

## Preparation and Properties of Novel Starch Derivatives Containing the Sulfonic Acid of the Group and Carboxymethyl

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Received: 5 June 2013;

Accepted: 5 September 2013;

Published online: 25 May 2014;

AJC-15206

In this study, novel anionic starch derivatives (2,4-bis(diiminobenzenesulfonic acid disodium salt)[1,3,5]triazine-6-yl)-carboxymethyl starch (BSTS-CMS) were prepared by the reaction of 2,4-bis(diiminobenzenesulfonic acid disodium salt)-6-chloro[1,3,5]triazine (BSTS) with carboxymethyl starch. The molecular weight of the samples with different degrees of substitution (DS) was analyzed by GPC and the structure was characterized by FT-IR. The thermal stability was investigated by non-isothermal thermogravimetry. The results showed that the BSTS-CMS had higher molecular weight ( $M_w \times 10^6 = 3.12-3.56$ ). The different degrees of substitution sample exhibited better temperature resistance properties compared with carboxymethyl starch. The viscosity of sample has the excellent stability towards pH 2-12. In addition, the thermogravimetric analysis of BSTS-CMS proved that it has good thermal stability compared with starch and carboxymethyl starch.

**Keywords:** Carboxymethyl starch, Sulfonic acid group, S-Triazine, Thermal stability.

### INTRODUCTION

Carboxymethyl starch (CMS) is one of the most important anion starch derivatives, that was usually synthesized by the reaction of starch with monochloroacetic acid or its sodium salt based on Williamson's ether synthesis<sup>1,2</sup>. Carboxymethyl starch has been extensively used in industry such as textile sizing, thickening of food, drug release, paper additives, thickening agent and water-based adhesives<sup>3-6</sup>. Carboxymethyl starch is also used in recovery of metals from waste water and auxiliary agents in petroleum<sup>7,8</sup>. However, there are still some problems during applications of CMS due to its low salt-tolerance, heat-resistance and pH-resistance. Subsequently modified water-soluble CMS have attracted considerable attention due to their outstanding solution properties and potential practical applications. The solutions of the hydrophobically modified CMS possess enhanced viscosity efficiency, improved shear and salt stability and shear-thickening rheology compared to the CMS<sup>9</sup>.

Some combination modified starch have been reported in the literature. These include cross-linked carboxymethyl starch (CL-CMS)<sup>10-12</sup>, carboxymethyl hydroxyethyl starch<sup>13</sup>, octenyl-succinates of carboxymethyl starch (OS-CMS)<sup>14</sup>, acetylated carboxymethyl starch (ACMS)<sup>15</sup>, enzyme carboxymethyl starch

(ECMS)<sup>16</sup>, carboxymethyl cassava starch (CMCS)<sup>17</sup>, carboxymethyl starch-g-poly (lactic acid) (CMS/LA)<sup>18</sup>, radiation-modified carboxymethyl starch<sup>19</sup> etc. However, the increasing demand for starch derivatives and derivatized starch derivatives justifies the need for exploration of new modification method, either one of these, sulfonic acid group was introduced into starch that makes the starch derivative more soluble, acid-base resistance and salt tolerant<sup>20</sup>. Sulfonated starch is traditionally prepared using a sulfonating agent<sup>21-23</sup>, such as sulfuric acid, chlorosulfonic acid, sulfuryl chloride, sulfur trioxide and sulfamic acid. However, with direct sulfonation, extreme hydrolysis or degradation of the starch chains usually occurs during the reaction, which also considerably affects their properties for applications<sup>24</sup>.

In this work, we attempt to explore the possibility of a new type of combination modified starches, which contain carboxymethyl and sulfonic acid group, as the above mentioned multifunctional polymeric additive. Such modified starch were prepared in dimethyl sulfoxide solutions by etherification reaction the mixed monomer system of 2,4-bis(diiminobenzenesulfonic acid disodium salt)-6-chloro-[1,3,5]-triazine (BSTS) and monochloroacetic acid or its sodium salt onto carboxymethyl starch to improve its thermal stability and salt-tolerance.

## EXPERIMENTAL

The materials and reagents used in this study were purchased from the following companies: food-grade corn starch (12 % moisture) from the Huang Long Food Company (Changchun, P.R. China); Cyanuric chloride(2, 4, 6-trichlorotriazine) and metanilic acid from the Tianjin Fuchen Chemical Reagent Factory (Tianjin, P.R. China); and all other chemicals were analytical grade quality and supplied by the Tianjin Plant of Agents (Tianjin, P.R. China).

