

# Structural Transitions in Commercial Cellulose Systems

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Received 17 July 2002; accepted 3 October 2002

**ABSTRACT:** The problems of phase transitions in commercial cellulose systems during processing are considered. The formation of structures in regenerated cellulose from viscose solutions during precipitation in different regenerated baths and in highly concentrated solutions of cellulose in *N*-methylmorpholin-*N*-oxide at different temperatures and shear deformations has been selected for this review. The difficulties in defining the type of structural ordering in

these systems are demonstrated. Fractal analysis is used to study the structures. A close relationship between the characteristics of the structures and the fractal dimensions is elucidated. The prospects for the different methods of regulating structures in cellulose systems are discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 22–32, 2003

**Key words:** cellulose; fractal; liquid crystal

## INTRODUCTION

In recent years, studies of structural transitions in commercial cellulose systems during their industrial processing have attracted increasing attention. This intense interest demonstrates the impelling need to reduce the quantity of synthetic fibers and films and to increase the quantity of cellulosic materials. The necessity of such substitutions is defined by the ecological problems of using and recycling synthetic polymers. Therefore, the replacement of synthetic material by biopolymers has been a priority since the 1970s.<sup>1</sup>

Currently, only two commercial methods of processing cellulose in regenerated cellulose are of practical importance. These are the viscose process and the *N*-methylmorpholin-*N*-oxide (MMO) process (processing cellulose through a solution in MMO).<sup>2</sup> Soon, the cuprammonium process will not be able to compete with these methods because of its low-grade physicomechanical properties and high cost.<sup>2</sup> Therefore, we consider both of the aforementioned basic commercial methods of processing regenerated cellulose.

The main objective of studying the structural transitions in cellulose systems is determining the conditions for the formation of the liquid-crystal (LC) state during one of the processing stages of the production of regenerated cellulose. In agreement with modern theoretical propositions, it is possible to accomplish this both when the solution of cellulose is being prepared (a viscose solution or a solution of cellulose in MMO) and when the cellulose solution coagulates in a

precipitation bath by the regulation of the conditions during coagulation. Up to the present day, we cannot obtain LC structures in industrially regenerated cellulose using a comparatively wide selection of methods for the regulation of structure formation.

It is difficult enough to consider all recent research in this field because there are many more patents than useful articles or books. We cannot evaluate such works. Therefore, it seems efficient to consider only theoretical and recent original studies.

Cellulose is a biopolymer, and so its properties are defined by some factors. It is necessary to determine exactly the type of raw cellulose used in scientific research and processing. In general, only baikal spruce cellulose has been used in this research, with a degree of polymerization greater than 200.

## STRUCTURAL TRANSITIONS DURING THE PREPARATION OF CELLULOSE SOLUTIONS FOR PRECIPITATION

There is no fundamental difference between solutions of cellulose in water-containing solvents and solutions of cellulose in organic solvents.<sup>3</sup>

A qualitative model of the dissolution of cellulose during the viscose process and during a number of MMO processes includes the following stages:

1. The penetration of the solvent into cellulose fibers, which induces swelling.
2. The breaking of hydrogen bonds with the formation of unstable compounds or without it (for the case of a direct solution).
3. The solvation of unstable compounds or molecular chains of cellulose and their subsequent stabilization.

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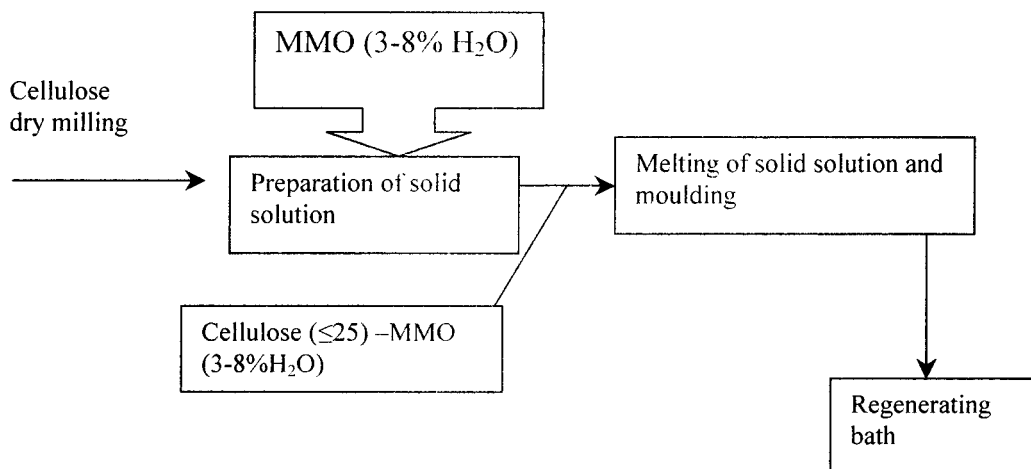


Figure 1 Schematic circuit of the solid-phase MMO process.<sup>10</sup>

4. The breaking of cellulose chains by hydrolysis and mechanoactivation effects.
5. The uniform disposition of structural units of cellulose of different sizes in a volume of the solvent by mechanochemical effects with the formation of a solution of cellulose.

The given scheme has been used in the viscose process for a long time<sup>4</sup> and in some types of MMO processes.<sup>5–8</sup> The so-called solid-phase MMO process does not have the first stage (swelling) because it is absent.<sup>9,10</sup> The viscose solutions or cellulose pulps for the usual MMO processes are homogeneous and unstructured systems with cellulose concentrations of 10–23%. To create an LC phase in these solutions before the formation of solid-structure regenerated cellulose is clearly quite impossible.

In that respect, the solid-phase MMO process has potential because it allows solutions with cellulose concentrations of up to 50%.

The scheme shown in Figure 1 represents the principal basis of the solid-phase MMO process.

