Derivatization of cellulose in lithium chloride and *N*-*N*-dimethylacetamide solutions

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The derivatization of cellulose in mixtures of lithium chloride and *N*,*N*-dimethylacetamide (LiCl/DMAc) is described. A wide range of cellulose derivatives, including cellulose esters, carbamates, sulphonates and ethers, have been synthesized in homogeneous solution using the LiCl/DMAc solvent. In most cases, a high degree of substitution was achieved, and the degree of substitution could be controlled accurately. Compared to current heterogeneous synthesis of cellulose derivatives, reactions conducted in homogeneous solutions of LiCl/DMAc have many advantages: (1) reactions may be conducted at moderate temperatures; (2) less reagent is required; (3) less degradation of the cellulose occurs; and (4) substitution is uniformly controllable.

(Keywords: cellulose solvent; cellulose derivatization; homogeneous solution reactions; cellulose ester; cellulose carbamate; cellulose sulphonate; cellulose ether)

INTRODUCTION

Controllable, uniform derivatization of unmodified cellulose has been hampered by the availability of suitable, non-degrading organic solvents. Although a number of solvents have been reported[1-5], the dissolution step usually proves to be cumbersome or expensive, or results in extensive degradation of the macromolecular backbone. Additionally, these solvents are seldom useful for a wide range of synthetic reactions.

A number of cellulose derivatives are currently prepared under heterogeneous conditions. Aside from the inherently unfavourable reaction kinetics, problems arise such as poor uniformity of substitution, low yields and extensive by-product formation. Also, characterization of the starting material (cellulose) and the product derivatives is tedious if not impossible in many cases.

In this work we report optimized synthetic conditions for preparing cellulose carbamates, esters and other derivatives by reactions of unmodified cellulose conducted in homogeneous solutions of lithium chloride and *N*,*N*-dimethylacetamide (LiCl/DMAc). Since the first report of this cellulose solvent by our laboratories[6], we have subsequently reported synthesis of derivatives[7-9] and characterization of unmodified cellulose by viscometry, carbon-13 nuclear magnetic resonance spectrometry, and low-angle and quasi-elastic light scattering[10-11]. References 10 and 11 also describe the appearance of an anisotropic phase at concentrations approaching 15% (w/w) cellulose. Since our initial report[10], Ciferri *et al.* have also reported similar findings[12-14]. Additionally, Turbak *et al.*[15,16] have reported improved properties of cellulose fibres spun from solutions of LiCl/DMAc.

EXPERIMENTAL

Materials

Purified, reagent grade cellulose used in this study was obtained from J. T. Baker. Reagent grade acid chlorides and isocyanates were vacuum distilled before use. Other reagent grade chemicals were used without further purification.

Elemental analysis. Polymer samples for elemental analysis were dried for 24 h at 60°C over P_2O_5 at less than 1 mmHg ($\simeq$ 133 Pa) pressure and then sealed in ampoules. Analyses were performed by M-H-W Laboratories of Phoenix, Arizona.

Spectroscopy. I.r. spectra were recorded on a Perkin–Elmer Model 283B spectrophotometer. Polymer samples for analysis were prepared by casting films in appropriate solvents onto NaCl windows and drying.

LiCl/DMAc solvent. Lithium chloride (LiCl) solutions, reagent grade from J. T. Baker, of concentrations 5–9% (w/w) and *N*,*N*-dimethylacetamide (DMAc), from Aldrich, were made by dissolving the appropriate amount of LiCl in DMAc at 100°C. The solvent was allowed to cool to room temperature before use. In all cases 9% LiCl/DMAc was the solvent chosen.

Synthesis

Cellulose dissolution. Into a dry, 250 ml three-necked flask fitted with a nitrogen inlet, addition funnel, mechanical stirrer and drying tube were added 100 ml 9% LiCl/DMAc and 3.3 g solvent-exchanged cellulose (2.0 g actual cellulose weight or 0.04 mol of hydroxyl functionality). The solvent-exchange technique used for cellulose pre-treatment is described in detail in ref. 11. The mixture was stirred at room temperature until clear (approximately 1 h for cellulose powder at 25°C or 48 h for cotton fibres at 60°C).

