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Homogeneous hydroxyethylation of cellulose in NaOH/urea aqueous solution

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Summary

The 6 wt.% NaOH/4 wt.% urea aqueous solution was proved to be an aqueous non-derivatizing solvent for cellulose by ^{13}C NMR. O-(2-hydroxyethyl)cellulose (HEC) was prepared by a totally homogeneous hydroxyethylation of cellulose using this new solvent for the first time, and the distribution of substituents within anhydroglucose units (AGU) was examined by ^{13}C NMR. It was found that the relative reactivity of the hydroxyl groups within AGU and the new hydroxyl group was in the order C-x > C-6 > C-2 > C-3, an analogous functionalization pattern as HEC obtained by the heterogeneous slurry process. The ethylene oxide efficiency in this homogeneous etherification reaction was 20 – 30%.

Introduction

Chemical modification continues to provide a dominant route towards cellulose utilization in polymeric materials. 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.[1] Considerable attention has been devoted to the investigations on cellulose solvents able to provide homogeneous reactions, e.g. lithium chloride (LiCl)/N,N-dimethylacetamide (DMAc),[2] LiCl/1,3-dimethyl-2-imidazolidinone (DMI)[3] and dimethyl sulfoxide (DMSO)/SO_2/diethylamine[4].

Aqueous non-derivatizing solvents for cellulose, such as cuprammonium hydroxide (Cuam), cupriethylenediamine hydroxide (Cuen) and even 10% aqueous NaOH solution, were widely used for cellulose regeneration, characterization and fiber spinning.[5,6] However, the application of these aqueous solvents as medium for completely homogenous functionalization reactions is of limited interest, due to their high toxicity, high reactivity of the solvents leading to undesired side reactions and tendency to become inhomogeneous during the reaction. Nevertheless, a novel aqueous solution of Ni(tren)$(OH)_2$ (tren = tris(2-aminoethyl)amine) were studied in terms of the mechanism of dissolution and their potential as medium for homogenous etherification reactions compare with simple aqueous NaOH activation. It is possible to convert cellulose dissolved in Ni-tren in a fully homogeneous process to carboxymethyl cellulose.[7]

In our previous work, 6 wt.% NaOH/4 wt.% urea aqueous solution[8] was proved to be a good solvent for cellulose and can completely dissolve cotton linters (cellulose I) with a viscosity-average molecular weight (M_η) of up to 6.7×10^4 g/mol and cellulosic nonwovens (cellulose II, *Bemliese*®, provided by Asahi Kasei Fibers Corporation, Japan) with M_η of up to 11.2×10^4 g/mol. Regenerated cellulose films with typical cellulose II crystalline form were successfully prepared from cotton linters in this new solvent system.[9] In this work, O-(2-hydroxyethyl)cellulose (HEC), a representative cellulose derivative, was prepared using the 6 wt.% NaOH/4 wt.% urea aqueous solvent system. The characteristics of this solvent system as a new homogeneous reaction medium for the etherification of cellulose were examined.

Experimental

Materials and Dissolution of Cellulose

Whatman CF-11 fibrous cellulose powder was used as a starting material. All other chemicals were reagent grade and used without further purification. A homogeneous cellulose solution (2 wt.%) in a 6 wt.% NaOH/4 wt.% urea aqueous solution was prepared according to our previous work.[8] 6 g of NaOH and 4 g of urea were dissolved in 90 g distilled water, 2 g of cellulose were then added with stirring to get a slurry. In order to prepare clear and homogeneous solution and avoid cellulose gel formation, a freeze-thaw cycle was employed in the cellulose dissolution. The cellulose slurry was held at –20°C for 4 h and then thawed with stirring in an ice-water bath to obtain a transparent solution without particles.

Preparation of O-(2-hydroxyethyl)cellulose

Ethylene oxide with known amount was added by portions (i.e. 0.5 mL every other 10 min) to an aliquot (50 g) of the homogeneous cellulose NaOH/urea aqueous solution (containing 1 g of cellulose) with stirring at 0°C and no precipitation occurred. The solution was then heated to 50°C and kept for 4 h with stirring. After cooled to room temperature, the solution was neutralized with acetic acid and was precipitated into a large excess of acetone. The precipitate was filtered off, washed with acetone and dried in vacuum at 60°C. The product was redissolved in deionized water, dialyzed against deionized water and lyophilized. With 3, 6 and 9 mol equivalent of ethylene oxide to the anhydroglucose units (AGU) of cellulose, three HEC samples were prepared and coded as HEC-1, HEC-2, and HEC-3.

