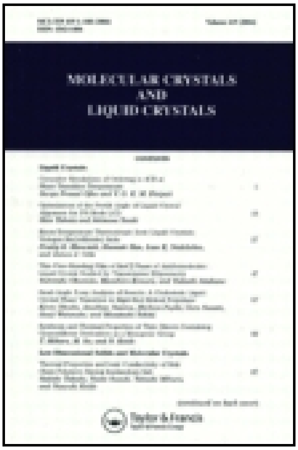

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# Study of Phase Transitions in Liquid Crystal Systems of Polysaccharides and their Derivatives

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# Study of Phase Transitions in Liquid Crystal Systems of Polysaccharides and their Derivatives

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The phase transformations in hydrocellulose were studied by method of determination of fractal dimension. The hydrocellulose was prepared by precipitation from viscose in model precipator. The films contained elements of spherulite structure. We are analyzed the spherulite structure in terms of Mandelbrot's simple model. The fractal dimension on base micrographs was estimated. It is shown the high correlation meaning of fractal dimension with physical and mechanical properties of samples.

*Keywords:* hydrocellulose; fractal; phase transitions; fractal dimension; spherulite; polysaccharides

## I. INTRODUCTION

### A. Objectives

At the present time the polysaccharides and its derivatives are the most use of nature polymers. The materials on basis of it have a good fields of application in all branch's of industry and so the polysaccharides until now remain the main objects of study in the world [1, 2]. The research in the past decades have allowed to get the new materials and modernize the old ones. It was to attain due to conversion polysaccharides objects in liquid crystal (LC) state. Already in the early sixties the theoretical ability of realization mesophase in cellulose and other polysaccharides has been predicted. Since that time well-defined LC solutions and films of most complex and simple cellulose ethers have successfully obtained. It was shown that it formed cholesteric mesophase, contained spherulites and other supermolecular textures [3,4]. However, until now at investigate the most practical significant cellulose materials, i. e. hydrocellulose obtained from viscose, concentrated solutions of cellulose in direct solvents and some other systems the exactly defined LC phase could not found. The results obtained different methods have brought to contradictive and mutually exclusive conclusions. Especially apparently it should be noted in concentrated solutions cellulose in N-methylmorpholin-N-oxide. For example, the nematic mesophase was shown by optical analysis and cholesteric by rheological methods. The daybreak and sunset of manufacture hydrocellulose from viscose was into twentieth century but to present day we may not speak nothing about contingency getting or kind of LC state in this system. Now we may see the analogous situation in study of new methods of manufacture hydrocellulose at direct dissolution [5,6,7]. The practical decision of this problem wasn't up to date. It is known from experience that type of mesophase define by super-molecular structure of investigated material. A spherulite or spherulitelike texture is characteristic element of mesophase in biopolymers [5]. Originally the spherulitelike texture in polysaccharide was obtained for LC system of cellulose ethers [8,9,10]. After that a long time it have undertook attempts to prepare similar structure in usual hydrocellulose objects. Some of the nisus were crowned with success and it was noted that such fact is not sufficient warranty for existence of LC state in hydrocellulose. Therefore the spherulite structure not define kind of mesophase or possibility of it realization in that case. Although the behavior of spherulite structure in hydrocellulose have much in common with similar structures of usual LC polymer materials. But the complexity super-molecular structures of such system forbid to establish more exactly structure parameters of hydrocellulose systems.

### B. Problem of alternative methods of define of structural parameters in hydrocellulose

Usual the majority of researchers note the inconsistency of results study of hydrocellulose and generally they aren't offer a way of solving this baffling problem. We also have noted contradictoriness of results by diverse methods during study of formation pseudo-spherulite structure at precipitation of hydrocellulose from viscose in bath of dimethylformamide which is advantaged such structures. In the capacity of new way of description such cases by method estimation of fractal dimension the micrographs of super-molecular spherulite structure was offered [11]. In ordinary use of the method estimation of fractal dimension decide three main tasks [12]:

1) verify a self-similarity
2) define boards of a self-similarity
3) calculate of a fractal dimension.