*Cellulose triacetate (**1a**): acetyl chloride method.* To the cellulose solution, 15.5 ml (0.11 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 7.9 ml (0.11 mol) acetyl chloride in 25 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The reaction solution was

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filtered to remove the pyridine salt. The product was isolated as a white powder by precipitation of the reaction solution into hot distilled water and purified by Soxhlet extraction with methanol for 24 h. The product was dried at 60°C for 48 h in a vacuum oven to constant weight, with a yield of 3.3 g (93%). The product was soluble in DMAc and acetone with $[\eta]=3.20$ and 2.50 dl g^{-1}, respectively. Elemental analysis: C, 49.39; H, 6.52; O, 44.09 (calc. degree of substitution (*DS*)=2.4). I.r.: ester C=O, 1750 (s); methyl C–H, 2960 and 2870 cm^{-1}.

Cellulose triacetate (***1b***)*: acetic anhydride method.* To the cellulose solution, 6 ml (0.11 mol) sulphuric acid in 25 ml DMAc were added dropwise. A solution of 10.5 ml (0.11 mol) acetic anhydride was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was isolated, purified and dried as compound **1a** with a yield of 3.4 g (95%). The product was soluble in DMAc and acetone with $[\eta]=2.60$ and 2.35 dl g^{-1}, respectively. Elemental analysis: C, 49.45; H, 6.46; O, 44.09 (calc. *DS*=2.4). I.r.: see compound **1a**.

Cellulose tripropionate (***2***). To the cellulose solution, 15.5 ml (0.11 mol) triethylamine (TEA) in 25 ml DMAc was added slowly in one portion. A solution of 9.6 ml (0.11 mol) propionyl chloride in 25 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was filtered, isolated, purified and dried as compound **1a** with a yield of 4.0 g (97%). The product was soluble in acetone with $[\eta]=2.1$ dl g^{-1}. Elemental analysis: C, 53.97; H, 7.50; O, 38.53 (calc. *DS*=2.6). I.r.: ester C=O, 1750; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Cellulose tributyrate (***3***). To the cellulose solution, 15.5 ml (0.11 mol) TEA in 25 ml DMAc was added slowly in one portion. A solution of 11.5 ml (0.11 mol) butyryl chloride in 25 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was filtered, isolated, purified and dried as compound **1a** with a yield of 4.0 g (94%). The product was soluble in acetone with $[\eta]=2.7$ dl g^{-1}. Elemental analysis: C, 57.55; H, 8.32; O, 34.13 (calc. *DS*=2.7). I.r.: ester C=O, 1750; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Cellulose caproate (***4***). To the cellulose solution, 15.5 ml (0.11 mol) TEA in 25 ml DMAc was added slowly in one portion. A solution of 15.6 ml (0.11 mol) hexanoyl chloride in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was filtered, isolated, purified and dried as compound **1a** with a yield of 5.5 g (97%). The product was soluble in DMF with $[\eta]=1.7$ dl g^{-1}. Elemental analysis: C, 62.74; H, 9.36; O, 28.90 (calc. *DS*=2.8). I.r.: ester C=O, 1745; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Cellulose caprylate (***5***). To the cellulose solution, 15.5 ml (0.11 mol) TEA in 25 ml DMAc was added slowly in one portion. A solution of 17.2 ml (0.11 mol) heptanoyl chloride in 50 ml DMAc was then added dropwise over a period of 2 h, and the stirring was continued for 8 h at 25°C. The product precipitated out of solution as a white solid and was washed with hot water. The product was purified and dried as compound **1a** with a yield of 5.6 g (90%). The product was soluble in toluene with $[\eta]=1.3$ dl g^{-1}. Elemental analysis: C, 63.71; H, 9.61; O, 26.68 (calc. *DS*=2.4). I.r.: ester C=O, 1747; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Cellulose octanoate (***6***). To the cellulose solution, 15.5 ml (0.11 mol) TEA in 25 mol DMAc was added slowly in one portion. A solution of 19.0 ml (0.11 mol) octanoyl chloride in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product precipitated out of solution as a white solid and was washed with hot water. The product was purified and dried as compound **1a** with a yield of 5.4 g (81%). The product was soluble in toluene with $[\eta]=1.4$ dl g^{-1}. Elemental analysis: C, 64.78; H, 9.85; O, 25.36 (calc. *DS*=2.2). I.r.: ester C=O, 1752; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Cellulose benzoate (***7***). To the cellulose solution, 9.0 ml (0.11 mol) pyridine (PYR) in 25 ml DMAc was added slowly in one portion. A solution of 13.0 ml (0.11 mol) benzoyl chloride in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was filtered, isolated, purified and dried as compound **1a** with a yield of 5.6 g (96%). The product was soluble in acetone with $[\eta]=2.1$ dl g^{-1}. Elemental analysis: C, 67.92; H, 5.25; O, 26.84 (calc. *DS*=2.8). I.r.: ester C=O, 1750; aromatic C–H, 3100–3000; aromatic C=C, 1600, 1495 and 1455 cm^{-1}.

