Synthesis of Amphiphilic Starch Derivatives Using One-pot Synthesis Procedure

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Abstract: Amphiphilic starch derivatives with high content of functional groups were prepared from potato starch using a one-pot synthesis method with a single reaction medium for the entire procedure. Potato starch was benzylated, followed by the introduction of hydroxypropyltrimethylammonium (HPMA) moieties without the purification of intermediates. The synthesis was performed under heterogeneous conditions, leading to the formation of benzyl 2-hydroxypropyltri methylammonium starch chloride (BnHPMAS) with a total degree of substitution (DS) of up to 1.4. This process improved the efficiency of the preparation of amphiphilic starch derivatives and reduced the time and resources consumed by avoiding a separation process and purification of the intermediate compounds. The DS of BnHPMAS was in the range of 0.36 to 1.4, which could be tuned by varying the molar ratio of the reagents to repeating unit or by changing the reaction temperature, time, and medium. The structure of the amphiphilic starches was characterized using elemental analysis, size exclusion chromatography, fourier transform infrared spectroscopy (FT-IR), and nuclear magnetic resonance (NMR) spectroscopy. Moreover, the surface tension and turbidity of the solutions of the products were measured for their potential application in the removal of dissolved and colloidal substances in paper cycling water.

Keywords: amphiphilic starch derivatives; chemical modification; degree of substitution; turbidity



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1 Introduction

Starch is one of the most dominant natural polymers in the planet. It is not only the main component in people's staple food, but also widely used in industries for many applications in both natural and derivative forms[1-3]. Starch has large amounts of hydroxyl groups on its surface, which facilitate the easy preparation of starch derivatives with chemicals or grafting with other mono-/polymers[4-7]. Starch derivatives have significantly different physicochemical properties from starch, which broaden their applications in many fields such as food, pharmacy, paper, and textile industries[3, 8-10].

Amphiphilic starches are derivatives modified by introducing chemicals with polar groups such as hydrophilic carboxymethyl (CM) or hydroxypropy ltrimethy lammonium (HPMA) moieties, and non-polar groups such as benzyl or alkyl groups. Their simultaneous hydrophilic/hydrophobic properties have attracted increasing interest in many fields. For example, amphiphilic starches based on O-(carboxymethyl) starch exhibit excellent emulsifying ability compared to commercial surfactants[11-12]. One of the most popular approaches for the synthesis of amphiphilic starches is the etherification of hydroxyalkyl starch with long-chain alkyl halides and epoxides[13]. There are also amphiphilic starch products based on HPMA starch derivatives with a C12 to C18 alkyl moiety[14-15]. Novel amphiphilic starch derivatives based on starch from potato, pea, and waxy maize containing hydrophobic benzyl and hydrophilic CM or HPMA groups with a high degree of substitution (DS) have been studied by Thomas Heinze et al[16]. However, the processes of synthesis of amphiphilic starch derivatives are expensive and time-consuming, involving several steps in different reaction vessels, including the recycling and purification of intermediate products such as benzyl starch.

In this paper, the synthesis of amphiphilic starch derivatives with lipophilic benzyl (Bn) and hydrophilic HPMA moieties using a one-pot procedure is proposed. The effects of reaction conditions such as the medium and reaction time on the DS of products are evaluated. The obtained amphiphilic starch derivatives are characterized using elemental analysis, fourier transform infrared spectroscopy (FT-IR), and nuclear magnetic resonance (NMR) spectroscopy, and size exclusion chromatography (SEC). Moreover, the properties of amphiphilic starch derivatives are further investigated in terms of surface tension and turbidity.

2 Experimental

2.1 Materials

The starch samples used were potato starch provided by CHP Carbohydrate Pirna (GmbH & Co.KG, Pirna, Germany). Benzyl chloride (BnCl) and 2,3-epoxypropy ltrimethylammonium chloride (EPTMA, 70% aqueous solutions) were purchased from Aldrich and used without further purification. The other chemicals were used as received.

2.2 Measurements

Elemental analysis was carried out using a Vario ELIII (Elementaranalysensysteme, Hanau, Germany). FT-IR spectra were measured using a Nicolet Avatar 370 spectrometer (Thermo Electron GmbH, Bremen, Germany) with the KBr pellet technique. ^{1}H and ^{13}C NMR spectra were acquired using a Bruker AMX400 spectrometer (Rheinstetten, Germany) with dimethyl sulfoxide-d_6 (DMSO-d_6) or D_2O as the solvent.

