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Homogenous modification of cellulose with acrylamide in NaOH/urea aqueous solutions

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Abstract

A series of cellulose polyelectrolytes, containing acylamino and carboxyl groups, were homogenously synthesized from cellulose with acrylamide in NaOH/urea aqueous solutions. The structure and solution properties of the polyelectrolytes were characterized with elemental analysis, FTIR, NMR, viscometer and zeta-potential measurement. The nitrogen content and total degree of substituent (DS) of the derivatives increased with increasing of the molar ratio of acrylamide to the anhydroglucose unit (AGU) and the cellulose concentration. The DS of carboxyl groups hardly changed because of the similar reaction and hydrolysis conditions, while the DS of acylamino groups increased with increasing of the total DS values of the products. The polyelectrolytes are soluble in water at a total DS as low as 0.36, and the zeta-potential values in pure water are in the range of −15 to −25 mV. The [η] values of the polyelectrolytes in NaCl aqueous solutions increased apparently with an increase of the pH value in the lower pH region, and reached the maximum value at the pH range from 5 to 6, and while hardly changed at the pH range from 7 to 12. This work provided a facile method for the synthesis of cellulose polyelectrolytes with two different functional groups.

Keywords: Cellulose; Polyelectrolytes; Homogeneous synthesis; NMR; Viscosity

1. Introduction

Cellulose is one of the most common organic polymers, and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm, Heubletin, Fink, & Bohn, 2005; Schurz, 1999). However, cellulose still has not reached its potential applications in many areas because it is difficult to process in general solutions or in the melting state on account of its strong intermolecular and intramolecular hydrogen bonding. Based on the unique structure and reactivity of cellulose, chemical modification reactions continue to play a dominant role in improving the overall utilization of this biomacromolecules (Heinze, 1998; Heinze, Liebert, Klüfers, & Meister, 1999). Nowadays, all commercial cellulose derivatives have been prepared with heterogeneous procedures with the cellulose slurry in industry. In case of heterogeneous reactions, the accessibility and reactivity of the OH groups are clearly determined by hydrogen bond-breaking activation steps through alkaline compounds and by interaction with the reaction media, which permits effective synthesis of cellulose products with desired degrees of reaction, reproducible substitution patterns, and targeted properties at both the laboratory and industry scales (Klemm et al., 2005). Therefore, homogenous modification of cellulose has been one focus of cellulose research for a long time. The discovery of novel solvents and solution complexes for cellulose in the past three decades has created opportunities for the application of significantly more diverse synthesis pathways and derivative types (Heinze & Liebert, 2001). For example, various cellulose derivatives have been successfully synthesized through homogenously methods in *N*, *N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) (Dawsey & McCormick, 1990; McCormick & Callais,

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1987; Schaller & Heinze, 2005; Tosh, Saikia, & Dass, 2000) and DMSO/tetrabutylammonium fluoride trihydrate (TBAF) (Ass, Frollini, & Heinze, 2004; Hussain, Liebert, & Heinze, 2004; Liebert & Heinze, 2001) solvent systems. More recently, ionic liquids (ILs) were found to dissolve cellulose efficiently, and they are considered to be "green" solvents on account of their non-volatility, non-flammability and thermally stability (Swatloski, Spear, Holbrey, & Rogers, 2002; Zhang, Wu, Zhang, & He, 2005; Zhu et al., 2006). ILs as the "green" reaction media for homogenous cellulose derivations have drawn much attention around the world (Barthel & Heinze, 2006; Cao et al., 2007; Heinze, Schwikal, & Barthel, 2005; Liu et al., 2007; Schlufter, Schmauder, Dorn, & Heinze, 2006; Wu et al., 2004).