Cellulose phenylacetate (***8***). To the cellulose solution, 15.5 ml (0.11 mol) TEA in 25 ml DMAc was added slowly in one portion. A solution of 14.5 ml (0.11 mol) phenyl acetyl chloride in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was filtered, isolated, purified and dried as compound **1a** with a yield of 6.0 g (92%). The product was soluble in acetone with $[\eta]=2.2$ dl g^{-1}. Elemental analysis: C, 69.35; H, 5.97; O, 24.79 (calc. *DS*=2.8). I.r.: ester C=O, 1750; methylene C–H, 2940; aromatic C–H, 3100–3000; aromatic C=C, 1600, 1495, 1450 cm^{-1}.

Cellulose methyl carbamate (***9***). To the cellulose solution, 5.0 ml (0.064 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 6.5 ml (0.11 mol) methyl isocyanate in 25 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was isolated as a white swollen gel by precipitation of the reaction solution in a water/methanol mixture (50:50) and purified by Soxhlet extraction with methanol for 24 h. The product was dried at 50°C in a vacuum oven to constant weight with a yield of 4.0 g (94%). The product was soluble in DMSO with $[\eta]=3.0$ dl g^{-1}. Elemental analysis: C, 43.88; H, 6.54; N, 12.29; O, 38.28 (calc. *DS*=2.7). I.r.: amide N–H, 3600–3300; methyl C–H, 2960; amide C=O, 1680 cm^{-1}.

Cellulose ethyl carbamate (***10***). To the cellulose solution, 5.0 ml (0.064 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 8.7 ml (0.11 mol) ethyl isocyanate in 25 ml of DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was isolated, purified and dried as compound **9** with a yield of 4.1 g (88%). The product was soluble in DMSO with $[\eta]=2.9$ dl g^{-1}. Elemental analysis: C, 47.60; H, 7.40; N, 11.03; O, 33.97 (calc. *DS*=2.1). I.r.: amide N–H, 3600–

3300; methyl C–H, 2960; methylene, 2820; amide C=O, 1675 cm^{-1}.

Cellulose propyl carbamate (**11**). To the cellulose solution, 5.0 ml (0.064 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 10.3 ml (0.11 mol) propyl isocyanate in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was isolated, purified and dried as compound **9** with a yield of 5.1 g (95%). The product was soluble in DMSO with $[\eta]=2.9$ dl g^{-1}. Elemental analysis: C, 51.45; H, 8.05; N, 9.95; O, 30.55 (calc. $DS=2.6$). I.r.: amide N–H, 3600–3300; methyl C–H, 1960; methylene C–H, 2820; amide C=O, 1680 cm^{-1}.

Cellulose p-tolyl carbamate (**12**). To the cellulose solution, 5.0 ml (0.064 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 13.2 ml (0.11 mol) *p*-tolyl isocyanate in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was isolated, purified and dried as compound **9** with a yield of 6.8 g (95%). The product was soluble in chloroform with $[\eta]=2.2$ dl g^{-1}. Elemental analysis: C, 63.23; H, 6.03; N, 7.21; O, 23.52 (calc. $DS=2.7$). I.r.: amide N–H, 3400–3200; methyl C–H, 2940; aromatic C–H, 3100–3030; amide C=O, 1730; aromatic C=C, 1600 cm^{-1}.

Cellulose phenyl carbamate (**13**). To the cellulose solution, 5.0 ml (0.064 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 12 ml (0.11 mol) phenyl isocyanate in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 8 h at 25°C. The product was isolated, purified and dried as compound **9** with a yield of 6.3 g (97%). The product was soluble in acetone with $[\eta]=2.0$ dl g^{-1}. Elemental analysis: C, 59.23; H, 5.48; N, 8.28; O, 27.00 (calc. $DS=2.8$). I.r.:amide N–H, 3400–3200; aromatic C–H, 3100–2990; amide C=O, 1730; aromatic C=C, 1600 cm^{-1}.

