

Synthesis of Cationic Hemicellulosic Derivatives with a Low Degree of Substitution in Dimethyl Sulfoxide Media

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ABSTRACT: A series of water-soluble cationic 2-hydroxypropyltrimethylammonium hemicellulosic derivatives with low average degrees of substitution (DS's) were prepared by the incorporation of the cationic moiety 2,3-epoxypropyltrimethylammonium chloride (ETA) onto the backbone of hemicelluloses in the presence of NaOH as a nucleophilic catalyst in homogeneous dimethyl sulfoxide (DMSO) media. The dependence of the homogeneous reaction on the different affecting factors was investigated. The average DS was calculated from the N/C ratio in the products and from the weight gain. The degree of substitution determined by the nitrogen content (DS_N) values up to 0.25 in a one-step synthesis of the etherified hemicelluloses

could be controlled by the adjustment of the amount of solvent used and the molar ratio of NaOH or ETA to the anhydromonomer units in the hemicelluloses. The structure of the cationic hemicellulosic derivatives formed was determined by Fourier transform infrared spectroscopy and further confirmed with solution-state ¹³C-NMR spectroscopy. In comparison, no significant degradation of the hemicellulosic derivatives occurred during the etherification of the polymers in the homogeneous DMSO system. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2711–2717, 2008

Key words: FTIR; functionalization of polymers; gel permeation chromatography (GPC); polysaccharides; synthesis

INTRODUCTION

The chemical modification of polysaccharides is the most important route for modifying the properties of naturally occurring biopolymers and for using this renewable resource in the context of sustainable development. Recent research and development has focused on the improvement of known products and synthesis paths and on new derivatives and alternative synthesis concepts.¹ For example, the quaternization of natural hemicelluloses enhances their solubility in water. The first report on the quaternization of hemicelluloses isolated from pulps concerned the preparation of flocculants and adhesives.² Two years later, Antal et al.³ prepared cationic polymers by the quaternization of hardwood hemicelluloses as beater additives. Recently, research on this aspect has

become more interesting, and more and more attention has been paid to the quaternization of hemicelluloses.^{4–6} Synthesis was carried out with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC) or 2,3-epoxypropyltrimethylammonium chloride (ETA) in an alkaline medium.

The overall aim of this research into sugarcane bagasse (SCB) hemicelluloses in our laboratories was to prepare new polymers from hemicelluloses as additives in papermaking and as replacements for polymers prepared from petrochemicals. Of particular interest to our group was the investigation of the effects of various reaction media on the yield and structural features of water-soluble cationic hemicellulosic derivatives. In the first article of this series,⁷ we reported the synthesis and structural characterization of cationic SCB hemicellulosic derivatives containing quaternary ammonium groups with average degrees of substitution (DS's) between 0.01 and 0.54, prepared by etherification with CHMAC or preferably with ETA in an aqueous alkaline solution. We found that a significant degradation of the hemicellulosic polymers occurred during the etherification under the strong alkaline conditions used. To reduce the substantial degradation of the macromolecular hemicelluloses, the quaternization was performed in aqueous organic solvents under relatively low concentrations of alkali. In the second article of this

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series,⁸ we reported the synthesis of cationic hemicelluloses by quaternization with CHMAC in a heterogeneously aqueous ethanol solution. The results show that cationic hemicelluloses with a noticeable degradation were obtained, and they had a rather low average DS, ranging from 0.063 to 0.19. To further reduce the degradation of the hemicelluloses and their derivatives by extensively decreasing the concentration of alkali used, we performed the etherification of the SCB hemicelluloses in a homogeneously organic solvent system. In this article, therefore, we describe the synthesis of cationic hemicellulosic derivatives with a low average DS by the reaction of SCB hemicelluloses with ETA homogeneously in dimethyl sulfoxide (DMSO). To optimize the synthesis procedure, the reaction parameters, including the amount of reaction media and the molar ratios of sodium hydroxide to anhydromonomer (AM) units and ETA to AM units in hemicelluloses, were investigated. The products were characterized by the recovery of the hemicelluloses and average DS with elemental analysis, ¹³C-NMR and Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography, and thermal analysis.

