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LIQUID-CRYSTAL STATE IN THE SYSTEM POLYSACCHARIDE–MESOPHASOGENIC SOLVENT

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Data on the influence of vapors of nitromethane — a mesophasogenic solvent, i.e., a solvent forming with a polymer a lyotropic liquid-crystal phase — on the structure of acetate fibers are presented. It has been established that nitromethane in the vaporous state initiates in the polymer matrix orientation processes: induced anisotropy, spontaneous elongation of the fiber (which, in terms of Flory, is considered to be the transition to the nematic phase), as well as the process inverse to the self-elongation discovered for the first time, etc. It has been shown that the realization of both the direct and inverse processes of spontaneous deformation of cellulose acetate in mesophasogenic solvent vapors is associated with the optical asymmetry, i.e., the optical activity of the polysaccharide.

Intensive experimental and theoretical studies of liquid-crystal (LC) polymer systems of synthetic origin, whose macromolecules are characterized by a high rigidity of the chain, date back to the 1950s [1, 2]. Later, the LC state was also revealed for natural polymers, e.g., such as cellulose and its derivatives [3, 4], the conformation of whose macromolecules is far from a rigid rod and is closer to the conformation of a semirigid chain.

Because the melting temperatures are much higher than the temperatures of intensive thermal decomposition, most cellulose derivatives cannot go to the LC state in melts and create only lyotropic LC systems. The formation of mesomorphous solutions of this class of substances is complicated because of the necessity to use high polymer concentrations (over 25 mass %) and in a rather limited range of solvents, in which the LC phase is formed [3–5]. The best studied in this respect are systems based on cellulose ethers: oxypropyl-, oxymethyl-, ethylcellulose, and ethers in such solvents as water, dimethylacetamide, dimethylsulfoxide, acetic, dichloracetic, and formic acids [3, 5]. The series of polymer LC systems based on natural polysaccharides that have received fairly complete and detailed studies includes cellulose esters, in particular, cellulose acetates [4, 6, 7] having in the composition of the macromolecular chain (depending on the degree of etherification of the samples) a different ratio between acetate and hydroxyl groups. It has been established that in the presence of a solvent specifically interacting with the functional groups of the polymer acetic-acid cellulose esters can form systems with phenomena and signs characteristic of the LC state [6–11]. Among such criteria are, for example, the distinguishing features of the rheological behavior of mesomorphous solutions [6–9]. For the solid-like state these are induction of time-independent optical anisotropy in acetate films [7, 10], the phenomenon of spontaneous elongation of fibers of the same nature [11], which according to Flory, directly confirms the transition of the polymer–solvent system to the nematic phase [1, 12], etc.

The effect of spontaneous elongation of fibers and films based on cellulose acetates at higher temperatures in liquid media, e.g., in aqueous solution of phenol or dioxane, is also known from [13–18]. The fact of immediate hydrothermal elongation of the fiber has been ascertained [13–15], the energy has been studied and the self-elongation work has been calculated [16], proofs of natural orientation of macromolecules have been given [17], methods for obtaining thin and high-strength fibers have been proposed [18], etc. Since the elongation described in these papers occurred directly in the solvent medium, where the processes of swelling and partial dissolution can proceed, which is difficult to control, the features of this phenomenon have not been clarified.

We have managed to not only find the conditions for detailed and stage-by-stage observation of the process of spontaneous elongation of the fiber but also investigate the process of polymer–solvent interaction [11]. This, in turn, made it possible to discover new phenomena and mechanisms that have not been reported in the literature before

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[11, 19, 20]. In this paper, we present the results of the investigation of the influence of vapors of the mesophasogenic solvent nitromethane, forming with a polymer a lyotropic LC phase, on the structure of acetate fibers widely manufactured by modern industry.

Experimental. We investigated diacetylcellulose (DAC) fibers with a linear density of 6.7 and 11 tex obtained in the Khimvolokno stock company (Engels) by dry forming. The content of bound acetic acid in the samples was 54.47–54.51%.