Cellulose methyl thiocarbamate (**14**). To the cellulose solutions, 5 ml TEA in 25 ml DMAc was added slowly in one portion. A solution of 7.6 ml (0.11 mol) methyl isothiocyanate in 50 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 12 h. The product was isolated, purified and dried as compound **9** with a yield of 4.2 g (89%). The product was soluble in DMAc. Elemental analysis: C, 38.16; H, 5.77; S, 22.61; N, 9.90; O, 23.55 (calc. $DS=2.6$). I.r.: amide N–H, 3400–3200; methyl C–H, 2960; thiocarbonyl C=S, 1170 cm^{-1}.

Cellulose tosylate (**15**). To the cellulose solution, 9.0 ml (0.11 mol) pyridine in 25 ml DMAc was added slowly in one portion. A solution of 21.2 g (0.11 mol) *p*-toluene sulphonyl chloride in 75 ml DMAc was then added dropwise over a period of 1 h, and the stirring was continued for 12 h at 0–15°C. The product was isolated as a white powder by precipitation of the reaction solution in cold water and washed with cold methanol. The product was dried in a vacuum oven for 24 h at 25°C with a yield of 6.7 g (80%). The product was soluble in DMAc. Elemental analysis: C, 49.14; H, 4.31; S, 16.09; O, 30.46 (calc. $DS=2.4$). I.r.: aromatic C–H, 3100–3000; aromatic C=C, 1600; sulphonate (asymmetric) $S(=O)_2$, 1350; sulphonate (symmetric) $S(=O)_2$, 1170 cm^{-1}.

Chlorodeoxy cellulose (**16**). A solution of compound **15** was heated at 100°C for 3 h. The product was isolated as a white powder by precipitation of the reaction solution in hot water and washed with hot methanol. The product was dried in a vacuum oven for 24 h at 60°C with a yield of 2.5 g (90%). The product was soluble in DMAc. Elemental analysis: C, 39.18; H, 3.29; O, 14.71; Cl, 42.85 (calc. $DS=2.3$). I.r.: C–Cl, 1250 cm^{-1}.

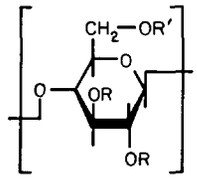
Methyl cellulose (**17**). This compound was prepared by the method of McCormick[8] with minor modifications. To the cellulose solution, 0.75 g (0.018 mol) sodium hydroxide powder was added, and the solution was heated to 80°C for 4 h. The reaction mixture was cooled to 25°C, and a solution of 2.3 ml (0.11 mol) iodomethane or 10.5 ml (0.11 mol) dimethyl sulphate in 25 ml of DMAc was added over a period of 1 h. An additional 0.75 g of sodium hydroxide was added and the stirring was continued for 24 h at 60–80°C and then for 48 h at 25°C. The product was isolated by precipitation of the reaction solution in a mixture of isobutanol and acetic acid (90:10). The filtered polymer was washed with hot ethanol and dried in a vacuum oven for 48 h at 50°C with a yield of 2.2 g (75%). The product was soluble in water with $[\eta]=2.0$ dl g^{-1}. Elemental analysis: C, 48.52; H, 7.76; O, 43.71 (calc. $DS=1.1$). I.r.: O–H, 3500–3200; methyl C–H, 2960 cm^{-1}.

Hydroxyethyl cellulose (**18**). This compound was prepared by the method of McCormick[8] with minor modifications. To the cellulose solution, 0.75 g (0.018 mol) sodium hydroxide powder was added, and the solution was heated to 80°C for 2 h. The reaction mixture was cooled to 10°C, and a solution of 6.4 ml (0.11 mol) ethylene oxide in 25 ml DMAc was added dropwise over a period of 1 h. An additional 0.75 g sodium hydroxide was added and the stirring was continued for 24 h at 60–80°C and then 48 h at 25°C. The product was isolated, washed and dried as compound **17** with a yield of 2.5 g (68%). The product was soluble in water with $[\eta]=2.9$ dl g^{-1}. Elemental analysis: C, 47.41; H, 7.82; O, 44.77 (calc. $DS=1.3$). I.r.: O–H, 3600–3200; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Hydroxypropyl cellulose (**19**). To the cellulose solution, 0.75 g (0.018 mol) sodium hydroxide powder was added, and the solution was heated to 80°C for 2 h. The reaction mixture was cooled to 25°C, and a solution of 2.6 ml (0.11 mol) propylene oxide in 25 ml DMAc were added dropwise over a period of 1 h. An additional 0.75 g of sodium hydroxide was added and the stirring was continued for 24 h at 60–80°C and then for 48 h at 25°C. The product was isolated, washed and dried as compound **17** with a yield of 2.7 g (75%). The product was soluble in water with $[\eta]=2.7$ dl g^{-1}. Elemental analysis: C, 51.43; H, 8.57; O, 40.00 (calc. $DS=1.7$). I.r.: O–H, 3600–3200; methyl C–H, 2960; methylene C–H, 2920 cm^{-1}.

