



MAURITIUS RESEARCH COUNCIL
INNOVATION FOR TECHNOLOGY

**SYNTHESIS AND
CHARACTERISATION OF
ENVIRONMENTALLY
FRIENDLY POLYMERS
DERIVED FROM
CELLULOSE**

Final Report

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SYNTHESIS AND CHARACTERISATION

OF ENVIRONMENTALLY FRIENDLY

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FINAL REPORT
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General Introduction

Cellulosic materials are used in the polymer industry for a wide range of applications including fillers, laminates and panel products, wood-polymer composites (WPC), polymer composites, alloys and blends, and cellulose derivatives called cellulose. The derivatisation of cellulose has opened up tremendous marketing possibilities for the polymer processing, adhesives and pharmaceutical industries. Commodity products made from waste cellulosic materials also show a promising future.

Much effort has been devoted to the preparation of the wood-like composite materials (fabric laminates, plywood, particle board, medium density fiber board (MDF) that use wood waste or non-woody plants like sugar-cane bagasse.

The study of polymer composites that contain cellulosic materials is also another important area of research. Cellulosic materials are rigid as compared to synthetic polymers. When cellulose is used in polymer composites, it is of critical importance to reduce the free energy of the cellulose surfaces to reduce agglomeration. Composites prepared under optimum conditions show excellent properties. The obtention of cellulose-reinforced materials, particularly thermoplastics, proceeds through modification of the polar cellulose surface by grafting with compatible thermoplastic segments.

Natural cellulose has a melting point that is considerably higher than its decomposition temperature. Thus, natural cellulose cannot be used as a plastic material. However, cellulose is derivatised through the etherification or esterification, its properties are modified and it can then be melted and molded. Such cellulosic products are used in a large variety of applications. This report will focus mainly on the synthesis of such derivatives.

In a first part, it is important to have a close look at the structure of native cellulose and the techniques used for its characterisation.

CHAPTER 1

Literature Review

1.0. INTRODUCTION

Polysaccharide cellulose is the main constituent of the cell of woody plants. Because of its fibrillar morphology (fig. 1) it forms a natural polymer composite of excellent material properties with other plant polysaccharides (hemicellulose) and lignin.

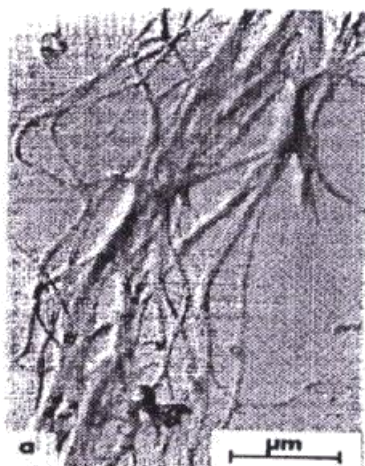


Fig 1: Fibrillar morphology of cellulose

Cellulose is prepared from wood by a process of dissolving and chemical softening. Depending on the solvent solution used, the following pulping processes are distinguished: sulfite process; soda process. The pulp is produced from cellulose-containing vegetable matter, such as sugar-cane waste, straw, reeds, maize and sunflower stalks. These materials are subjected to a preliminary cleaning treatment, chopped up by mechanical processes, and then boiled in large tans with hot solutions, sodium sulfide, sodium sulfate, sodium carbonate. The lignin, which causes the cellulose fibres to adhere together, is dissolved by this treatment and is, in part, chemically decomposed, leaving a soft pulp that consists of cellulose. The raw pulp thus obtained is reduced by mechanical processes, washed, bleached and again carefully cleaned. Finally, the pulp is dewatered and formed into strips or boards. Most of the cellulose produced is consumed by the textile industry and the paper industry. The outstanding properties of this material will guarantee large-scale applications of chemically converted cellulose, which means cellulose, reconstituted from solutions as well as cellulose derivatives.

During recent decades, the chemistry of cellulose has promoted by the discovery of nonaqueous systems for cellulose, which broadens the scope of derivatization reactions

under homogenous conditions as well as by the general progress in synthesis and characterization of saccharide derivatives.

1.1. STRUCTURE OF CELLULOSE

Cellulose is a linear 1,4- β glucan as shown in figure 2, biosynthesized by a regio- and stereoselective multistep polycondensation reaction. It is highly uniform polycetal containing three reactive uniform groups per 'anhydroglucose' unit.