The fiber was treated with solvent vapors under isobaric-isothermal conditions (in the temperature range between −15 and +50°C at normal atmospheric pressure) in a sealed vessel 1/5 of whose volume was filled with the solvent. As a sorbate, we used analytically pure nitromethane, d = 1.14 g/cm^3, T_{boil} = 101.2°C. We used nitromethane an — electron-donor, dipolar, aprotic solvent [21], in which cellulose acetates form a lyotropic LC phase [4, 8, 10]. Moreover, nitromethane specifically interacts with the functional groups of cellulose ester, solvating mainly hydroxyl groups [22, 23].

To study the phenomenon of spontaneous deformation, the fiber in a freely stretched state was located horizontally in the vessel at a distance of 4 cm over the liquid surface. This method proved to be more expedient compared to the usual swelling in the solvent medium, since it permits visual observation and evaluation of the self-elongation and makes it possible to break down this process into stages and study it at each stage, interrupting the interaction of vapors at any of them. Moreover, such a method simplifies further investigations of the modified fiber. Measurements of the fiber length were made in the usual way (by means of a rule) and by calibration graphs (calculated according to the model of free fiber sag*). The results obtained visually and by computing methods agreed. The resulting value of the spontaneous elongation was determined from 10 measurements.

Under spontaneous deformation of the fiber we determined the degree of sorption (C_s) of solvent vapors by the fiber by the gravimetric method (weighting accuracy of ±0.0001 g)

$$C_s = \frac{m - m_0}{m_0} \cdot 100\% \,.$$

In the swelling process, we took x-ray photographs of fibers on a DRON-3 diffractometer with Cu–K$_\alpha$ radiation at U = 22 kV and J = 20 mA. The orientation angle φ of the polymer in the fiber was determined by the half-width of the reflex intensity curve.

The thermodeformation characteristics of the starting fibers and those treated in nitromethane vapors were obtained by means of linear dilatometry — by measuring the fiber length with a temperature increase to 300°C. A load that did not exceed 0.1% of the breaking load was applied to the fiber. The heating rate was 2–2.5 deg/min, and the measurement error was 0.1%.

The optical rotary dispersion (ORD) of the solutions of the starting and modified samples were taken on an SPU-E automatic speckle opolarimeter in the range of wavelengths λ = 300–700 nm at a temperature of 20°C. As a solvent, we used chemically pure acetone. The concentration of the investigated solutions was 0.1 g/dl. We used glass thermostated 1-dm-long cells with windows. As a light source, a DRSh-250 high-pressure mercury lamp served. The specific optical rotation was determined by the formula

$$[\alpha]_\lambda^{20^\circ\text{C}} = \frac{100 \cdot (\alpha - \alpha_0)}{lC} \,.$$

The exact concentration was determined by the method of bringing a certain volume of the polymer solution to a constant weight (weighting accuracy of ±0.0001 g). The ORD curve was plotted proceeding from the data of three parallel experiments. The measurement error of rotation angles did not exceed 0.002 deg.

Results and Discussion. It has been established by experiment that the system DAC fiber–nitromethane vapors is characterized by the process of spontaneous elongation, whose value depends on the temperature [11]. As an example, Fig. 1 shows the process of spontaneous elongation for a fiber of linear density 6.7 tex depending on the temperature and time of treatment with mesophasogenic solvent vapors. The largest value of elongation (with respect

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*The program algorithm was developed by S. L. Shmakov.