Methods to control the degree of substitution. A series of reactions were conducted in attempts to achieve degrees of substitution of 1, 2 and 3, respectively, by adding stoichiometric molar quantities of reagent based on the molar hydroxyl functionality. Two reagents were studied, namely acetyl chloride and phenyl isocyanate, in attempts to produce cellulose acetate (compound **1a**) and cellulose phenyl carbamate (compound **13**), respectively, with DS

Table 1 Cellulose derivatives prepared in LiCl/DMAc solutions, degree of substitution *DS* and intrinsic viscosity [η]



Substituent	Compound no.	*DS*	[η] ($dl\,g^{-1}$)	Solvent
Esters				
$-CO-CH_3$	1a	2.4	3.2	DMAc
$-CO-CH_3$	1b	2.4	2.9	DMAc
$-CO-CH_2-CH_3$	2	2.6	2.1	Acetone
$-CO-(CH_2)_2-CH_3$	3	2.7	2.7	Acetone
$-CO-(CH_2)_4-CH_3$	4	2.8	1.7	DMF
$-CO-(CH_2)_5-CH_3$	5	2.4	1.3	Toluene
$-CO-(CH_2)_6-CH_3$	6	2.2	1.4	Toluene
$-CO-C_6H_5$	7	2.8	2.1	Acetone
$-CO-CH_2-C_6H_5$	8	2.8	2.2	Acetone
Carbamates				
$-CO-NH-CH_3$	9	2.7	3.0	DMSO
$-CO-NH-CH_2-CH_3$	10	2.1	2.9	DMSO
$-CO-NH-(CH_2)_2-CH_3$	11	2.6	2.9	DMSO
$-CO-NH-C_6H_5-CH_3$	12	2.7	2.2	Acetone
$-CO-NH-C_6H_5$	13	2.7	2.0	Acetone
$-CS-NH-CH_3$	14	2.6	[a]	DMAc
Sulphonate				
$-SO_2-C_6H_5$	15	2.4	[a]	DMAc
Ethers				
$-CH_3$	17	1.1	2.0	Water
$-CH_2-CH_2-OH$	18	1.3	2.9	Water
$-CH_2-CHOH-CH_3$	19	1.7	2.7	Water

[a] Intrinsic viscosity not determined

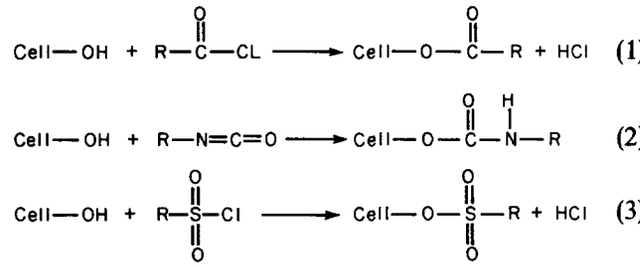
values of 1, 2 and 3 (*Table 1*). Reactions were conducted at 25°C for 48 h.

RESULTS AND DISCUSSION

Derivatization of cellulose in LiCl/DMAc solutions

The lack of suitable organic solvents has, in the past, prevented facile preparation of a wide range of derivatives from unmodified cellulose. Currently, the preparation of cellulose derivatives involves a heterogeneous reaction in which the cellulose is not solubilized in the initial reaction mixture. This usually results in an extremely inefficient process. Many of the problems encountered in preparation of cellulose derivatives can be greatly reduced or eliminated by the use of homogeneous organic solutions. The obvious advantages of a solvent system such as LiCl/DMAc for the preparation of cellulose derivatives lies in the ability to conduct a variety of organic reactions, produce high degrees of substitution under mild conditions, and increase the efficiency of such reactions in homogeneous solution. Additionally, LiCl/DMAc acts as the solvent for the synthesized derivative, which would ensure not only high substitution but also more uniform substitution due to greater accessibility of the reagent.

