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SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF CATIONIC STARCHES

S. M. Butrim,* **T. D. Bil′dyukevich,**
N. S. Butrim, and T. L. Yurkshtovich

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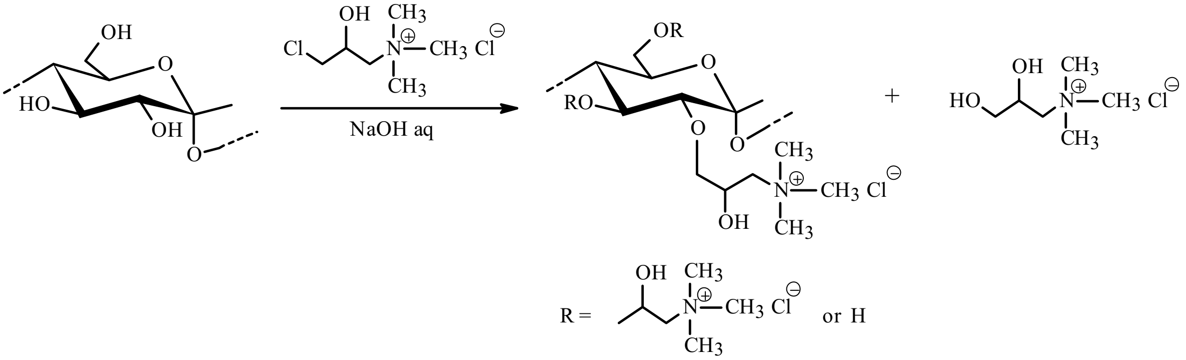
The reaction kinetics of an aqueous suspension of potato starch, various amounts of NaOH, and cationic 3-chloro-2-hydroxypropyltrimethylammonium (chloride) were studied in detail. It was found that the compositions of the sparsely substituted cationic starch ethers and the efficiency of the reaction depended strongly on the ratio of components in the alkylating mixture. The physicochemical properties of the synthesized samples were studied using chemical analysis, scanning electron microscopy, x-ray structure analysis, and thermogravimetry. It was shown that the temperature regime of the reaction had a determining influence on the thermal stability and structural changes of the cationic starch derivative.

Keywords: cationic starch derivative, kinetics, reaction efficiency, degree of substitution, diffraction patterns, thermal destruction.

Starch derivatives containing cationic groups are important commercial products that are widely used as effective additives in the cellulose and paper, textile, cosmetic, and other branches of industry. Cationic starches with quaternary ammonium ethers have the broadest application [1] and have been used effectively over the last decades in the production of paper and cardboard to increase the retention of fiber and filler, suppress the disintegration process, and increase the surface strength and rupture strength of paper [2]. Such cationic starches can be prepared by various methods (dry, wet, extrusion) by adding to the starch macromolecule functional groups carrying a positive charge [3–6]. Of the large number of available reagents, 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMAC) is used most often.

Cationic ethers are obtained via reaction of native starch with CHPTMAC under various conditions according to the general Scheme 1.



Scheme 1

The goal of the present work was to study the influence of various factors (mole ratio of reagents, temperature, starch suspension concentration, reaction time) on the preparation process and the properties of the cationic starch ethers.

Scientific Research Institute of Physical Chemical Problems, Belarusian State University, Minsk, e-mail: butryms@bsu.by. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 172–175, March–April, 2011. Original article submitted July 28, 2010.