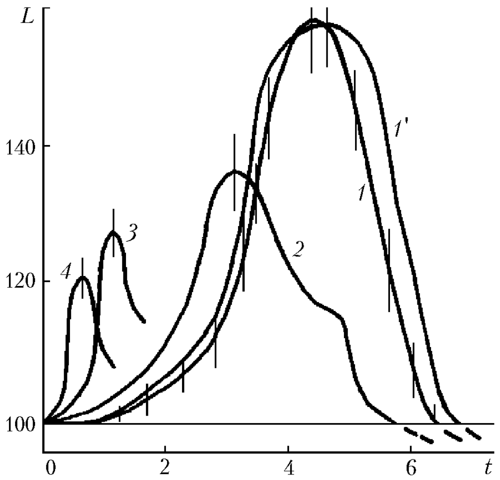
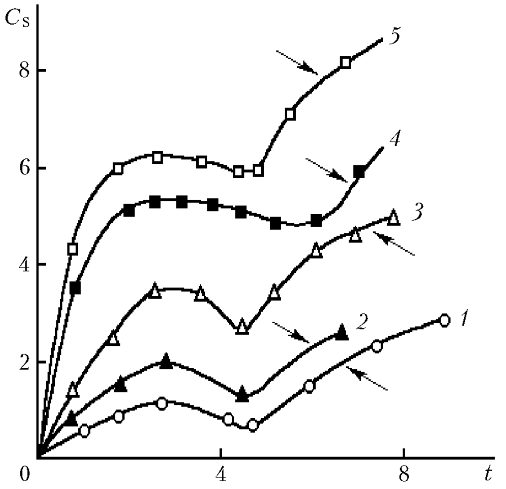


Fig. 1. Kinetics of spontaneous deformation (elongation–contraction) of the acetate fiber (6.7 tex) in nitromethane vapors at various temperatures: 1) 25; 2) 30; 3) 40; 4) 50°C; 1′) fiber with oil at 25°C.

to the initial length taken to be equal to 100%) corresponds to 20–30°C and constitutes 130–160% (curves 1 and 2). The maximum elongation of the fiber is realized within 3.0–4.5 min. The elongation values for fibers with 6.7 and 11 tex are approximately equal. No clear dependence of spontaneous elongation on the linear density within the investigated temperature range has been revealed. Oiling of fibers has no marked effect on the spontaneous elongation either (curve 1′). Elongation of the DAC fiber is observed even at temperatures of 3–5°C. As the temperature of fiber treatment is increased to 40–50°C, the self-elongation effect decreases and the process itself proceeds in a shorter time interval (curves 3 and 4).

Such an approach to the investigation of the phenomenon of spontaneous elongation of the fiber, namely, in specific liquid vapors, has revealed several previously unknown phenomena that have not been described in the literature. In particular, one striking feature of the fact of spontaneous deformation of the acetate fiber in nitromethane vapors distinguishing this process from the others [13–18] is kinetic "reversibility" of the process. A horizontally suspended fiber, having reached maximal elongation in the vapors, after a short pause (less than 10 sec) under the same thermodynamic conditions is able to regain its original linear dimension. After that, still being in the sort of "living" state, the fiber swells and breaks. Note that at low and high temperatures the "reversibility" of the process is partial, and at room temperatures (15–30°C) it is complete. The traditional notion "shrinkage" is unacceptable here, since the linear dimension of the length of the spontaneously elongated fiber rather than of the original fiber begins to decrease. Moreover, the of "shrinkage" in this case is not a result of the action of temperature or a relaxation reaction to the deformation elongation when the forces arising in the polymer are directed counter to motion. Both the elongation and the inverse process proceed spontaneously, in an experimentally short time (complete cycle takes 5–7 min) and, what is most important, under the same conditions: at the same temperature and pressure and in the presence of nitromethane vapors. The fiber elongated under the action of vapors is able to preserve for a long time this dimension with a slight time shrinkage in the absence of vapors (i.e., when removed from the vapor medium). The reason for the double influence of nitromethane on the polymer is likely the specificity of the polymer–solvent interaction [19, 22, 23]. Nothing of the kind has been revealed for acetate fibers swelling directly in liquid media [13–18].

The next feature is the fact that the process of spontaneous elongation of the fiber proceeds most intensively at room temperatures or temperatures close to them. In the given temperature range, in the process of elongation, the fiber first absorbs up to 6–8 mass % of solvent vapors and then loses 1–2 mass % of the absorbed quantity of vapors. After that, the elongated fiber begins to slowly regain its original linear dimension, absorbing vapors at an even higher rate and in larger quantities. If the fiber was initially in a fixed position (as in the experiment under consideration (Fig. 1, curves 1, 1′, 2)), then the process of fiber shrinkage finally terminates with its breaking, and under free swelling (e.g., in special sieves) — with its dissolution.