The DS of benzyl group (DS_{Bn}) was calculated by integrating the peaks in the ^{1}H NMR spectra of the peracetylated benzyl starch samples according to Equation (1)[17].

$$DS_{Bn} = \frac{1.4 I_{Bn}}{I_{AGU} - 0.4 I_{Bn}} \quad (1)$$

Where I_{AGU} is the integral value of the peaks between 3.0 and 6.0 ppm, and I_{Bn} is the integral value of the peaks between 7.0 and 7.8 ppm.

The MS (the average number of moles of the substituent groups per monomer unit) value of the HPMA groups (MS_N) was calculated from the nitrogen content according to Equation (2).

$$MS_N = \frac{M_{BnS} \cdot N}{1401 - 151.64N} \quad (2)$$

Where M_{BnS} is the molar mass of the modified repeating unit of benzyl starch and N (%) is the nitrogen content.

The weight average (Mw) and number average (Mn) molecular masses and polydispersity index (PDI) were determined using an SEC system (Model PU-980 pump and DG-980-50 degasser, JASCO Corp., Tokyo, Japan) equipped with a UV detector 975 (k=254 nm) and a refractive index detector 930. The system consisted of two columns (columns Suprema 1000+ and Suprema 100, Kromatek, Great Dunmow, Essex, UK). The eluent used in the system was aqueous DMSO solution containing 0.5% LiBr, and the flow rate of the eluent was 1 mL/min. Pullulan and dextran standards (M<104 g/mol) were used as the calibration for the calculation of Mw, Mn, and PDI.

The surface tension of the starch derivatives dissolved in water (dissolution was carried out at 25℃, 1%) was measured using a tensiometer (K100, Krüss GmbH, Hamburg, Germany) by applying a platinum plate with a moistened surface area of 40 mm^2. The aqueous solutions were measured at 25℃ for 6 h using a heating/cooling cycle.

The turbidity of the starch derivatives dissolved in water (1%) was measured using a turbidity meter (Turbiquant® 3000 IR, Merck KGaA, Germany) at room temperature.

2.3 Methods

Amphiphilic starch (BnHPMAS 1) was prepared using the one-pot process described as follows.

2.3.1 Synthesis of starch derivatives with benzyl group

First, 23.8 g of potato starch (16% water content corresponding to 20 g of dry material, 123 mmol) was dispersed in 80 mL of 2-propanol/water (50%, *V/V*) solution. Subsequently, 1.73 g of solid NaOH (0.043 mol, 0.35 mol/mol modified anhydroglucose unit (AGU)) was added to the dispersion and the mixture was stirred for 30 min at 60℃. Subsequently, 4.2 mL of benzyl chloride (37 mmol, 0.30 mol/mol modified AGU) was added and the mixture was further stirred for 24 h at 60℃.

2.3.2 Synthesis of benzyl-starch derivatives with EPTMA group

Further, 30 mL of 2-propanol/water (50%, *V/V*) and 0.49 g (12 mmol, 0.10 mol/mol modified AGU) of solid NaOH were added to the mixture obtained above. The mixture was stirred for 30 min at 60℃ followed by the addition of 12 mL of EPTMA (70% in water) (74 mmol, 0.6 mol/mol modified AGU). The mixture was stirred for 24 h at 60℃ to facilitate the reaction.

After cooling, the mixture was neutralized with 1 mol/L HCl. The synthesized starch derivatives were obtained by the precipitation of the mixture in 2-propanol solution, followed by the dissolution in water and precipitation again with 2-propanol.

The entire process was repeated twice and the product was finally obtained by drying in vacuum at 40℃ for 48 h.

Sample: BnHPMAS 1 (DS_{Bn}=0.29, MS_N=0.30). Yield: 24.1 g (89 % according to starch, white powder).

Elemental analysis: C 49.32%, H 7.14%, N 1.81%, Cl 7.45%.

IR (KBr, cm^{-1}): 3416 (OH), 2925 (CH), 1641, 1486 (C═C), 1417 (CH), 1356 (CH_3), 1154, 1086, 1020 (C—O—C_{AGU}), 756 (CH_{aromat}), 705 (CH_{aromat}).