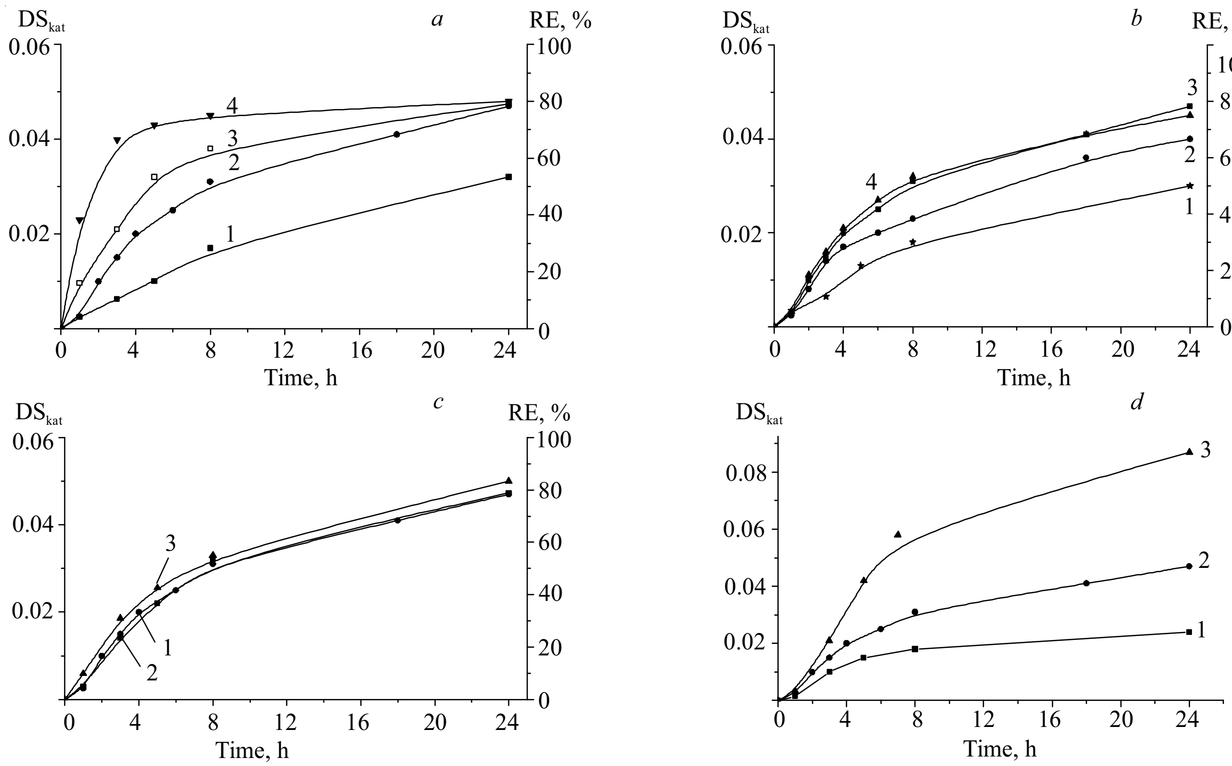


Fig. 1. Reaction kinetics of potato starch with cationic chloride as functions of reaction temperature (°C): 25 (1), 35 (2), 45 (3), and 55 (4) (concentration of aqueous starch suspension 33%; NaOH/CHPTMAC mole ratio 2.8; CHPTMAC/DS mole ratio 0.06) (a); NaOH/CHPTMAC mole ratio: 1.6 (1), 2.2 (2), 2.8 (3), 3.3 (4) (concentration of aqueous starch suspension 33%, 35°C, CHPTMAC/DS mole ratio 0.06) (b); concentration of aqueous starch suspension (%): 24 (1), 33 (2), 42 (3) (35°C, NaOH/CHPTMAC mole ratio 2.8, CHPTMAC/DS mole ratio 0.06) (c); CHPTMAC/DS mole ratio: 0.03 (1), 0.06 (2), 0.12 (3) (35°C, aqueous starch suspension concentration 33%, NaOH/CHPTMAC mole ratio 2.8) (d).

The efficiency of the cationic reagent was estimated by studying the reaction kinetics for preparing the potato starch cationic ethers using CHPTMAC in the temperature range 25–55°C, various mole ratios of components, and various concentrations. The alkylation rate of potato starch by CHPTMAC increased smoothly with increasing temperature (Fig. 1a). However, formation of cationic starch at >45°C, regardless of the use of NaCl, caused gelatinization of the polysaccharide in basic solution. This hindered significantly the isolation and purification of the final product from salts.

The rates of reaction in the initial portions were practically identical if the NaOH/CHPTMAC mole ratio was in the range 2.2–3.3 (Fig. 1b). Furthermore, the maximum rate and degree of starch substitution (DS) were achieved even at NaOH/CHPTMAC mole ratio 2.8. Therefore, the excess of base was not increased further. On the other hand, a deficiency of NaOH in the reaction mixture did not produce the desired results even if the reaction was carried out for an extended time.

The production of the cationic ethers depended least on the concentration of the starch suspension. Thus, varying this parameter in the range 24–42% with constant stirring did not produce any substantial differences in the reaction rate and maximum DS of cationic groups (Fig. 1c).

Use of the modifying agent synthesized by us to prepare cationic starches was rather advantageous because it could achieve high reaction efficiencies (RE = 70–80%) that, in turn, indicated that most of the CHPTMAC was consumed in binding to starch and not in forming side products (Fig. 1a-c).

The CHPTMAC/DS mole ratio had an important influence on both the reaction rate and the limiting DS (Fig. 1d). Increasing this ratio left the solution volume constant. Therefore the CHPTMAC concentration in solution increased. This increased the rate of starch alkylation. Increasing the CHPTMAC/DS mole ratio increased proportionally the limiting content of cationic groups in the polysaccharide.

TABLE 1. Quantitative Characteristics of Thermal Degradation of Studied Samples*

Polysaccharide	DS_{cat}	T_{init}, °C	$T_{50\%}$, °C	Residue at 500°C, %
Potato starch	0	287	303	21.0
Cationic pot. starch	0.035	267	300	26.7
Cationic pot. starch	0.045	244	313	33.1
Cationic pot. starch	0.061	220	292	23.1

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*T_{init} and $T_{50\%}$ are the temperatures of initial degradation (carbonization) and loss of 50% of the polymer mass, respectively.