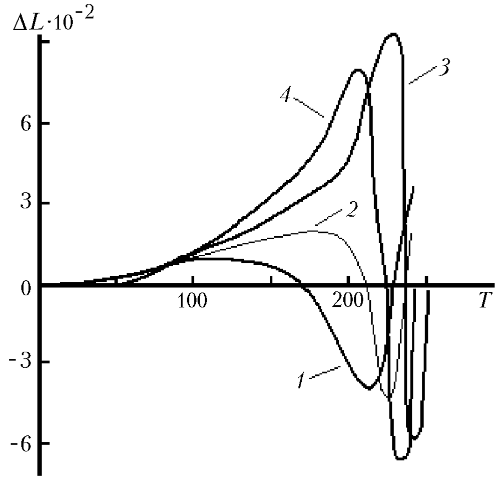


Fig. 2. Kinetic curves of sorption by the acetate fiber (6.7 tex) of nitromethane vapors at temperatures of: 1) –15; 2) 5; 3) 15; 4) 20; 5) 25°C.

Fig. 3. Thermodeformation curves for diacetate fibers (6.7 tex): 1) control industrial fiber; 2) fiber that has begun to elongate in nitromethane vapors (swelling time ≤1 min, $L \leq 105\%$); 3) fiber elongated in vapors to the maximum value; 4) fiber that elongated and regained its original linear dimension in nitromethane vapors.

Figure 2 shows the swelling curves of the DAC fiber of linear density 6.7 tex in nitromethane vapors at different temperatures [19, 24]. The data presented clearly show the two-stage character of sorption that appears even at negative temperatures. The desorption branch on the swelling curves corresponds to the maximum rate of fiber elongation. The arrows mark the process of sorption corresponding to the spontaneous "shrinkage" of the elongated fiber. Probably, precisely because nitromethane is a specific solvent of cellulose acetates [22, 23], the behavior of fibers in its vapors is unusual. The anomalous character of the swelling curves, i.e., the extreme sorption kinetics, the squeezing out of the solvent reflected by the "dropping" sections of the curves $C_s = f(t)$, as well as the sharp increase in the rate of absorption of the solvent vapors at the final stage, point to a structural transformation in the polymer matrix in the diffusion process [19, 25]. It should be noted that the influence of vapors at the first stage of sorption corresponding to the induction period preceding the elongation (see Fig. 1) initiates orientation processes [24, 26]. In the given case, nitromethane vapors act as a kinetic stimulator of the phase transition, providing the segmental mobility necessary for the unfolding of chains and further spontaneous orientation ordering of macromolecules [16].

From Fig. 3, which presents the thermodeformation curves for control and modified DAC fibers, it is seen that for the sample obtained under industrial conditions by dry forming (curve 1) only shrinkage indicative of a weakly oriented structure is observed. For the samples that have absorbed a dose of solvent vapors the deformation–temperature curves have a radically different shape, which is characteristic of polymers having a preliminary orientation [27]. The sample elongated in nitromethane vapors has the greatest self-orientation effect (curve 3). For the elongated fiber that has regained in vapors its original linear dimension (curve 4) a high level of orientation is also preserved, though to a lesser extent compared to sample 3. The thermodeformation curve of sample 4 is blurred and a decrease in the vitrification temperature is observed, which is likely to be due to the superposition on the orientation process of the processes of swelling and polymer dissolution.

The realization of the ordered state is also evidenced by the decrease in the disorientation angle at different stages of the spontaneously deformed fiber [24]. For the original DAC fiber φ = 60–65°C, upon its treatment for ~1 min in nitromethane vapors φ = 40°C, upon maximum elongation (treatment for ~4 min) φ = 45°C, and when the fiber regains its original dimension φ has the same value. The greatest effect of the orienting influence of nitromethane is attained in the initial period of treatment (<1 min). In the region of maximum elongation, as well as in the region of fiber shrinkage, the orientation somewhat decreases, although the values of angles φ remain much smaller than the initial value.

