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Soviet-era science, translated into English

# CHEMISTRY

B. A. ZAKHAROV, V. I. IVANOV, G. A. KRYLOVA, and N. G. VYUNOVA

1958

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**Abstract**

**Full Text**

## **CHEMISTRY**

**B. A. ZAKHAROV, V. I. IVANOV, G. A. KRYLOVA, and N. G. VYUNOVA**

# **MOLECULAR HOMOGENEITY AND PROPERTIES OF CELLULOSE**

*(Presented by Academician P. A. Reh binder, 3 VI 1958)*

At one time the opinion became established that the molecular weight of cellulose, as a high-molecular compound<sup>(1-4)</sup>, is<sup>(5)</sup> about 500,000. Studies of the retardation of oxidative degradation of cellulose and viscometric measurements led to a value of the molecular weight<sup>(6-8)</sup> close to 1,600,000; this value was confirmed in recent works<sup>(9-11)</sup>. As early as 1939, strange and difficult-to-explain observations were made<sup>(12-13)</sup>: the strength properties of natural cellulose fibers in the solid state are revealed at an average molecular weight ( $\bar{M}$ ) of about 32,000 and rapidly increase as  $\bar{M}$  rises to 113,000; then, as  $\bar{M}$  rises to 160,000, the increase becomes progressively less sharp; a further increase in  $\bar{M}$  has no effect on strength.

It was also established<sup>(14,15)</sup> that cellulose is heterogeneous with respect to the length of its chain molecules. Therefore the indicated value of the molecular weight should be regarded as an average value, definitely dependent on the method of measurement.

A general idea of the heterogeneity of cellulose is given by the average coefficient of heterogeneity  $\bar{U}$

$$\bar{U} = \frac{\bar{M}_w}{\bar{M}_n} - 1,$$

where  $\bar{M}_w$  and  $\bar{M}_n$  are, respectively, the weight-average and number-average molecular weights. For homogeneous cellulose  $\bar{U} = 0$ .

In modern studies the heterogeneity of cellulose is described more fully and accurately mathematically by means of the functions of integral and differential distribution<sup>(16)</sup>.

At the present time, individual attempts are being made to evaluate changes in heterogeneity in various processes of cellulose isolation and processing, and to relate heterogeneity to the quality of cellulose and to the properties of cellulose

Figure 1

Figure 1: Figure 1

products. The main result of these studies is the recommendation to free cellulose from very short and very long chain molecules. The proposed evaluation of heterogeneity and of its relation to the mechanical properties of films of cellulose esters, with the aid of the shape factor of the mass-distribution curve, is rather complicated and not very promising.

We set ourselves the aim of detailing more fully the problem of the length of chain molecules by refining the concepts and significance of the homogeneity of cellulose. In our view, the following two characteristics of homogeneity, obtained from the mass-distribution curve, are of decisive importance: the degree of homogeneity (monodispersity) reveals the physical essence of the phenomenon—the preferential concentration of the substance near the maximum on the mass-distribution curve; this characteristic is described by the height and base of the maximum on the curve. The second characteristic

is determined by the value of the degree of polymerization ( $P$ ) corresponding to the maximum.

The following considerations indicate the decisive importance of molecular homogeneity for the strength properties of artificial fibers. Cellulose chain molecules having the same length will have the same form in solution. Therefore the viscosity of such a solution, homogeneous with respect to molecules, will be uniform at different concentrations in each elementary unit of volume of the solution. In turn, the uniform viscosity of the spinning solution will ensure, in the process of spinning artificial fibers, greater uniformity of orientation and a high uniformity of packing of the molecules in the elementary fiber, which should lead to a high value of the strength properties of the fiber. As is known, the high strength of a fiber is associated with a uniform distribution of the applied stress<sup>(17)</sup>. This uniform distribution attains limiting importance in the case of a homogeneous fiber prepared from homogeneous cellulose.

**Fig. 1.** Molecular homogeneity of cellulose, expressed as the mass-distribution function  $m_p = f(P)$ .

1 —homogenization of cotton cellulose with dilute nitric acid; 2 —homogeneity of the cellulose of an artificial fiber, meril, with breaking length 54 km; 3 —homogeneity of wood cellulose obtained by the chlorocellulose method (paper from this cellulose has a breaking length of 9 km); 4 —heterogeneity of the original cotton cellulose.

It follows from the views set out above that the supramolecular structure of cellulose (the mutual arrangement of molecules and intermolecular bonds) must be determined and can be regulated by the magnitude of the molecular homogeneity.

For an experimental verification of the ideas proposed, we used the following approach. By fractionating, by the precipitation method<sup>(18)</sup>, nitrofibers obtained from cellulose in finished articles (natural or artificial fibers, papers) and possessing a decreasing magnitude of strength properties, we should obtain mass-distribution diagrams showing a decrease in molecular homogeneity.

From curve 2 in Fig. 1 it follows that the high breaking length of meril fiber (54 km) corresponds to a high degree of homogeneity at  $P = 450$ . Curve 3 in Fig. 1 shows considerable homogeneity of chlorocellulose at  $P = 2800$ . Paper manufactured from this cellulose has a high breaking length (9 km).

Our investigations showed the presence, in a number of celluloses, of a high degree of homogeneity at the following values of the degree of polymerization: Swedish cord celluloses 900-1200, Canadian cord cellulose 2000, domestic

domestic cellulose (sulfate cellulose, refined by the IOKh method) is 850, and Syas unbleached cellulose is 2800. Cellulose acetate films have an average degree of homogeneity at  $P = 250$ .

Quite naturally, the question arises as to what means are available for the controlled change of molecular-weight heterogeneity in order to obtain a high degree of homogeneity at a given value of the degree of polymerization. Our recalculations of experimental data<sup>19</sup> on fractionation showed that hydrolysis with dilute hydrochloric acid and alkaline pre-ripening do not ensure the production of cellulose with a high degree of homogeneity.

We treated cotton cellulose prepared according to Corey and Gray (its heterogeneity is shown by curve 4 in Fig. 1) with dilute nitric acid. As can be seen in Fig. 1 (curve 1), the cotton cellulose acquired a high degree of homogeneity at  $P = 400$ . The homogenizing effect was also established with wood cellulose.

The results obtained are the first confirmation of the importance of cellulose homogeneity for strength and indicate one of the possible ways of attaining the required homogeneity.

It should be assumed that molecular homogeneity is of great importance for the chemical and physical properties of cellulose and for the behavior of natural and synthetic high-molecular compounds.

N. D. Zelinsky Institute of Organic Chemistry  
Academy of Sciences of the USSR

Received  
25 V 1958

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