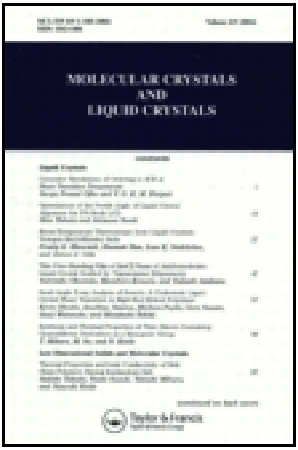

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Liquid Crystal Systems of Cellulose and its Derivatives

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Liquid Crystal Systems of Cellulose and its Derivatives

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The present work makes an attempt to estimate the prospects of liquid crystal state realization in cellulose systems based on cellulose esthers and cellulose in direct solvents.

The study was conducted mainly by means of polarization-optical methods such as polarized microscopy intensity measurement of passing light by crossed polaroids and small angle scattering of polarised light.

Keywords: hydrocellulose; cellulose esthers; phase transitions; direct solvents; spherulite; polysaccharides

The experimental and theoretical studies have allowed to characterize liquid crystal (LC) state for the great number of cellulose esthers. The information on the possibility of obtaining LC cellulose solutions in a number of solvents is have appeared [1, 2]. But the conditions of transition into the LC phase have not been ascertained yet for cellulose xanthate which is widely used in order to obtain the hydrated cellulose yarns. The present work makes an attempt to estimate the prospects of LC state realization in cellulose systems based on cellulose esthers: ethylcellulose EC, oxypropylcellulose OPC celluloseaccetate CA; labile esthers (cellulose xanthate) CX; cellulose in direct solvents.

The study was conducted mainly by means of polarization-optical methods such as polarized microscopy intensity measurement of passing light by crossed polaroids and small angle scattering of polarised light [3].

As it is shown in the lowest critical concentration of transition into LC phase have the solutions of cellulose derivative in trifluoroacetic acid (TFAA). The transition is revealed by the appearance of interference coloration of microscopic pictures which are observed by crossed nicols polarized microscope (extinguishing pictures). Pictures of small angle scattering of polarized light with such samples have usually 4-petal form (X-type) (Fig. 1 a, b). Small shear forces are quite enough for sharp change of the optical properties of cellulose derivatives LC solutions (Fig. 1 c, d).

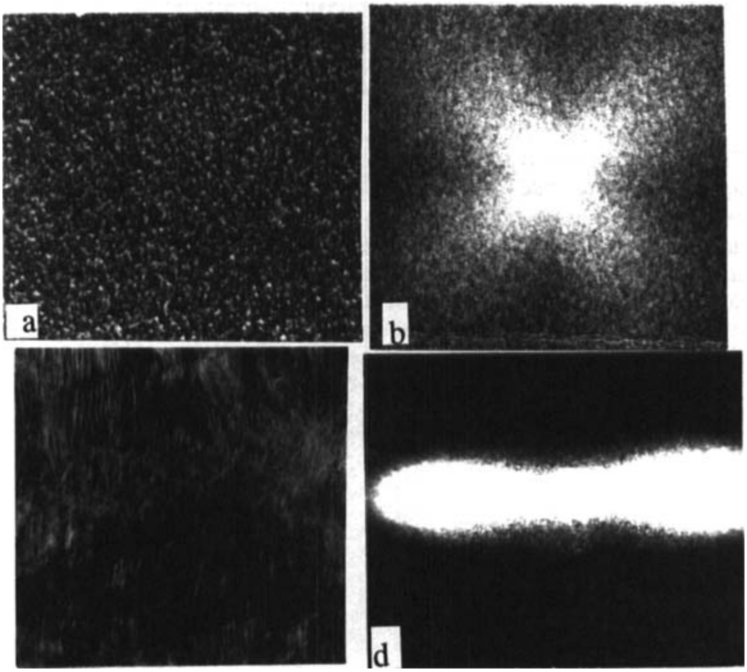

FIGURE 1.

Microphotographs (nicols are crossed) (a c) and pictures of small angle scattering of polarized light (b d) 30 % solutions of OPC in TFAA. The magnification is x200.

The analysis and calculation of light scattering diffractograms of nonoriented samples of cellulose derivatives LC solution have allowed to calculate some parameters of anisotropic structures in such systems and to make a conclusion about cholesteric nature of formed liquid crystals.

Side by side with liotropic mesomorphism cellulose derivatives LC system have thermotropic properties there is phase transition into isotropic state during the heating of such systems. Application of polarized optical methods has allowed to determine the technologically important field of LC state existance in spinning solutions of cellulose derivatives at the changing of polymer concentration in a solution and of temperature [4, 5] (Fig. 2).