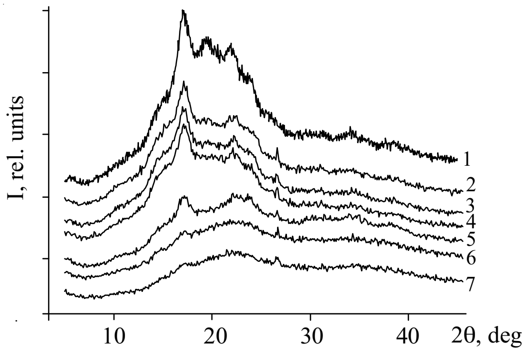

Fig. 2. Diffraction patterns of potato starch (1) and cationic potato starches 2-7 prepared at various temperatures (°C): 35 (2–5), 45 (6), 55 (7).

Carrying out the starch alkylation with CHPTMAC in basic medium could change substantially the supramolecular structure of the polysaccharide, primarily as a function of the reaction temperature. Thus, the diffraction patterns shown in Fig. 2 (6 and 7) indicated that the degree of crystallinity (DC) of the starch decreased substantially after forming the cationic derivative at temperatures that caused gelatinization in the reaction mixture. These changes were more significant as the reaction temperature increased. The principal reflections characteristic of native potato starch (2θ = 17.0, 19.5, and 22.1°) were practically absent in samples of cationic starch (Fig. 2, 6 and 7) synthesized at ≥ 45°C. Because modification of the starch under such conditions affected not only amorphous but also crystalline structures, it was obvious that the 2-hydroxypropyltrimethylammonium groups introduced into the sample were distributed rather unevenly. Diffraction patterns of cationic starch with different DS (Fig. 2, 2–5) that were obtained at 35°C were typically missing the reflection at 2θ = 19.5° and showed distinct peaks with maxima at about 2θ = 17.0 and 22.1°. However, a calculation of the relative DC of these cationic starches showed that the DC for samples 2 and 3 were greater and for samples 4 and 5 less than that of native starch (Table 1).

The DC values of the studied samples* are given below:

Sample	*DC, %*	*Sample*	*DC, %*
Native potato starch – 1	33.2	Cationic starch (DS_{cat} = 0.035) – 5	28.0
Cationic starch (DS_{cat} = 0.0041) – 2	39.5	Cationic starch (DS_{cat} = 0.061) – 6	X-ray amorphous
Cationic starch (DS_{cat} = 0.021) – 3	36.5	Cationic starch (DS_{cat} = 0.045) – 7	X-ray amorphous
Cationic starch (DS_{cat} = 0.047) – 4	32.4		

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*Numbering of samples corresponds with that in Fig. 2.

This type of change in the DC of the cationic starches may be related to the fact that the more soluble (amorphous) part of the modified polysaccharide remained in the filtrate upon washing the aqueous isopropanol mixture. Therefore, the fraction of crystalline regions in the isolated and studied cationic starch increased, slightly increasing the DC. Furthermore, the results suggest that changing the reaction temperature can produce cationic starches with similar contents of cationic groups but different DC (Fig. 2, 4 and 7). This could ultimately be responsible for the different physicochemical properties.

Figure 3a shows that granules of native potato starch have variable sizes and shapes. They include very small granules (d ≈ 5 μm) of primarily round shape and very large ones (d ≈ 60 μm) of oval shape. The destructive action of NaOH, the ions of which are capable under certain conditions of causing starch in solution to form a gel, was consistent with the observed changes in the morphology of the starch granules (Fig. 3).

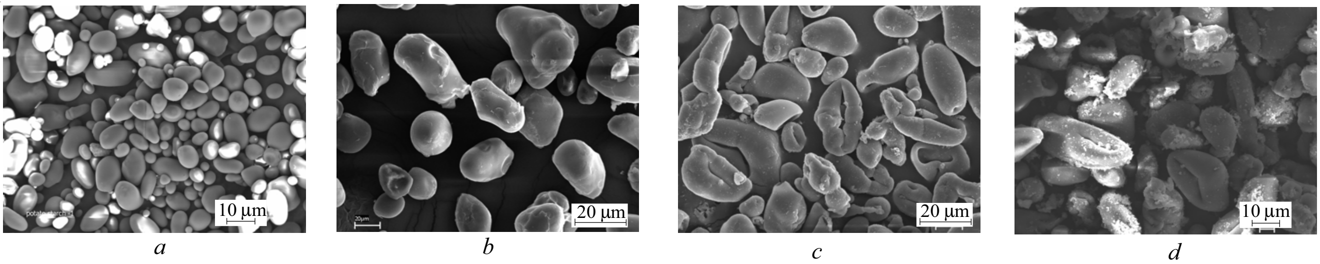

Fig. 3. Scanning electron microphotograph of potato starch granules (*a*) and cationic potato starch (*b*, *c*, *d*) prepared at various temperatures (°C): 35 (*b*), 45 (*c*), 55 (*d*).