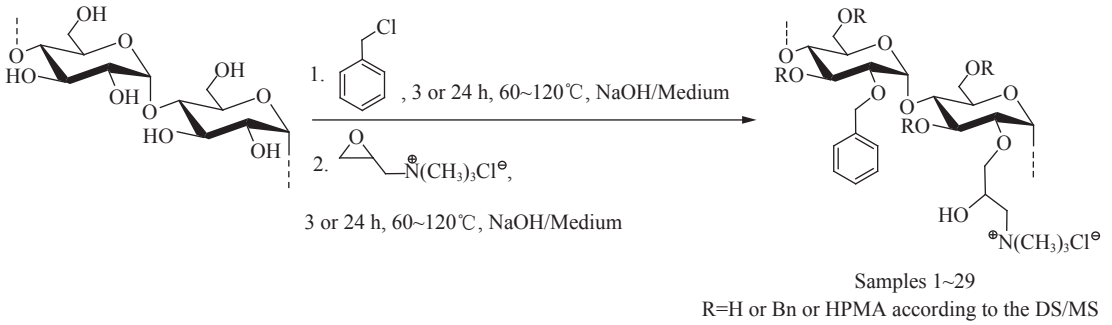
^{1}H-NMR (D_2O, ppm): 3.23 (H15), 3.33~4.43 (H2~6, H12~14), 5.49 (H1), 5.77 (H1'), 7.43 (H8~11).

^{13}C-NMR (D_2O, ppm): 54.3 (C15), 60.6 (C6), 65.3 (C13), 68.1 (C14), 68.4 (C6s), 70~78 (C2~5, C7), 73.2 (C12), 80.4 (C2s), 96.7 (C1'), 128.8 (C9~11), 137.4 (C8).

3 Results and discussion

3.1 Synthesis of amphiphilic starch derivatives

The conventional method to introduce both hydrophobic and hydrophilic groups into starch molecules is expensive and time-consuming. In the present study, amphiphilic starch was synthesized first via the reaction with benzyl chloride to achieve the hydrophobic



Scheme 1 Synthesis of benzyl 2-hydroxypropyltrimethylammonium starch chloride (BnHPMAS 1~29) from starch using the one-pot process

property, followed by the introduction of hydrophilic HPMA moieties directly on the benzyl starch formed. The two reactions were carried out in the same reaction medium using a one-pot procedure without the purification of intermediate benzyl starch (Scheme 1).

The potato starch reacted with benzyl chloride and EPTMA (70% in water) of different molar ratios with 2-propanol/water (50%, *V/V*) as the reaction medium. Table 1 presents the products of BnHPMAS obtained under different reaction conditions and molar ratios.

Amphiphilic BnHPMAS (1~21) with the total DS values in the range of 0.36~1.40 was obtained. The value of DS_{Bn} and MS_N of BnHPMAS obtained was strongly depended on the amount of corresponding reagent used under the same reaction conditions. The highest DS_{Bn} value of BnHPMAS achieved was 0.87 when the highest molar ratio of BnCl was used in the reactant mixture of in this work.

Applying a molar ratio of AGU∶BnCl∶EPTMA of 1∶0.3∶0.6, BnHPMAS with DS_{Bn} of 0.29 and MS_N of 0.30 (sample 1) was obtained. With the increase in the molar ratio of BnCl∶AGU up to 0.9∶1 at a comparable molar amount of EPTMA, the DS_{Bn} of BnHPMAS obtained could reach 0.87 (BnHPMAS 9). Alternatively, with the increase in the molar ratio of BnCl to repeating unit, MS_N decreased at a comparable molar amount of EPTMA. Thus, sample 1 had DS_{Bn} of 0.29 and MS_N of 0.30 by applying a molar ratio of 1∶0.3∶0.6 (AGU∶BnCl∶EPTMA). Sample 9 had MS_N of 0.08 and DS_{Bn} of 0.87 at a molar ratio of 1∶0.9∶0.6 (AGU∶BnCl∶EPTMA). However, with the increase in the molar ratio of EPTMA∶AGU up to 3∶1, the MS_N of BnHPMAS achieved could reach 1.00 (BnHPMAS 4) although the DS_{Bn} was 0.28, i.e., comparable to that of sample 1. MS_N strongly depends on the molar ratio of BnCl per repeating unit applied and the resulting DS_{Bn} under specific conditions. For comparable molar amounts of EPTMA, the increase in the molar ratio of BnCl∶AGU resulted in a higher DS_{Bn} value and lower MS_N value.