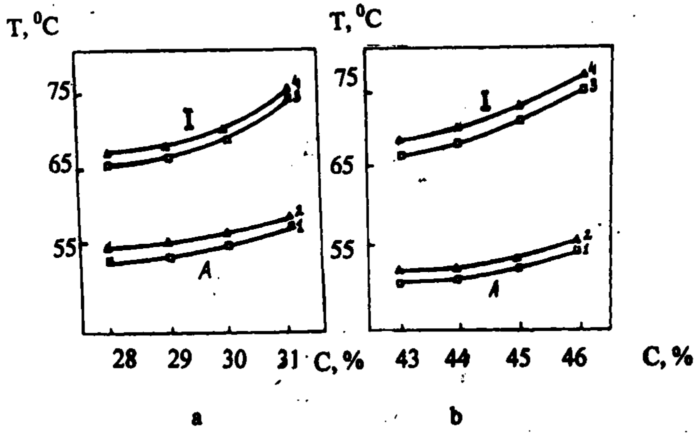

FIGURE 2.

Phase diagrams sections of systems: DAC TFAA (a) and DAC N-methylpyrrolidone (b)

The inter effect was discovered during the study of LC state realization conditions at the evaporation of solvent from isotropic solutions of cellulose derivatives. It was established that OPC transforms into LC state in all used solvents and at all initial concentrations of isotropic solution under the solvent evaporation.

Structure formation is going on in two stages. At the first stage rodlike structures with orientation of optical axis along the big axis of rod are formed. At the second stage the system of cholesteric mesophase domains with the step of spiral twisting in the order of 10 µm is formed.These stages become distinctly apparent in the change of intensity of light scattering pictures and their transition from X-type into +-type. The behaviour of AC solutions which show the LC transition dependence on polymer concentration is different. It was shown that when its concentration is lower than 23 % isotropic solutions don't form LC phase at evaporation of TFAA.

The observed phenomena must be stipulated by the differences in mechanism of OPC and AC molecular rigidity and is connected with kinetic limitations of the possibility of LC phase realization from isotropic solution. In other words during the evaporation of volatile solvent (TFAA) AC macromolecules can be late for taking the equilibrium conformations necessary for formation of regulated system. At the same time the probability of LC transition for AC solutions increases with the rise of polymer concentration in initial solution owing to more equilibrium molecular conformations.

The obtained results show that the transition into LC state from isotropic solution is quite widespread phenomenon for cellulose derivatives.

Proceeding from these relusts the ways of realization of such state for another technologically important polymer cellulose xanthate can be determined. The first method can evidently be based on the obtaining of viscose solutions with high polymer concentration and high degree of etherification by analogy with earlier described liotropic transition into mesophase that is going on in solutions of s cellulose esthers. But in practice the realization of this method meet with some difficulties connected with high tenacity of viscose solutions at quite low polymer concentrations. The other method which is more realizable consists in the possibility of LC state realization in the process of xanthate precipitation from viscose solution in consequence of raising the polymer concentration at phase dissociation. At such method the proper choice of precipitator and conditions of cellulose xanthate coagulation has the decisive importance. These parameters should be selected in such a way that during phase dissociation in the process of precipitating the polymer concentrations necessary for LC phase realization would be obtained.

The theoretical estimation given in this work shows that the critical volumetric concentration of transition into LC state is equal to 0.7 for cellulose. In the process of precipitation it might be as well desirable to prevent the xanthate decomposition and cellulose crystallization because they reduce the possibility of LC phase realization. That's why the most accep precipitators are alcohols and amid solvents that ensure the attainment of high polymer concentration in coagulation process and at the same time this precipitators prevent the xanthate decomposition and cellulose crystallization. The carried out studies confirm this supposition. Watching The pictures of extinguishing and scattering of hydrated cellulose films formed in coagulation baths of various compositions it is not difficult to notice that
overmolecular structure forming in acid-salt precipitators and in organic ones has essential differences. In the first case the morphology of hydrated cellulose films obtained from wood and bagasse cellulose has some differences owing to local crystallization but it has not anisotropic structures indicative of phase formation. In the second case anisotropic films having rodlike morphology are formed. Scattering pictures of such films have round form.

The carried out structural investigations of hydrated cellulose films have shown that the formation of anisotropic structures does not take place when the water precipitator containing 300 g/l H_2SO_4 are used. The films obtained by precepitation in dimethylformamid (DMFA) had spherolit structure when H_2SO_4 content was equal to 60 150 g/l. At low H_2SO_4 concentration we can watch the extinguishing picture formed by chaoticly disposed small structure elements having sizes from 10 to 5m. H_V scattering diffractograms of such structures are evident of spiral twisting of optical axises. Their distorted form is evidence of the presence of optical rotation. In the range of H_2SO_4 concentrations from 70 to 140 g/l the clearly marked spherolit structure is seen. When H_2SO_4 concentration is higher than 150 g/l this structure becomes disordered and transforms into texture formed by chaoticly disposed species of micron sizes.

