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Research Article

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Molecular-Weight Characteristics of Chitosan Sulfate *Bombyx mori*

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Abstract The molecular mass characteristics of chitosan sulfate obtained from chitin extracted from silkworm pupae were studied using fractionation and viscometry methods. Its polydispersity and medium-viscosity molecular weight were identified, the found values of length of segment A and their number in the chain indicate a high stiffness of the chains.

Keywords chitosan sulfate, chlorosulfonic acid, molecular mass distribution

Introduction

Natural polysaccharide - chitin of silkworm pupae *Bombyx mori* is a very promising source for the production of chitosan and its water-soluble derivatives, in particular, chitosan sulfate (CS), which is of great interest for medicine [1]. Substitution of sulfogroups occurs mainly due to C-2, C-3 and C-6 hydroxyl and amino groups of chitosan under the influence of high temperatures [2-5]. Samples of SC with a high degree of substitution (DS≥1) and solubility (P>99%), recommended for medicine, can be obtained by sulfating in chlorosulfonic acid (CSA) at 55÷80 °C for at least 3.5 hours. However, such reaction conditions are quite strict, occurring with the destruction of polysaccharide chains and changes in the molecular mass distribution (MMD) and polydispersity (P), as well as the number (N) of segments [6]. In this case, it is very important to identify the optimal reaction conditions for obtaining a SC sample with the necessary molecular-weight characteristics for practical use, however, this issue has not yet been studied at a sufficient level. This work is performed in this aspect, in which the molecular mass characteristics of the samples of Bombyx mori SC were studied using methods of fractionation and viscometry of polymer solutions [6-9].

Objects and methods

The initial sample of chitosan was obtained by deacetylation of chitin isolated from silkworm pupae according to [1]. The value of the characteristic viscosity [η] = 1.2 DL/g of chitosan in 2% CH_3COOH+NaCl was determined according to the Huggins law [9]. Based on [η], the values of the molecular weight of chitosan $(M_\eta)_{x3} \approx 53100$ were calculated using the Mark-Kuhn-Hauvink formula [1].
The resulting *Bombyx mori* chitosan was sulfated according to [2,3] in CSA medium at 50 ^oC for 3 hours. The given reaction condition is considered optimal. The results of elemental analysis showed that the obtained sample of SC is characterized by the degree of substitution of sulfogroups DS≈1,2. The solubility of the sample in water is 99.3%, the resulting SC shows a polyelectrolytic effect, which was excluded by adding 0.25 M NaCl during viscometric experiments. According to the value of the characteristic viscosity of the SC [η] ≈ 0.14 dl/g in water+NaCl (0.25 M), the molecular weight was calculated using the equation $[\eta] = 4.97\times10^{-5}M_\eta^{0.77}$ dl/g [4,7,8], which was $M_\eta \approx 30200$. The results obtained show that M_η SC decreases by 1.75 times compared to $(M_\eta)_{chitosan}$ of the original chitosan. This indicates that there is a noticeable degradation of the SC molecules when sulfated in chlorosulfonic acid compared to other sulfating reagents.

Depending on the destruction, the molecular mass distribution changes, which can be estimated by diffraction and determination of the molecular weight by viscometry [4,6].

Results and Discussion

Fractionation of the aqueous solution of the initial SC sample was performed by fractional precipitation using acetone as the precipitator. In this case, 9 fractions were obtained, the characteristics of which, in particular, mass (m_i), mass fraction (f_i), as well as cumulative mass fractions ($W'(M_i)$), calculated using the expression (1), are shown in the table 1.

$$W'(M_i) \approx 0{,}5f_i + \sum f_i - f_{i-1} \qquad (1)$$

where *i* – number of a fraction [9].

Table 1: Mass and molecular-mass characteristics of SC fractions

Number of a fraction	Mass of fraction, m_i, g	Mass fraction, f_i	Cumulative mass fraction, $W'(M_i)$	$[\eta]$, dl/g	M_η
1	0.5160	0.2755	0.8620	0.16	35900
2	0.4551	0.2430	0.6027	0.14	30200
3	0.2512	0.1341	0.4141	0.12	24700
4	0.1277	0.0681	0.3130	0.11	22100
5	0.1448	0.0773	0.2404	0.10	19500
6	0.1125	0.0601	0.1716	0.09	17000
7	0.1046	0.0558	0.1137	0.07	12300
8	0.0866	0.0462	0.0627	0.06	10000
9	0.0742	0.0396	0.0198	0.05	7900
Sum, Σ	**1.8727**	**0.9997**	**-**	**-**	**-**

Curves of the integral and differential molecular mass distribution of the SC sample are constructed, which are shown in Fig. 1. It can be seen that the SC sample is characterized by a certain molecular mass distribution. Low molecular weight plot for the differential of the curve is comparatively large. This indicates a noticeable destruction of chains with the formation of a set of SC fractions characterized by a low molecular weight [9].