EXPERIMENTAL

Materials

SCB was obtained from Huwei sugar factory (Guangzhou, China). It was dried in sunlight and then ground to pass a 0.8-mm screen. The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50°C. ETA was purchased from Dongying Fine Chemicals, Ltd. (Shandong, China). The other chemicals used in this study were analytical reagent grade and were purchased from Guangzhou Chemical Reagent Co. (Guangzhou, China).

Synthesis of the cationic hemicellulosic derivatives

The hemicelluloses were isolated from SCB after the removal of lignin by the methods described in one of our previous articles.⁸ In a typical synthesis, 0.33 g of hemicellulose (equal to 0.0054 mol of hydroxyl functionality in the hemicellulose) was suspended in 4 mL of water and then heated at 85°C until the hemicellulose dissolved completely; then, we added the required amount of DMSO (10–25 mL) under continuous stirring. After the solution was cooled, the required quantity of sodium hydroxide was added. As the temperature was increased to 50°C, the required amount of ETA was added dropwise under stirring within 30 min. The mixture was kept at 50°C for 8 h under stirring. After it was cooled to ambient temperature, the solution was slowly poured into 100 mL of 80% ethanol with stirring.

The product that separated from the solution was filtered off and washed thoroughly with 95% ethanol to eliminate residual reagents and byproducts. Finally, the cationic hemicellulosic derivatives obtained were first air-dried for 12 h and then further dried in an oven for 24 h at 45°C.

Determination of the recovery of the hemicelluloses and the average DS

The recovery percentages were calculated on the basis of the assumption that all of the hemicelluloses were fully converted to etherified hemicelluloses. In this case, the recovery percentage and the average DS (DS_Y) would have been 100% and 2.3, respectively, and the recovery of the hemicelluloses was assumed to be 100% in these calculations. The unreacted cationic agent in the reaction mixture was separated from the product by dissolution in ethanol. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would have been 28.1% with a DS_Y value of 0.0. The contents of nitrogen and carbon in the cationic hemicellulosic derivatives were determined with a Vario ELIII elemental analyzer (Elementar, Jena, Germany). DS_N of the cationic hemicellulosic derivatives was calculated from the ratio of the nitrogen to the carbon content according to the following equation:⁶

$$DS_N = (60 \times \%N) / (14 \times \%C - 72 \times \%N)$$

To reduce error and confirm the results, each experiment was repeated in duplicate under the same conditions. The standard errors or deviations of the yield, DS_Y , and DS_N were observed to be lower than 5.5, 5.1, and 4.9%, respectively.

Characterization of the cationic hemicellulosic derivatives

The neutral sugar composition of the isolated native hemicelluloses was determined by gas chromatography analysis of their alditol acetates.⁹ The content of uronic acids in the native hemicelluloses was estimated colorometrically by the method of Blumenkrantz and Asboe-Hanson.¹⁰ Methods for the measurement of the molecular weights, the recording of the FTIR and solution-state ¹³C-NMR spectra, and the determination of the thermal stability of both the native and etherified hemicelluloses were described in one of our previous articles.⁸

RESULTS AND DISCUSSION

Sugar composition of the native SCB hemicelluloses

Hemicelluloses possess different sugar side chains, and their composition can vary depending on the