**Preparation of carboxymethyl starch:** Carboxymethyl starch was prepared by reacting starch with the sodium salt of monochloroacetic acid (SMCA) in the presence of NaOH and the DS<sub>CMS</sub> was determined using the method reported by Kessel<sup>25</sup>. The IR spectrum (KBr) of the CMS is shown in Fig. 1. The molecular weights of CMS is presented in Table-1.

**Preparation of 2,4-bis(diiminobenzenesulfonic acid disodium salt)-6-chloro[1,3,5]triazine:** Cyanuric chloride (0.01 mol) was dissolved in 20 mL of ice-cold acetone and then metanilic acid (0.01 mol) solution was added slowly with constant stirring. The reaction was performed at 0-5 °C for 10 h. During the course of the reaction the pH was maintained at 4.5-5.5 by the addition of 10 % Na<sub>2</sub>CO<sub>3</sub> solution. Thin layer chromatography was used to monitor the completion of the reaction (R<sub>f</sub> = 0.85). The mobile phase was a mixed solvent of isopropyl alcohol:propanol:ethyl acetate:deionized water = 2:4:1:3). Then, the temperature of the reaction solution was increased to 30 °C and 0.01 mol of metanilic acid solution was added and stirred at a pH of 6 by the addition of 10 % Na<sub>2</sub>CO<sub>3</sub> solution. After the reaction, the 2,4-bis(diiminobenzenesulfonic acid disodium salt)-6-chloro[1,3,5]triazine (BSTS) product was isolated by adding potassium acetate, collected by filtration, washed with ethanol after filtration to remove potassium acetate and then dried in vacuum (Yield: 93 %). The purity of the product was determined using the validated protocol with a high performance liquid chromatography/mass selective detector, obtaining 98.8 % purity, for quantifying purposes. MS (+ESI): 455.99 (M-H)<sup>-</sup>, 227.4 ([M-2H]<sup>2-</sup>). The FT-IR spectrum of BSTS is shown in Fig. 1.

**Preparation of sulfonic acid group-carboxymethyl starch:** 2,4-bis(diiminobenzenesulfonic acid disodium salt)-[1,3,5]-triazine-6-yl)- carboxymethyl-starch was prepared *via* an etherifying reaction between carboxymethyl starch and BSTS in dimethyl sulfoxide. Briefly, dry carboxymethyl starch (8.3 g, 0.05 mol) and solid sodium hydroxide (1.2 g, 0.03 mol) were dissolved in 120 g dimethyl sulfoxide and heated to 70 °C for 0.5 h. Subsequently, BSTS (12.5 g, 0.025 mol) was added. The reaction solution was stirred at 120 °C for 4-6 h. The product was isolated by filtration, washed with methanol and then separated using the dialysis method to remove the unreacted BSTS and NaCl. The final product with DS = 0.41 was obtained after washing with acetone to remove water and then dried in vacuum. The samples with different degrees of substitution in Table-1 were prepared according to the above mentioned method.

**Measurement of the degrees of substitution of the sulfonic acid group-carboxymethyl starch:** The extent of amination was traced by determining the nitrogen content (N %) using the semi-micro Kjeldahl method. The degree of

the substitution, which is the number of substituted hydroxyl groups per AGU in the starch polymer, was calculated using the following equation:

$$N\% = \frac{2 \times 14C(V_1 - V_0)}{m} \quad (1)$$

$$DS_{BSTS} = \frac{(162 - DS_{CMS}) \times \frac{N\%}{5}}{14 \times 100 - 481 \times \frac{N\%}{5}}$$

$$\begin{aligned} &= \frac{(162 - DS_{CMS}) \times \frac{2 \times 14C(V_1 - V_0)}{5m}}{14 \times 100 - 481 \times \frac{2 \times 14C(V_1 - V_0)}{5m}} \\ &= \frac{(162 - DS_{CMS}) \times 2 \times 14C(V_1 - V_0)}{14 \times 100 \times 5m - 481 \times 2 \times 14C(V_1 - V_0)} \quad (2) \end{aligned}$$

where V<sub>1</sub> and V<sub>0</sub> are the volumes of the consumed standard aqueous solution of H<sub>2</sub>SO<sub>4</sub> (L) during the titration of the samples and blank, respectively; m is the dry weight of the sample (g); 481 is the molar quantity of the substituted group and c is the concentration of the H<sub>2</sub>SO<sub>4</sub> standard aqueous solution (mol/L).