Faced with the serious pollution produced by the viscose method worldwide, our laboratory developed a non-polluting and non-toxic solvent system for cellulose, that is, a NaOH/urea aqueous solution (Zhang, Cai, & Zhou, 2005; Zhang & Zhou, 2003; Zhou & Zhang, 2000). Cellulose (cotton linter pulp) could be completely dissolved in a 7–8 wt% NaOH/11–12 wt% urea aqueous solution precooled to −10 to −13 °C within 5 min at the ambient temperature (Cai & Zhang, 2005; Zhang et al., 2005), and the regenerated cellulose fibers and films with excellent mechanical properties have been prepared from the solvent system on a pilot scale (Cai, Zhang, Zhou, Chen, & Jin, 2004; Cai et al., 2007; Zhang, Mao, Zhou, & Cai, 2005). The solvent is also a suitable homogenous reaction medium for the etherification of cellulose; cellulose ethers such as methylcellulose, hydroxyethylcellulose and hydroxypropyl cellulose as well as hydrogels have been successfully synthesized under mild conditions (Zhou, Chang, Zhang, & Zhang, 2007; Zhou, Qin, Liu, & Zhang, 2006; Zhou, Zhang, Deng, & Wu, 2004). Cellulose-based polyelectrolytes, such as carboxymethyl cellulose and cellulose grafted copolymers, have been found a wide range of industrial applications in flocculation, drag reduction, detergents, textiles, paper, foods, drugs, and oil well drilling operation (Biswal & Singh, 2004; Dönges, 1990; Wei & Cheng, 2007). In this paper, a series of cellulose-based polyelectrolytes were homogenous synthesized in the novel NaOH/urea aqueous solutions. Acrylamide was used to modify cellulose, and the structure and properties of the obtained polyelectrolytes were investigated.

2. Experimental

2.1. Materials and preparation of the cellulose solutions

The cellulose (cotton linter pulp) was supplied by Hubei Chemical Fiber Group Ltd. (Xiangfan, China), and the viscosity-average molecular weight (M_η) of the cellulose was determined by viscometry in cadoxen (Brown & Wiskstön, 1965) to be 10.3×10^4. Acrylamide and other reagents were analytical grade and were used without further purification.

Cellulose solution was prepared according the previous method (Zhang et al., 2005). Into a 250 mL beaker, an adequate amount of NaOH, urea and distilled water (7:12:81 by weight) were added, and the resulting mixture aqueous solution was stored in a refrigerator. After the solution was precooled to −12.3 °C, cellulose was added immediately into it with stirring vigorously for 5 min at ambient temperature to obtain the transparent cellulose dope. Before use, the cellulose solution was subjected to centrifugation at 8000 rpm for 20 min at 5–10 °C to exclude the slightly remaining undissolved part.

2.2. Homogenous modification of cellulose with acrylamide

In a typical reaction procedure, a certain amount of acrylamide dissolved in water was added dropwise into the 100 g cellulose solution mentioned previously, and the mixture was stirred at 25 °C for 6 h. The reaction product was neutralized with acetic acid, and dialyzed with regenerated cellulose tubes (M_w cut-off 8000, USA) against distilled water for 7 days. The solution was finally freeze-dried with lyophilizer (Christ Alpha 1–2, Osterode am Harz, Germany) to obtain the purified cellulose derivative (white powder). According to Table 1, seven samples were prepared by changing the mole ratio of the anhydroglucose unit (AGU) to acrylamide from 1:3 to 1:9, and the cellulose concentration from 2 to 4 wt%.

Table 1
Synthesis and properties of the cellulose polyelectrolytes

Sample	$c_{cellulose}$ (wt%)	Molar ratio[a]	Nitrogen content[b] (wt%)	Solubility in water[c]	ξ[d] (mV)	$[\eta]$[e] (mL/g)
1	2	1:3	0.986	Δ	–	–
2	2	1:5	1.320	+	−25.43	387.8
3	2	1:7	1.942	+	−15.05	398.5
4	2	1:9	2.496	+	−16.98	410.3
5	4	1:3	1.755	+	−23.57	357.6
6	4	1:5	2.907	+	−23.41	358.0
7	4	1:7	3.603	+	−22.84	370.6

[a] Mole ratio of AGU to acrylamide.
[b] Determined by elemental analysis of the acidic derivatives.
[c] + Soluble, Δ swelling for a 1% (w/v) solution at 25 °C.
[d] Determined by the 0.1 mg/mL aqueous solutions at 25 °C.
[e] In 0.2 mol/L NaCl aqueous solution at 25 °C.

