Preparation of Cationic Starch Ether: A Reaction Efficiency Study*

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Cationic starch ether, important as a papermaking additive, was prepared from native corn starch and 2-chloro-3-hydroxypropyltrimethylammonium chloride in aqueous media in a study to ascertain conditions yielding maximum reaction efficiency (RE). Based on the amount of monomer retained after exhaustive washing procedures, RE values of 84–88% were achieved with 0.025–0.05 mole of monomer/mole of starch. Degrees of substitution of up to 0.075 were investigated. A number of variables were studied that allow high RE under a variety of reaction conditions, including those involving low energy input. The excellent stability of the monomer during etherification suggests that the water-soluble active monomer and salts could be recycled in subsequent reactions.

1 Introduction

The United States produces over 3.7 billion lb (1,681 metric tons) of corn starch, of which almost two-thirds is absorbed by the U. S. paper and corrugating industries [1]. Probably their most important starch derivatives are cationic ethers containing tertiary amino or quaternary ammonium groups with degrees of substitution (DS) of about 0.02–0.04. Recently, our colleagues reported a dry-state method of preparing these derivatives, in which the monomer 3-chloro-2-hydroxypropyltrimethylammonium chloride has been investigated extensively [2,3]. In conjunction with this work we now report our etherification results using this monomer in aqueous starch slurries, which reveal up to 88% reaction efficiency (RE). The primary reaction mechanism is suggested by the following scheme (1) where $R = -\text{CH}_2\text{N}(\text{CH}_3)_2\text{Cl}^-$ and $R' = -\text{CH}_2\text{N}(\text{CH}_3)_2\cdot\text{HSO}_4^-$.

\[
\text{OH}^- + \text{H}_2\text{C}^-\text{CHR} \xrightarrow{\text{reactant}} \text{H}_3\text{C}^-\text{CHR} + \text{H}_2\text{O} \quad \text{(I)}
\]

\[
\text{H}_2\text{C}^-\text{CHR} + \text{Cl}^- \xrightarrow{\text{aqueous NaCl}} \text{Starch-OCH}_2\text{CHOHR'} + \text{NaCl}
\]

2 Experimental

2.1 Materials

The following materials were used for preparation of the cationic starch ether. Starch: Native corn starch 3005, CPC International. Quat 188: Aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride as the reactive monomer supplied at 53–58% active monomer concentration, Dow Chemical Company, Freeport, Texas. Our analysis indicated that a 2-year old sample used in this work contained 50% active monomer concentration [4]. NaOH: 98.2% assay, J. T. Baker Chemical Company. Na$_2$SO$_4$: Anhydrous, certified A. C. S. grade, Fisher Scientific Company.

* The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.
2.2 Procedures and Analyses

Preparation of Cationic Starch Ether

The primary procedure selected for preparation of the cationic starch ether of various DS is exemplified as follows: To a closed 250-ml container, equipped with stirrer and secured in constant-temperature water bath at 51°C (slurry temperature, 50°C), were added 133 ml distilled H₂O, 50 g Na₂SO₄, and 2.8 g (0.07 mole) NaOH pellets. Following dissolution of the above, 81.0 g (0.5 mole) starch, d. b., was added and slurred 5 min at 50°C, after which 8.3 ml Quat 188 (Density 1.135 g/ml at 40°C) containing 4.71 g (0.025 mole) of active monomer was admixed during 1 min. Starch concentration was 35% (starch/starch + H₂O basis). Periodically, a 10-ml sample was withdrawn and mixed with 200 ml of 25% ethanol and 0.75 ml 3-N HCl in a 250-ml centrifuge bottle. By centrifugation-decantation procedures, each sample was subsequently washed 5 times with 200 ml of 25% ethanol. A test for sulfate ion (added 0.1 molar BaCl₂ to the supernatants) was weakly positive on the third wash and negative on the fourth. Following their fifth wash, the starch derivatives were slurried in 95% ethanol, filtered and allowed to equilibrate to about 89% solids. Subsequent analyses indicated that the products contained enough sulfur to exist as the cationic sulfate salt. No attempt was made to convert the products to the chloride salt.

Elemental Analyses

Nitrogen was determined by the Kjeldahl method and sulfur by the Schöniger combustion method. DS: The DS of each derivative was based on nitrogen increase of the exhaustively washed product, and was calculated from the formula DS = 162(%N)/(1,400 - 117(%N)).

