Chemistry of Natural Compounds, Vol. 30, No. 4, 1994

HYDROLYTIC SPLITTING OF CARBOXYMETHYLCELLULOSE

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UDC 541.6.69:614.01

The possibility has been shown of using hydrolytic splitting to regulate the degree of polymerization and the molecular and compositional homogeneity of carboxymethylcellulose, which makes it suitable for the production of medico-biological polymers.

In the creation of physiologically active polymers the problem of using a molecularly homogeneous biodestructable polymeric matrix acquires enormous importance, since it determines their toxic and cumulative properties and the rates of resorption and elimination from the organism [1].

With the aim of obtaining molecularly homogeneous carboxymethylcellulose (CMC) with different degrees of polymerization (DPs) we have investigated the acid hydrolytic splitting of an industrial CMC with DP 530 and a degree of substitution with carboxymethyl groups (DS) of 80 ± 2.

On the hydrolytic splitting of cellulose and its derivatives in the presence of mineral acids a decrease in the DP takes place as a result of the cleavage of the 1,4-β-anhydroglucopyranose bond [2]. Hydrolytic splitting was conducted under heterogeneous conditions in isopropyl alcohol in the presence of hydrochloric acid. The influence of the temperature, the concentrations of the reactants, and the duration of the reaction on the DP of the hydrolyzed CMC was investigated.

As can be seen from the kinetic curves of the hydrolytic splitting of CMC (Fig. 1), the reaction proceeded initially at a fairly high rate, and with an increase in the molar ratio of HCl to CMC the rate of the reaction rose. It must be mentioned that at a CMC:HCl ratio of 1:3 the rate of the reaction was low and it rose sharply at a ratio of 1:5. A further decrease in the ratio had no effect on the rate of hydrolysis.

Since the hydrolytic degradation of cellulose is a 1st-order reaction, the semilogarithmic anamorphosis of the kinetic curve should be rectilinear [2]. The form of the curves for the hydrolytic splitting of CMC shown in Fig. 2 is due to the fact that the reaction takes place initially in comparativley readily accessible disordered regions of the material under investigation; i.e., it shows the influence of the supermolecular structure on the rate of the process. With a rise in the temperature of the reaction from 10 to 85°C the relative catalytic activity of the acid increased, which led to a more intensive nature of the hydrolysis.

X-Radiographic studies of samples of CMC with different DPs obtained by hydrolytic splitting showed that at a DP of 450-200 their degree of orderedness scarcely changed and amounted to 45%. Increases in the depth of splitting to DP 100 and to DP30 were accompanied by a rise in the crystallinity of these samples to 54%. This therefore confirmed the conclusion that in the course of acid hydrolysis there is a faster dissolution of the amorphous regions and samples of CNC with a more ordered structure are obtained, as the result of which there is a passage from a less dense to a more dense sructure.

Also in agreement with these results was the change in the sorption properties of the samples of hydrolyzed CMC investigated – with a decrease in DP from 530 to 30 the sorption of water vapor at a relative humidity of 65% fell from 4.30 to 1.50% as a result of the elimination of the amorphous fraction. A successive decrease in the specific surface (S_{sp}) and in the size (r_k) and volume (W_0) of the pores with a decrease in the DP was also detected for samples of CMC subjected to heterogenous hydrolytic splitting (Table 1).

A study of the molecular mass distribution (MMD) of the hydrolyzed CMC samples in comparison with the initial material showed that it contracted in the course of hydrolytic splitting (Fig. 3). Thus, while the initial CMC was character-

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0009-3130/94/3004-0499$12.50

TABLE 1. Sorption of Water Vapor by Samples of Hydrolyzed CMC, %

Relative humidity	Degree of polymerization of the CMC samples		
	530	200	30
10	1.60	1.35	0.45
30	2.90	2.55	0.95
50	3.80	3.25	1.20
65	4.30	3.90	1.50
80	5.40	4.80	2.00
90	7.00	6.10	2.55
100	12.40	10.30	3.60
Sorption characteristics			
Ssp, m^2g	83.29	74.86	30.03
Wo, cm^3/g	0.12	0.10	0.03
r_K, Å	30	27	24