2.3. Characterizations

IR spectra of samples were performed with a Nicolet 170SX Fourier transform infrared spectrometer. The test specimens were prepared by the KBr-disk method.

^{13}C NMR and ^{1}H NMR measurements of the samples in D_2O at 25 °C were carried on a Varian INOVA-600 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe at ambient temperature, and the sample concentration was about 3.5 wt%. The chemical shifts were referenced to the signals of D_2O and tetramethylsilane (TMS).

The derivatives were dissolved in distilled water, and the pH of the solutions were adjusted to 1 by the addition HCl solution for dealing with 30 min, and then the acidic solutions were dialyzed with distilled water and freeze-dried. The elemental analysis of the acidic derivatives was measured with an elemental analyzer (CHN-O-Rapid, Foss Hera us GmbH, Hanau, Germany). Based on the structure of the acidic derivatives, the content of nitrogen ($N\%$) could be defined as following,

$$N\% = \frac{14x}{162 - (x+y) + 72x + 73y} \times 100$$

where x is the DS of acylamino groups, y is the DS of carboxyl groups. The ratio of x to y could be determined by the peak intensity of ^{13}C NMR spectra for the two carbonyl peaks or the methylene peaks that connect to acylamino and carboxyl groups.

The solubility of the samples in water was measured at 25 °C, and the concentration was about 1% (w/v). The zeta potential of the samples in distilled water ($c_{polymer} =$ 0.1 mg/mL) was performed on a MALVERN ZETASIZER (Malvern Instruments, Malvern, UK) at 25 ± 0.1 °C.

The viscosity of the samples in different solvents was measured at 25 ± 0.1 °C with an Ubbelodhe capillary viscometer. The kinetic energy correction was always negligible. The pH values of the 0.1 mol/L NaCl aqueous solutions were adjusted by the addition of HCl or NaOH aqueous solution. Huggins equation was used to estimate the intrinsic viscosity ($[\eta]$) value by extrapolation to concentration (c) to be zero as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

where k' is a constant for a given polymer at a given temperature in a given solvent and η_{sp}/c the reduced specific viscosity.