The modification of starch also depends on other reaction conditions, including reaction time and temperature. It was observed that changing the reaction time had a significant influence on the DS of BnHPMAS. With a shorter duration (such as 3 h) of each reaction in the one-pot synthesis, BnHPMAS (samples 13~16, seen in Table 1) with lower DS of 0.22~0.52 was produced compared with the samples prepared with the same molar ratio of reactants. Furthermore, the reaction temperature affected both the reaction steps. It was observed that the reagent conversion increased with the increase in the reaction temperature as demonstrated by the DS of entries 13~16 (Table 1). However, the mixture of reactants turned to gel state at high temperature.

The yield of BnHPMAS was 85%~90%, which is much higher than that of BnHPMAS prepared using the two-step reaction (approximately 73%)[16]. Surprisingly, the reactions of BnCl with starch exhibited high reagent conversion of above 90% in 2-propanol/water (50%, *V/V*) at 60℃ for 24 h with the molar ratios of 0.3 and 0.6 mol BnCl/mol AGU. The efficiency of benzylation decreased to 78% in the case of a higher molar ratio of 0.9 mol BnCl/mol AGU (sample 10). However,

Table 1 Reaction conditions and resulting BnHPMAS products in 2-propanol/water (50%, *V/V*) obtained from starch using the one-pot process

Sample No.	Molar ratio[a]	Reaction conditions		Products	
		T/℃	Time[b]/h	DS_{Bn}[c]	MS_N[d]
1	1∶0.3∶0.35∶0.6∶0.1	60	24-24	0.29	0.30
2	1∶0.3∶0.35∶1.0∶0.2	60	24-24	0.28	0.48
3	1∶0.3∶0.35∶2.0∶0.3	60	24-24	0.27	0.86
4	1∶0.3∶0.35∶3.0∶0.4	60	24-24	0.28	1.00
5	1∶0.6∶0.70∶0.6∶0.1	60	24-24	0.56	0.23
6	1∶0.6∶0.70∶1.0∶0.2	60	24-24	0.59	0.35
7	1∶0.6∶0.70∶2.0∶0.3	60	24-24	0.57	0.43
8	1∶0.6∶0.70∶3.0∶0.4	60	24-24	0.58	0.71
9	1∶0.9∶1.05∶0.6∶0.1	60	24-24	0.87	0.08
10	1∶0.9∶1.05∶1.0∶0.2	60	24-24	0.70	0.20
11	1∶0.9∶1.05∶2.0∶0.3	60	24-24	0.83	0.37
12	1∶0.9∶1.05∶3.0∶0.4	60	24-24	0.74	0.68
13	1∶0.6∶0.70∶1.0∶0.2	60	3-3	0.22	0.23
14	1∶0.6∶0.70∶1.0∶0.2	80	3-3	0.26	0.26
15	1∶0.6∶0.70∶1.0∶0.2	Reflux[e]	3-3	0.52	0.40
16	1∶0.6∶0.70∶1.0∶0.2	Reflux[f]	3-3	0.51	0.45

a. AGU: BnCl:NaOH: EPTMA: NaOH; b. The reaction times for step 1 and step 2 were 24 h and 24 h (or 3 h and 3 h), respectively; c. Degree of substitution of benzyl groups (DS_{Bn}) determined using ^{1}H NMR spectroscopy after peracetylation; d. Molar degree of substitution of HPMA groups (MS_N) determined using nitrogen content; e. Bath temperature 100℃; f. Bath temperature 120℃.

