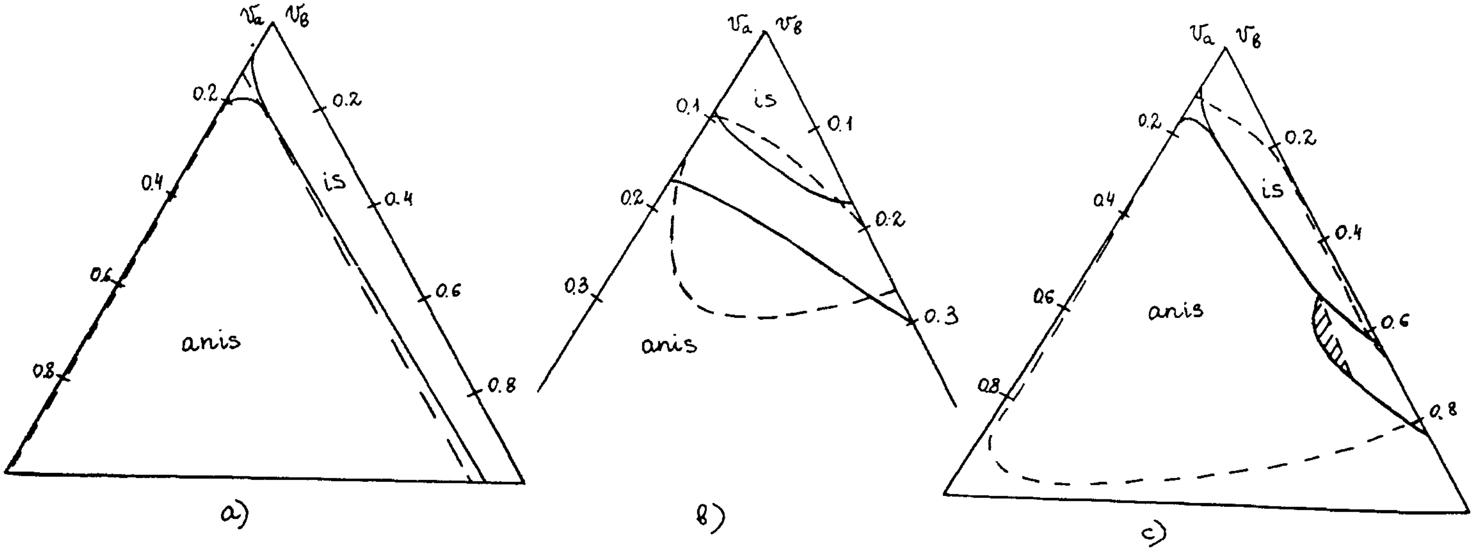

FIGURE 2 Ternary diagrams for the solutions of chains consisting of the segments x_a and x_b: a) $x_a > x_{\min} > x_b$; b) $x_a > x_b > x_{\min}$, $x_b/x_a > 0.2$; c) $x_a > x_b > x_{\min}$, $x_b/x_a < 0.2$. Dashed curves represent ternary diagrams for the solutions of rodlike particles of the same lengths.

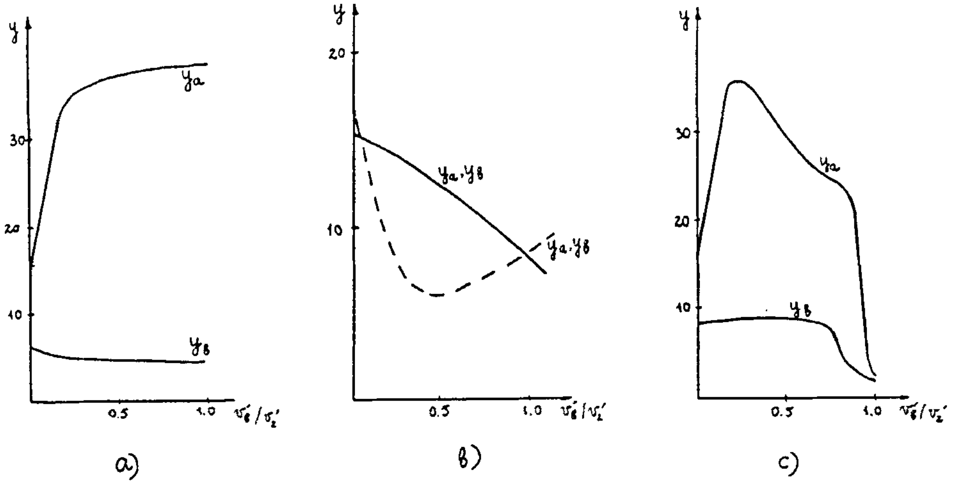

FIGURE 3 Dependences of the parameters y_x at the anisotropic boundary on the volume fraction of short segments v_b/v_2: a) $x_a > x_{\min} > x_b$; b) $x_a > x_b > x_{\min}$, $x_b/x_a > 0.2$ (corresponding dependences for the solution of rodlike particles are represented by dashed curves); c) $x_a > x_b > x_{\min}$, $x_b/x_a < 0.2$.