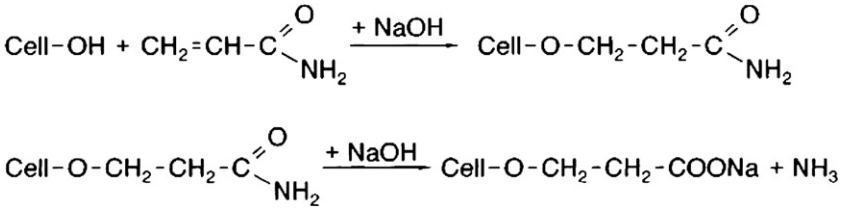
3. Results and discussion

3.1. Homogenous synthesis of cellulose polyelectrolytes

Usually, vinyl monomers can be grafted onto cellulose by graft copolymerization through various methods. On the other hand, acrylonitrile and acrylamide etc. can also be served as etherification reagents and reacted with cellulose in an alkaline medium. In a Michael addition, acrylamide can be added to cellulose with formation of the carbamoylethyl ether of cellulose. Moreover, the acylamino group can be easily saponified to a carboxyl group and to give carboxyethyl cellulose as the stable end-product in a higher alkaline aqueous medium at elevated temperature (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). Scheme 1 illustrates the homogenously modification of cellulose with acrylamide in NaOH/urea aqueous solution, and the reaction conditions are listed in Table 1. Under the reaction conditions for the etherification, the solution was transparent and remained completely homogenous as the reaction proceeded. As shown in Table 1, the N content of the derivatives increased with increasing of molar ratio of acrylamide to AGU and the cellulose concentration. Except for sample 1, samples 2–7 showed good solubility in water. Because acylamino groups of the substituent have been partially saponified to carboxyl groups, the derivatives display the typical solution behavior of anionic polyelectrolytes. The zeta-potential values for the water-soluble derivatives in pure water are shown in Table 1. The derivatives display negative charges of −15 to −25 mV, indicating that the carboxylic groups have been dissociated into $-COO^-$ groups. Therefore, cellulose polyelectrolytes containing two different functional groups of acylamino and carboxyl were successfully synthesized in NaOH/urea aqueous solutions, and without addition of an extra catalyst because of the basicity of the solvent system.

3.2. Structure analysis

Fig. 1 shows the FTIR spectra of the native cellulose and its derivative samples. The peaks at 1670 and 1375 cm^{-1} for the derivatives represent amide I (C=O stretching) and amide II (C–N stretching) bands, respectively. Two peaks at 1566 and 1416 cm^{-1} are observed due to the asymmetrical and symmetrical stretching of $-COO^-$ groups, respectively. Comparing the relative inten-



Scheme 1. Homogenous modification of cellulose with acrylamide in NaOH/urea aqueous solutions.

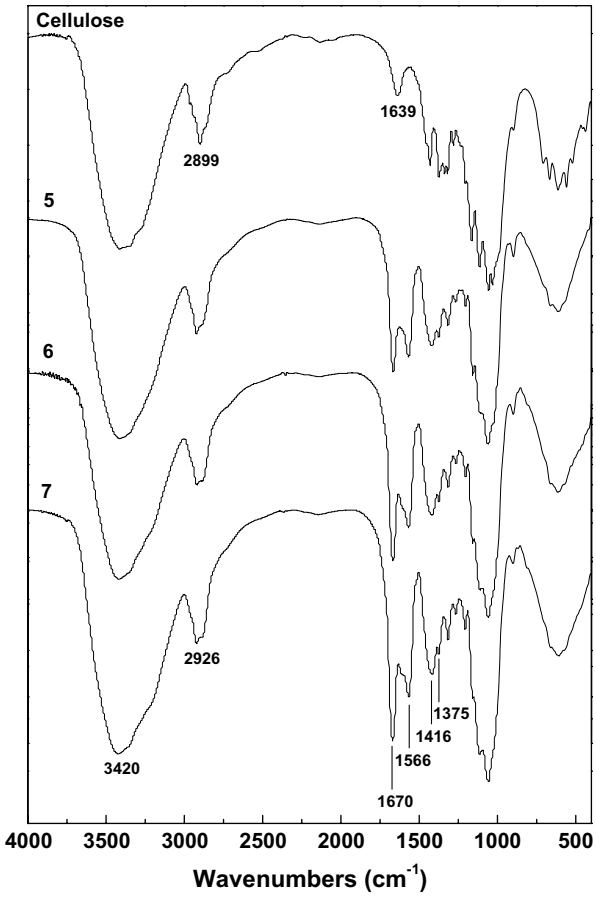


Fig. 1. The IR spectra of the native cellulose and its derivative samples.

sity at 1566 and 1670 cm^{-1}, the intensity at 1670 cm^{-1} apparently increased for sample 5–7, indicating an increase in the ratio of acylamino to carboxyl groups for the derivatives. Moreover, a broad absorption band around 3100–3500 cm^{-1} for the derivatives are ascribable to the stretching frequency of the –OH and $–NH_2$ groups, which become stronger than the band of the stretching vibration of –OH of the native cellulose. It suggested the strong inter- and intramolecular hydrogen bands and electrostatic interaction formed in the derivatives.