upon applying such a high amount of reagent (samples 9~12, DS_{Bn} ranges from 0.70 to 0.87), the reaction appeared to be not as reproducible as the reactions with a lower molar ratio (samples 1~4, DS_{Bn} 0.27~0.29). The reagent conversion of EPTMA is depended on the prior benzylation. The cationization of the benzylated intermediate formed had the highest efficiency at a molar ratio of BnCl to AGU of 0.3∶1 starting with the conversion efficiency of EPTMA of 50% (0.6 mol EPTMA/mol AGU). With the increase in the molar ratio of EPTMA, the reagent conversion decreased to 33% (3 mol EPTMA/mol AGU). At a comparable molar amount of EPTMA (0.6 mol/mol AGU), the efficiency of the EPTMA conversion decreased with the increase in the starting amount of BnCl, e.g., to 50% (sample 1, 0.3 mol BnCl/mol AGU) and to 38% (sample 5, 0.6 mol BnCl/mol AGU). The overall efficiency of the reagent conversion was 65% at a low molar ratio (0.3 mol BnCl and 0.6 mol EPTMA per mol AGU, sample 1). It decreased to 36% at the molar ratios of 0.9 mol BnCl and 3.0 mol EPTMA per mol AGU (sample 12). The longer the reaction time and the higher the reaction temperature, the higher was the efficiency of the synthesis. Notably, the reagent conversion was slightly higher at a low molar ratio for the one-pot procedure, and with the increase in the molar amount, it was in the same range as described for the two-step synthesis of BnHPMAS[16]. At a comparable molar ratio of 0.55 mol BnCl/mol AGU for the two-step procedure and 0.6 mol BnCl/mol AGU for the one-pot process, the reagent yields were 91% and 97%, respectively, for benzylation. For the cationization, the reagent yield (EPTMA) depends on the prior benzylation (comparable amount of BnCl 0.55 mol/mol AGU for the two-step procedure; 0.6 mol/mol AGU for the one-pot process); it was 50% for the one-pot procedure and 42% for the two-step procedure, if 0.6 mol EPTMA/mol AGU and 0.5 mol EPTMA/mol AGU, respectively, were used. At the molar ratio of 0.55 mol BnCl/mol AGU for the two-step procedure and 0.6 mol BnCl/mol AGU for the one-pot reaction, the reagent yield for the conversion of EPTMA was 38% (one-pot) and 52% (two step synthesis) at comparable molar amounts of EPTMA (0.6 mol/mol AGU for the one-pot process, 0.5 mol/mol AGU for the two-step procedure). The by-products of the benzylation appeared to have a significant influence on the resulting DS and efficiency of reagent conversion.

Further investigations were carried out by using different reaction media including aqueous methanol and aqueous ethanol. As presented in Table 2, BnHPMAS with different DS[17-24] was also prepared from starch using the one-pot process with different media. Compared to the results of the products prepared under comparable reaction temperatures and times, e.g., BnHPMAS 19 (DS_{Bn} 0.24, MS_N 0.28) and 23 (DS_{Bn} 0.27, MS_N 0.38), the DS was slightly higher by using aqueous ethanol than methanol. Under these conditions,

Table 2 Reaction conditions and results of synthesis of BnHPMAS using different reaction media via the one-pot process

Sample No.	Molar ratio[a]	Reaction conditions			Products	
		Medium	*T*/℃	Time[b]/h	DS_{Bn}[c]	MS_N[d]
17	1∶0.6∶0.70∶1.0∶0.2	80% methanol	80	3-3	—	0.09
18	1∶0.6∶0.70∶1.0∶0.2	60% methanol	80	3-3	0.12	0.24
19	1∶0.6∶0.70∶1.0∶0.2	50% methanol	80	3-3	0.24	0.28
20	1∶0.6∶0.70∶1.0∶0.2	50% methanol	80	24-24	0.18	0.25
21	1∶0.6∶0.70∶1.0∶0.2	80% ethanol	80	3-3	0.13	0.36
22	1∶0.6∶0.70∶1.0∶0.2	60% ethanol	80	3-3	0.26	0.39
23	1∶0.6∶0.70∶1.0∶0.2	50% ethanol	80	3-3	0.27	0.38
24	1∶0.6∶0.70∶1.0∶0.2	50% ethanol	80	24-24	0.39	0.43

a. AGU: BnCl:NaOH: EPTMA: NaOH; b. The reaction times for step 1 and step 2 were 24 h and 24 h (or 3 h and 3 h), respectively; c. Degree of substitution of benzyl groups (DS_{Bn}) determined using ^{1}H NMR spectroscopy after peracetylation; d. Degree of substitution of HPMA groups (MS_N) determined using nitrogen content.