as a combination of the results of a) and b) (Figure 2a–c). For the left-hand side of the boundary of the anisotropic region we have, just as in case a): $y_a < x_a$, $y_b \simeq x_b < y_a$, i.e., only long segments are noticeably oriented. For the right-hand side, just as in case b), we have $y_a \simeq y_b < x_a, x_b$, i.e., both types of segments are appreciably oriented. It should be noted that the orientation of short segments is also observed in case a). However, it exists only in the range of high concentrations far from the boundary of anisotropic phase (Figure 4). The detailed analysis of ternary diagram in the intermediate case c): $x_a > x_b > x_{\min}$ at $x_b/x_a < 0.2$ shows[12] that appreciable ordering of short segments may occur as phase transition with biphasic region (dashed region in ternary diagram, Figure 2c).

Now we will pass from the general numerical considerations to a more detailed analysis by using various approximations based on the results of numerical calculations. As before, the solutions of polymers with a bimodel lengths distribution of freely jointed segments will be considered.

IV ORIENTATIONAL ORDER IN ANISOTROPIC SOLUTIONS

It is clear from Figures 3 and 4 that the segments of polymer chains in anisotropic solutions may exhibit different degrees of order. Let us consider the parameters of orientational order, Equations (2)–(4), in the limits of highly ordered and weakly ordered (or disordered) segments.

At $\alpha_x >> \pi/2$ (highly ordered segments), the functions $f_i(x)$ in Equation (3) may be represented in the form of rapidly converging series.[7]

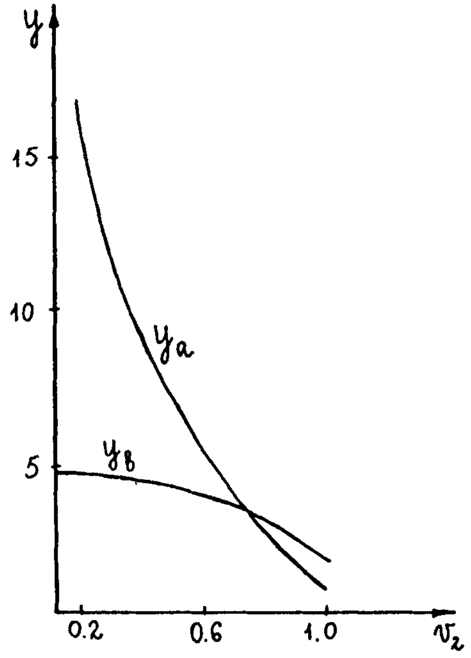

FIGURE 4 Dependences of y_x on the volume fraction of polymer v_2 in the case $x_a = 80$, $x_b = 5$ and $v_a/v_2 = 1/2$.

$$f_1(x) = \frac{1}{\alpha_x^2} + \frac{3}{\alpha_x^4} + \dots$$

$$f_2(x) = \frac{2}{\alpha_x^3} + \frac{1}{\alpha_x^5} + \dots \tag{6}$$

Then we have from Equations (2) and (4)

$$y_x \simeq \frac{8}{\pi}\frac{x}{\alpha_x}\left(1 + \frac{3}{\alpha_x^2}\right) \simeq -\frac{2}{\ln[1 - v_2(1 - \bar{y}/\bar{x})]} \tag{7}$$

which corresponds to the approximation used in Reference 4.

At $\alpha_x < 1$ (weakly ordered segments), the exponents in Equation (3) may be expanded into a series; then

$$f_1(x) = 1 - \frac{\pi}{4}\alpha_x + \dots$$

$$f_2(x) = \frac{\pi}{4} - \frac{2}{3}\alpha_x + \dots \tag{8}$$

We have from Equations (2) and (4)

$$y_x = x(1 - \delta), \tag{9}$$

where

$$\delta = \frac{4}{\pi} C\alpha_x = -Cx \ln[1 - v_2(1 - \bar{y}/\bar{x})] \tag{10}$$

and

$$C = \frac{32}{3\pi^2} - 1 \simeq 0.08.$$

Let us now consider the limiting orientational states of the anisotropic solution of macromolecules containing segments x_a and x_b.

REGIME I: $\alpha_a >> 1$, $\alpha_b < 1$. According to Equation (7), (9) and (10), we have

$$y_a \simeq -\frac{2}{\ln[1 - v_a(1 - y_a/x_a)]} \tag{11}$$

$$y_b \simeq x_b(1 - \delta) \tag{12}$$

In this case the indispensable condition $x_b \leqslant y_a$ should be fulfilled; this gives $\delta < 0.16$.