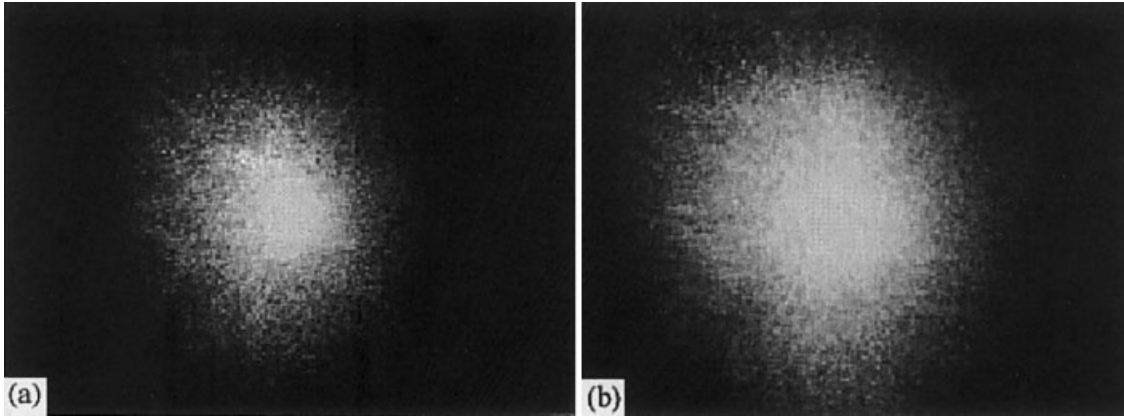
The stage including the melting of a solid solution and moulding attracts the greatest interest with respect to the preliminary regulation of the cellulose solution structure. A certain structure can be expected in this range of concentrations (30–50%), which is regulated by the temperature and shear deformation. It is possible to obtain an LC phase in such solutions after regulated melting and moulding.

An LC state in MMO solutions of cellulose containing up to 25% cellulose was first reported by Navard and Haudiu.<sup>9</sup> However, later investigations demonstrated that the optical anisotropy and specific rheological behavior observed by those authors were due to the phase inhomogeneity of high-concentration solutions and a photoelastic effect.<sup>10</sup>

Further developments in this direction gave a radically new solution for the problem of the direct disso-

lution of cellulose in MMO, allowing high-concentration solutions containing up to 50% cellulose to be prepared.<sup>11</sup> In the solid-state pretreatment of cellulose and crystalline MMO (water content = 1–3%) under the simultaneous action of shear strain, compression, and forced plastic yielding, a solid–solid complexation reaction proceeds between cellulose and MMO. Under the subsequent action of temperature and strain, the formed concentrated solid solutions melt and transform into a fluid state with a high degree of homogeneity. Calorimetry, X-ray diffraction, and rheological studies of such homogeneous solutions have revealed that the optical anisotropy of solutions containing less than 45% cellulose results from kinetic factors, namely, slow relaxation of orientation induced by the preparation of the solutions. The thermodynamic equilibrium anisotropic state is realized in solutions containing greater than 45% cellulose.<sup>12</sup>

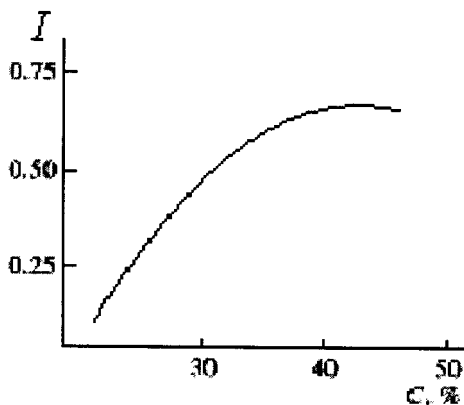
A comparative study of cellulose solutions with different concentrations in MMO has been carried out to show the temperature and concentration conditions for the emergence of optical anisotropic structures. Solutions containing 20% cellulose in MMO are fully isotropic after being treated by the aforementioned heating–cooling procedure and do not exhibit the  $H_V$  pattern of light scattering and transmission in crossed polaroids at any temperature. The  $H_V$  scattering pattern from 25% solutions is a weak diffuse spot [Fig. 2(a)], the intensity of which is significantly lower than that of the  $V_V$  pattern [Fig. 2(b)]. This suggests that the major contribution to  $V_V$  scattering is made by the density fluctuations of the medium. Comparable anisotropic structures with a wavelength of incident light of  $\lambda = 0.6328 \mu\text{m}$  are not observed. Meanwhile, a weak background is observed at large radial scattering angles (not visible in Fig. 2 because of the low intensity). An analysis of these scattering patterns shows that the solution contains regular macromolecular associates possessing some optical anisotropy per unit of



**Figure 2** (a)  $H_V$  and (b)  $V_V$  scattering patterns from 25% cellulose solutions in MMO at 20°C.

scattering volume even at concentration ( $c$ ) = 25%. However, such structures are much smaller than  $\lambda$ , so wide-angle light scattering should be used to characterize them. The emergence of some optical anisotropy with increasing concentration is also indicated by an increase in the integral light transmission at  $c = 25\%$  (Fig. 3).

$H_V$  and  $V_V$  scattering patterns from 50% solutions are comparable in intensity and have a circular shape [Fig. 4(a,b)]. It is known that light scattering in this case is due to the orientational fluctuations of the medium.<sup>13</sup>  $H_V$  patterns of this type are typical for optically anisotropic media with randomly distributed rodlike elements on a micrometer scale. This is typical of nematic LCs and was observed earlier in LC solutions of rigid-chain poly( $n$ -benzamide).<sup>14</sup> As demonstrated in Figure 3, when the concentration rises to 50%, the integral light transmission in crossed polaroids is actually saturated. This dependence of the relative transmitted intensity suggests the formation of an optically anisotropic texture in solution, as for the lyotropic transition to the nematic state. At the same time, other regions of the same solution exhibit



**Figure 3** Integral light transmission intensity ( $I$ ) as a function of the concentration ( $C$ ) of cellulose solutions in MMO at 20°C.