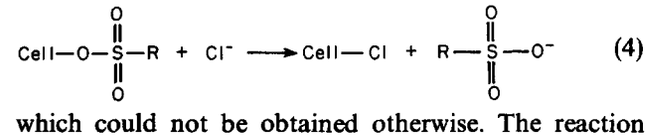
Preparation of cellulose esters, carbamates and sulphonates with high degrees of substitution. The first series of experiments investigated the reaction conditions that would yield high degrees of substitution (*DS*). Preparation of cellulose esters, carbamates and sulphonates was accomplished by the reaction of cellulose with acid chlorides (equation (1)), isocyanates (equation (2)) and organic sulphonyl chlorides (equation (3)), respectively, in the presence of tertiary amines.



Ester, carbamate and sulphonate derivatives were typically prepared by reacting cellulose with a three molar excess of the reagent based on the hydroxyl functionality. Triethylamine or pyridine was used as an acid acceptor or, in the case of isocyanate reactions, as a catalyst. The reagent in 25–50 ml of DMAc was added dropwise over a period of 1 h to the stirred solution at 25°C. The cellulose ester reactions were monitored by observing in the infrared spectra a reduction in the acid chloride carbonyl absorbance (1820–1790 cm^{-1}) and the appearance of an ester carbonyl absorbance (1760–1740 cm^{-1}). The carbamate reactions were monitored by observing the decrease in the isocyanate absorbance (2280–2260 cm^{-1}) and the appearance of a carbamate carbonyl absorbance (1730–1660 cm^{-1}). The sulphonate reactions were monitored by observing the decrease in the sulphonyl chloride absorbance (1350 cm^{-1}) and the appearance of a sulphonate ester absorbance (1290–1270 cm^{-1}). The reactions were usually complete within 4–8 h.

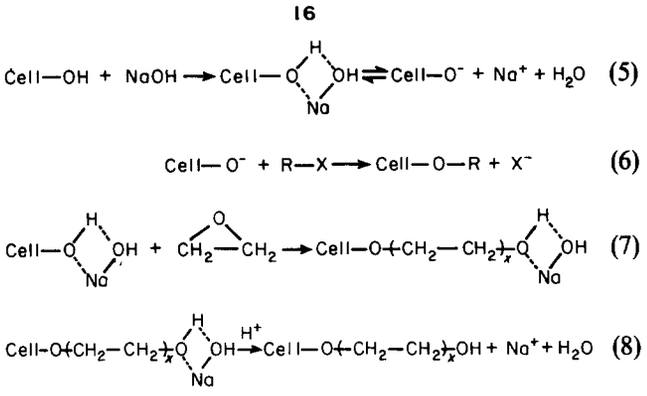
Table 1 lists the cellulose esters prepared, the *DS* values and intrinsic viscosities obtained. Analyses confirmed that cellulose esters with high degrees of substitution can be easily synthesized under homogeneous conditions in LiCl/DMAc solutions. In fact, degrees of substitution of 2.4–2.8 were easily obtained under these reaction conditions. The LiCl/DMAc solvent acts as a solvent both for the starting cellulose and the final product and reactions could be conducted at room temperature. These features assure uniform substitution and lessen the chance of degradation of the cellulose backbone by acid hydrolysis. The only products that were not soluble in the LiCl/DMAc solvent and precipitated from the reaction mixture were compounds **5** and **6**. These products reached degrees of substitution of 2.4 and 2.2, respectively.

In a related reaction, cellulose was successfully chlorinated by a homogeneous replacement of the sulphonate group of tosyl cellulose (compound **15**). Cellulose sulphonates may undergo exchange reactions with the chloride ion where the sulphonate is displaced nucleophilically to produce chlorodeoxy cellulose (compound **16**):



which could not be obtained otherwise. The reaction involved heating a solution of compound **15** with $DS = 2.4$ in 9% LiCl/DMAc to 100°C for 3 h. The results indicate that nearly all of the tosyl groups were displaced. The product **16** obtained a calculated $DS = 2.3$.

Preparation of cellulose ethers. Cellulose ether preparation was accomplished by the reaction of alkali cellulose (equation (5)) with an alkyl halide (equation (6)) and ring opening of alkylene oxides, as illustrated for hydroxyethyl cellulose in equations (7) and (8):



The reaction conditions were found to be adequate to produce water-soluble cellulose derivatives. However, there were a number of inherent problems that included:

(1) low solubility of the metal hydroxide in LiCl/DMAc;

(2) high reaction temperatures; and

(3) long reaction times.