Fig. 2 shows ^1H NMR spectra of the water-soluble cellulose derivatives in D_2O at 25 °C. The peaks from 2.3 to 2.5 ppm are assigned to protons of methylene that connected to acylamino (H-8) and carboxyl (H-8′) groups, whereas the broad peaks from 2.8 to 4.5 ppm are attributed to another methylene (H-7, H-7′) of the substituents and all the protons of the cellulosic skeleton. The chemical shift of the protons of acylamino and carboxyl groups usually lay at 7–12 ppm, which cannot be observed for theirs high activity. We can estimate the total DS of the derivatives from the peak area of 2.3–2.5 ppm and 2.8–4.5 ppm, and the results are listed in Table 2. The derivative is soluble in water starting from a total DS as low as 0.36, and the highest total DS as-obtained is 0.84. However, it is difficult to attain derivatives with higher DS values due to the hydrolysis of acrylamide in NaOH/urea aqueous solutions.

Fig. 3 shows the ^{13}C NMR spectra of water-soluble cellulose derivatives in D_2O at 25 °C. The chemical shift at 177.3 and 180.1 ppm are assigned to the carbon signal of carbonyl groups in acylamino (C-9) and carboxylate (C-9′) groups (Halverson, Lancaster, & O'Conner, 1985; Zurimendi, Guerrero, & Leon, 1984), respectively. Doublet at 35.8 and 37.8 ppm are attributed to methylene that connect to acylamino (C-8) and carboxyl (C-8′) groups, respectively. The peaks for the cellulose backbone and another methylene (C-7, C-7′) of the substituents are between 60 and 102 ppm. The DS of acylamino and carboxyl groups could be obtained according to the peak intensity of the two carbonyl peaks or the methylene peaks that connect to acylamino and carboxyl groups, and the results are listed in Table 2. The DS of acylamino increased with increasing of the total DS values of the derivatives. However, the DS of carboxyl groups hardly changed because of the similar reaction and hydrolysis conditions. According to the nitrogen content in the acidic derivatives (as shown in Table 1) and ^{13}C NMR spectra, the DS of acylamino and carboxyl groups were calculated and were also listed in Table 2, which were agreed well with the results determined using ^1H and ^{13}C NMR spectra. In Fig. 3, the peak intensity of C-6 (60.4 ppm), which reflects the unsubstituted hydroxyl groups at the C-6 position, become weaker apparently with increasing of the total DS. Moreover, a small new peak appeared at around 97 ppm (C-1′) in the high total DS values of the derivatives, which referenced the substituted hydroxyl groups at the C-2 position. Therefore, we can conclude that the relative reactivity of hydroxyl groups at the C-6 position is higher than those of C-2 and C-3 positions.

3.3. Viscosity behavior of dilute solution

The reduced viscosity η_{sp}/c of sample 5 (DS = 0.49) in water and NaCl aqueous solutions are shown in Fig. 4. In the absence of salt, the reduced viscosity of the cellulose derivative displayed typical polyelectrolyte behavior, which remarkably increases with decreasing polymer concentration due to the expanded polyelectrolytes chains and chain–chain repulsion (Zhou et al., 2001). As NaCl is added, the electrostatic repulsion is screened, leading to the macromolecules to a more flexible chain conformation. So the solution viscosity decreased gradually with the addition of NaCl.

Intrinsic viscosity is a measure of hydrodynamic volume of macromolecules. It is generally accepted that macromolecule conformation and molecular weight play a fundamental role, through their relationships with the molecular dimensions and shapes, in determining the value of intrinsic viscosity (Lapasin & Pricl, 1995; Michell, 1979). Therefore, the values of $[\eta]$ could reflect the expanded extent of the polymer chain. The $[\eta]$ values of the water-soluble derivatives in 0.2 mol/L NaCl aqueous solutions are