$H_V$  scattering patterns of an X type with a uniformly decreasing intensity with  $\theta$  at an azimuthal scattering angle of  $\mu = 45^\circ$  [Fig. 4(c)]. Such patterns, typical of cholesteric LCs with a pitch of  $P \gg \lambda$ ,<sup>15</sup> were observed earlier in solutions of polypeptides<sup>16</sup> and cellulose derivatives.<sup>17</sup> Usually, in the equilibrium state of LC solutions of cellulose derivatives,  $P$  is approximately the same as  $\lambda$ , and, correspondingly, an x-type  $H_V$  pattern [Fig. 4(d)] is observed. Calculations that follow the photometric analysis of the scattering pattern given in Figure 4(b) allow the evaluation of a length  $L$  and a diameter  $D$  of anisometric structures and the qualitative estimation of variations in these parameters during the heating-cooling cycle. We have used the following relationship:<sup>18</sup>

$$I_{H_V}^{diff} \sim \exp\left(-h \frac{\pi D}{2}\right) \frac{2 \cos^4 \frac{\theta}{2}}{Lh}$$

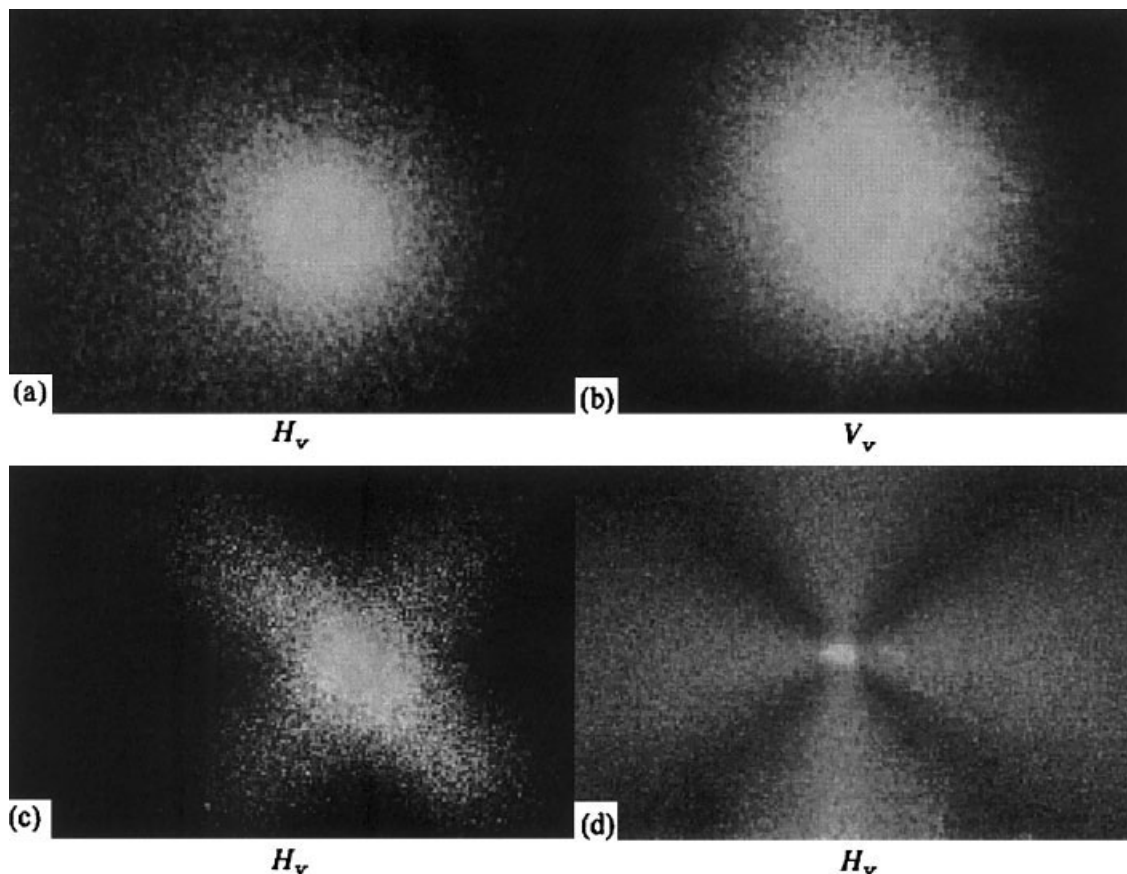
where  $I_{H_V}^{diff}$  and  $h$  are experimentally determinable values:

$$h = \frac{2\pi}{\lambda} \sin^2 \frac{\theta}{2}$$

$$I_{H_V}^{diff} = |I_{H_V}(\mu = 45^\circ) - I_{H_V}(\mu = 0)|$$

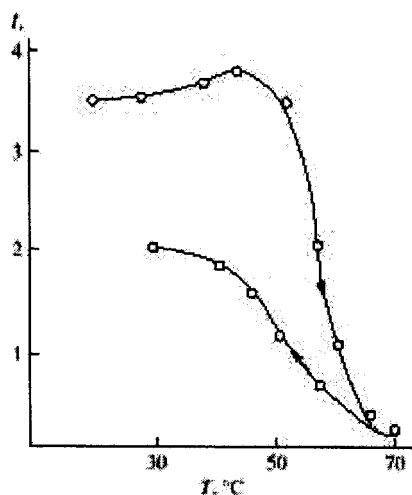
For 50% cellulose solutions in MMO, the calculations give  $L = 10.4 \mu\text{m}$  and  $D = 1.2 \mu\text{m}$ . These values are of the same order of magnitude as similar results obtained for reference samples of LC structures: cellulose diacetate solutions in trifluoroacetic acid and other cellulose derivatives.<sup>19</sup>

The heating of samples leads to a decrease in the transmission of polarized light in crossed polaroids (Fig. 5). Structure recovery to the initial form takes 8 h and is accompanied by a uniform increase in light transmission. A similar behavior for optical transmis-



**Figure 4** (a,c)  $H_V$  and (b)  $V_V$  scattering patterns from 50% cellulose solutions in MMO at 20°C and (d)  $H_V$  scattering pattern from a 40% solution of diacetate cellulose in trifluoroacetic acid at 20°C.

sion was observed earlier for the LC–isotropic liquid-phase transition in nematic LC solutions of polyheteroarylenes.<sup>20</sup> An analysis of changes in the scattering patterns during the heating–cooling cycle reveals that the vanishing of light from the sample upon heating is