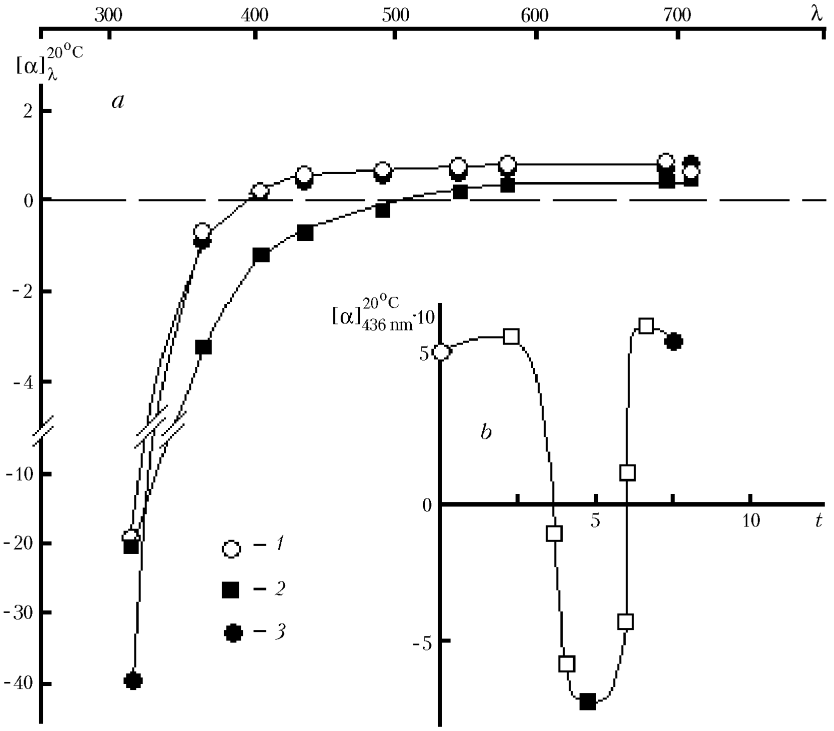


Fig. 4. ORD curves of acetate fiber (6.7 tex) solutions in acetone [1) control industrial fiber; 2) fiber elongated to the maximum value in nitromethane vapors; 3) fiber that elongated and regained its original linear dimension in nitromethane vapors] — *a* and kinetics of the change in the specific optical rotation in the process of spontaneous elongation and spontaneous contraction of the acetate fiber in nitromethane vapors — *b*; open and solid circles, as well as solid boxes correspond to the points of the dispersion curves of Fig. 4a at λ = 436 nm, i.e., to the original fiber that maximally elongated and regained its original linear dimension upon contraction; open boxes correspond to the points of the dispersion curves of modified samples extracted from the vapor phase at intermediate stages of the elongation–contraction cycles.

Note that acetate fibers of both 6.7 tex and 11 tex, regaining in nitromethane vapors their original linear dimensions, can lift a load of mass up to ~15 mg to a height of 1.5–1.7 cm. The specific work of self-elongation calculated by the deformation–time curves at various values of external loads was equal to 0.032 J/cm^3. It should be emphasized that this work is in no way associated with external forces and reflects only the change in internal energy (and, consequently, free energy) and, therefore, should be equal to the heat of the ordered-phase formation. The small value of the specific heat typical of the isotropic-to-LC transition once more points to the fact that the transition of the first kind is not associated with recrystallization [16].

We could give other examples confirming the transition from the amorphous glassy state to the highly ordered LC state that takes place in the process of spontaneous elongation of the DAC fiber in nitromethane vapors. But we decided to restrict ourselves to the foregoing and discuss in detail the experiment that has made it possible to explain the inverse process — the effect of spontaneous "shrinkage" of the elongated fiber. We could not explain this effect for a long time, since attempts to estimate the spontaneous deformation of the fiber only in terms of the thermodynamic polymer–solvent interaction did not give exhaustive explanations of the fact of process reversibility.