REGIME II: α_a, $\alpha_b >> 1$. Equation (7) gives

$$y_a \simeq y_b = -\frac{2}{\ln[1 - v_2(1 - \bar{y}/\bar{x})]} \tag{13}$$

The obtained results (Equations (11)–(13)) make it possible to draw some important conclusions about the orientational order of segments:

1. In an anisotropic solution all segments, both long and short, are characterized by a certain orientational order $y_a/x_a < 1$ and $y_b/x_b < 1$. Although the degree of order of short segments may be relatively low ($\delta << 1$), it always differs from zero. The order of short segments is not in the least related to their mesogeneity, i.e.

to the ratio of x_b to $x_{\min}$. Only completely isotropic short segments with $x_b = 1$ do not acquire the orientational order in the anisotropic phase.

2. Under regime I, which in principle can exist at a great difference between lengths of segments x_a and x_b, the degree of orientational order of long segments is in the first approximation the function of the concentration and length of these segments alone (Equations (11), (12)), see also Reference 9. Short segments are virtually unoriented and play the role of a quasi-isotropic bonded solvent.

3. In contrast, under regime II, short and long segments have approximately equal mean transverse projections y. The value of y is determined by the overall characteristics: the mean segment length $\bar{x}$ and the complete polymer concentration in solution v_2.

4. It can be seen from Equation (11) that with increasing polymer concentration v_2, the value of y_a decreases. At any given ratio of segment lengths, $x_a > x_b > 1$, beginning from a certain polymer concentration, inequality $x_b \leqslant y_a$ is no longer obeyed. Moreover, the degree of orientational order of short segments will increase, their anisotropy will be clearly manifested (at $x_b > 1$) and the system will pass to regime II.

5. In the region of the crossover between regimes I and II, the approximations used in Equations (6) and (8) are not valid, and initial Equations (2)–(5) should be used. This refers to all cases in which the segments in an anisotropic solution exhibit an intermediate degree of orientation, References 7, 10, and 13. Numerical calculations of phase separation have been carried out according to Equations (2)–(5) in References 10 and 12; the transition between regimes I and II is the phase transition if the region of the crossover (shaded region in the ternary diagram, Figure 2c) adjoins the region of phase transition from an isotropic solution to an anisotropic one, Reference 12; in the other cases the transition between regimes I and II is smooth and does not have the phase character.

6. All the considerations in this section deal only with the orientational structure of an anisotropic solution at a given concentration and refer to equal extents to a solution of polymer chains consisting of freely-jointed segments x_a and x_b and to that of a mixture of rods x_a and x_b. These cases differ, however, in the thermodynamic stability of solutions. For a solution of a mixture of rods, the concentration range corresponding to regime I is always located inside a broad two-phase region. The transition of the solution to the anisotropic phase occurs under regime II. The bonding of segments into a chain leads to the involvement of short segments in the anisotropic phase and hence to the appearance of conditions for regime I in the range of phase transition.

V PHASE SEPARATION. ANISOTROPIC SOLUTION UNDER REGIME I

Let us consider Equations (5) for the conditions of phase equilibrium. Under regime I, the value of y_a is determined by Equation (11) and $y_b \simeq x_b$.

Let us introduce the overall excluded volume of long segments in the coexisting phases $\vartheta_a = x_a v_a$, $\vartheta_a' = x_a v_a'$ and denote $\bar{\vartheta}_a = (\vartheta_a' + \vartheta_a)/2$, $\Delta\vartheta_a = (\vartheta_a' - \vartheta_a)/2$. Let $\omega_a = \vartheta_a/(\vartheta_a + \vartheta_b) = \vartheta_a'/(\vartheta_a' + \vartheta_b')$ be the fraction of monomers included in long segments and $F_a = y_a/x_a$ be the parameter of their disorientation at the boundary of the anisotropic phase.

We assume for simplicity that $x_a >> 1$. Then in the range of transition v_a, $v_a' <<$ 1 and $\ln[1 - v_a(1 - y_a/x_a)]$ in Equations (5) and (11) may be expanded in series (virial expansion, see also Reference 3); Equations (5) and (11) are rearranged to give

$$\bar{\vartheta}_a = \frac{1}{F_a(1 - F_a \ln 8/\pi F_a)} \tag{13'}$$

$$\omega_a^2 = F_a^2 \bar{\vartheta}_a \Delta\vartheta_a \tag{14}$$

$$\vartheta_a' = \frac{2}{F_a(1 - F_a)} \tag{15}$$

It is clear from Equations (13')–(15) that the characteristics of phase separation $\bar{\vartheta}_a$, $\Delta\vartheta_a$ and F_a (containing the value of x_a) are determined only by the monomer content in long segments ω_a but are independent of the length of short segments x_b quasi-isotropic under regime I.

Figure 5 shows the characteristics of phase transition under regime I plotted according to Equations (13')–(15) as functions of the chemical composition ω_a of the dissolved polymer (all values are referred to the corresponding values for a solution of a homopolymer consisting of segments x_a, i.e. $\omega_a = 1$).