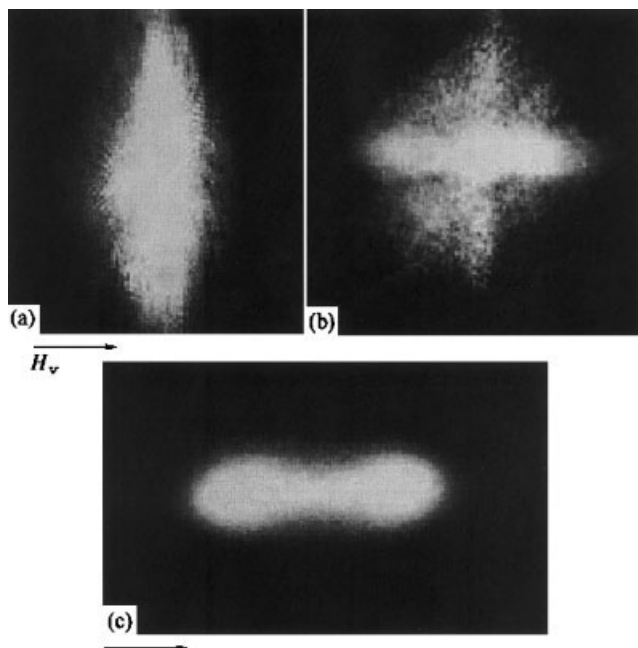
**Figure 5** Integral light transmission intensity ( $I$ ) as a function of the temperature ( $T$ ) of 50% cellulose solutions in MMO.

accompanied by structural transitions leading to a decrease in the linear dimensions of rodlike structures with a simultaneous increase in their length-to-diameter ratio. Upon cooling, the reverse process of these structures growing is accompanied by a decrease in their anisometry.

After the orientation of a 50% solution by sample deformation,<sup>21</sup> a circular or four-lobed scattering pattern [Fig. 6(a,b)] transforms into an elliptic one extended in the direction perpendicular to that of deformation [Fig. 6(a)]. This scattering pattern suggests the formation of anisometric elements oriented along the direction of shear.<sup>22</sup> Earlier, a similar behavior was observed in oriented solutions of nematic LC poly(*p*-benzamide).<sup>14</sup>

Light scattering by anisotropic structures of a regular shape is similar to scattering by a polymer film upon its deformation. Therefore, the photometric analysis of  $H_V$  and  $V_V$  elliptic scattering patterns and subsequent calculations by the formulas given in refs. 23 and 24 can give the size and root-mean-square angle of the orientation disorder ( $\langle c^2 \rangle^{1/2} = 1/2$  for such structures). For an oriented 50% cellulose solution in MMO,  $L$  is 35  $\mu\text{m}$ ,  $D$  is 0.75  $\mu\text{m}$ , and  $\langle c^2 \rangle^{1/2}$  is 8–9°.





**Figure 6**  $H_V$  scattering patterns from 50% cellulose solutions in MMO: (a) oriented, (b) 24 h after deformation, and (c) from a solution of diacetate cellulose in trifluoroacetic acid after deformation at 20°C.

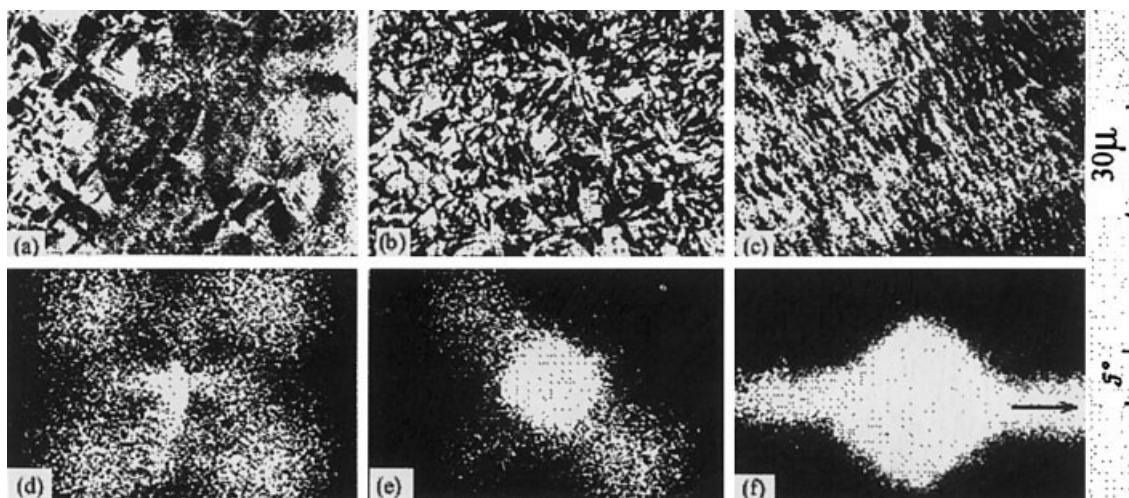
After long-term relaxation (for 24 h), some intensity redistribution over the angle  $\mu$  is observed in the elliptic  $H_V$  scattering pattern [Fig. 6(a)], with mutually perpendicular discrete lobes being formed [Fig. 6(b)]. The approximately equal dimensions of the transient scattering patterns observed over the course of relaxation demonstrate that structural transformations in different stages involve anisometric elements whose geometry is close to that characteristic of the structure of the nonoriented solution. Figure 6(c) shows an  $H_V$

scattering pattern that is typical of oriented LC solutions of cellulose derivatives, in which the positions of discrete maxima coincide with the strain direction. This scattering pattern corresponds to the anisotropic texture with structural elements oriented perpendicular to the shear direction, as is clearly visible in the crossed nicols of a polarizing microscope. However, such phenomena were not observed upon shear strain and subsequent relaxation of concentrated cellulose solutions in MMO.

The obtained experimental results suggest that the emergence of optical anisotropy in concentrated cellulose solutions in MMO is due to the presence of supermolecular structural entities appearing both in the nonoriented state and upon deformation. However, there is a fundamental difference between anisotropic systems based on MMO solutions of cellulose and LC solutions of cellulose derivatives. This is a peculiar structural response to external action. In the former case, according to the theory of rodlike scattering, the particles should orient their large axis along the shear direction, this being characteristic of nematic LCs. In the latter case, the observed formation of the perpendicularly oriented structure is more inherent to cholesteric LC solutions.