Note once again that the alternative effects of fiber self-elongation and "shrinkage" discovered by us occur under the same conditions, i.e., the sample is always in the vapor medium and is not removed from it. This suggested that, under the influence of mesophasogenic vapors in the polymer, there appear not only orientational phenomena but also other processes that provide the inverse effect. Taking into account that cellulose acetates belong to the class of optically active substances, it is quite natural to suppose that under the action of vapors of a specific liquid acetic-acid ester can change its spatial structure and, accordingly, its optical activity. It turned out that for the modified samples the optical activity expressed in terms of the specific optical rotation [α] does vary over a wide range.

Figure 4a shows the ORD curves of solutions of the original DAC fiber and of the DAC fibers treated in active solvent vapors (at room temperature). The dispersion curve of the fiber elongated to the maximum value (curve 2) markedly differs from the industrial fiber ORD (curve 1) and in the 300–500-nm range of wavelengths is characterized by negative values of [α]. The ORD of the fiber that first elongated and then regained its original linear dimension in nitromethane vapors (curve 3) practically coincides with the dependence $[\alpha] = f(\lambda)$ for the control sample, except for the value of [α] at $\lambda = 313$ nm. Comparison of [α] of the solutions of the control and modified fibers at one of the spectrum wavelengths in the range $\lambda = 400–500$ nm clearly shows inversion of the sign of the specific optical rotation (Fig. 4b). The solution of the original fiber in this range of wavelengths is characterized by a positive value of [α], the solution based on the self-elongated fiber has a negative value, and the [α] value of the shrunken fiber solution is positive again. Inversion of the sign of [α] can only point to the fact that under the active action of mesophasogenic solvent vapors the cholesteric helix of cellulose ester changes the direction of rotation of the polarization plane, going, e.g., from counterclockwise to clockwise polarization, and vice versa. Analogous results were also obtained for acetate films which (as fibers) in nitromethane vapors experience spontaneous elongation and, moreover, acquire time-independent optical anisotropy [10]. Reversal of the sign of optical rotation is also observed for powdery DAC modified in nitromethane vapors [19, 20], which confirms the single mechanism of interaction of acetic-acid cellulose ester with mesophasogenic solvent vapors.

Of particular importance is the fact that the stagewise transition from one spatial state to another discovered for the system cellulose diacetate–nitromethane vapors obeys the "dose–effect" law with a great effect of the influence of small quantities of absorbed solvent vapors (no more than 6–8 mass %). Exactly this fact made it possible to monitor the structural changes in the system and, concurrently, the optical activity of the polymer, to establish their relationship and find an exhaustive explanation of the mechanism of spontaneous deformation of the fiber in vapors of an active medium, including the effect inverse to self-elongation, as well as gain an understanding of the nature of the LC state in the investigated system polysaccharide–mesophasogenic solvent.

Before turning to the description of the mechanism, let us once again follow the sequence of all transformations that take place in the process of spontaneous deformation of the fiber. For the sake of convenience of consideration, let us make use of the diagram given in Fig. 5. The position of the amorphous (AM) and LC state is marked by individual lines: the horizontal line before its intersection with the middle dashed vertical line represents the AM state, then comes the LC state, and the lower horizontal line represents the LC state. The time line gives sequentially the points corresponding to the initial instant of time (t_1), the time at which the fiber reaches maximum elongation (t_2) and the time at which the elongated fiber regains its original linear dimension (t_3).