TABLE I
Yield of Etherified Hemicelluloses and Average DS

Quaternization condition			Cationic hemicellulosic derivatives			
Volume of DMSO (mL)	NaOH/AM molar ratio ^a	ETA/AM molar ratio ^b	Sample no.	DS _N	DS _Y	Recovery (%) ^c
10	1.1	2.2	1	0.16	0.18	33.7
15	1.1	2.2	2	0.18	0.19	34.0
20	1.1	2.2	3	0.21	0.24	35.5
25	1.1	2.2	4	0.19	0.19	34.1
20	0.22	2.2	5	0.19	0.19	33.9
20	0.33	2.2	6	0.22	0.25	35.9
20	1.6	2.2	7	0.23	0.25	35.9
20	2.2	2.2	8	0.08	0.09	31.0
20	0.33	0.54	9	0.05	0.07	30.2
20	0.33	1.1	10	0.11	0.09	31.0
20	0.33	1.6	11	0.13	0.11	31.5
20	0.33	2.7	12	0.20	0.20	34.3
20	0.33	3.3	13	0.21	0.20	34.3
20	0.33	4.3	14	0.14	0.14	32.4

^a Represents the molar ratio of NaOH to AM units in the hemicelluloses.

^b Represents the molar ratio of ETA to AM units in the hemicelluloses.

^c On the basis of the assumption that all of the hemicelluloses were fully converted to etherified hemicelluloses (recovery = 100%, DS_Y = 2.30). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the recovery would be 28.1% (DS_Y = 0.0).

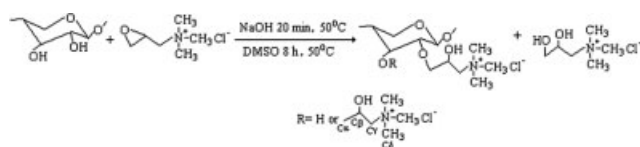
method of isolation, even when the isolation is performed under the same conditions with different extracting batches. The two hemicellulosic preparations, isolated by 10% KOH for 10 h at 25°C with a solid-to-liquid ratio of 1–20 (1 g/20 mL) from the holocellulose in two batches showed minor differences in their sugar compositions.⁸ The sugar composition of the native SCB hemicelluloses, obtained in this study and in the first study of this series with the same batch, showed that xylose was the main neutral sugar component (55.2%), and glucose (27.8%) and arabinose (13.0%) appeared as the second and third major sugars. Uronic acids (3.0%), mainly, 4-*O*-methyl glucuronic acid, galactose (2.6%), and mannose (1.5%), were present in small amounts. In this case, the xylose/glucose/arabinose/galactose/mannose/4-*O*-methyl glucuronic acid molar ratio in the native hemicelluloses was found to be 57.0 : 24.0 : 13.4 : 2.2 : 1.3 : 2.2. The high amount of glucose was probably due to the degradation of cellulose during the treatment of the holocellulose with 10% KOH for a longer duration.

Yield and DS of the cationic hemicellulosic derivatives

As is well known for the modification of polysaccharides, the efficiency of the heterogeneous system is lower than that of the homogeneous system.¹¹ This may be explained by the fact that in the first case, the charged groups are accumulated on the surface

of the hemicelluloses and the diffusion of further cationic agent into the inner parts is increasingly hindered. With processes with homogeneous sequences, cationic hemicelluloses are dissolved, and the reaction on the new surface of the hemicelluloses is less impeded. Therefore, to increase the product yields, we adopted a procedure of quaternization of the hemicelluloses in DMSO as a homogeneous reaction media in our experiment. In all of the water/DMSO volume ratios used, the suspended hemicelluloses in waterlike gel completely dissolved at 85°C for 20 min; then, DMSO was added, and the solution was stirred until it was transparent. The reaction was, therefore, performed in a homogeneous system. In comparison with the procedure of the etherification of hemicelluloses in a heterogeneously aqueous ethanol solution,⁸ sodium hydroxide in a small amount was used to activate the hemicelluloses by increasing the accessibility of the polymer for further chemical modification in this study. The commercially available ETA was used as the etherifying reagent with 0.54–4.3 molar ratios of cationization agent per AM unit in the hemicelluloses (Table I). The reactive species was the epoxide, which was formed *in situ* from ETA with a stoichiometric amount of a base. The main reaction was the quaternization of hemicelluloses, but also, some diol was formed as a result of a side reaction (Scheme 1).