The considered cellulose solutions in MMO are high-viscosity liquids. Solutions with such concentrations, in addition to a high viscosity, have a characteristic high-phase heterogeneity. These properties impede the identification of the phase state and the type of supramolecular structure formed.

Polarization optical methods such as small-angle light scattering and the measurement of the integral intensity of light scattering are convenient for quickly analyzing the structural state in such complex systems, along with optical microscopy. The essential



**Figure 7** Microphotographs (400 $\times$ ) in (a–c) polarized light and (d–f) small-angle light of  $H_V$ -scattering patterns of CH films obtained in (a,d) the beginning stages and (b,e) the final stages of the coagulation process and (c,f) orientated during the coagulation process.<sup>35</sup>

characteristics of LC solutions of polymers are precited linear dimensions of anisometric elements of the supermolecular structure. The calculation of linear dimensions is a laborious procedure because it is necessary to assay the small-angle light scattering patterns. The heterogeneity of concentrated solutions of cellulose determines the specificity of the approach used to analyze the results of scattering studies. In that case, the structure of investigated solutions is considered as mass fractals.<sup>25,26</sup> It should also be stated that there are well-ordered LC structures (spherulites) in certain sections of samples. The ordered structures appreciably reduce the precision of estimating the fractal dimensions of entire samples.<sup>27</sup>

A series of samples of up to 50% cellulose solutions in MMO have been considered. In the investigated samples, so that the influence of the ordered structure on the values of the fractal dimensions would be avoided, the spectra of fractal dimensions for different sections of samples of cellulose solutions were estimated under various scales of microscopic observations. The fractal dimensions were in the range of  $D = 2.3 \pm 0.2$ . The calculations of the dimensions were based on the measurement of the integral intensity light scattering.

Preliminary data have shown that the fractal dimensions obtained from 50% cellulose solutions by the measurement of the integral intensity of light scattering have a certain effect on the length  $L$  and diameter  $d$  of anisometric elements of the structure.

The linear sizes of elements of the supermolecular structure were estimated by the photometric measurement of patterns of small-angle scattering. It was convenient to use a length-to-diameter ratio ( $L/d = P$ ) for this consideration instead of separate linear sizes of the anisotropic structure.

The dependence  $D$  (fractal dimension) as a function of  $P$  during the cycle of cooling and heating is retained as  $D = f(P)$ . The inverse function is obtained from a given function by the interchanging of the roles of the independent and dependent variables.

The defined dependence  $D = f(P)$  allows us to conclude that  $P$  can serve to estimate the fractal dimensions in some instances for concentrated LC polymeric solutions and vice versa.

Consequently, the dynamics of fractal dimensions are among the many characteristics of dispersion of LC phases in concentrated polymeric solutions, including the random orientation correlation function.

Therefore, optical studies do not provide unambiguous conclusions concerning the nature of the mesomorphic texture of concentrated cellulose solutions in MMO. The ambiguity in the interpretation of the observed optically anisotropic structure is due to the phase inhomogeneity of high-concentration cellulose solutions at concentrations greater than 45%. Probably, in addition to the mesophase, nonequilibrium

structures hampering more accurate identification of the system are present in such solutions. Nevertheless, the optical polarization studies may provide evidence for the formation of a thermodynamically stable LC phase in MMO solutions of cellulose (at a cellulose concentration  $> 45\%$ ).

Certainly, there is no reason to expect the use of highly concentrated LC cellulose solutions in industry in the years ahead. However, the predicated concentrations of lyotropic LC transitions of cellulose solutions in MMO have now been confirmed.

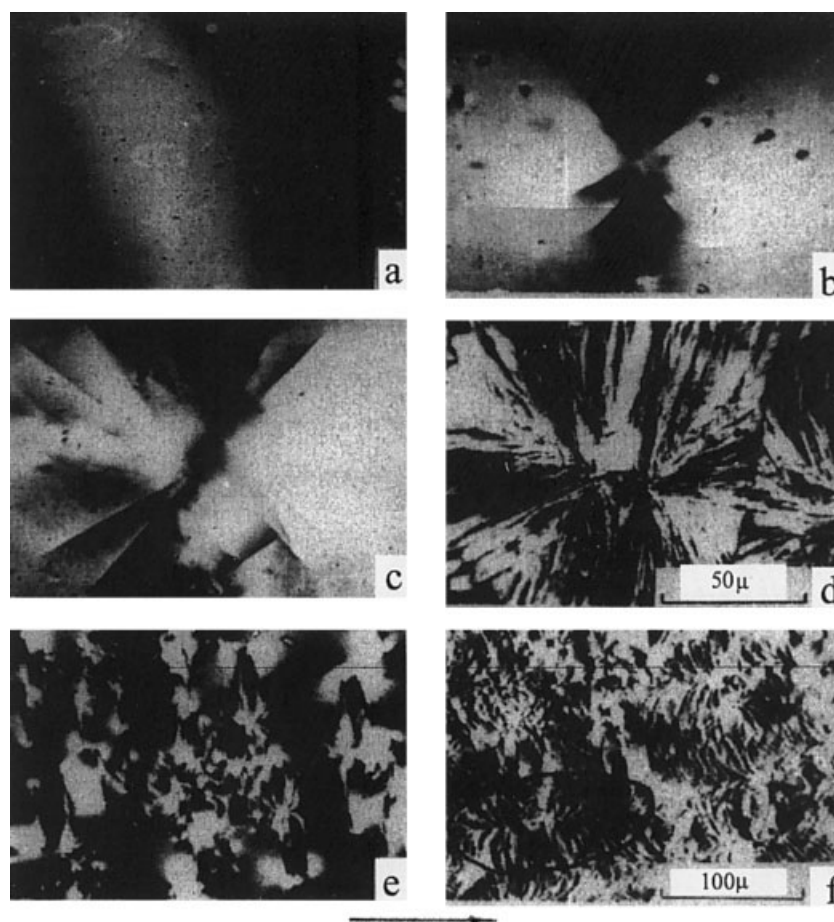
Further research in this field must be directed to the conservation of the LC state in the solid phase after the coagulation of concentrated cellulose solutions in a regenerated bath. Although studies in this range of concentrations of cellulose during the coagulation process have not been carried out, it is known that there is an ordered structure in regenerated cellulose from cellulose solutions in MMO for a concentration range of 18–25%.<sup>28–32</sup> Hopefully, we will soon obtain successful developments concerning the regenerated cellulose LC structure in the field of high-concentration cellulose solutions.