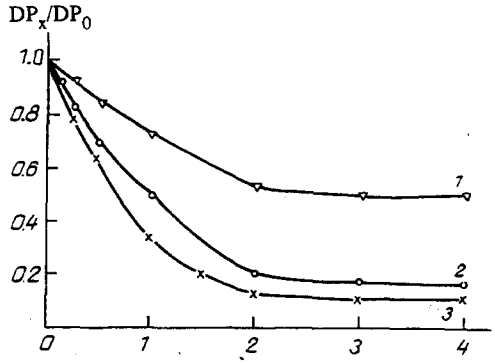

Fig. 1

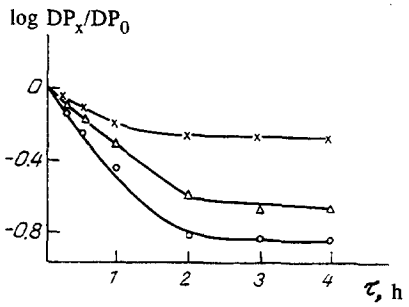

Fig. 2

Fig. 1. Kinetic curves of the hydrolytic splitting of CMC. Conditions: T = 75°C; CMC:HCl = 1:5 [1) C_{HCl} = 1 N; 2) C_{HCl} = 2 N] and 1:10 [3) C_{HCl} = 2 N].

Fig. 2. Semilogarithmic anamorphosis of the kinetic curves for the hydrolytic splitting of CMC. Conditions: T = 75°C; CMC:HCl = 1:5 [1) C_{HCl} = 1 N; 2) C_{HCl} = 2 N] and 1:10 [3) C_{HCl} = 2 N].

ized by a broad MMD and the DPs of individual fractions ranged from 150 to 1400 (curve 1), at a low degree of hydrolysis (curve 2) the maximum on the differential curve had shifted in the direction of lower DPs and showed bimodality. This was due to the fact that the least ordered amorphous sections underwent hydrolysis initially, which led to low-molecular-mass degradation products. On more profound splitting, the process also affected the more ordered structures, which considerable increased the homogeneity of the sample (curve 3).

Thus, in the course of hydrolytic splitting it is posible to obtain CMC samples more homogeneous in terms of molecular mass that are of undoubted interest in the development of medico-biological polymers and, in particular, surgical articles with regulable rates of resorption and medicinal polymers with definite rates of elimination from the organism.

EXPERIMENTAL

The x-radiographic studies* of the CMC samples were carried out on a DRON-2 diffractometer using CuK_α radiation. The degrees of crystallinity of the samples were determined by means of Segal's formula [3]. The degrees of polymerization of the samples were determined viscosimetrically [4]. Sorption properties were investigated by means of a McBain vacuum balance with a quartz spiral [5].

*The x-radiographic investigations and the study of sorption properties were carried out under the direction of N. D. Burkhanova.

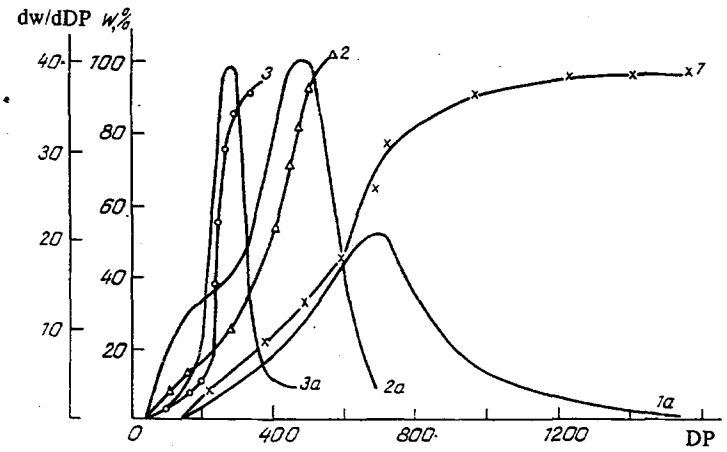

Fig. 3. Integral (1, 2, 3) and differential (1a, 2a, 3a) curves of the MMD of the CMC: 1, 1a) initial CMC, DP 530; 2, 2a) after hydrolysis, DP 440; 3, 3a) after hydrolysis, DP 127.

In the study of MMDs we used a KhZh-1304 liquid chromatograph with a 4 × 300 mm stainless-steel column filled with the sorbent G-40-OH having a pore diameter of 240 Å and a mean particle size of 3-5 μm. The eluent used was 0.5 N aqueous sodium nitrate at a rate of flow of 10 ml/h. Refractometric detector.

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