Measurements

^{1}H and ^{13}C NMR spectra were measured with a Varian Mercury VX-300 spectrometer by using a standard 5 mm probe at room temperature. For the ^{13}C NMR measurement of the cellulose solution in 6 wt.% NaOH/4 wt.% urea in D_2O, deuterated dimethylsulphoxide (DMSO-d_6) sealed in a glass capillary was used as an internal standard. The HEC samples were measured directly in DMSO-d_6. The quantitative-mode ^{13}C NMR measurement conditions closely followed those in the structural analysis of the cellulose derivatives.[10] The relative DS value at an individual hydroxyl group was determined from the ratio between peak areas. The peak areas were measured by the weight cut from photocopies. The elemental analysis was

measured with an elemental analyzer (CHN-O-Rapid, Foss Heraeus GmbH, Hanau, Germany).

Results and Discussion

As shown in Figure 1, the ^{13}C NMR spectrum of cellulose in 6 wt% NaOH/4 wt% urea/D_2O solution gave well resolved spectrum with signals at 103.9 ppm (C-1), 79.2 ppm (C-4), 75.6 ppm (C-5, C-3), 74.2 ppm (C-2) and 60.8 (C-6). These chemical shifts were almost the same as those of cellulose in LiCl/DMAc[11], LiCl/N-methylpyrrolidone (NMP)[11] and LiCl/DMI[3] solvent systems, as summarized in Table 1. No additional signal was observed, indicating that the NaOH/urea aqueous solution is a non-derivatizing solvent, i.e. a real solvent of cellulose.[12] The signal for C-4 (79.2 ppm) shifted to the higher magnetic filed than those of cellulose in solid state (87.9 and about 84 ppm) and in NaOH/D_2O (1/9, w/w; 79.9 ppm), indicating that the intramolecular hydrogen bonds of cellulose were destroyed.[13] The signal of the carbonyl group of urea in the cellulose solution was 162.7 ppm (not shown in Figure 1), which shifted to the higher magnetic field than that of only urea in D_2O (163.4 ppm), indicating an interaction between urea and NaOH occurs in this solution. This interaction played an important role in the dissolution of cellulose, i.e. breaking the inter- and intra- molecular hydrogen bond of cellulose and enhancing the interaction between cellulose and urea molecules, which effectively prevented the self-association of cellulose macromolecules in NaOH aqueous solution and improved the stability of the cellulose solution.

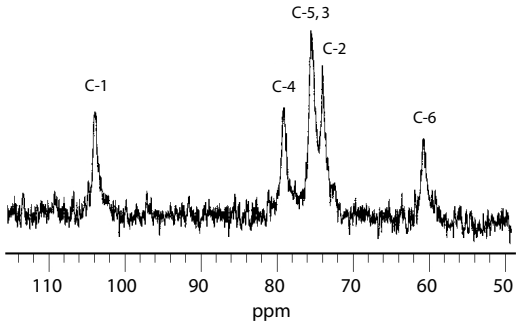

Figure 1. ^{13}C NMR spectrum of cellulose in 6 wt% NaOH/4 wt% urea/D_2O solution at 25°C.

Table 1. ^{13}C NMR chemical shifts of cellulose in various solvents.

Solvents (ratio by weight)	^{13}C NMR chemical shift (ppm)					Reference
	C-1	C-4	C-5, C-3	C-2	C-6	
NaOH / urea / D_2O (6/4/90)	103.9	79.2	75.6	74.2	60.7	This work
LiCl / DMAc (1/10)	103.1	79.2	76.0	74.3	60.5	[11]
LiCl / NMP (1/10)	103.2	79.2	76.2	74.4	60.7	[11]
LiCl / DMI (1/10)	103.2	79.3	76.3	74.3	60.5	[3]
NaOH / D_2O (1/9)	104.7	79.9	76.4	75.0	61.9	[14]

In order to elucidate this new non-derivatizing aqueous solvent as medium for homogenous phase reactions for cellulose, we first studied hydroxyethylation of

cellulose. The etherification experiment was carried out without addition of an extra base because of the basicity of the solvent system (12 mol of NaOH per AGU). Ethylene oxide was added by portions into the cellulose solution at 0°C and the viscosity of the reaction mixture obviously increased without the loss of homogeneity. Precipitation may occur in case of a rapid addition of the reagent. However, the precipitate redissolves in the course of reaction.