The DS_N and DS_Y values agreed well in most cases. Obviously, the amounts of reaction media had a great effect on the DS's of the products. As shown



Scheme 1 Mechanism of the quaternization of the hemicelluloses with ETA.

in Table I, the DS_N values increased from 0.16 to 0.18 to 0.21 with increasing volume of the reaction media from 10 (sample 1) to 15 (sample 2) to 20 mL (sample 3), respectively. This increase was probably due to the fact that the more homogeneous reaction media were obtained with an increment in volume of DMSO from 10 to 20 mL, which raised the reaction rate and efficiency. On the other hand, when the volume of reaction media was increased further, DS_N decreased from 0.21 in sample 3 to 0.19 in sample 4. This decrease in the DS values could be interpreted in terms of a lower availability of ETA molecules in the proximity of the hemicellulosic molecules at higher volumes of DMSO. Obviously, the amounts of solvent had an effect on the reaction efficiency by influencing the concentration of the hemicelluloses, NaOH, and ETA in DMSO. Thus, an optimized volume of reaction media, 20 mL, was used in further samples.

To obtain a maximum value of DS in the samples, the one-step reaction of ETA with the hemicelluloses was conducted under the variation of the amounts of the catalyst NaOH. Table I also shows the effect of the molar ratio of NaOH to AM on the value of the DS. Clearly, with an optimized volume of reaction media (20 mL), a molar ratio of ETA to AM of 2.0, a temperature of 50°C, a reaction time of 8 h, an alkalization temperature of 50°C, and an alkalization time of 20 min, a molar ratio of NaOH to AM of 0.22 in the homogeneous system yielded a relatively high DS_N of 0.19 (sample 5). When a greater amount of NaOH was added (0.33 mol of NaOH/mol of AM units in the hemicelluloses), the result was an increase in the DS_N value to 0.22 (sample 6). Similarly, a further increase of the amount of NaOH (1.6 mol of NaOH/AM), the DS_N of the product was increased slightly to 0.23 (sample 7). In contrast to this increasing trend, the DS_N values decreased from 0.23 to 0.08 as the amount of NaOH was raised from 1.6 to 2.2 (mol of NaOH/AM). This could be explained as a consequence of the increasing hydrolysis of ETA to the corresponding diol in a high concentration of alkali under the reaction conditions given. Therefore, the hydrolysis of the reagent should be controlled as lowly as possible. On the other hand, a certain amount of NaOH was necessary to activate the hemicelluloses. As a result, a low molar ratio of 0.3 (mol of NaOH/AM) was used in samples 9–14.

With reference to the reaction results, we stress that the DS values increased with increasing amount of cationic agent per AM unit in the hemicelluloses. In this case, the DS could be simply controlled by the adjustment of the molar ratio of ETA to AM units in the hemicelluloses. As shown by the data given in Table I, increasing the molar ratios of ETA to AM from 0.54 (sample 9) to 1.1 (sample 10) to 1.6 (sample 11) to 2.2 (sample 6) led to an increase in the DS values from 0.05 to 0.11 to 0.13 to 0.22, respectively. These increases in DS by increases in the reactant concentration could be interpreted in terms of the greater availability of ETA molecules in the proximity of the hemicellulosic molecules at relatively higher concentrations of the etherifying agent. In contrast, as the molar ratio of ETA to AM was further increased from 2.2 to 2.7 (sample 12) to 3.3 (sample 13) to 4.3 (sample 14), the DS decreased from 0.22 to 0.20 to 0.21 to 0.14, respectively. This may have resulted from insufficient mixing between the ETA and hemicellulose phases. Thus, sufficient time should be given for large extents of etherification at higher ETA concentrations. In comparison, the DS obtained in the homogeneous DMSO system in this study with a low molar ratio of NaOH to AM (0.33) was higher than that of the cationic hemicelluloses prepared in the heterogeneously aqueous ethanol solutions with molar ratios of NaOH to AM 0.8–2.0 but lower than that of the hemicellulosic derivatives performed in a strong aqueous alkaline solution (molar ratio of NaOH to AM = 20).⁷