The polarized microscope was used to obtain this signs at precipitation of hydrocellulose in the wide interval of resolution and magnifying power. Fig. 1, 2 illustrates the growth of some spherulites in film of hydrocellulose. The weak self-similarity was observed during all process of growth.

*FIGURE 1.*

Microphotographs (x400) showing formation of spherulites in cellulose hydrate gel.

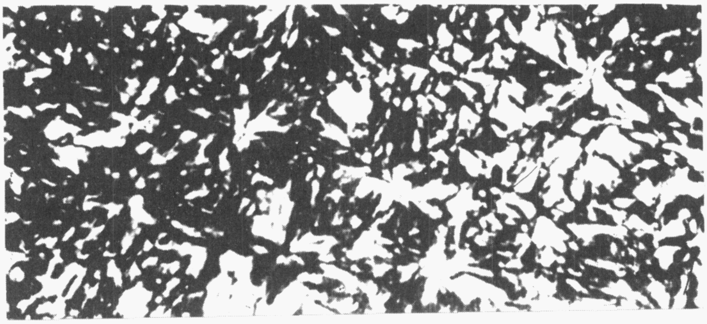

FIGURE 2.

The formed central-symmetrical structure in films hydrocellulose. (Microphotographs x 200 in polarized light).

The growth of solid phase at precipitation was considered for proof the existence of the fractal dimension in spherulite structure as a non-equilibrium phase transition in the points of nuclei formation, then it is necessary to determine the fractal dimension of structures which control the free spherulite growth in the points of nuclei formation, then it is necessary to determine the fractal dimension of structures which control the free spherulite growth. The structures around the nuclei are the dynamic multitude possessing properties of universality and invariability and also ability to self-analogous growth. The fractal structures possess the same abilities. Because of this, we tried to use the concept of fractals for quantitative description of spherulite structures. This is the basis for determination of universal relationship between parameters of dynamic structure and physical properties.

It is known that the character of growth a new phase on micro- and macrolevels possible to describe with the help of function $\Delta^{1/M}$, where M is changed in a manner of geometric progression and corresponding to the cycles' periodicity in the self-organizing systems. Using of this function would allow to analyse the dynamics of growth LC phase at conditions it free growth in polymer systems.

According of Mandelbrot, the self-analogy means that there is a function which copies the universality on itself with help of scalar Z which is an auto-model ratio. For non-standard self-analogous shapes, the whole can be divided on M parts obtaining throughout auto-model ratio Z and connected with a fractal dimension by expression:

$$Z^D = 1/M \tag{1}$$

at $0<D<3$.

To use the expression at analysis of self-organizing structures, it is necessary to determine the physical meaning of parameter M. With this object in mind an analysis was made of the growth of singular spherulite from point of nucleation to beginning of secondary structure formation. For analysis of fractal dimension in point nucleation it necessary select two scale of observation: $r^{max}$ – maximum size of auto-model zone of nucleation (fluctuation) and $r_{oc}$ – critical size of nuclei in this zone, when it became stable. Then the spherulite during the auto-model increment achieve meaning $r_C^{max}$, that correspond strictly to beginning of secondary structure formation. The scale of observation $r_{oc}$ is critical size of nuclei of spherulite within the limits of which ratio surface energy and volume energy have constant meaning. Within the limits $r_{oc}$ the processes of structure formation is determined non-equilibrium phase transitions between isotropic phase to quasi-amorphous phase and from quasi-amorphous phase to anisotropic phase. Seeing that $r_{01}$ ; $r_{02}$; $r_{03}$… $r_{0N}$ – is critical sizes of nuclei's able to auto-model grow. The $r_c^{min}$ and $r_C^{max}$ – are minimal and maximal size of spherulite. The ration $r_c^{min}/r_C^{max}$ characterise extremal level of coefficient of scale ($i^{Cmax}_r$) at free growth from nuclei able to formation spherulite $r_0$ until $r_C^{max}$.