#### STRUCTURAL TRANSITIONS DURING THE COAGULATION OF VISCOSE SOLUTIONS IN A MODEL REGENERATED BATH

The stage of coagulation is the most convenient phase for forming highly ordered structures or an LC state in regenerated cellulose when a jet of viscose enters a coagulating bath of acids and salts, in which it is reconverted into cellulose, which coagulates to form a solid material.<sup>33</sup> Preliminary studies have shown well-ordered and optical anisotropic (spherulitic) structures analogous to LC structures formed by the coagulation of viscose solutions in a regenerated bath of dimethylformamide (DMFA).<sup>34,35</sup> The formation of optical anisotropic structures in CH films from wood cellulose were reported for the first time in ref. 35. There was a disagreement between the unusual nature of spherulitic structures of such samples and the fundamental formation of polymer supermolecular structures.

The greatest interest in such systems concerns the behavior of the formation of spherulitic morphology and the types of new structures. With this design, the comparative study of the structures and properties of regenerated cellulose formed by the coagulation of viscose solutions in regenerated baths of DMFA was carried out.

Microscopic investigations have shown that during the precipitation of cellulose hydrate from solutions, the coagulation processes and structure formation are separate in time. The solution coagulation is accompanied by the formation of an optically isotropic gel [see Fig. 8(a)] consisting predominantly of cellulose



**Figure 8** Microphotographs (400 $\times$ ) showing the formation of spherulites in cellulose hydrate gel (a–d) in the absence of orientation and (e,f) during preliminary orientation: (a) an optically isotropic gel, (b,c) an increase in centrosymmetrical structures, (e) an increase in fibrillar elements perpendicular to the stretching direction, and (d,f) formed spherulites. The times from the moment of coagulation were (a) 0, (b) 30, (c) 45, (d) 90, (e) 35, and (f) 90 s.

xanthate; this is confirmed by the solubility of the gel-type film in water or aqueous alkalis. From the beginning of the film formation (depending on the water and precipitating mixture content), an increase is seen of the centrosymmetrical radial structures [Fig. 8(b)]. Consecutive light and dark film portions with clearly defined dividing borders appear [Fig. 8(c)]. The points dividing the border crossover are the spherulite centers or their fragments.

The obtained pictures mostly have a polarization optical character, and in natural light, the films seem to be homogeneous. The next step is the material ordering inside the space between the radial structures: the angle sizes of the sectors and their amount increase, and the inner spherulite packing is perfected, with this leading to the formation of perfect spherulites of high density [Fig. 8(d)]. Spherulite fragments are formed inside the borders, which are determined by the sizes of the initial anisotropic sections. At this point, the rate of the radial structure increase is unusually high for processes taking place in very viscous gels and at low water contents in the precipitator and can reach tens of micrometers per second.

It is obvious that during precipitation, two processes occur simultaneously: an increase in the polymer solid phase according to the laws of primary structure formation from the nucleus centers and the formation of ordered macromolecular sectors (the initial structure elements) through the whole volume of the solid phase.

A comparative study of the physical properties of ordinary and spherulite-containing cellulose hydrate films has shown that such samples have approximately the same strength but different values of the elongation at break. This is typical for spherulite-containing-polymer elongation mechanisms: the rotation and mutual movement of fibrils made of spherulites, without a change in their fine molecular structure.<sup>36</sup>

By the transition from wholly isotropic films to ones containing perfect spherulites, there are intermediate shapes of spherulite organization that are characterized by similar sizes but different states of inner ordering. Physical tests of a set of samples showed that the film strengths in all the samples were approximately the same, but the elongation at break gradually



increased in proportion to the perfection of the spherulite structure.

At an elongation of an isotropic film [Fig. 8(a)] of 40–50%, radial structures and spherulites form [Fig. 8(e,f)] that are characterized by the growth of perpendicularly oriented fibrillar elements. Such a phenomenon is usually peculiar to structure formation under conditions of preliminary orientation. However, in a deviation from what is commonly described in the literature, the large axes of the spherulites are directed along the applied elongating force. The regularities of the structure formation during the coagulation and orientational elongation of cellulose hydrate into fiber and films have certain similarities to the crystallization mechanism of synthetic polymers from solutions and melts,<sup>37</sup> but they also have some unique features. The unusual two-step character of spherulite structure formation, the location of spherulites in preliminary oriented films along the orientation direction, and the similarity of the tensile strengths of samples having rather different supermolecular structures, cannot satisfactorily be interpreted on the basis of the traditional models of structure formation during the phase decomposition of polymer solutions and spherulite growth due to autoepitaxy, doubling, and branching.<sup>38</sup>

The spherulite organization perfection can be explained by the influence of DMFA in the precipitating bath, which acts as a crystallization suppressor<sup>39</sup> and, possibly, as a plasticizer operating according to the structure plasticization mechanism. However, in the framework of the doubled structure formation model, the effect of sulfuric acid cannot be ignored. The acid accelerates the coagulation and helps the partial crystallization. For this reason, as compensation for the mutual influence of the basic coagulation variable, the

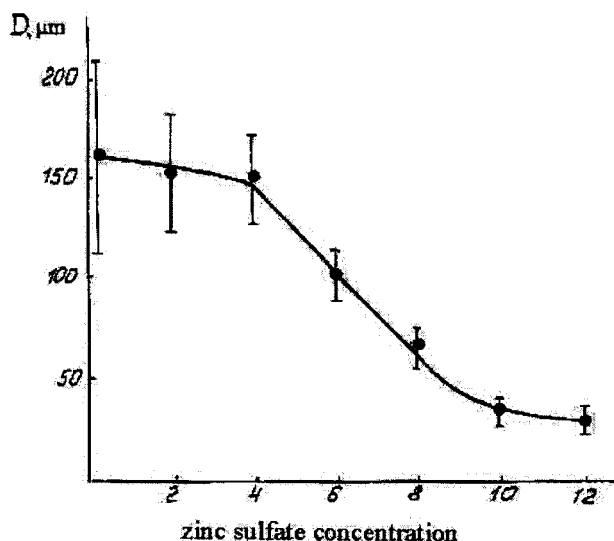


Figure 9 Dependence ( $D$ ) of the spherulite size on the zinc sulfate concentration in the precipitating bath.