When short segments are added to the polymer chain (decreases), the middle of the biphasic region $\bar{\vartheta}_a$ is weakly displaced towards lower concentrations of long segments in solution. The value of this displacement does not exceed ~12%. The boundary of the anisotropic phase ϑ_a' is displaced to a greater extent (up to ~30%) in the same direction. This displacement leads to a decrease of the orientational order of long segments: the value of $F_a = y_a/x_a$ increases from $F_{a_1} = 0.19$ to $F_{a_0} = 0.31$. The width of the biphasic region depends on the chemical composition of chains ω_a to the greatest extent: with decreasing ω_a the value of $\Delta\vartheta_a/\Delta\vartheta_a(\omega_a = 1)$ decreases sharply (at $0.1 < \omega_a \lesssim 0.7$ approximately as ω_a^4 and then slightly weaker). As example, when 15% and 50% of units are included in the short segments, $\Delta\vartheta_a$ decreases twice and by one order of magnitude, respectively. However, $\Delta\vartheta_a$ remains finite up to $\omega_a \rightarrow 0$, and the transition to the anisotropic phase retains the character of the first-order phase transition.

VI PHASE SEPARATION. ANISOTROPIC SOLUTION UNDER REGIME II

Under regime II we have $y_a \simeq y_b = y$ (Equation (13)), and the value of y is determined by the overall concentration of solution $v_2 = v_a + v_b$ and the number-average segment length $\bar{x}$. Hence, it is appropriate to take as the reduced values $\vartheta_2 = v_2\bar{x}$, $\vartheta_2' = v_2'\bar{x}$ and $F = y/\bar{x}$ (it should be noted that the number-average value of x is directly related to the weight-average value, denoted by $\langle x \rangle$: $1/\bar{x} = \langle 1/x \rangle$;

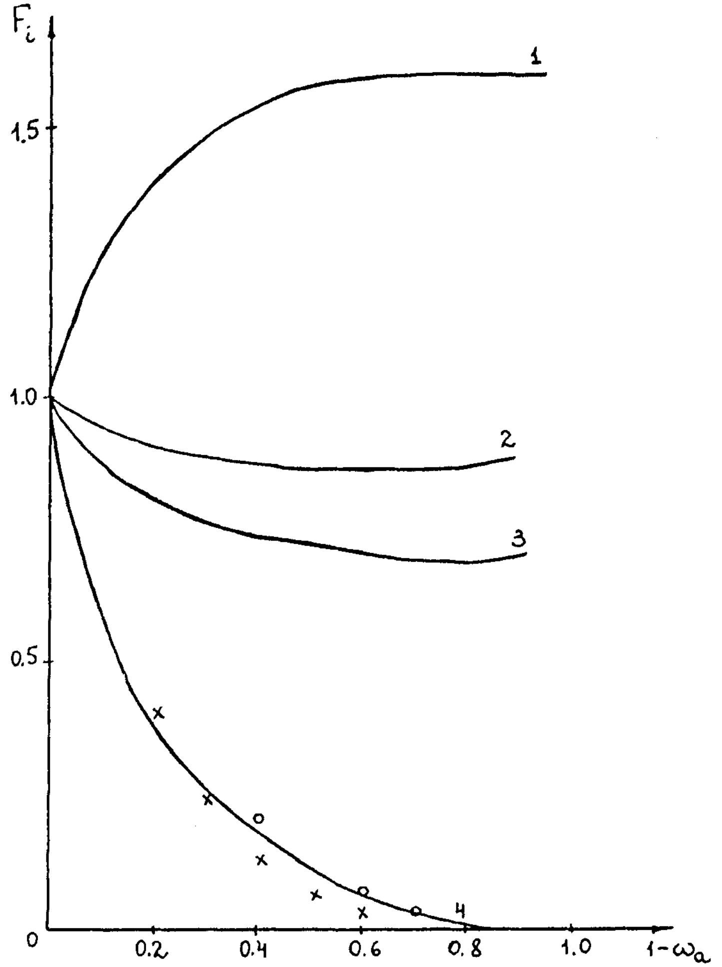

FIGURE 5 Characteristics of phase transition under regime I in dependence on the chemical composition ω_a of the dissolved polymer (all values are referred to the corresponding values for a solution of homopolymer consisting of segments x_a, i.e. $\omega_a = 1$): curve 1 – $(y/x)/(y/x, \omega_a = 1)$; curve 2 – $\bar{\vartheta}_a/(\bar{\vartheta}_a, \omega_a = 1)$; curve 3 – $\vartheta_a'/(\vartheta_a', \omega_a = 1)$; curve 4 – $\Delta\vartheta_a/(\Delta\vartheta_a, \omega_a = 1)$, functions ω_a^4 and ω_a^3 are shown by x and o correspondingly.

so the reduced values may also be treated as $F = y\langle 1/x \rangle$, etc.). Assuming that v_2, $v_2' << 1$ the expansion of $\ln[1 - v_2(1 - \bar{y}/\bar{x})]$ in Equations (5) and (13) gives

$$\bar{\vartheta}_2 = \frac{1}{F\left[1 -. F \ln\left(\frac{8}{\pi F} \cdot \frac{\bar{x}_G}{\bar{x}}\right)\right]} \tag{16}$$

$$F^2 \bar{\vartheta}_2 \Delta\vartheta_2 = 1 \tag{17}$$

$$\vartheta_2' = \frac{2}{F(1 - F)} \tag{18}$$

where $\bar{x}_G = x_a^{n_a/(n_a+n_b)} \cdot x_b^{n_b/(n_a+n_b)}$ is the geometric mean length of segments. Hence, Equations (16)–(18) are not single-parameter equations with the parameter $\bar{x}$ contained in the reduced values of ϑ_2, ϑ_2' and F. The conditions of phase separation also depend on the second parameter of the chain structure: the $\bar{x}_G/\bar{x}$ ratio.