**Fourier transform infrared (FT-IR) spectroscopy:** The change in the chemical structure of the starch was qualitatively analyzed using FT-IR spectroscopy (FT/IR-430, JASCO, Japan). The samples were prepared by grinding the finely powdered starch with KBr.

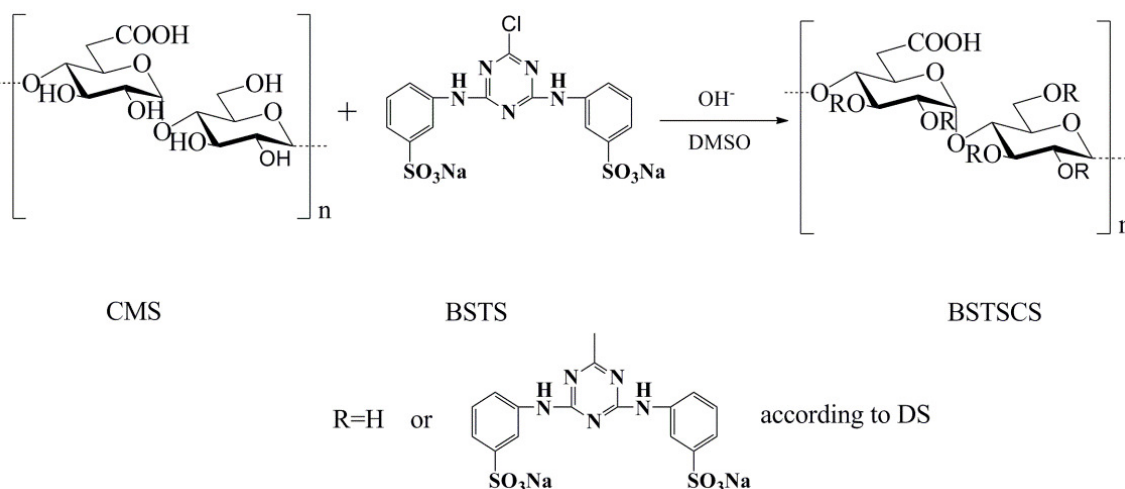
**Thermal analysis:** The thermal analyses were performed using a TGA/SDTA 851 simultaneous thermal analyzer (Perkin-Elmer, USA). Samples (20 mg) were placed in corundum crucibles that were non-hermetically closed with lids and heated under argon from room temperature to 400 °C at a rate of 10 °C/min.

**Determination of the molecular weight distribution:** The samples were dissolved in deionized water (1 wt. %) at room temperature, to obtain a final extract concentration of 8 to 15 mg mL<sup>-1</sup>. Prior to injection, the sample solutions were filtered through a 0.45 μm cellulose acetate filter.

HPLC analysis of the sample was performed by using a liquid chromatograph (Agilent 1200 series), containing Chemstation Software (Agilent Technologies), a binary pump, an online vacuum degasser, an autosampler and a thermostated column compartment, TSK gel columns (ultrahydrogel 1000, 7.8 × 300 mm and ultrahydrogel 1250, 7.8 × 300 mm) in combination with a M32 workstation. A Dawn-DSP-F multiangle laser light scattering detector (Wyatt Technology, Santa Barbara CA, USA) equipped with He-Ne laser emitting at 630.0 nm and a differential refractive index detector (L-7490, Merck, Darmstadt, Germany) were connected to the columns. The eluent and flow rate were high pure demineralised water and 0.5 mL/min, respectively.

## RESULTS AND DISCUSSION

**Characterization of BSTS-CMS:** Novel anionic starch derivatives {2,4-bis(diiminobenzenesulfonic acid disodium salt)[1,3,5]-triazine-6-yl}carboxymethyl-starch (referred to as BSTS-CMS) with different degrees of substitution were



**Scheme-I:** Synthetic procedure for producing BSTS-CMS

designed and synthesized by reacting 2,4-bis(diiminobenzenesulfonic acid disodium salt)-6-chloro[1,3,5]triazine (BSTS) with carboxymethyl starch. The synthesis reaction of BSTS-CMS was as follows (**Scheme-I**).