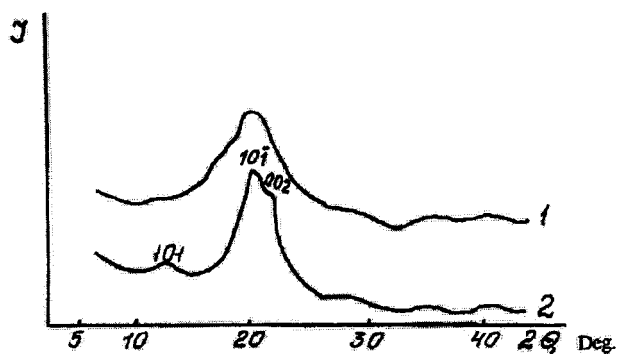


Figure 10 X-ray irradiation dissipation intensity curves for cellulose hydrate films obtained at certain zinc sulfate concentrations in a precipitator based on DMFA: (1) 0.1 g/L and (2) greater than 2.0 g/L.

following series of tests were conducted in a precipitation bath with DMFA and sulfuric acid in the presence of zinc sulfate.

With a change in the concentration of zinc sulfate in the bath from 0 to 12 g/L, the spherulite size was reduced by an order of magnitude (Fig. 9).

On the basis of the data, for zinc sulfate concentrations of 0–4 g/L, the spherulite diameter practically did not change. The data scatter shows a trend of reduction with an increase in the  $\text{ZnSO}_4$  concentration, and the inner structure of the spherulites changed. The latter was determined by small-angle light dispersion and X-ray analysis. The essence of the transformations was probably related to the transition from mesophase cellulose (Fig. 10, curve 1) to cellulose II (Fig. 10, curve 2). The X-ray patterns of films containing spherulites had shapes characteristic of the patterns of cellulose II (Fig. 10, curve 2) with a certain degree of crystallinity. The character of the molecular conformational ordering, evaluated by spectroscopy, was practically unchanged and was characteristic of mesomorphic cellulose. As the zinc sulfate concentration in the precipitating bath increased further, the parameters of the spherulite structure inner ordering did not change noticeably.

Therefore, changes in the sizes of the spherulites and their inner structure occur separately (on the basis of the zinc sulfate concentration scale), this presents an opportunity to evaluate the influence of each of these factors on the physical properties of the samples.<sup>36</sup> The test results are given in Table I.

The tensile strength and elongation at break of cellulose hydrate films and fibers formed in a DMFA medium clearly increase only in the range of zinc sulfate concentrations exceeding 6–8 g/L, corresponding to a significant decrease in the spherulite size (Fig. 9). Therefore, during the formation in zinc-containing baths, not only is cellulose xanthate decomposition retarded, but the obtained films and fibers with a small-spherulite structure have improved ten-



**TABLE I**  
**Effect of Zinc Sulfate Concentration on the**  
**Physical Properties of hydrocellulose**  
**(Orientational Extension-80%)**

Concentration of ZnSO <sub>4</sub> (g/L)	Tensile strength (MPa)	Elongation at break (%)	Strength loss in wet state (%)
0	19.1	6.3	56.4
2	17.9	7.4	50.1
4	19.8	6.1	43.4
6	21.0	6.8	40.9
8	25.4	8.2	38.6
12	30.4	14.5	34.7

sile and strain properties.<sup>40,41</sup> From data in Table I, it also follows that the addition of a small amount of zinc sulfate to the precipitating bath leads to a significant increase in the tensile properties in the wet state but does not change the tensile and strain properties in the dry state. This is very important, for example, in the packaging of food products.

It was very difficult to directly observe the existence of amorphous supermolecular pseudospherulite structures by the physical methods available to us. Nevertheless, an investigation, for example, of the structure of ethyl cellulose films obtained by the spreading of a drop of a 10% solution in CH<sub>3</sub>COOH over a water surface showed that on the film surface there was a relief in the shape of central radial structures (Fig. 11). Such formations were found only during investigation under natural light; this indicated the amorphous character of the investigated samples.

In polarized light, it is possible to determine that the centers of the structure formation are mostly undissolved polymer fibers. Such effects can easily be explained by the growth of the amorphous polymer concentration in the polymer phase near the nucleus centers, which are sections with supercritical concentrations.

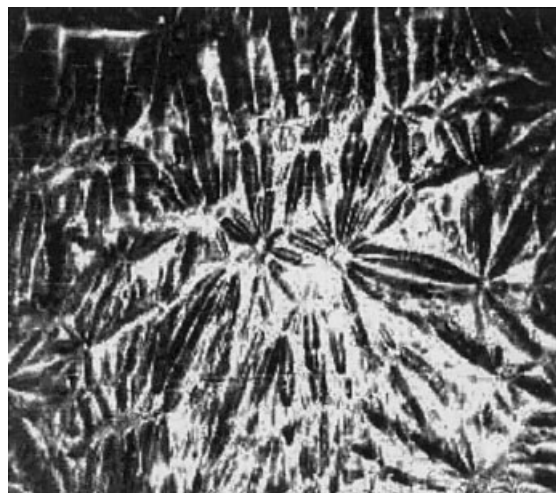
It is possible that the phase decomposition occurs according to the mechanism of the predominant growth of nuclei of a concentrated polymer phase. There are reasons for such an assumption:

1. The rate of solvent molecule diffusion is two to three orders of magnitude higher than the rate of macromolecules. The size of a molecular chain is several times larger than the size of molecules of a low-molecular-weight compound in the coagulating mixture. The low growth rate of the phase formed by large particles corresponds to the fast growth of the phase formed from the small particles.
2. The molecular chains are interpenetrated in the concentrated solution. Because of this, it is necessary to consider not only diffusion<sup>42</sup> but also the possible movement of macromolecules or

their segments caused by chain interactions during the analysis of the structure transformation during phase transitions. The process started in one nucleus center can quickly propagate to other ones.