The value of $\bar{h}^2/L$ where $\bar{h}^2$ is the mean square end-to-end distance and L is the contour length of the chain is usually considered as the characteristic of polymer chain rigidity. In our model, $\bar{h}^2 = n_a x_a^2 + n_b x_b^2$, $L = n_a x_a + n_b x_b$ and $\bar{h}^2/L = \langle x \rangle$.

Figure 6 shows "ternary" diagrams calculated for homopolymers with segment lengths $\langle x \rangle$ and $\bar{x}$ depending on composition ω_a of bimodel copolymer. For a homopolymer with a segment length $\bar{x}$, the boundaries in "ternary" diagrams Figure 6 are noticeably curvilinear with strong downward curvature. For a homopolymer with a segment length $\langle x \rangle$ the boundaries of two-phase region in Figure 6 are virtually linear. The analysis of Equations (16)–(18) shows that the existence of the second parameter $\bar{x}_G/\bar{x}$ apart from $\bar{x}$ leads to a considerable (although incomplete) increase in the rectilinearity of phase equilibrium curves. The boundaries of biphasic region are found to coincide approximately with those calculated for a homopolymer consisting of segments $\langle x \rangle$, although complete reduction to one parameter does not occur (Figures 2b and 6). Thus, in the case $x_a = 80$ and $x_b = 10$, the diagram for homopolymers consisting of segments $\langle x \rangle$ does not exhibit a characteristic narrowing of the biphasic region (the result of a precise calculation, Figure 2c).

The solution of approximate Equations (16)–(18) for a homopolymer gives the values of $\vartheta_2' \simeq 13.4$ and $\vartheta_2 \simeq 10.5$ independent of segment length x. Figure 7a shows the results of numerical calculations of ϑ_2' and ϑ_2 according to Equations (5) for homopolymers; it is clear that approximate Equations (16)–(18) may be

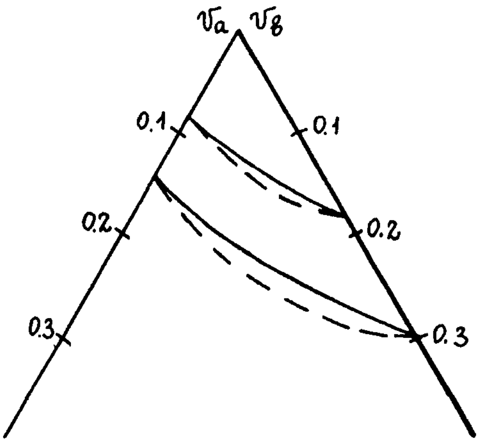

FIGURE 6 Ternary diagrams for homopolymers with segment lengths $\langle x \rangle$ (solid curves) and $\bar{x}$ (dashed curves).

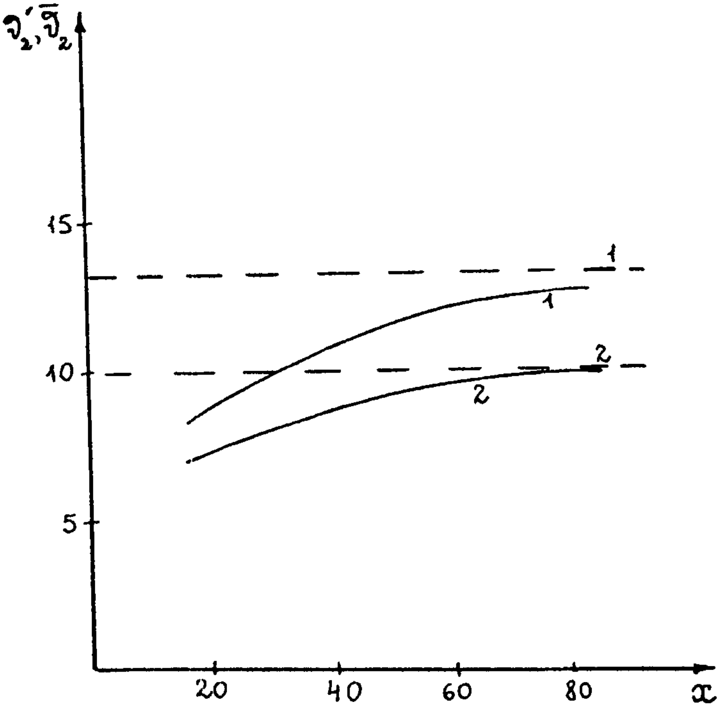

FIGURE 7a Dependences of ϑ_2' (curves 1) and $\bar{\vartheta}_2$ (curves 2) on the segment length x for the solution of homopolymer: results of numerical calculations (solid lines) and of approximate consideration (dashed lines).