3 Results and Discussion

3.1 NaOH/Monomer Mole Ratio and Reaction Time

Figure 1 shows the effect of NaOH/monomer mole ratio and reaction time on RE. The % RE is equal to the DS x the monomer/starch mole ratio x 100. With use of 0.05 mole of monomer/mole of starch, 35% starch concentration, and 50°C, the RE values improve dramatically (for any given reaction time up to 6 h) as the NaOH ratio is increased to 2.8. With the 2.8 ratio, an RE of 84% was reached in 4 h and 88% in 24 h. Slightly lower results were obtained using a ratio of 3.6. Presumably, OH concentration at the highest alkali level evaluated is sufficient to accelerate the competitive reaction of OH for epoxy ring opening. For the lower ratios (1.2 and 2.0), significant increases in DS occur between 6 and 24 h.

3.2 Temperature and Reaction Time

Figure 3 illustrates the effect of temperature (from 40 to 70°C) on the reaction of 0.05 mole monomer/mole starch, 35% starch concentration and 2.8 mole NaOH/mole monomer. With respect to the first hour, reaction proceeds in order of increasing temperature. During a 5- to 6-h period, in which time nearly maximum substitution occurs, 50°C is favored over 60-70°C. Apparently, under these particular reaction conditions ring inactivation by alkali was slightly increased at 60-70°C, with peak substitution occurring in about 2 h. As previously indicated, longer reaction periods can be used at lower temperatures to yield nearly similar DS. Approximately 1 day was required at 40°C and 2 days at 25°C to reach an 84% RE.

3.3 Starch Concentration and Reaction Time

The effect on RE of starch concentration from 20 to 45% is presented in Figure 4, using the ratios 2.8 NaOH and 0.05.
monomer at 50°C. The concentration is critically important between 20 and 35% for any given reaction time up to 24 h. For example, RE values are 36 and 62% for 2 and 24 h at 20% concentration compared to 74 and 88%, respectively, at 35% concentration. There was no RE benefit by increasing from 35 to 45%. However, evaluations at 45% and above deserve investigation with special mixing equipment to overcome any deleterious effect of starch viscosity.

3.4 Monomer/Starch Mole Ratio and Reaction Time

The effect of monomer/starch mole ratio from 0.025 to 0.10 and reaction time is shown in Figure 5 (2.8 NaOH ratio, 35% starch concentration and 50°C). Cationic starch derivatives of DS 0.02 to 0.04, which are considered adequate for wet-end papermaking applications, were rapidly obtained in 12 to 30 min with a ratio of 0.10. Although only 20 to 40% RE were obtained in this time interval, it appears technically feasible to obtain these DS with an excess of monomer when the time factor is paramount and then to reuse the aqueous media containing the active monomer and Na₂SO₄ in a recycling system. The highest RE values obtained with reaction periods of up to 2 h were with the 0.025 monomer ratio (64 to 84% in 30 min to 2 h) with no increase beyond 2 h. The RE was 75% with the 0.1 mole ratio during 4 to 24 h.

3.5 Other Variables

Although Na₂SO₄ was used in excessive amounts to ensure minimum swelling of the starch granules under all conditions, the RE at low DS (0.01 — 0.03) was not significantly affected by absence of this salt.

In preparation of cationic starch of DS 0.02 without the use of Na₂SO₄, the derivative exhibited poor dispersion until washed. This property is apparently significantly affected by residual NaCl formed in the reaction system.

Sequence of chemical addition was important. To minimize starch swelling during derivatization, Na₂SO₄, water and starch are first combined in any order to form a uniform slurry, followed by alkali and then monomer. The addition of monomer before alkali resulted in significantly lower RE.

Summary

The reaction efficiency (RE) of native corn starch and 2-chloro-3-hydroxypropyltrimethylammonium chloride was evaluated in aqueous systems to form lowly substituted (DS about 0.01—0.07) cationic starch ether. The study was prompted by widespread interest in these derivatives as wet-end papermaking additives and by the demand for more efficient reaction systems. Variables, including low energy input, were identified which allow high RE of 84—88% (% of monomer reacted). For example, a DS of 0.044 representing an RE of 84% was achieved at either 25°C in 48 h or 50°C in 4 h using 0.05 mole of monomer/mole of starch. Rate of reaction was greatest with the lowest monomer incorporation (0.025 vs. 0.05 and 0.10 mole ratio).

Bibliography


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