On the basis of theory developed in the calculation of diffractograms of small angle scattering of polarized light with hydrated cellulose films was made [4]. The films were formed at the different conditions of precipitation. From this data it can be made the deduction while the concentration of H_2SO_4 in precipitator is increased the pitch of twisting of cholesteric spiral increases (Fig. 3).

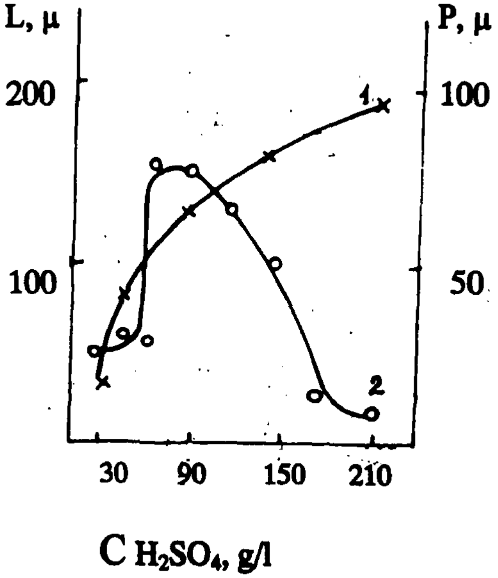

FIGURE 3.

Twisting step of cholesteric spiral (1), and species diameter (2) are a function of H_2SO_4 concentration in precipitator.

Structure elements sizes as a function of H_2SO_4 concentration have maximum in concentration range from 70 to 140 g/l. In this range as fig. 8 b e show the distinctly marked spherolit structure is observed. The studies of phase state of spherolit containing hydrated cellulose films were executed by means of the complex of polarized-optical, X-rays and spectroscopic methods. These studies have allowed to characterize the films structure as liquid crystalline one.

High values of round dichroism in such hydrated cellulose films in also evidence of the formation of cholesteric LC structure in media containing alcohols and DMFA. This high values are comparable with analogous characteristics of DNC films formed from anisotropic solutions. At low H_2SO_4 concentrations in the composition of coagulation bath the highest degree of LC state realization is obtained. It is stipulated by the creation of "soft" conditions of coagulation and by the elimination of factors promoting to crystallization. At the same time in the process of precipitation in precipitator containing DMFA cholesteric mesophase formation does not influence the essential increasing of strength characteristics of fibres spun in such baths. LC state allows to increase strength characteristics of fibres and films.

Obviously in order to realize such possibility of LC state it is necessary to fulfil the conversion of the system from cholesteric into nematic mesophase that is in possession of high parameters of molecular orientation. Partial realization of nematic mesophase explains the observed effect of double increase of hydrated cellulose films strength. These films are obtained in the process of precipitation into isopropyl alcohol (IPA) and H_2SO_4 in proportion 9:1. It should be also noted that 15 times increase of strength characteristics approximately can be obtained by the addition of zinc sulphate into precipitator. It must be connected with decrease of spherolit sizes.

The obtaining of cellulose in direct solvents having independant practical importance in connection with the prospective of viscose fibre production without carbon bisulphide application is one of the ways of LC state realization. The solvent type and polymer concentration in a solution are the main factors of mesophase formation for such systems. In a number of scholarly works it is said about the transition of high concentrated cellulose solutons into LC state in the mixture of TFAA and chlorinated low alkanes in N-methylmorpholin-N-oxide in the system dimethylacetamide LiCl [6, 7].

It was shown that optical anisotropy in high concentrated cellulose solutions in triethylaminoxide is not connected with LC phase presence because there are no typical oriented effects peculiar to liquid crystals. In this connection it could technologically be more accep to realize LC phase in such systems directlty in the process of polymer precipitation in isotropic solution as it was mentioned earlier [8, 9].

The analysis of available literature data and the studies presented in this report show that it is difficult to realize as a whole practical possibilities of cellulose LC systems today. A few experiments are known when the acetate fibres of about 30 cN/tex have been obtained by spinning in solutions of N-methylpyrrolidone by processing through LC state[10] and it is also known that the hydrated cellulose fibres of about 100 cN/tex have been obtained by saponificating triacetate fibres spun in LC solutions [11]. This new prospective direction of improvement of physical mechanical properties of natural polymer fibres and films [12] will obviously lead to interesting scientific and practical results in the near future.

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