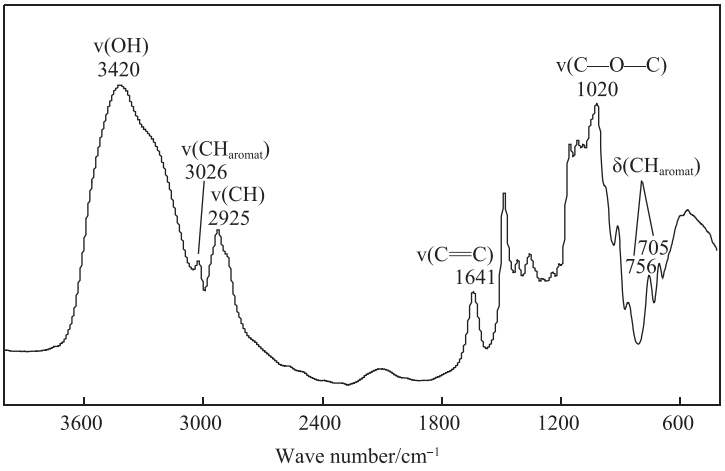


Fig.1 FT-IR spectrum of BnHPMAS sample 4 (DS_{Bn} 0.28, MS_N 1.00)

the DS of the product was also higher for products prepared in aqueous ethanol (23, DS_{Bn} 0.27, MS_N 0.38) than those prepared using aqueous 2-propanol as the slurry medium (compare BnHPMAS 14, DS_{Bn} 0.26, MS_N 0.26). However, for the fast volatilization of solvent and especially strong gelation trend of starch, in addition to lower boiling temperature, it was difficult to carry out the reaction at a higher temperature in aqueous methanol or aqueous ethanol. Thus, for the one-pot process, it was more efficient to apply 2-propanol/water (50%, *V/V*) as the reaction medium.

3.2 Characterization

3.2.1 FT-IR and NMR Spectroscopy

The structure of BnHPMAS was confirmed using FT-IR and NMR spectroscopy. Fig.1 shows the FT-IR spectrum of the prepared BnHPMAS 4 (DS_{Bn} 0.28, DS_N 1.00). The residual OH groups exhibited stretching vibration at approximately 3420 cm^{-1} and typical absorption bands of the polymer backbone were detected at 2925 (CH), and 1154, 1086, and 1020 cm^{-1} (C—O—C). Moreover, the vibrations of the benzyl moiety were detected at 3026 cm^{-1} (C—H of aromatic ring), 1641 cm^{-1} (C═C), and 756 and 705 cm^{-1} (CH).

The ^{13}C NMR spectra in combination with the Distortionless Enhancement by Polarization Transfer (DEPT) ^{13}C technique in D_2O at 300 K allowed the assignment of structural features of BnHPMAS 8 (DS_{Bn} 0.58, MS_N 0.71, Fig.2). The carbon atoms of the modified AGU (2~5) were detected between 70 and 78 ppm. A signal at 60.6 ppm indicates the unsubstituted position 6 of the repeating unit. The chemical modification of the AGU in the primary position resulted in a significant shift of the signals to 68.6 ppm. The peak of position 1 was influenced by a substituent at position 2 resulting in the C1'-signal at approximately 96.7 ppm, whereas a signal for C-1 (unmodified position 2) was not visible, which appeared with a down-field shift of 3~5 ppm. The signal of the functionalized position 2 was observed at approximately 80.4 ppm. Moreover, the aromatic resonances of the benzyl ether were observed at 128.8 (C9~11) and 137.4 ppm (C8). The CH_2 group (C7) overlapped with the AGU carbon atoms and could not be assigned. Further peaks appeared in the ^{13}C NMR spectrum of BnHPMAS 8 (Fig.2) at 65.3 ppm and 68.1 ppm (C13 and C14 of the cationic substituent), and at 54.3 ppm (CH_3 group C15 of the HPMA substituent). The chemical shift of C12 was 73.2 ppm, which was also in the range of the AGU carbon atoms. From the