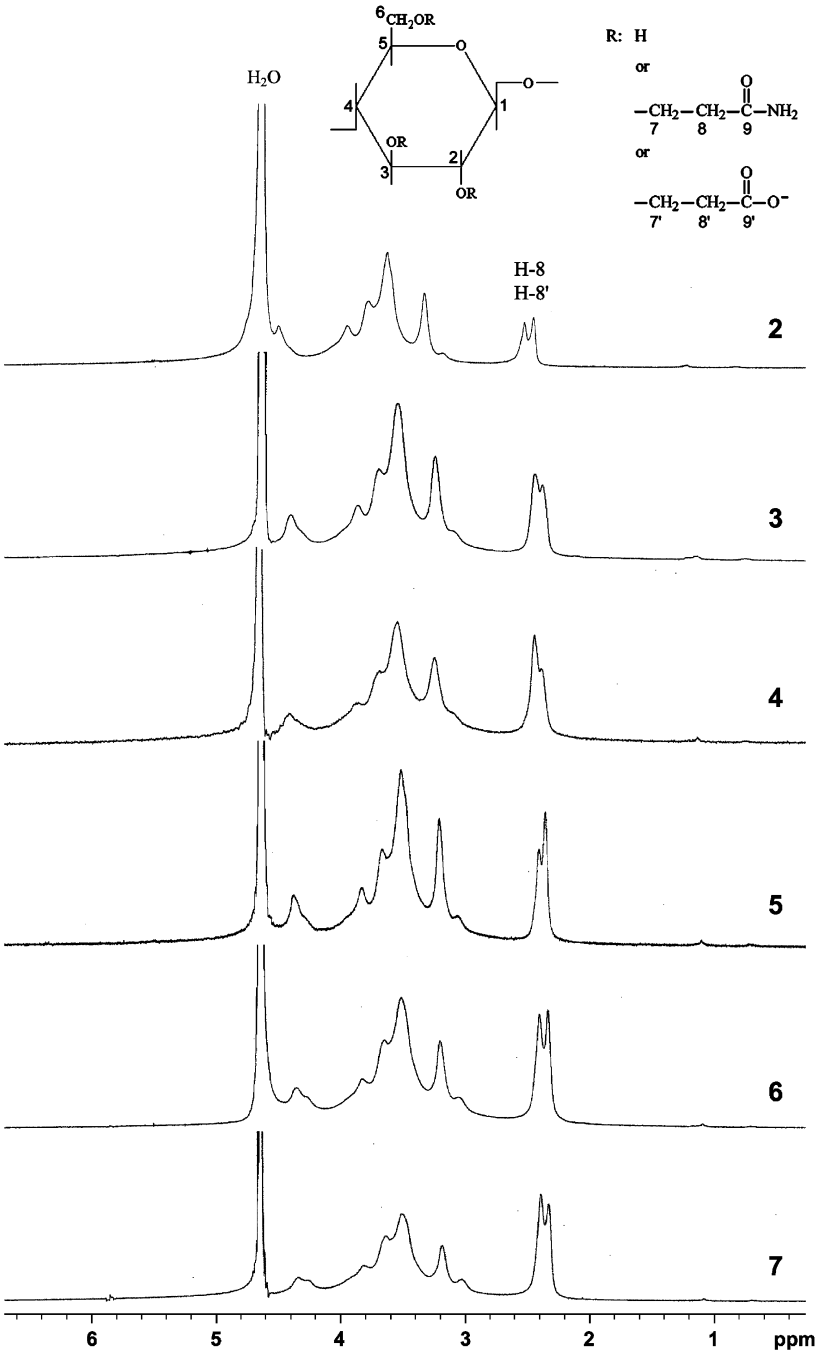


Fig. 2. ^{1}H NMR spectra of the derivative samples in D_2O at 25 °C.

Table 2
Structure analysis of the cellulose polyelectrolytes

Sample	Degree of substituent[a]			Degree of substituent[b]		
	Acylamino	Carboxyl	Total	Acylamino	Carboxyl	Total
2	0.18	0.18	0.36	0.18	0.17	0.35
3	0.29	0.20	0.49	0.27	0.18	0.45
4	0.39	0.20	0.59	0.36	0.18	0.54
5	0.25	0.24	0.49	0.25	0.24	0.49
6	0.40	0.27	0.67	0.45	0.30	0.75
7	0.54	0.30	0.84	0.58	0.32	0.90

[a] Determined by ^{1}H and ^{13}C NMR.
[b] Calculated from the content of nitrogen in the acidic derivatives and ^{13}C NMR.