FTIR spectra

FTIR spectra of the native hemicelluloses [Fig. 1(a)] and cationic hemicellulosic sample 3 [Fig. 1(b)] confirmed the extent of quaternization, depicting some representative spectra of the hemicelluloses ethers. In the spectrum of the native hemicelluloses, the absorbance at 3423, 2918, 1620, 1468, 1266, 1165, 1043, and 892 cm^{-1} were associated with native hemicelluloses in Figure 1(a).¹² Compared with the Figure 1(a), Figure 1(b), showing the spectrum of the cationic hemicellulose sample 3, provides evidence of quaternization by an increase in the intensity of the major ether bands at 1165 and 1039 cm^{-1} . In addition, the appearance of a small sharp band at 1463 cm^{-1} in the etherified hemicelluloses [Fig. 1(b)] was assigned to the CH_2 bending mode and methyl groups of the substituent.¹³ The presence of an additional band at 1413 cm^{-1} , assignable to the C–N stretching vibration, was clear proof of the incorporation of a cationic moiety onto the backbone of the hemicelluloses.¹⁴ The intensity of the symmetric C–H vibration band at 2923 cm^{-1} increased, which implied that CH_3 groups were introduced.

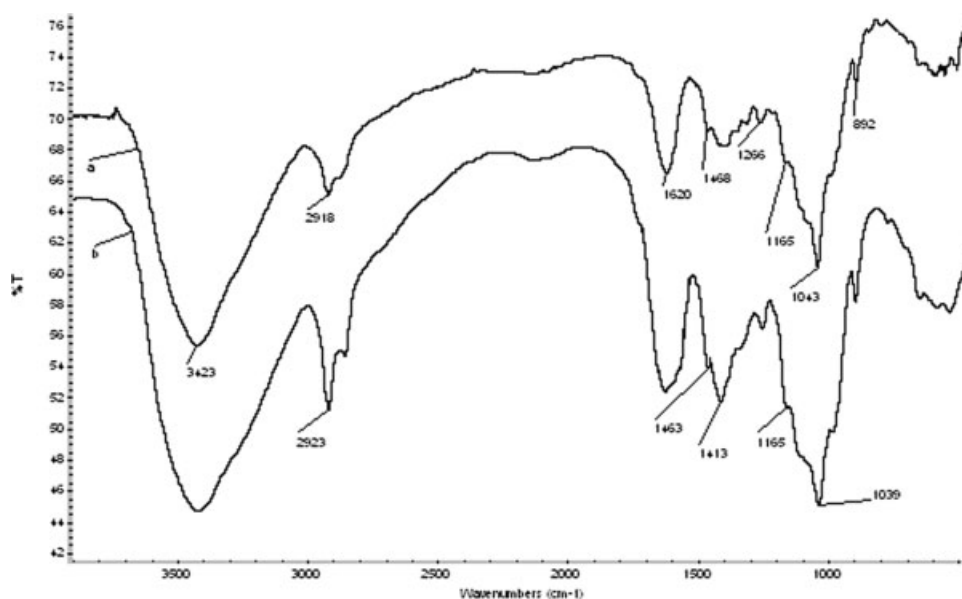


Figure 1 FTIR spectra of (a) the native hemicelluloses and (b) cationic hemicellulose sample 3.