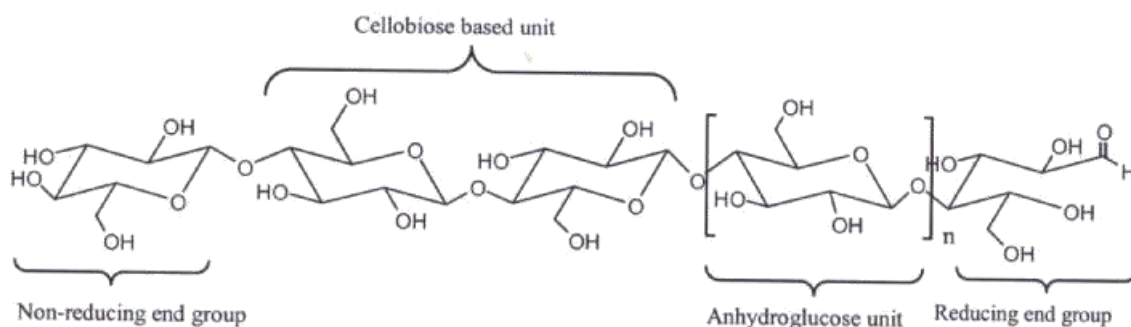


Fig. 2: Molecular representation of 1,4- β glucan

Based on this molecular structure, ordered hydrogen bond systems (figure 3) for various types of supramolecular semicrystalline structures, which are essential for the natural functions and commercial applications of cellulose.

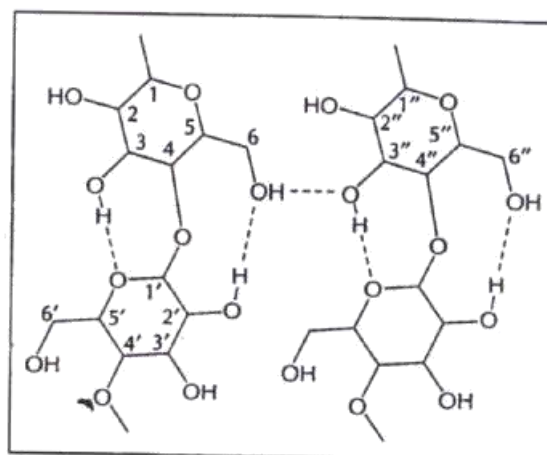


Fig 3: Network of Intra- and Intermolecular H- bonds

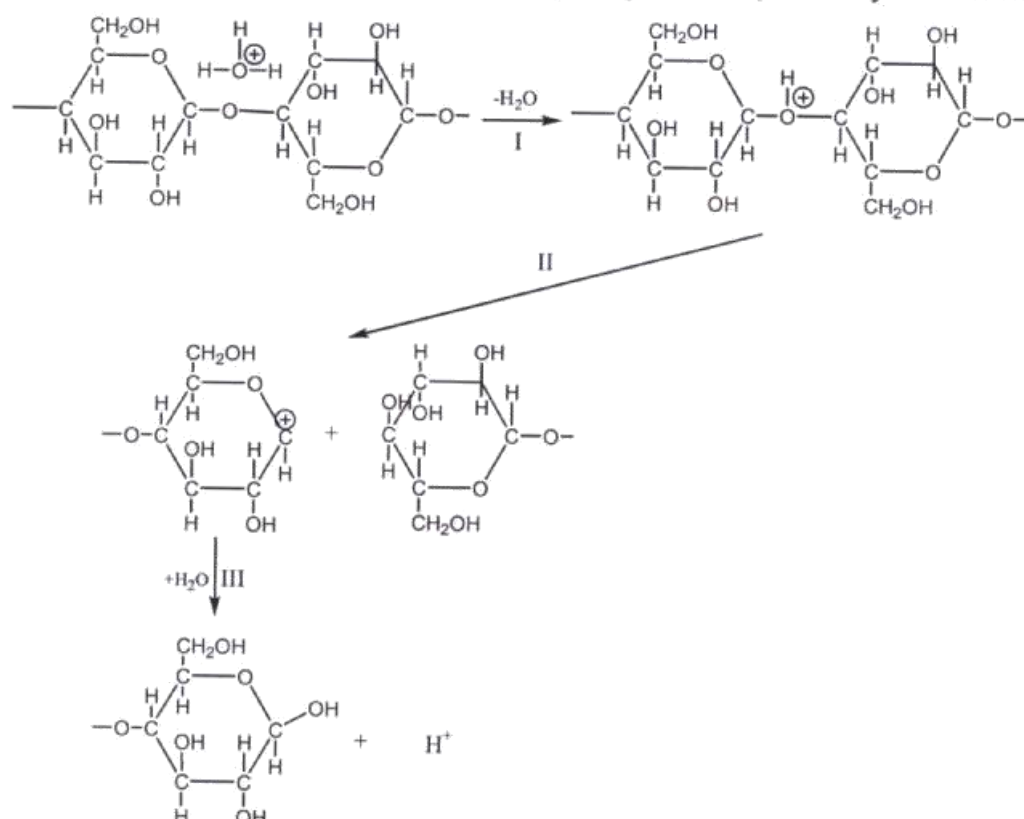
The three OH-groups in the 2-, 3- and 6-positions can be derivatized by etherification, esterification, oxidation and grafting. Besides covalent derivatization, the H-groups, as well as the ring and bridge O-atoms, can participate in intermolecular interactions