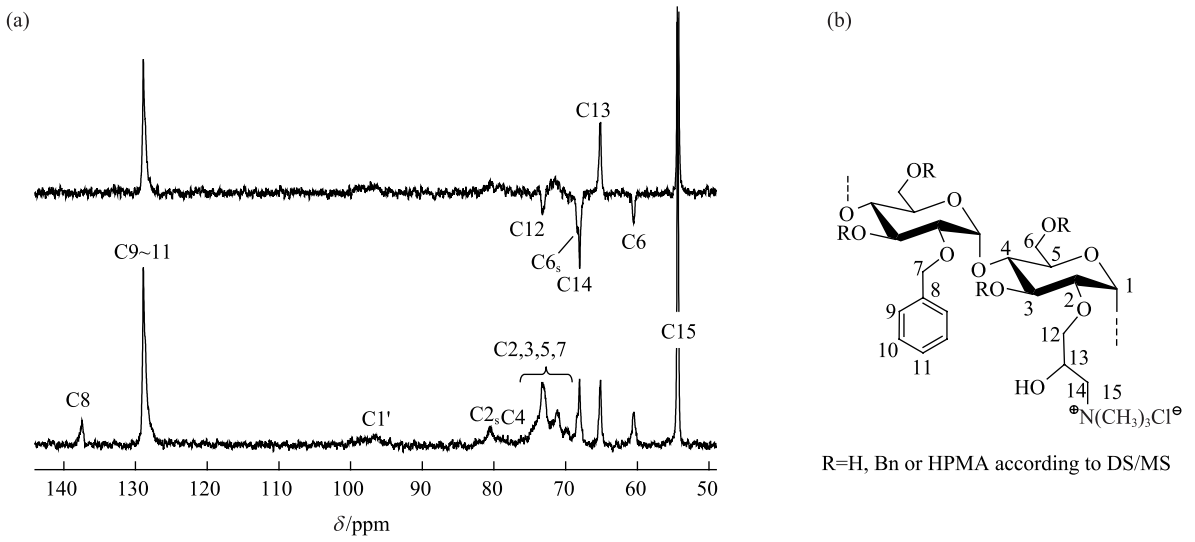


Fig.2 ^{13}C NMR (a) and DEPT spectrum (b) of BnHPMAS sample 8 (DS_{Bn} 0.58, MS_N 0.71) recorded in D_2O at 300 K

NMR spectra, it could be concluded that a substituent distribution within the AGU occurred in the order O-2 >>O-6>O-3.

3.2.2 Properties

Amphiphilic polyelectrolytes are used as solvents and thickeners owing to their ability to drastically change the rheological properties of aqueous solutions and suspensions[18-19]. The toxicity of native or modified starch used during paper production is classified as non-hazardous[20]. Owing to its cationic and hydrophobic groups, BnHPMAS obtained has significant potential to be used in the removal of dissolved and colloidal substances in paper cycling water[21].

Table 3 Surface tension and turbidity of BnHPMAS samples prepared using the one-pot process (measured in 1%)

Sample No.	DS_{Bn}	MS_N	Surface tension /(mN · m^{-1})	Turbidity /NTU
1	0.29	0.30	42.3	16.3
2	0.28	0.48	53.7	12.1
3	0.27	0.86	49.6	12.9
4	0.28	1.00	55.1	12.8
5	0.56	0.23	43.1	10.5
6	0.59	0.35	42.2	9.8
7	0.57	0.43	46.3	16.8
8	0.58	0.71	41.9	9.6
9	0.87	0.08	—	7800
10	0.70	0.20	—	6500
11	0.83	0.37	—	6300
12	0.74	0.68	49.5	30.4

Table 3 summarizes the results of the surface tension and turbidity measurement of the selected amphiphilic starch derivatives with different DS prepared using the one-pot synthesis. Apparently, the DS of moieties determines the values of turbidity. BnHPMAS samples (1~8) with DS below 0.59 and MS starting from 0.23 could be well dissolved in water, with turbidity in the range of 10~17 NTU. However, HPMAS samples with DS_{Bn} more than 0.70 (9~11) with MS_N below 0.37 could not be dissolved in water; the turbidity values were more than 6000 NTU. Sample 12 with MS_N of 0.68, which could be dissolved in water, possessed higher turbidity than BnHPMAS with lower DS_{Bn} (MS_N 0.08~0.37, samples 9~11). As summarized in Table 3, the surface tension values of amphiphilic starch derivatives were in the range of 41.9~55.1 mN/m, which were significantly lower than that of water (72.8 mN/m). However, no clear correlation among DS_{Bn}, MS_N, and surface activity could be observed for BnHPMAS (samples 1~12), which was similar to the data reported previously for BnHPMAS samples obtained using the two-step procedure[16]. At comparable DS_{Bn} of approximately 0.3 and low MS_N values, the surface tension of the BnHPMAS synthesized using the one-pot process (MS_N 0.30, 42.3 mN/m, 1) was lower than that of BnHPMAS obtained using the two-step procedure (MS_N 0.22, 58.7 mN/m). At higher MS_N values, the