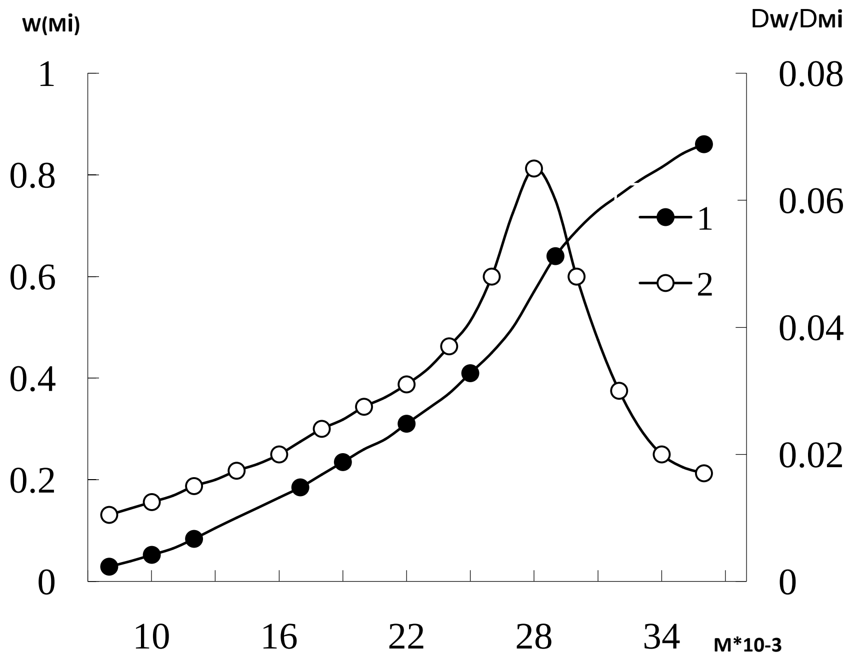

Figure 1: Integral (1) and differential (2) curves of molecular-weight distribution of SC Bombyx mori

According to [9], based on the data in table 1, the values of the average weight M_w=19900 and the average number M_n=15900 molecular weight SC were calculated, and the polydispersity of this sample was determined M_w/M_n=1.25. The found values of M_w/M_n allow us to refer the test sample SC obtained under the specified conditions of sulfation to polymers characterized by a narrow polydispersity by molecular weight.

It was found that the average molecular weight of $M_\eta \approx 30200$ is noticeably greater than the average mass molecular weight of $M_w \approx 19900$. This indicates a high stiffness of the chains, which is in good agreement with the data of the calculation carried out on the basis of the theory of translational and rotational friction of the model of persistent chains [9].

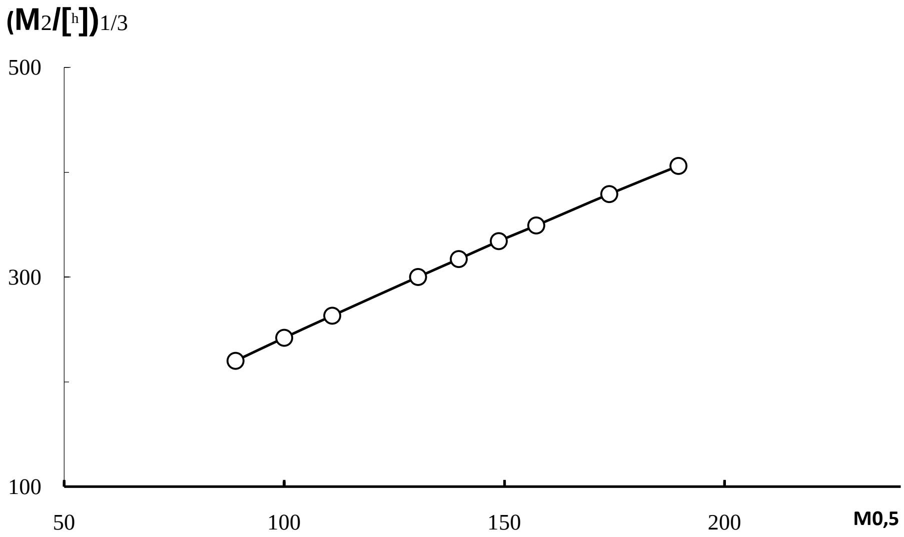

Figure 2: Dependence of $(M^2/[\eta])^{1/3}$ from $M^{0,5}$ for solutions of SC samples

You can see from Figure 2, the dependence of $(M^2/[\eta])^{1/3}$ от $M^{0,5}$ are presented, in accordance with the equation $(M^2/[\eta])^{1/3} \approx F^{-1/3}(M_o/\lambda_s A)^{0,5}M^{0,5} + M_o/\lambda_s (k/3\pi A_o 100^{1/3})(lg(A/d) - 1,056)$

Where $F \approx 2,21*10^{23}$ – hydrodynamic constant; $M_o \approx 401$, $\lambda_s \approx 0,51$ nm and $d \approx 1$ нм, weight, length and diameter of an elementary link, respectively; $A_o \approx 3,7*10^{-10}$ erggrad-1 mol-1/3 – hydrodynamic invariant; k - constant.

The value of the slope $F^{-1/3}(M_o/\lambda_s A)^{0,5} \approx 1.83$ was determined and the length of the chain segment $A \approx 15$ nm was calculated for the SC *Bombyx mori*. The obtained value of A is typical for polysaccharides of this class [6,7]. Since, the contour length of the chains $(M_i/M_o)\lambda_s \approx L$ of the studied SC fractions ranges from 10-50 nm, then the number of n segments is no more than 3. This, according to [6,10], indicates the high rigidity of the chains obtained by the SC *Bombyx mori*.

Conclusions

Thus, the results of studies to determine the molecular mass characteristics of Bombyx mori SC, namely, the fractional composition and molecular mass distribution of this polysaccharide by fractionation and viscometry show that the resulting SC sample with the degree of substitution S=1,2 and water solubility P = 99,3% is a low-molecular sample characterized by an average molecular weight of $M_\eta \approx 30200$, a narrow molecular mass distribution ($M_w/M_n \approx 1,25$) and high chain stiffness ($A \approx 15$ mn, $N \approx 1 \div 3$). These results are valuable for identifying the optimal conditions for the synthesis of SC samples that are characterized by certain values of molecular weight necessary for the recommendation of practical application. According to [11], SC samples with such molecular mass characteristics can be used in the field of biomedicine, pharmaceuticals, cosmetology, etc.

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