¹³C-NMR spectra

The chemical changes in the structure of the hemicelluloses were verified by ¹³C-NMR spectroscopy. The ¹³C-NMR spectra of the native hemicelluloses and cationic hemicellulose sample 6 with a DS_N value of 0.22 are shown in Figure 2. In comparison with Figure 2(a) of the native hemicelluloses, the presence of three signals at 68.4, 65.3, and 53.3 ppm was characterized by the carbon resonances of C_γ(CH₂-N⁺), C_β(CHOH), and C_δ(CH₃)₃N⁺ moieties, respectively, which again confirmed the occurrence of quaternization in the hemicelluloses.⁴ The occurrence of five signals at 101.8, 76.5, 73.8, 72.8, and 63.0 ppm related to the carbon atoms of C-1, C-4, C-3, C-2, and C-5 in the β-D-xyl-p units of the hemicelluloses.¹⁵

Thermal analysis

Thermogravimetric (TG) analysis and differential thermal analysis (DTA) are analytical experimental techniques that investigate the behavior of substances as a function of temperature, and their ability is to characterize, quantitatively and qualitatively, huge varieties of materials over a considerable temperature range.¹⁶ In this study, the effect of chemical modification on the thermal properties of SCB hemicelluloses was examined by thermogravimetric analysis and DTA in the temperature range 0–600°C, and the thermograms of native hemicelluloses and the etherified hemicellulosic sample 6 are given in Figure 3. The early minor weight loss observed for both samples was attributed to the desorption of water from the polysaccharide structure. Sample 6 in this

stage showed a higher perceptual loss weight than the native hemicelluloses, which indicated that the modified hemicelluloses had more absorbed water than the native hemicelluloses. This fact was in agreement with the observations about crystallinity disappearance after chemical modification.⁶ In addition, this figure gave clear evidence that the native hemicelluloses had a higher thermal stability up to 225°C than the modified hemicelluloses at 200°C when decomposition began. Beyond these

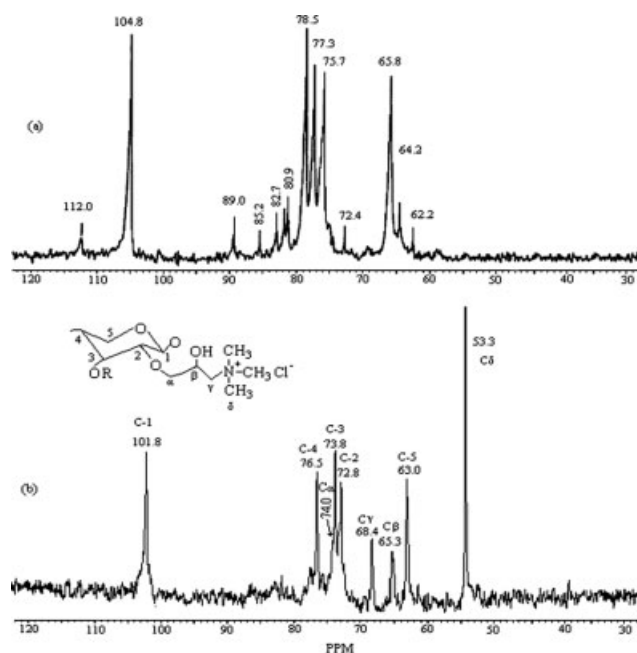


Figure 2 ¹³C-NMR spectrum of (a) the native hemicelluloses and (b) cationic hemicellulose sample 6.

temperatures, there was a sharp weight loss in both the native and etherified hemicelluloses. At 50% weight losses, the decomposition temperature occurred at 302°C for the native hemicelluloses and at 285°C for the modified hemicelluloses. These decreasing trends of decomposition temperature implied that the thermal stability of the modified hemicelluloses was lower than that of the native hemicelluloses. However, this thermal stability of the etherified hemicelluloses over 200°C would be rather satisfactory in additives in papermaking.

Figure 3 also shows the DTA curves of the native hemicelluloses and the modified hemicelluloses. Notably, the exothermic peak, which represents heat released from the product, was observed at a maximum temperature of 305°C for the native hemicelluloses and at 290°C for sample 6. This decrement in temperature was due to the fact that the hydrogen bonds were destroyed by chemical modification. Therefore, the thermal stability of the modified hemicelluloses decreased.