The presence of carboxymethyl substituents might enhance the starch granules swelling<sup>26,27</sup>, under alkaline conditions, the negative oxygen ion of the starch attacks the carbon atom bound to the chlorine atom on the triazine group of BSTS, namely, a nucleophilic substitution reaction occurred on the triazine group of BSTS and hydrogen chloride was produced. In consideration of the solubility and reactivity of starch and BSTS, DMSO was selected as a solvent and 10 % sodium carbonate was used as an acid-binding agent. In this study, BSTS-CMS with different degrees of substitution was synthesized by varying the ratio of carboxymethyl starch and BSTS. The DS,  $M_w$ ,  $M_n$  and  $M_w/M_n$  values of the products are summarized in Table-1.

In Table-1, as the degrees of substitution of BSTS-CMS varied from 0.10 to 0.41, the  $M_w$  of the product always maintained an order of magnitude of  $10^6$ , which was the same as that of CMS with a degrees of substitution of 0.40. It was because that the BSTS-CMS was synthesized by the etherification substitution reaction between BSTS and carboxymethyl starch under alkaline conditions, which was similar to the synthesis of CMS. To obtain starch derivatives with a high DS, more BSTS and alkali need to be added. However, under a reaction temperature of 120 °C (The characteristics of BSTS), adding more alkali will result in a certain degree of decomposing of the starch chain. But the  $M_w$  caused by increasing degrees of substitution can offset this degree of decomposing of the starch chain in certain extent. As shown in Table-1,

increasing the degrees of substitution from 0.10 to 0.41 resulted in the  $M_w$  of BSTS-CMS Slight increasing from  $3.12 \times 10^6$  to  $3.56 \times 10^6$  using this indirect sulfonation method. These data were used only for comparison. The results suggested that severe degradation of starch chains didn't occur in the etherification process or washing process of BSTS-CMS.

**FT-IR:** The IR spectra of the native corn starch, BSTS, CMS with DS 0.40 and BSTS-CMS with degrees of substitution 0.41 are shown in Fig. 1. The bands at  $1604 \text{ cm}^{-1}$  and  $1420 \text{ cm}^{-1}$  were the characteristic adsorptions of  $-\text{COONa}$  group, which indicated the introduction of  $-\text{COO}-$  group on the starch molecules. The IR results of CMS were consistent with that reported in the literature<sup>28</sup>. Upon comparison of the IR spectra of BSTS-CMS and starch, it was very clear that BSTS-CMS exhibits some new absorption peaks. The peak located at  $1577 \text{ cm}^{-1}$  was the characteristic absorption of s-triazine ring stretching vibration, the peak near  $1486 \text{ cm}^{-1}$  was attributed to the bending vibration of N-H, the peaks at  $1232 \text{ cm}^{-1}$  and  $1036 \text{ cm}^{-1}$  were the stretching vibration absorption peaks of S=O, the peak at  $807 \text{ cm}^{-1}$  was the stretching vibration absorption peaks of S-O<sup>29</sup> and the peaks at  $1669 \text{ cm}^{-1}$  and  $1486 \text{ cm}^{-1}$  were stretching vibration absorption peaks of benzene ring. All these results indicated that sulfonic acid groups were introduced into the corn starch molecules.

**Effect of pH on the viscosity properties of the BSTS-CMS solution:** Polymers that contain sulfonic groups are a type of strong electrolyte and their viscosity is not sensitive to the pH conditions when the  $\text{pH} > 1$ <sup>30</sup>. Similar results were also obtained in this study, as shown in Fig. 2. Fig. 2 displays the influences of pH on the viscosity of BSTS-SMS solution. As can be seen, the influence of the pH value on the viscosity of

TABLE-1  
SYNTHESIS DETAILS AND MOLECULAR WEIGHT OF BSTS-CMS

Sample	Actual DS	Yield (%)	$M_w (\times 10^6)$	$M_n (\times 10^6)$	$M_w/M_n$
Corn starch	–	–	3.21	–	–
CMS	$0.40 \pm 0.01$	–	2.94	–	–
BSTS-CMS 1	$0.10 \pm 0.01$	66.7	3.12	1.04	3.01
BSTS-CMS 2	$0.15 \pm 0.01$	75.0	3.16	0.95	3.33
BSTS-CMS 3	$0.20 \pm 0.01$	75.8	3.24	0.93	3.48
BSTS-CMS 4	$0.30 \pm 0.01$	75.0	3.37	0.96	3.51
BSTS-CMS 5	$0.41 \pm 0.01$	72.3	3.51	0.97	3.62