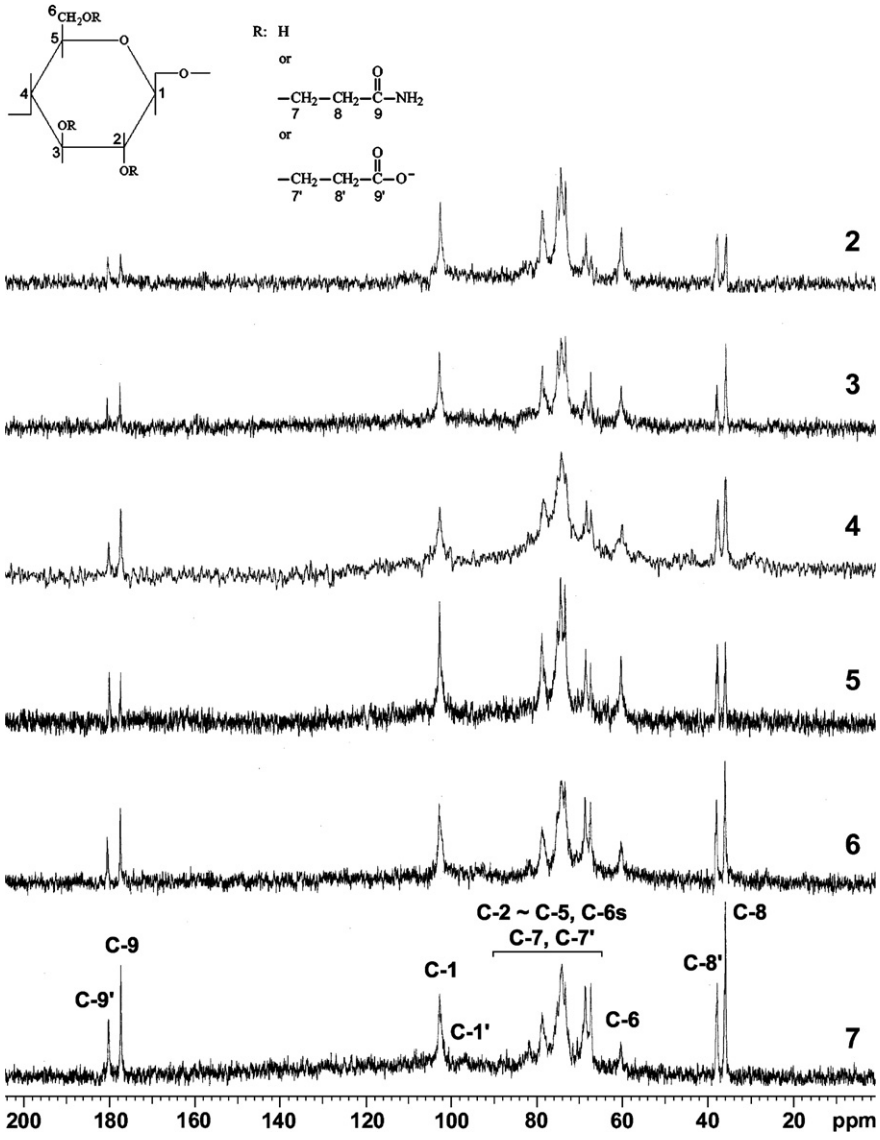


Fig. 3. ^{13}C NMR spectra of the derivative samples in D_2O at 25 °C.