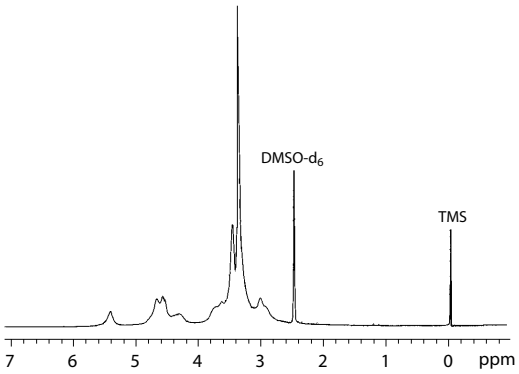

Figure 2. ^{1}H NMR spectrum for HEC-3 in DMSO–d_6 at 25°C.

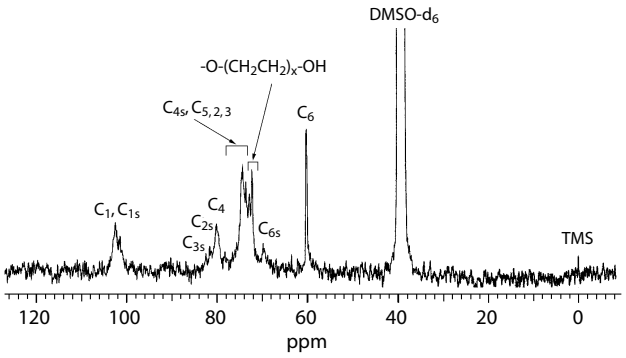

Figure 3. ^{13}C NMR spectrum for HEC-3 in DMSO–d_6 at 25°C.

O-(2-hydroxyethyl)-cellulose was successfully prepared using 6 wt.% NaOH/4 wt.% urea aqueous solution as medium. The ^{1}H NMR spectrum of the HEC-3 sample was shown in Figure 2. The methylene proton signals at 3.35 and 3.45 ppm overlapped with the broad ring proton signals (2.80 – 5.60 ppm) of the cellulose skeleton. The mole substitution (MS) values of the HEC samples were estimated from the ratio between these two peak areas and further confirmed by the results of the elemental analysis.[15] The total degree of substitution (DS) values and the relative DS at three different types of hydroxyl groups can be estimated by a ^{13}C NMR method.[10,16,17] Figure 3 demonstrate the ring carbon spectrum of a representative sample, HEC-3 in DMSO-d_6 at 25 °C. The peaks C_6 and C_{6s} are due to the C-6 carbons bearing an unsubstituted and a substituted hydroxyl group, respectively. The peak designated by C_{1s} in the spectrum is assignable to C-1 carbons adjacent to C-2 carbons bearing a substituted hydroxyl group, and a peak designated by C_1 is assignable to C-1 carbons

adjacent to C-2 carbons with a free hydroxyl group, respectively. The same discussion may be also applied to the peaks of C-4 carbons designated by C_4 and C_{4s}.

Table 2. Values of MS (mole substitution), DS (degree of substitution), distribution of substituents and solubility of the HEC samples.

Samples	MS[a]	Total DS[b]	DS at position[c]				Solubility[e]		
			C-2	C-3	C-6	C-x[d]	H_2O	Acetone	DMSO
HEC-1	0.9	0.5	0.15	0.06	0.28	0.4	○	×	○
HEC-2	1.3	0.7	0.23	0.10	0.34	0.6	○	×	○
HEC-3	1.9	0.9	0.30	0.14	0.43	1.0	○	×	○

[a] Estimated by ^{1}H NMR and elemental analysis.
[b] Sum of the degree of substitution at C-2, C-3 and C-6.
[c] Determined by ^{13}C NMR.
[d] DS at new hydroxyl group, C-x = MS – total DS
[e] × insoluble, ○ soluble, for 1% (w/w) solution at 25 °C.

The MS value, the total DS value, the distribution of substituents within the AGU and solubility of the HEC samples were summarized in Table 2. The relative reactivities of the hydroxyl groups at positions 2, 3, 6 and the new hydroxyl group of the substituents were in the order C-x > C-6 > C-2 > C-3. They posses the same funtionalization pattern and solubility properties as the hydroxyethylcellulose obtained by the totally heterogeneous slurry process, i.e. prepared from ethylene oxide and alkali-cellulose in a suspension with isopropanol, tert-butanol or aceton as the suspension medium.[18] This result further proves that both simple activation of cellulose with aqueous NaOH and the completely dissolution of the polysaccharide leads to reactive sites with an almost even accessibility and hence there is no particular advantage of a conversion of the dissolved polymer, which was first proposed by Heinze[19]. Furthermore, the ethylene oxide efficiency in this homogeneous etherification reaction was 20 – 30%, which is lower than that of the heterogeneous process (40 – 75%) as applied for commercial production of HEC. This lower yield of ethylene oxide is because of the high alkali concentration per AGU of cellulose, which leads to the formation of polyglycol as a side reaction.

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