$$r_c^{min}/\ r_C^{max} = i^{Cmax}_r \tag{2}$$

The growth of zone from $r_0$ to $r_C$ is modelled by at auto-model growth of boundaries anisotropic phase in terms of function $\Delta^{1/M}$. The physical significance of parameter M is possible to describe with help of function of self-similarity for that the scalar quantity $i^{Cmax}_r$ is replaced on function $\Delta$. It is coming out from equation of singular spherulite growth kinetics which is described by the growth of self-analogy:

$$r^i\ /\ r^{i-1} = \Delta^{1/M} \tag{3}$$

where $r^i$ and $r^{i-1}$ are next and previous spherulite size in direction of the crystal phase growth correspondingly. The M is number which is changing according the law of geometric progression and corresponding to the cycles' periodicity in the self-organizing systems [13]. The number determines the upper border of the intermediate asymptotic block at M →∞ 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 determined the periodicity of repetition of an intermediate asymptotic block at self-analogous spherulite growth. The function gives a 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 to the next size. Because of this, the self-analogous spherulite growth can be represented as blocks of intermediate asymptotics in which the consequence of spherulite sizes thresholds is taken place. At the consequence, in each exit from the block of intermediate asymptotics , the spherulite size increases on value $\Delta^{-N}$, where: N - iterations. This will allows to use the auto-model function $\Delta^{1/M}$ at $M \to \infty$ as a self-analogy function Z in expression (1) expressing it as follows:

$$Z^D = \Delta^D = 1/\, i^C{}_r \qquad (4)$$

Where : $i^C{}_r$ - scale coefficient taking into account the ratio of maximal scale to minimal scale of observation and characterizing the spherulite critical parameters - is maximal increase r max as the result of self-analogy growth of micro-spherulite of initial size $r_0$ to $r_C{}^{max}$.
Regardless of that whether or no existence spherulite is possible physical or it is abstract construction but such conclusion is obtained as result of statistical averaging-out elements of structure formed solid phase. Therefore a measurement of some structure sensible physical or physicochemical quantities refers to spherulite in its statistical representation i. e. to statistical spherulite. Apparently this model not deny possibility selective filling up inter-spherulite space by amorphous and quasi-amorphous phase. Certainly, in this context on fixed stage of growth already not will satisfy condition decrease of density of set with increase of size. All the more this condition in reality this sort of fractal model practical not satisfy. But from mathematical point of view so model is correct towards fractal theory and after that we may use it as base to calculate fractal dimension pictures of spherulites.

## II. EXPEREMENTAL SECTION

General ideas and detailed descriptions of the apparatus and materials were reported previously and will not be repeated here [11]. All the experiments reported herein were conducted at room temperature. The patterns of spherulite structures were recorded on photographic films.

The fractal dimension was calculated by Fractal Dimension Calculator. Fractal Dimension Calculator takes a black and white image in the form of a file or clipboard contents and uses the box counting algorithm to estimate the fractal dimension of the object represented in the image. It creates a text file containing the various box sizes and resulting counts (and their appropriate logarithm values).

## III. RESULTS AND DISCUSSION

In that way the body of experimental data on different stages of growth presumable LC phase at precipitation was analyzed with help above described method, i. e. suitable program system. In concordance with peculiar properties of LC objects we have made some changes into work of the program system in order to described its complex morphology and defined a fractal dimension. After that comparative researches between mechanical properties of simples and its values of fractal dimension super-molecular structures was made. On the basis of such studies it was shown that at approach the fractal dimension to integral values the strength increased on average up to 15-30% and vice versa. That indirect it have confirmed the relationship between the morphology features and physical properties of cellulose and its derivatives LC simples [14].

## IV. CONCLUSION

Proposed approach in restrained terms allow to use the method of fractal dimension for study of phase transitions in polysaccharides as independent characteristic degree maturity of super-molecular spherulite structures. The method showed a good correlation with strength properties that enable in practice using it as unific characteristic at study LC biopolymers and others LC polymer systems.

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