relevant to cellulose dissolution. The glucosidic linkage between the monomer units in the anhydroglucose is easily cleaved in an acidic medium or by enzymic hydrolysis.

The mechanism of the hydrolytic reaction consists in the attack of the acid to the polar - β -glucosidic link that splits heterolytically, and fixes to the end of the fragment thus formed, according to the scheme 1 described by Vasuiliu-Opera *et al.*, *Cellulose Chem. Technol.*, **14**, 65 (1980).

The H^+ proton forms, together with water, the H_3O^+ ion, that attacks the extra-cyclic oxygen of the β (1-4) bridges and protonizes effectively the hemiacetal link, which causes a strong deformation of the valency links, as well as release of the water molecule from the acid complex.

Under the action of the tensions thus formed, the bridge between the links cleavage, which is accompanied by the formation of a chain fragment, with a non-reducing end (N), as well as of the carbonation placed in position (I) of the other fragment, resulted from splitting, to which the water molecule is added. In this way, the second segment of the polysacchride chain-having, this time, a reducing end (R) is generated, along with the separation of the H^+ ion. This ion is not consumed during the reaction, thus becoming available for resuming other elementary hydrolysis operations (the catalytic character).



Scheme 1: Mechanism of the reaction of cellulose hydrolysis

1.1.1. Microcrystalline Cellulose

In natural cellulose the microcrystals are packed tightly in the fiber direction in a compact structure. This fibrillar structure can be destroyed under either mechanical stirring or by chemical methods, thereby leading to a highly dispersed powder containing particles under 100 μ . This powder is called microcrystalline cellulose. The microcrystals are rehydrogen bounded together, and a spongy, porous, random fine structure replaces the highly ordered pattern. Microcrystalline cellulose can be prepared from all forms of natural cellulose or from wastes such as fibres resulting from textile spinning mills. This powder possesses unique properties due to its unique particle size and its very narrow particle size distribution.

According to some authors (Cellulose Chem. Technol., 28, 155-119, 1994), the mechanical process presents some shortcomings in that the products get mixed with the metal from the installation, thus limiting considerably their domain of utilizations. Special interest is paid to chemical methods which consist in their hydrolytic attack usually in an acid medium.

1.2. CHARACTERISATION OF CELLULOSE

1.2.1. ^{13}C -NMR Spectroscopy

During the last two decades, high resolution NMR spectroscopy, has become a powerful tool for molecular characterization of cellulose. NMR techniques have been extensively applied to the study of cellulose and its derivatives. Spectral resolution is often poor due to incomplete dissolution and high viscosity of the cellulose solution. Line broadening and overlapping resonance bands add to analysis problems. However, some of these difficulties have been overcome using two-dimensional (2D) COSY NMR techniques [R. Nardin and M. Vincondon, *Macromolecules*, **19** 2452-2454 (1986); C. Buchanan, J. Hyatt, and D. Lowman, *Macromolecules*, **20**, 2750-2754 (1987); C. Buchanan, K. Edgar, J. Hyatt, and A. Wilson, *Macromolecules*, **24**, 3050-3059 (1991)].