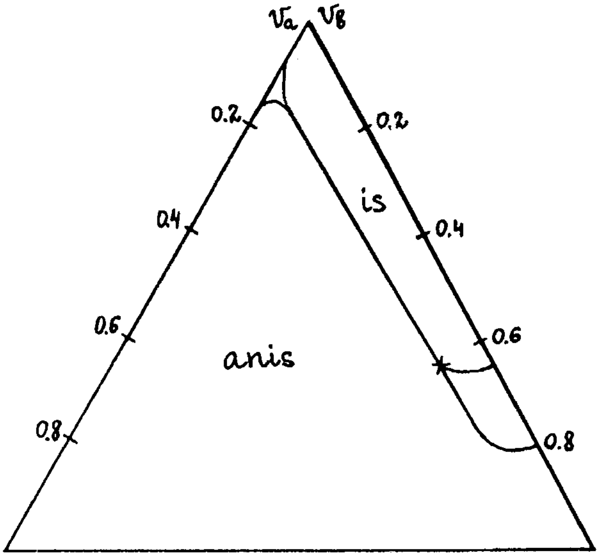

FIGURE 7b Ternary diagram for the solutions of chains ($x_a = 80, x_b = 10$) as a result of the crossover of the diagram under regime 1 and the diagram for homopolymer of segments; x — the crossover point ω_{a0}.

used only at relatively large values of $x (x \gtrsim 40)$. Hence, the phase diagram for the intermediate case $x_{\min} < x_b < y_a(\omega_a = 1)$ at $x_b \lesssim 40$ may be represented as a result of the crossover of the diagram under regime I at $\omega_a > \omega_{a0}$ and the diagram for homopolymer consisting of segments of length $\langle x \rangle$ at $\omega_a < \omega_{a0}$. The crossover point of diagrams ω_{a0} is determined from the condition of equality of the volume fraction of the polymer at the boundary of the isotropic phase v_2. The diagram obtained for the case $x_a = 80$ and $x_b = 10$ is shown in Figure 7b. It is in fairly good agreement with the results of precise calculations (Figure 2c), except of the dashed region in Figure 2c.

VII DISCUSSION

In this paper we have shown that two regimes of the anisotropic phase of an athermal solution of macromolecules containing segments x_a and $x_b < x_a$ are possible. Under regime I which may be called the regime of "bonded quasi-isotropic solvent," short segments x_b are almost completely disordered. As a result, the chemical potentials of macromolecules in isotropic and anisotropic solutions approach each other, which in turn leads to a sharp decrease in the width of the biphasic region in the regime of bonded solvent.

Under regime II, the regime of the "common tube," the anisotropy of both long and short segments becomes apparent; all segments are characterized by approximately equal transverse projections y. The scheme of segment orientation is shown in Figure 8.

In conclusion several points should also be mentioned.

1. *Order parameter.* Under both regimes, the values of the order parameters for segments of two types S_a and S_b ($S = (3 \cos^2 \Psi - 1)/2$, Ψ is the orientation angle with respect to the nematic axis) always differ. As follows from Equation (1), we have $S_a > S_b$. Under regime I, $y_b \simeq x_b$ and $S_b \simeq 0$. Under regime II, $y_a \simeq y_b$. However, $y_a/x_a < y_b/x_b$ so that in this case $S_a > S_b$. Hence, the average order parameter S of freely jointed segments at boundary of the anisotropic region is always lower for a copolymer than for a homopolymer.

2. *Low molecular weight mesogenes.* In this paper the solutions of polymer chains were considered. The results may be extended to the solutions of "small" molecules containing only one or several long segments x_a and one or several segments x_a. (In this case, ω_a of course cannot be considered as an independent quantity.)

In the case of a small segment number in the chain, Equations (5) contain additional terms in which the entropy of segment mixing is taken into account.[8,10] As has been shown in Reference 8, these terms affect only slightly the conditions of phase equilibrium in the solution of homopolymer consisting of segments of equal lengths as compared to the solution of rods of the same length. The boundaries of the biphasic region are displaced by no more than ~3% for v_2 and ~10% for v_2'. This conclusion is also valid for the case of "small" molecules.