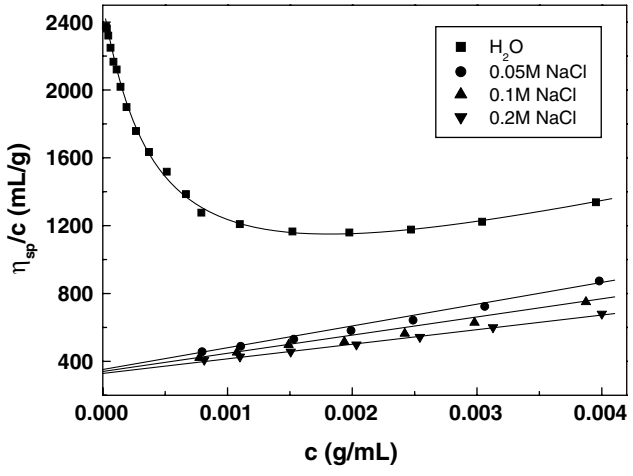


Fig. 4. η_{sp}/c *vs* c of sample 5 (DS = 0.49) in different solvent at 25 °C.

listed in Table 1. For the electrostatic interaction and the strong hydrogen bands between acylamino and carboxyl groups, macromolecules of the derivatives formed large aggregates and led to large [η] values. Fig. 5 shows the [η] values of the derivative samples in 0.1 mol/L NaCl aqueous solutions with different pH value. With an increase of the pH value of the solution, the [η] values of the derivatives increased apparently, and reached the maximum values at the pH range of 5–6. As the pH value of the solution increased to 7, the [η] values of the derivatives slightly decreased, and then hardly changed with the increased pH value of the solution from 7 to 12. It could be explained that in the lower pH region, the cellulose-based polyelectrolytes were in coiled conformation because of the decrease of the ionized carboxyl groups and of weak charge repulsion. As the pH values higher than 7, the derivatives were in randomly extended conformation both by hydra-

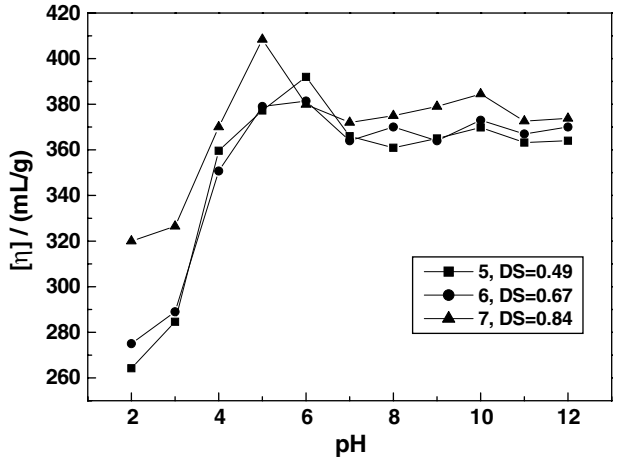


Fig. 5. Intrinsic viscosity ([η]) of the derivative samples in 0.1 mol/L NaCl aqueous solutions with different pH value.

tion of the carboxyl groups and by a strong charge repulsion between the $-COO^-$ groups (Lai & Chiang, 2002).

4. Conclusions

Based on the Michael addition and the saponification of acylamino groups to a carboxyl groups in alkaline media, cellulose polyelectrolytes containing acylamino and carboxyl groups were homogenously synthesized from cellulose with acrylamide in NaOH/urea aqueous solutions. The total DS and the DS of acylamino groups for the derivatives increased with increasing of the molar ratio of acrylamide to AGU and the cellulose concentration, while the DS of carboxyl groups hardly changed because of the similar hydrolysis conditions. The total DS values of the water-soluble derivatives are in the range of 0.36–0.84. The zeta-potential values of derivatives are in the range of -15 to -25 mV, which display negative changes in water for the dissociation of carboxylic groups into $-COO^-$ groups. The [η] values of the polyelectrolytes in NaCl aqueous solutions increased apparently with an increase of the pH value in the lower pH region and reached a relatively stable value at the pH range from 7 to 12.

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