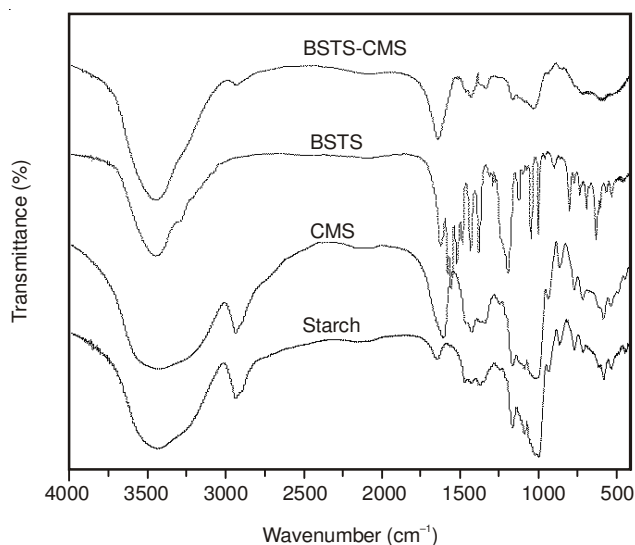


Fig. 1. IR spectrum of starch, CMS, BSTS and BSTS-CMS

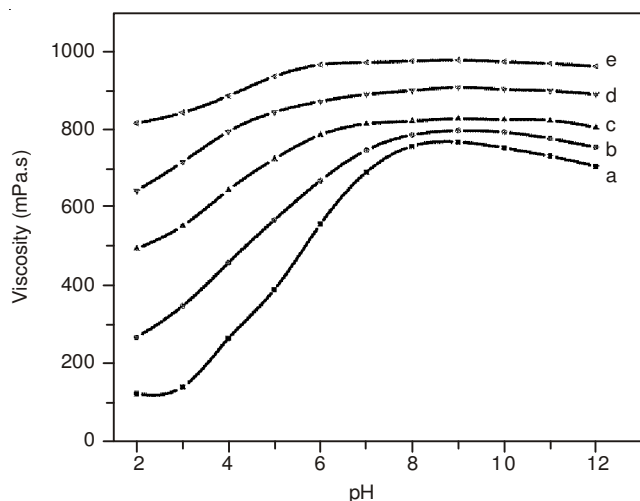


Fig. 2. Effect pH on the composite starch derivatives (25 °C, C = 2.0 wt. %) (a:  $DS_{CMS} = 0.40$ ; b:  $DS_{CMS} = 0.40$ ,  $DS_1 = 0.10$ ; c:  $DS_{CMS} = 0.40$ ,  $DS_1 = 0.20$ ; d:  $DS_{CMS} = 0.40$ ,  $DS_1 = 0.30$ ; e:  $DS_{CMS} = 0.40$ ,  $DS_1 = 0.41$ )

the BSTS-CMS solution was little and the general trend was that the viscosities of the BSTS-CMS solutions remained almost constant over a wide pH range for different degrees of substitution at a certain concentration.

The effect of pH on the viscosity of polysaccharide solutions has been widely researched<sup>31-35</sup>. But for the reported solutions of polysaccharides, the initial pronounced increase and subsequent decrease of the viscosity with pH increasing were discovered. In addition, it can be seen from Fig. 2 that with the increasing of the sulfonic acid group substitution degree, the influence of the pH value on the viscosity of the BSTS-CMS solution was very small. It may be due to the

sulfonic acid group was introduced into carboxymethyl starch, molecule of sulfonic acid group increase with the increase of degree of substitution, the charge repulsion of the sulfonate groups, the molecule chains of BSTS-CMS could always keep stretch and the viscosity of BSTS-CMS was less affected.