As the acetate fiber swells in nitromethane vapors, it self-elongates (interval t_1–t_2) and goes from the amorphous glassy state to the highly ordered LC state (Fig. 5a), which is confirmed by the data of the x-ray structural, thermodeformation, and other analyses [11, 19, 24, 26] (Fig. 5b) and works [12–18]. It is at this stage that the first inversion of the sign of the specific optical rotation is observed (Fig. 5c), pointing to the fact that the polymer macromolecules not only elongate and are oriented, but they also unfold. As the fiber stays further in the vapor medium of nitromethane (interval t_2–t_3), the elongated fiber shrinks and reaches its original linear dimension (Fig. 5a) and the quantity [α] regain its initial values (Fig. 5c). In so doing, no transition to the amorphous state is observed and the polymer system continues to be in the oriented state (Fig. 5b). Thus, both the direct process of fiber elongation and the inverse process of regaining its original dimension are associated not only with the phase transition of the polymer from the disordered amorphous state to the LC state but also with the conformation transformation of macromolecules.

The mechanism of the process of spontaneous deformation of the acetate fiber in vapors of a specific liquid can be described as follows. At the initial instant of time, while the polymer system is vitrified and the macromolecular mobility is limited, it is in the nonequilibrium conformation state (even despite some preliminary orientation acquired in the process of fiber formation). Since nitromethane belongs to selective solvents interacting mainly with OH-groups of DAC [19, 22, 23], upon absorption by the fiber of the first small portions of specific solvent vapors, disruption of the intermolecular hydrogen bonds occurs, whereas the intermolecular bonds (or at least some of them) remain intact, which preserves natural rigidity of the ester cellulose chains [5]. Upon removal of kinetic distur-

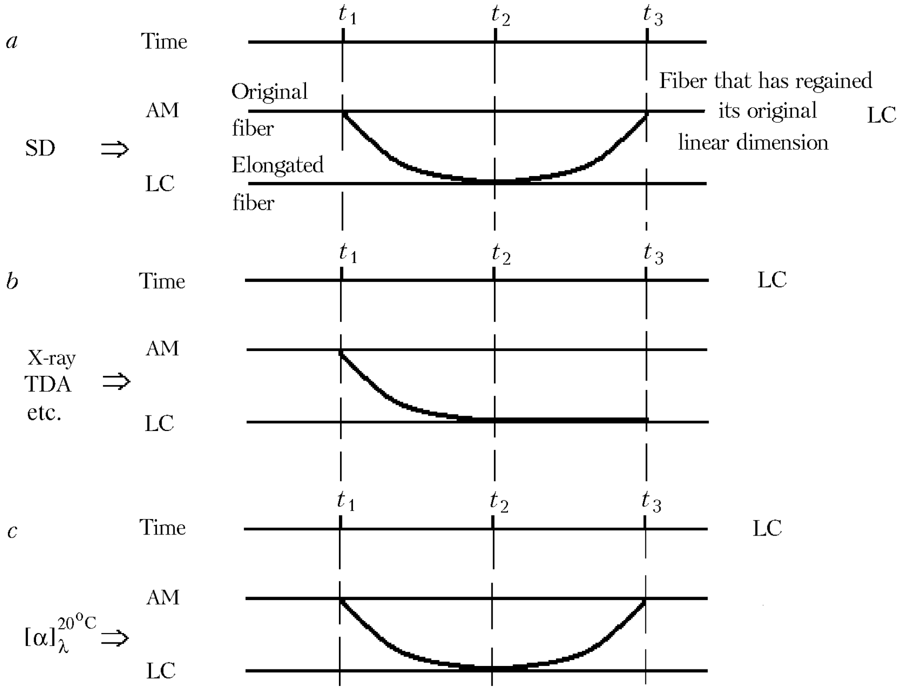


Fig. 5. Schematical representation of the phase and conformation transitions in the process of spontaneous deformation of the acetate fiber in nitromethane vapors: t_1–t_2 is the cycle of self-elongation of the original fiber; t_2–t_3 is the cycle of self-contraction of the elongated fiber; a) spontaneous deformation (SD) kinetics of the fiber; b) results of the investigation of modified samples by direct structural methods (x-ray structural analysis, thermodeformation analysis (TDA), etc.); c) kinetics of the change in the specific optical rotation.