Etherification without added base yielded no derivative; apparently, the hydroxyl functionality of cellulose is not a strong enough nucleophile even in homogeneous solution to initiate reaction. A base must be used to increase the reactivity. Sodium and potassium hydroxide, which are typically used in the production of alkali cellulose, were not very soluble in LiCl/DMAc solutions. A number of other bases were substituted for the metal hydroxides, but no derivative formation resulted. These bases included lithium hydroxide, tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, barium oxide, zinc oxide, triethylamine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-ene, sodium methoxide and sodium ethoxide.

Under the most favourable reaction conditions methyl cellulose (compound **17**), hydroxyethyl cellulose (compound **18**) and hydroxypropyl cellulose (compound **19**) were produced. Cellulose ethers were typically prepared by reacting cellulose with a 3–5 molar excess of the appropriate reagent in the presence of stoichiometric quantities of sodium or potassium hydroxide. The reaction mechanism involves a nucleophilic substitution reaction with the alkyl halide or an SN_2 displacement by the alkali complex on the epoxide. The reagent in 25–50 ml DMAc was added dropwise over a period of 1 h to the stirred solution at 0–15°C and then the mixture was heated to 60–80°C. The reactions were usually complete in 48–72 h. The maximum *DS* values obtained for compounds **17**, **18** and **19** were 1.1, 1.3 and 1.7, respectively (*Table 1*).

Conclusions are that the cellulose ethers may be produced in the LiCl/DMAc solutions; however, degrees of substitution were much lower than expected based on the amounts of base and reagent in the reaction mixture. Additionally, reaction times exceeded 4 days in most cases. Added base or reagent neither increased the *DS* nor decreased the reaction time. Therefore, the reaction appears to be solely dependent on the solubility of the base and the ability to form the alkali complex.

Regulation of the DS *in homogeneous solutions.* Since these reactions are conducted in homogeneous solutions, the *DS* can be controlled by varying the stoichiometry of the reagents. Reactions were conducted with two reagents, acetyl chloride and phenyl isocyanate at stoichiometric ratios to produce *DS* values of 1.0, 2.0 and 3.0, respectively. Cellulose acetate (compound **1a**) and cellulose phenyl carbamate (compound **13**) derivatives were obtained with degrees of substitution as indicated in *Table 2*. Despite homogeneous reaction conditions, complete substitution did not occur within 48 h at 25°C. However, only a small excess of reagent is necessary to produce esters and carbamates with mono- or di-substitution. Interestingly, *DS* values of 2.6 and 2.8 were obtained in attempts to produce the cellulose triacetate and cellulose tricarbamate under these conditions. Subsequent reactions with a three-fold excess of the respective acid chloride or isocyanate reagents failed to produce degrees of substitution of three (*Table 1*).

One possible reason for the lack of complete substitution may be the relatively high molecular weight of the cellulose substrate, which is not degraded by the LiCl/DMAc solvent. Derivatization in other systems may be aided by partial decomposition of the molecular chain. A second explanation for incomplete substitution may be the high viscosity of the reaction medium leading to diffusion controlled kinetics. Neither the molecular weight nor viscosity dependence on reaction kinetics was studied in this work.

With the exception of complete substitution ($DS > 2.8$), the LiCl/DMAc solvent allows controllability not possible in heterogeneous reactions of cellulose. The derivatization of cellulose in a heterogeneous process relies on the advancement of the reaction from layer to layer through the solid cellulose structure. Since the crystalline regions of cellulose are less accessible to reagents than either the amorphous or surface regions, non-uniform substitution during derivatization is likely. In most heterogeneous systems, pre-swelling or activation of the cellulose before reaction is needed. Common activation agents include water, aqueous acid,

Table 2 Reaction conditions and observed degrees of substitution for cellulose acetate and cellulose phenyl carbamate[a]

[OH][b] (mol)	[Reagent][c] (mol)	[Pyridine] (mol)	Target *DS*	Cellulose acetate *DS* (obs.)[d]	Cellulose phenyl carbamate *DS* (obs.)[d]
0.037	0.013	0.025	1.0	0.8	0.9
0.037	0.025	0.050	2.0	1.7	1.8
0.037	0.037	0.100	3.0	2.6	2.8

[a] Reaction conducted for 48 h at 25°C
[b] Concentration of hydroxyl functionality
[c] Concentration of acetyl chloride or phenyl isocyanate
[d] Determined by elemental analysis

liquid ammonia and organic solvents. The pre-treatment reduces intermolecular hydrogen bonding, thus increasing the rate of diffusion of the reactants; however, with cellulose that has been pretreated the activation agent must be removed with an appropriate solvent before reaction. Additionally, the effects of failing to achieve uniform swelling and decrystallization are manifested by poor solubility of the product. Those areas which are not properly swollen do not react and appear as insolubles.