**Thermogravimetric analysis:** The differences in the thermal behaviors of BSTS-CMS, CMS and starch may be clearly seen in Fig. 3, which presents the TG curves of the samples recorded at a heating rate of 10 °C/min. As shown in Fig. 3, the introduction of BSTS affected the thermal characteristics of starch, especially the temperature of mass loss onset and the mechanism of thermal degradation. The mass loss of the BSTS-CMS samples commences at a considerably higher temperature, at approximately 320 °C, than that for the native starch (290 °C) and CMS (275 °C). Furthermore, the thermal stability of BSTS-CMS increased as the degrees of substitution increased. Thus, it could be concluded that the substitution of hydroxyl groups of starch with BSTS improved the thermal stability of starch. The main reason for the result was because that BSTS containing the s-triazine ring and the phenyl groups which favored inducing of van der Waals interactions due to its plane and polarizable structure. Therefore, the phenyl groups and s-triazine ring can act as spacer to increase the rigidity of the structure and the thermal stability of BSTS-CMS<sup>36,37</sup>. the introduction of a strongly polar sulfonic acid group can increase the thermal degradation temperature because of the formation of internal hydrogen bonds between the starch chains.

The characteristic degradation temperatures taken from the TG curves recorded at a heating rate of 10 °C/min for all three samples are given in Table-2. It is obvious that the temperature of mass loss onset is dependent on the degrees of

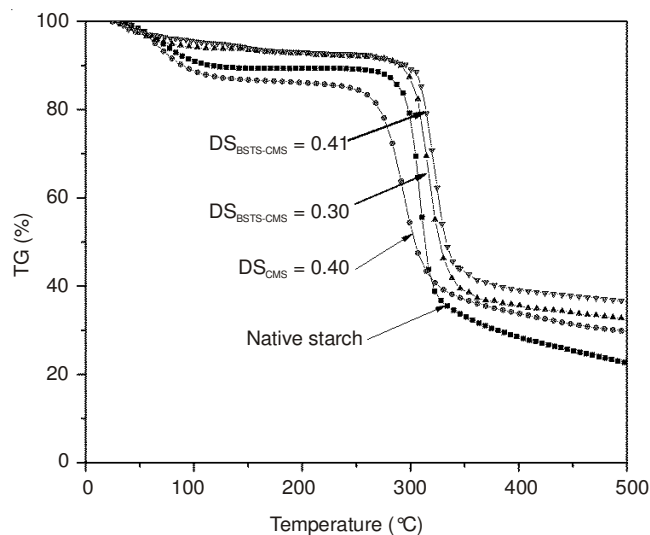


Fig. 3. TG curves of starch, CMS and BSTS-CMS samples

TABLE-2

CHARACTERISTIC DEGRADATION TEMPERATURES OF THE EXAMINED SAMPLES TEMPERATURE AT 10 AND 50 % MASS LOSS,  $T_{10\%}$  and  $T_{50\%}$ , RESPECTIVELY, AND THE AMOUNT OF RESIDUE AT 500 °C (HEATING RATE) 10 °C/min

Sample	DS	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue at 500 °C (%)
Starch	0	118.3	315.6	22.6
CMS	$0.40 \pm 0.01$	88.4	304.8	29.8
BSTS-CMS	$0.30 \pm 0.01$	308.3	354.5	33.4
BSTS-CMS	$0.41 \pm 0.01$	349.5	388.1	40.3

substitution, decreasing with increasing amount of substituted OH groups in the starch molecules. Starch bonds between the OH groups from the starch molecules and the BSTS from the substituent are probably broken in the degradation. Consequently, in the second stage of the degradation, in the temperature range of 310-380 °C, predominantly starch molecules degrades regardless of the original degrees of substitution of the sample<sup>36</sup>.

### Conclusion

In this paper, the preparation and performance of a novel anionic starch derivative, (2,4-bis(diimino benzenesulfonic acid disodium salt)-[1,3,5]-triazine-6-yl)-carboxymethyl-starch (BSTS-CMS) were described and discussed. The BSTS-CMS had high molecular weights ( $M_w \times 10^6 = 3.12-3.56$ ). It was also proved that the investigated BSTS-CMS samples exhibited excellent viscosity stability towards pH 2-12. The thermal analysis of BSTS-CMS indicated that these derivatives had enhanced resistance to thermal degradation compared with native starch and the carboxymethyl starch (CMS) that had the same degree of substitution. These parameters and the desirable properties of BSTS-CMS would provide relevant information for useful applications of the starch derivatives.

### ACKNOWLEDGEMENTS

The authors thank the Natural Science Foundation of China (20836001) for financial support of this research.

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