Weight-average molecular weight (M_w)

To check the extent of the polymer degradation during the reaction, the molecular weights of the native hemicelluloses and the modified hemicellulosic preparations with different average DS's were further determined by gel permeation chromatography, and their M_w , number-average molecular weight (M_n), and polydispersity (M_w/M_n) are given in Table II. As clearly shown, the native hemicelluloses had an average molecular weight 28,900 g/mol with a 3.2 polydispersity. Compared with that of the native hemicelluloses, the M_w of the modified hemicellulosic derivatives decreased slightly, which was due to the minor degradation of the hemicelluloses during chemical modification. Moreover, the M_w 's of the modified hemicelluloses with high DS values were

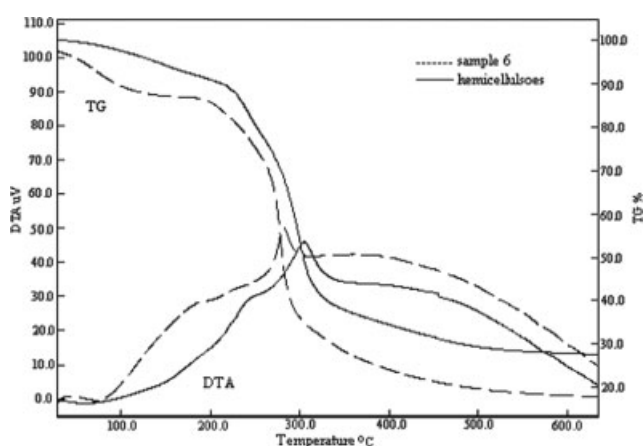


Figure 3 Thermograms of the native hemicelluloses and modified hemicellulose sample 6.

TABLE II
 M_w of the Native Hemicelluloses and Their Derivatives with Different Average DS Values

Sample no.	DS _N	M_w	M_n	M_w/M_n
Native hemicelluloses	0.00	28,890	9000	3.2
6	0.22	26,900	8100	3.3
8	0.08	25,200	7400	3.4
11	0.13	25,900	8100	3.2
13	0.21	26,900	8300	3.3

higher than that of the modified hemicelluloses with low DS values. For example, sample 6 (DS = 0.22) displayed a M_w value of 26,900 g/mol, whereas sample 11 (DS = 0.13) showed a M_w value of 25,900 g/mol. As was also observed, the polydispersity (M_w/M_n) of the modified hemicelluloses was higher than that of the native hemicelluloses in most case, which indicated that the molecular weight distribution of the modified hemicelluloses was wider than that of the native hemicelluloses. Interestingly, the cationic hemicellulosic derivatives, obtained in a homogeneous DMSO system, showed higher values of M_w (25,200–26,900 g/mol) than the etherified polymers, which were prepared in heterogeneously aqueous ethanol systems ($M_w = 23,200$ – $25,900$ g/mol),⁸ and the quaternization of SCB hemicelluloses in a strong aqueous alkaline solution resulted in a substantial degradation of the polymers, as shown by their M_w values between 15,400 and 19,400 g/mol.⁷ From this point of view, the homogeneous DMSO system was found to be an optimum reaction medium for the production of water-soluble cationic hemicellulosic derivatives without significant degradation of the macromolecular hemicellulosic polymers.

CONCLUSIONS

These results show that the cationic hemicellulosic polymers with a low average DS could be prepared by quaternization with ETA without substantial degradation in the homogeneous DMSO medium. The DS values reached by these reactions could be adjusted by the amount of reaction media, sodium hydroxide, and cationic agent used in the reactions. Under optimized conditions (reaction temperature = 50°C, reaction time = 8 h, volume of reaction media = 20 mL, molar ratio of NaOH to AM = 0.33, and molar ratio of ETA to AM = 2.2), cationic hemicellulosic derivatives with a DS value of 0.22 were synthesized. FTIR and solution-state ¹³C-NMR spectroscopy studies produced clear evidence that the quaternization occurred in the hemicelluloses. The thermal stability of the cationic hemicellulosic derivatives decreased after chemical modification.

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