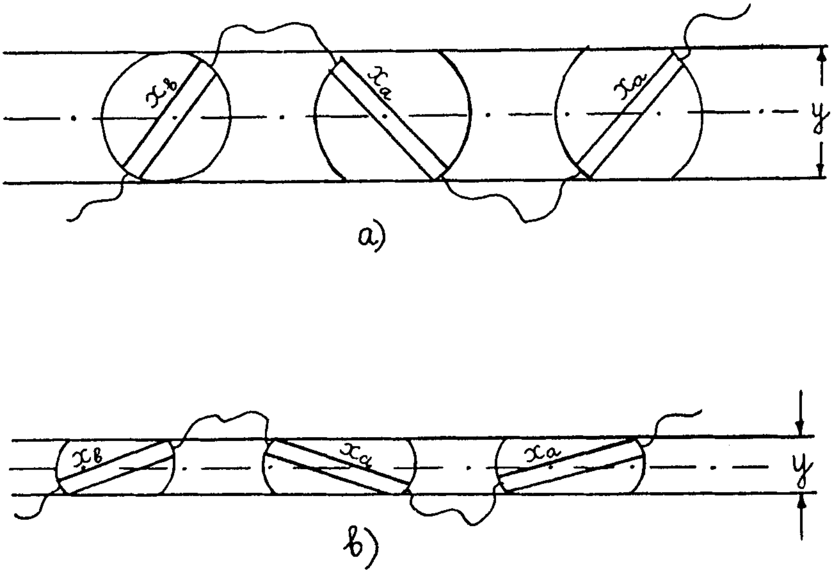

FIGURE 8 The orientations of segments: a) regime I (regime of the "bonded quasi-isotropic solvent"); b) regime II ("common tube").

Hence, in solutions of "small" molecules two regimes of the anisotropic phase are also possible. The transition to regime I, that of the "bonded quasi-isotropic solvent," should be characterized by a very narrow biphasic region.

It is noteworthy that in the thermotropic phase transition of low molecular weight compounds, the density of the system undergoes little change $\Delta\rho = \rho_{\text{anis}} - \rho_{\text{is}}$ (ρ is the number of particles in unit volume) in the transition range: $\Delta\rho/\bar{\rho} \sim 0.01$.[14] Several attempts to treat these data in the framework of athermal solution models have been made (point 4). The value of $\Delta\rho/\bar{\rho}$ is similar to $(v_2' - v_2)/\bar{v}_2$. In particular, it has been shown in Reference 15, that the insertion of a flexible tail into a stiff molecule always leads to a decrease in $(v_2' - v_2)/\bar{v}_2$. The calculation in Reference 15 has been based on the lattice model in Di Marzio's scheme[16] in which a discrete set of orientations of rigid segments (along the three axes of a simple cubic lattice) is assumed. The agreement between our conclusions about a drastic decrease in the width of the two-phase region under regime I and the data in Reference 15 shows that these results do not depend on the choice of the model.

3. *Intra- and intermolecular heterogeneity.* The results obtained show that the structure of the anisotropic athermal solution on the phase boundary is profoundly affected by the type of heterogeneity of the solute.

It should also be emphasized that the effect of the type of intramolecular heterogeneity, i.e. of the distribution of flexible joints along the chain, upon the curves of phase separation is a manifestation of a more general effect, that of the mechanism and not only that of chain flexibility. In the case considered here, it is just the change in the distribution of flexible joints at a fixed flexibility (fixed value of $\bar{h}^2/L = \langle x \rangle$) that may lead to a change in the regime of the anisotropic phase. Moreover, it follows from the considerations in section VI that the distribution of joints affects the position of the boundaries of phase separation even within regime II alone.

It is noteworthy that the existence of two regimes in the anisotropic phase for polymer chains consisting of rigid segments with semiflexible spacers has also been considered in Reference 17. The rotational isometric mechanism of orientational order of semiflexible spacer similar to that considered in Flory's paper[18] (see also References 8 and 9) leads to the existence of the phase transition separating these regimes.

4. *Temperature of thermotropic transition*. A scheme has been proposed in Reference 19 which makes it possible to determine the relative temperature of the thermotropic phase transition on the basis of the calculation of characteristics of phase transition in an athermal solution. The scheme is based on the introduction of a dimensionless parameter

$$\varphi = \frac{PV_0}{kT} = \frac{1}{kT}\left(\frac{\partial F}{\partial n_0}\right)_{T,\{n_x\}} \tag{19}$$

where F is Helmholtz free energy, n_0 is the total number of places on the lattice, V_0 is the volume of one cell, $\{n_x\}$ is the number of all dissolved particles, $(n_0 - \{n_x\})$ is the number of solvent molecules, P is the pressure and T is the solution temperature.

At an equilibrium orientational distribution φ is the chemical potential of the solvent

$$\varphi = -\frac{(\mu_1 - \mu_1^0)}{kT} \tag{20}$$

The relative temperature, T^*, of the phase transition from the anisotropic to isotropic state ($A - I$) at P = const in a heterogeneous systems (systems of rods of lengths x_a and x_b or of chains consisting of freely jointed segments of the same lengths) is given by

$$T^* = \frac{T_{A-I}}{T_{A-I}(\omega_a = 1)} = \frac{\varphi_{A-I}(\omega_a = 1)}{\varphi_{A-I}} \tag{21}$$

Figure 9 shows the plots of the temperature T^* vs ω_a for systems with intra- and intermolecular heterogeneity ($x_a = 80$ and $x_b = 40, 10$). It is clear that when a mixture with a fixed composition is heated (ω_a = const) above the melting temperature, T_{melt}, in the case of intermolecular heterogeneity the isotropic phase is formed, and at $T = T_{\text{is}}$ the anisotropic phase disappears. A broad temperature range of phase coexistence is the result of the redistribution of rods according to phases. In the case of intramolecular heterogeneity of a solution with a fixed