bances, macromolecules, by virtue of their natural rigidity and acquired mobility, to attain an equilibrium, more straightened conformation, elongate, unfold (which is evidenced by the inversion of the sign of [α]), and self-orientate themselves. Macroscopically, this shows up as an increase in the linear dimension of the fiber. And the fiber structure thereby densifies, which leads to a squeezing of the solvent out of the polymer matrix. At this point the process of orientation probably terminates, and the process associated with stereometric transformations of the system persists. Obviously, this just explains the effect of spontaneous "shrinkage." According to Flory [12], Frenkel' et al. [16], Papkov [27], and other authors, at the final stage of elongation the stretched macromolecules are densely packed in parallel to one another. However, the presence of chiral centers in the glucopyranose rings of the polysaccharide generates weak asymmetric forces between segments of adjacent chains, leading to the appearance of a macroscopic helicoidal structure. This, in turn, predetermines the realization of the cholesteric LC phase rather than the nematic one [3, 5, 28], which is also confirmed by our investigations [10, 19]. Consequently, it may be suggested that the parallel packing of molecules is preserved only at the supermolecular level within the LC domains and at the macroscopic level domains with oriented and straightened molecules are arranged relative to one another at a small angle, which leads to a cholesteric twist.

Moreover, if we take into account that the fiber, returning to its initial state under the same conditions under which it experienced elongation, does work, it is possible that the solvent vapors at the first stages of sorption (corresponding to the initial moment of self-elongation) energetically promotes the transformation of the "bath" form (*cis*-form) of the link that is usual for cellulose acetates to the more prolate "chair" form (*trans*-form). Exactly such a state, where intermolecular bonds in the polymer can be disrupted with the preservation of intramolecular ones, provides the realization of the *trans*-form of the glycopyranose ring and the transition of ultimately oriented macromolecules to the LC state [5, 29]. As a rule, for most polymers with a developed system of hydrogen bonds upon swelling and dissolution there occurs disruption of not only intermolecular contacts, but also intramolecular ones due to the solvation by the solvent of the functional groups in macromolecules, which impedes the formation of the true LC phase. Probably by means of aprotic, dipolar solvents interacting mainly with a certain kind of functional groups of the type of nitromethane and being in the vapor state it is possible to realize selective disruption of H-bonds by creating conditions for the realization of native rigidity of polysaccharide molecules and, accordingly, for their self-ordering. At the same time, because the system tends to the least volume (minimum of free energy), a repeated change in the conformation of macromolecules followed by a shrinkage of the elongated fiber takes place.

Since the process inverse to spontaneous elongation proceeds against the background of the structural changes that have already taken place in the polymer matrix, taking into account the high level of acquired orientation, we think that the process of spontaneous shrinkage of the elongated fiber is most likely to be due to the spiralization of macromolecules and their more compact packing. We also believe that the polymer–solvent system continues to tend to a state with a still lesser minimum of free energy but by virtue of objective limitations associated with the experimental conditions does not reach it. As a result, the polymer system with the sorbed solvent should take spheric form. Note that we have managed to realize such conditions, but the results of this investigation will be described in detail in a separate paper. Here we only report that the process of phase transition (AM–LC) in the investigated system is multistage, with each stage having its own characteristics and an individual internal structure, and the LC phase itself is characterized by a diversity of spatial structures.

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NOTATION

C, solution concentration, g/dl; C_s, degree of sorption of solvent vapors, mass %; d, solvent density, g/cm^3; J, current intensity, A; L, value of fiber elongation (or contraction), %; l, optical path, dm; ΔL, change in the sample length under linear heating, μm; m_0 and m, mass of the starting polymer sample and of the sample that has received a portion of solvent vapors, g; T, temperature, ^{o}C; T_{boil}, boiling temperature of solvent, ^{o}C; t, time, min; U, voltage, V; $[\alpha]$, specific optical rotation of solution, deg·cm^2/g; α and α_0, measured angles of rotation of polymer solution and solvent, deg; λ, wavelength, nm; φ, angle of orientation, deg. Subscripts: boil, boiling; s, sorption.

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