Molecular weights of cellulose derivatives produced from LiCl/DMAc solutions. The molecular weights of selected cellulose derivatives were determined to illustrate the extent of degradation that occurred during the reaction in LiCl/DMAc. The molecular weights were estimated using well established Mark–Houwink–Sakurada (MHS) parameters (*Table 3*). Relationships were derived from light scattering data and established for the *DS* of the derivative.

The intrinsic viscosities of compounds **1a**, **13**, **17** and **18** were carefully determined in the solvents listed in *Table 3*. The theoretical molecular weights were based on the molecular weight of the starting cellulose ($M_w = 182000$)[11] and the DS. *Table 4* lists the molecular weights estimated by the MHS relationships compared with the expected values.

The cellulose derivatives **1a** and **13** were within 15% of the calculated value. In contrast, the cellulose derivatives **17** and **18** were 54% and 42%, respectively, below the expected value. The results indicate that little degradation occurs during the reaction to produce cellulose esters and cellulose carbamates, whereas it must be concluded that a significant amount of degradation occurs during the reaction to produce cellulose ethers. The large decrease in viscosity observed in the cellulose ether reactions is not totally unexpected since cellulose is very susceptible to degradation in the presence of metal hydroxides[21].

CONCLUSIONS

A wide range of cellulose derivatives have been prepared in homogeneous solution utilizing the LiCl/DMAc solvent; this is significant because most cellulose derivatives are produced under heterogeneous reaction conditions. Cellulose esters, carbamates and sulphonates were prepared using highly reactive reagents, such as acid chlorides, isocyanates and sulphonyl chlorides, respectively. The reaction conditions were optimized to give high degrees of substitution under mild reaction conditions. Under these reaction conditions, the degree of substitution (*DS*) ranged from 2.1 to 2.8; the LiCl/DMAc acts as the solvent for the derivative, ensuring uniform substitution by greater accessibility of the reagent. Additionally, reactions to produce cellulose esters and carbamates can be controlled with high accuracy by adjusting the molar ratio of reagent and hydroxyl functionality; no significant degradation occurs during the reaction.

When compared to synthesis in heterogeneous reactions of cellulose esters and carbamates, homogeneous derivatization yields the following advantages:

(1) the reaction may be conducted at room temperature;

(2) less reagent is necessary;

(3) there is less degradation of the cellulose; and

(4) the degree of substitution may be accurately controlled up to values of 2.8.

Cellulose ethers, such as methyl, hydroxyethyl and hydroxypropyl cellulose, were also produced in the LiCl/DMAc solvent. However, low solubility of the metal hydroxides needed in the reaction limits yields. Unfortunately, no other effective bases have yet been found that can be substituted for the metal hydroxides. Additionally, the *DS* cannot be regulated, and significant degradation of the derivatives occurs. Therefore, the production of cellulose ethers in LiCl/DMAc does not appear to have advantages over conventional processes, at least under our reaction conditions.

Table 3 MHS parameters for cellulose derivatives in various solvents at 25°C

Compound	*DS*	Solvent	K (cm^3 g^{-1})	a	Ref.
1a	2.9	DMAc	0.026	0.75	17
		Acetone	0.029	0.73	17
13	3.0	Acetone	0.0012	0.91	18
		Dioxane	0.0008	0.97	18
17	1.7	Water	0.316	0.55	19
18	1.0	Water	0.0074	0.89	20

Table 4 Comparison of viscosity average molecular weight calculated from MHS relationships, M_w (MHS), and theoretical molecular weight, M_w (th.), for cellulose derivatives produced in LiCl/DMAc solutions

Compound/*DS*	Solvent	$[\eta]$ (dl g^{-1})	M_w (MHS)	M_w (th.)
1a/2.6	DMAc	3.20	280000	310000
	Acetone	2.50	270000	310000
13/2.8	Acetone	2.00	530000	520000
	Dioxane	2.95	540000	520000
17/1.1	Water	2.00	92000	200000
18/1.3	Water	2.91	145000	250000

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