Therefore, it is possible to use an approach based on the predominant growth of nuclei of a concentrated polymer phase along with the known models of gel formation. As it is analogous to the fractal propagating process from one point in isotropic media, the growth of polymer phase fragments must have a centrosymmetrical character. The continuity of the transition from one fragment to another one is provided by mutual interpenetration of molecular chains. Such a model is close to the classical views on the structures of amorphous polymers described in ref. 43. However, there is an exclusion, in that in this case the existence of any intermolecular or intersegmental interaction is not assumed. We discuss only the general regularities of the isotropic process of propagation in an isotropic medium. However, the modified model of phase decomposition suggested by us can conveniently explain the phenomena associated with the growth of correct structures in polymeric gels after the decomposition of amorphous phases.

By the application of the model to the case of a rayon-precipitator system, it is easy to explain the fast growth of anisotropic structures in the highly viscous gel as the result of intermolecular ordering of supermolecular pseudospherulite forms on the traces of the amorphous phase decomposition. The spherulite arrangement in the oriented gel along the stretching direction seems to be the only possible case because the pseudospherulite structures must transform exactly so at orientation. The imposed sizes of the



**Figure 11** Microphotograph (200×) in nonpolarized light of a centrosymmetrical structure in an ethyl cellulose film.

spherulites (see Fig. 9) can provide a small increase in the fiber and film strength at extension.

According to the data in Table I, the character of the physical properties of cellulose hydrate fibers and films practically follows the regularities known for ordinary rayon films.<sup>44</sup> The difference between isotropic and spherulite-containing samples appears only in the character of the consecutive ordering based on the traces of the initial structure formation. The conditions of precipitation in an aqueous medium are less favorable for the proper ordering because the water activity helps the crystallization of cellulose crystallites. On the contrary, the organic solvents retard the cellulose crystallization, and the ordering occurs because of the transition into the mesomorphic state.

The description of a suggested mechanism is possible with the synergetic approach to the structure formation process analysis, with consideration given to the collective effects and self-ordering of the spherulite structures. In this experimental investigation, we have found that the scale hierarchy of ordered structural elements growing in cellulose hydrate films may serve as the basis for the determination of the relationship between microparameters and macroparameters of spherulite growth with fractal theory to describe the self-similar ordering elements and the fractal dimension as the characteristics of the dynamic object structure.

If we consider the crystal phase growth as a non-equilibrium phase transition at the points of nucleus formation, then it is necessary to determine the fractal dimensions of the structures, which control the free spherulite growth. The structures around the nuclei are the dynamic multitude possessing properties of universality and invariability and also an ability of self-similar growth. The fractal structures possess the same abilities. Because of this, we tried to use the concept of fractals for the quantitative description of spherulite structures. This is the basis for the determination of the universal relationship between the parameters of the dynamic structure and physical properties.

According to Mandelbrot,<sup>45</sup> the self-similarity means that there is a function that copies the universality on itself with the help of a scalar  $Z$ , which is an automodel ratio. For nonstandard self-similar shapes, the whole can be divided into  $M$  parts obtained throughout automodel ratio  $Z$  and connected with a fractal dimension by the following expression at  $0 < D < 3$ :

$$Z^D = 1/M \quad (1)$$

To use the expression for the analysis of self-organizing structures, we must determine the physical meaning of parameter  $M$ . It comes from an equation of

singular spherulite growth kinetics, which are described by the growth of self-analogy:

$$r^{i-1}/r^i = \Delta^{1/M} \quad (2)$$

where  $r^{i-1}$  and  $r^i$  are the previous and next spherulite sizes, respectively, in the direction of the crystal phase growth.  $M$  is a number that changes according to the law of geometric progression and corresponds to the periodicity of the cycles in the self-organizing systems. The number determines the upper border of the intermediate asymptotic block at  $M \rightarrow \infty$  and the lower border at  $M = 1$ . The function  $\Delta^{1/M}$  is just the function of self-analogy, which copies the multitude on itself and determines the periodicity of repetition of an intermediate asymptotic block at self-similar spherulite growth. The function gives compressed information on different scale levels. The possibility of information compression is determined by the scale invariance of the previous spherulite size in the spectrum for the next size. Because of this, the self-similar spherulite growth can be represented as blocks of intermediate asymptotics in which the results of spherulite size thresholds have taken place. As a result, in each exit from the block of intermediate asymptotics, the spherulite size increases in value as  $\Delta^{-N}$ , where  $N$  is the number of iterations. This allows us to use the automodel function  $\Delta^{1/M}$  at  $M \rightarrow \infty$  as a self-analogy function of  $Z$  in eq. (1):

$$Z^D = \Delta^D = 1/i_r^c \quad (3)$$

where  $i_r^c$  is the scale coefficient representing the ratio of the maximal scale to the minimal scale of observation and characterizing the spherulite critical parameters, including the maximal increase  $r^{\max}$  as the result of the self-analogy growth of microspherulites of initial sizes  $r_0$  to  $r_{0c}$ .

To provide a quantitative description of spherulite structure growth, we must give numbers to the nucleus center image, for example, by replacing it with a lattice of  $n$  points ( $n$  is usually ca.  $10^{16}$ ).<sup>46</sup> The generalized dimension can then be calculated by several independent methods: the sand box methods, the density-density correlation function method, and the radius gyration method.<sup>46</sup> In this work, we used the radius gyration method. The results show that the dimension is 1.8–1.9.

## CONCLUSIONS

We can make the following general conclusions on the basis of this overview of the state of the art of structure formation in commercial cellulosic systems.

In cellulose solutions in MMO with cellulose concentrations greater than 45%, a stable LC phase arises.

This type of mesophase state is not set because of the high viscosity of the cellulose solutions. No examples are known of the commercial use of concentrated anisotropic cellulose solutions. Nevertheless, regenerated cellulose materials have a number of extra properties not peculiar to common rayon.

The modification of the regenerated bath in the viscose process allows us to fix peculiar supermolecular structures, such as LC structures. The strength of preproduction samples of new regenerated baths already has been reported by scientists in industry.

Nonspecial methods for the analysis of hydrated cellulose samples based on fractal theory have been developed. In the future, we can expect the convenience of the proposed fractal method for working with the polymer structure as a basis for a new applied polymography.

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