surface tension of the BnHPMAS synthesized using the one-pot process (MS_N 0.48, 53.7 mN/m, 2) was slightly higher than that of a comparable sample obtained using the two-step process (MS_N 0.40, 48.6 mN/m). With the increase in MS_N, the surface tension of BnHPMAS synthesized using the one-pot process (MS_N 0.86, 49.6 mN/m, 3) was lower than that of a comparable sample obtained using the two-step procedure (MS_N 0.85, 50.8 mN/m). The solutions of samples 5~8 (one-pot process) with DS_{Bn} of 0.56~0.59 and MS_N of 0.23~0.71 exhibited lower surface tension (41.9~46.3 mN/m) than comparable samples obtained using the two-step synthesis (DS_{Bn} 0.50, MS_N 0.26~0.69) exhibiting surface tension in the range of 52.3~54.0 mN/m[16].

The molar mass distribution of starch and selected amphiphilic starch derivatives was measured using SEC in DMSO containing 0.5% LiBr. Fig.3 shows the typical molar mass distribution of BnHPMAS (sample 6) compared with that of the starting starch. Both samples

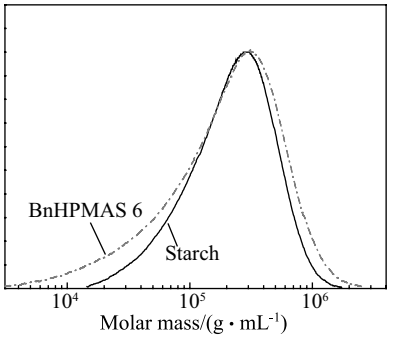


Fig.3 SEC of starch and BnHPMAS sample 6 (DS_{Bn} 0.59, MS_N 0.35) measured in DMSO/LiBr

Table 4 SEC data of BnHPMAS samples prepared using the one-pot process measured in DMSO/LiBr

Sample No.	Molar mass[a] /10^5 (g • mol^{-1})			PDI[b]	DP_w[c]	DP_n[d]
	*M*w	*M*n	*M*p			
Starch	2.81	1.47	2.76	1.9	1735	9074
2	3.18	0.52	3.27	6.2	1225	1992
4	3.43	1.05	3.32	3.3	1015	3108
6	2.98	0.85	3.14	3.5	1112	3189
8	3.07	0.51	3.18	6.0	955	1584
14	2.91	0.96	2.93	3.0	1295	4270
23	3.13	1.25	3.17	2.5	1285	5132
24	2.80	0.49	2.96	5.7	1069	1874

a. Weight average (*M*w), number average (*M*n), and peak maxima (*M*p) molar mass; b. Polydispersity index; c. Weight average degree of polymerization; d. Number average degree of polymerization.

possessed a unimodal molar mass distribution. The data of SEC (*M*w and *M*n) are summarized in Table 4. With respect to the initial DP_n and DP_w of the starting starch, there was a degradation of polymer during the reaction especially for a longer reaction time and possibly also during purification. The PDI of BnHPMAS samples was higher than that of starting starch. However, a tendency of polymer aggregation could not be detected.

4 Conclusions

Amphiphilic starch derivatives containing hydrophobic benzyl and hydrophilic HPMA groups with different ratios and high total DS were prepared successfully using a one-pot process. This process improved the efficiency of preparation of amphiphilic starch derivatives and reduced the consumption of time and resources by avoiding a separation process and the purification of the intermediate compounds. The DS could easily be adjusted by varying the molar ratio of reactants or by changing the reaction conditions. 2-propanol/water (50%, *V/V*) was more efficient as the reaction medium for this one-pot process than both aqueous methanol and aqueous ethanol because the reaction could be carried out at higher temperature and consequently, the conversion was more efficient. Moreover, there was only slight polymer degradation during the reaction and all the amphiphilic starch derivatives possessed a unimodal molar mass distribution. For solubility in water, the ratio of Bn and HPMA moieties had to be adjusted in the range of DS_{Bn}>0.85 and MS_N<0.40. No clear correlation among DS_{Bn}, MS_N, and surface tension could be observed for BnHPMAS. With the introduction of both hydrophobic benzyl and hydrophilic HPMA groups, the obtained amphiphilic starch derivatives have significant potential to be used in the removal of dissolved and colloidal substances in paper cycling water.

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