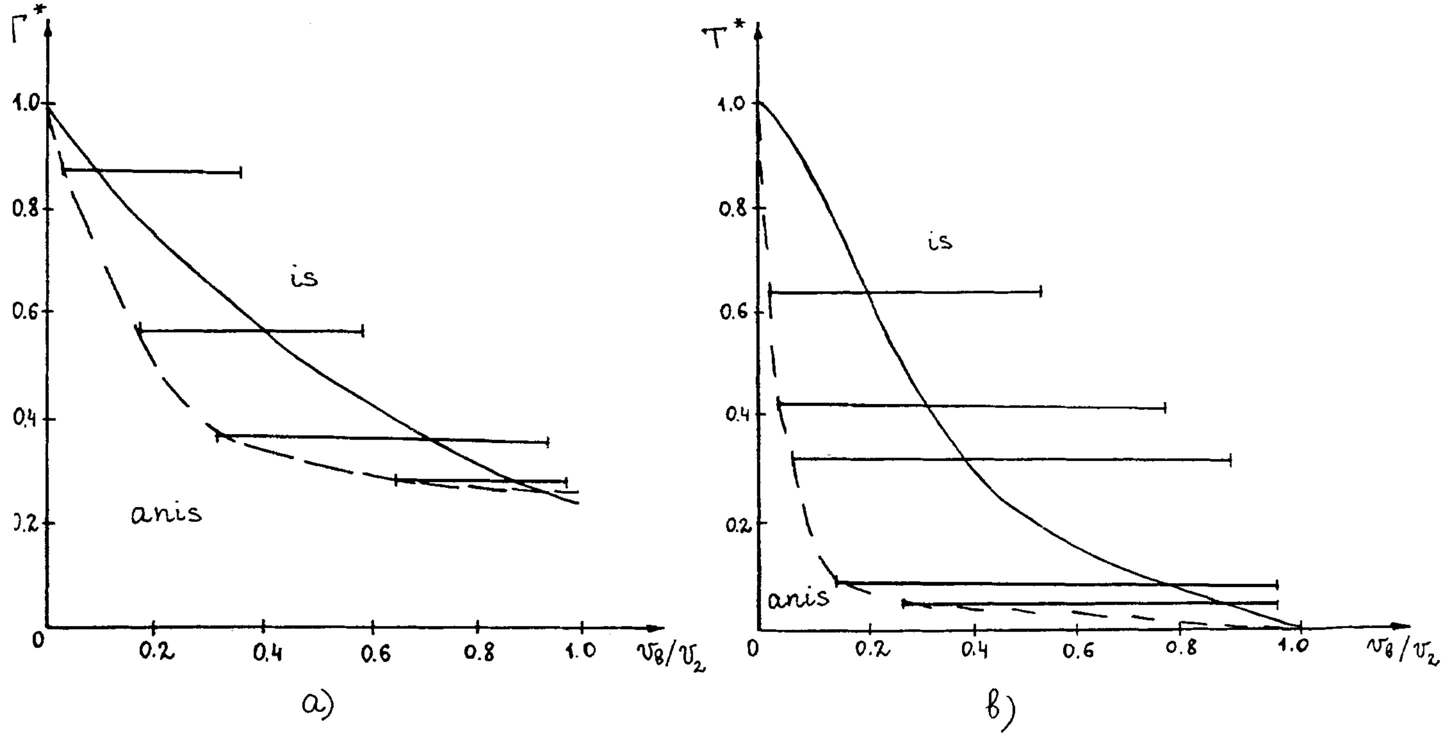

FIGURE 9 The relative temperature T^* of the phase transition vs ω_a for solutions of chains (solid lines) and rods (anisotropic boundary is shown by dashed line, the points of phase transition are conjugated by the straight lines): a) $x_a = 80$, $x_b = 40$; b) $x_a = 80$, $x_b = 10$.

composition (ω_a = const), the transition from the anisotropic to the isotropic phase occurs at $T_{\text{melt}} = T_{\text{is}}$ because the segments cannot be redistributed.

The temperature dependences obtained for systems of rigid rods of different lengths are in reasonable agreement with the results in References 19 and 20 in which the calculations have been based on the lattice model in Di Marzio's scheme.[16] The agreement between the results of theoretical calculations using different physical models and the qualitatively correct reproduction of experimental data (see References 19 and 20) indicate that these results do not depend on the choice of a specific model but reflect the general properties of systems of rigid particles.

In conclusion it should be emphasized that in this paper solutions of chains consisting of freely jointed segments of a fixed length have been considered. The establishment of the orientational order in these systems occurs only by segmental ordering.[8,9,21] In the general case of chains with statistically distributed segment lengths, another ordering mechanism is possible, which leads to the stretching and orientation of chains as a whole.[17,18]

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