The starch granules changed more, the more the reaction temperature increased. Depressions, fractures, and wrinkles appeared and grew. These changes were more evident as the temperature increased. Thus, at 35°C, where cationic starch was synthesized over the whole reaction in a suspension (without gelatinization), the granules of cationic starch differed little in shape and size from the initial ones. Only small depressions and surface defects were observed (Fig. 3a and 3b). At ≥45°C in basic medium, the reaction caused gelatinization of the starch. The granules were highly swelled and destroyed. As a result, electron microphotograph of the cationic starch showed more significant defects in the granules (Fig. 3c and 3d). Large depressions up to openings through the granules and fine fragments of granules can be seen.

Table 1 presents the results from a study of the thermal stability of native starch and three samples of cationic starch. It can be seen that introducing cationic groups into the starch macromolecule had a great influence on the thermal characteristics of the starch, mainly on the initial temperature and degradation mechanism. All studied samples lost mass in two stages. The first (70–100°C) was related to loss of adsorbed moisture; the second (220–287°C), to direct degradation and decomposition of the polymer (carbonization). All samples of cationic starch began to carbonize at lower temperatures than native starch. The mass of resulting carbonized residue at 500°C was greater for all cationic starches than for native starch. The carbonization temperature decreased with increasing content of cationic groups. However, the temperature at which the samples lost 50% of their mass depended weakly on the DS of the cationic starch.

Thus, the results led to the conclusion that the cationic potato starch derivative can be efficiently produced using CHPTMAC. The studied alkylation conditions enabled cationic starches with the required DS (DS_{cat} = 0.02–0.06) to be prepared and a high reaction efficiency (RE = 80%) to be obtained. The structure and properties of the cationic starch depended mainly on the reaction temperature for modifying the native starch.

EXPERIMENTAL

We studied potato starch (GOST 7699-78, contents of amylase 23.8%; P, 0.08; N, 0.03; ash, 0.31; moisture, 12.0). All reagents were chemically pure or analytically pure grade.

Alkylation of Starch by the Cationic Reagent. A round-bottomed flask (500-mL) was placed in a water bath; equipped with a mechanical stirrer, dropping funnel, and thermometer; and treated with starch (81.0 g, 0.50 mol), distilled water (200 mL), and NaCl (35 g). The resulting suspension was stirred at room temperature and treated slowly from the dropping funnel with the required amount of aqueous NaOH (10%). The water-bath temperature was increased to the set point with constant stirring, after which the calculated amount of cationic reagent was added. Samples of the suspension (about 10 mL) were taken during the course of the reaction at certain time points and placed in a beaker with distilled water (200 mL) that was treated beforehand with HCl solution (0.2 mL, 25%). Then, the precipitate of cationic starch was separated by decantation, washed on the filter with aqueous isopropanol (1:1) until a qualitative reaction for Cl^- in the rinsings was negative, and dried in a drying cabinet at 50°C. The N content (N, %) was determined by the Kjeldahl method [7]. The DS (DS_{cat}) and RE (%) were calculated from the increase of N content after forming the cationic derivative.

Diffraction patterns were recorded on an HZG-4A x-ray diffractometer (Carl Zeiss, Jena) using Cu K_α-radiation, a Ni filter, and digital recording. The morphology of the structural elements was studied using a LEO 1420 scanning electron microscope (Germany). Thermal decomposition of samples was studied on an STA 449C synchronous thermal analyzer (Netzsch, Germany) (heating rate 5 deg/min in a dynamic N_2 atmosphere at flow rate 22 cm^3/min, sample mass 50 mg, and calcined Al_2O_3 as a standard).

REFERENCES

1. D. B. Solarek, in: *Modified Starches: Properties and Uses*, O. B. Wurzburg (ed.), CRC Press, Inc., Boca Raton, Florida, 1986, p. 113.
2. W. Nachtergaele, *Starch/Starke*, **41**, 27 (1989).
3. S. Radosta, W. Vorwerg, and A. Ebert, *Starch/Starke*, **56**, 277 (2004).
4. F. Xie, L. Yu, H. Liu, and L. Chen, *Starch/Starke*, **58**, 131 (2006).
5. G. Hellwing, D. Bischoff, and A. Rubo, *Starch/Starke*, **44**, 69 (1992).
6. S. M. Butrim, N. S. Butrim, and T. D. Bil′dyukevich, *Zh. Prikl. Khim.*, **81**, 1911 (2008).
7. J. Houben and T. Weyl, *Methoden der organische Chemie*, Thieme, Stuttgart, 1959.