In 1982 the first ^{13}C -NMR solution spectrum of cellulose in LiCl/DMAc (Fig. 4) was reported by McCormick and T.S. Shen, *Macromolecular Solutions* (R. B. Seymour and G. S. Stall, eds., Pergamon, New York, 1982, pp. 101-107). The spectrum shows five distinct peaks ranging from the anomeric carbon (C-1) at 103.5 ppm to the primary

carbon (C-6) at 60.7 ppm. The three interior peaks from the low to high field have been assigned to the C-2, the C-3 and the C-5 overlap, the C-4 carbon respectively. The aprotic character of LiCl/DMAc allows observation of individual labile hydroxyl proton resonance by ^1H -NMR. Homonuclear ^1H studies and two dimensional ^{13}C -H correlation experiments have been conducted [R. Nardin and M. Vincendon, *Macromolecules*, **19**, 2452-2454 (1986)].

Figure 5 is a schematic representation of the ^{13}C -NMR spectrum of cellulose. The general pattern of the cellulose is characterized by an isolated C-1 signal at low-field (~ 103 ppm), a number of closely spaced signals in the range of 70-80 ppm corresponding to the C-atoms, 2, 3, and 5 and an isolated signal for the C-6 atoms at high field (~ 61 ppm).

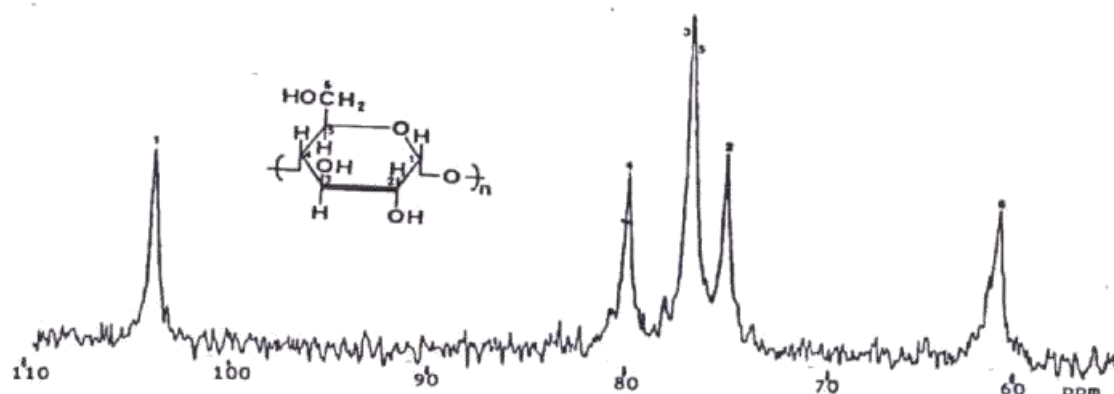


Fig. 4: ^{13}C NMR spectrum of a 3% w/w solution of cellulose in a 5% LiCl/DMAc solvent with 1-s pulse repetition, 90° pulse angle, obtained at 90°C

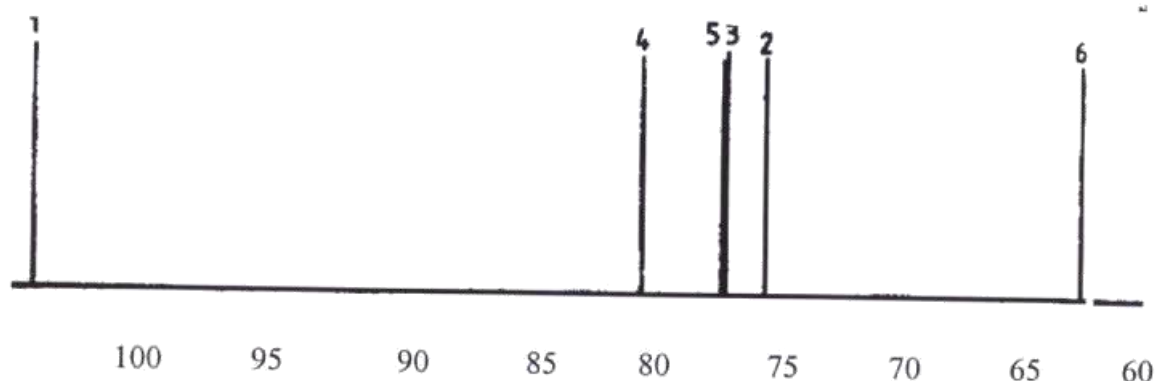


Fig 5: Schematic representation of the ^{13}C NMR spectrum of cellulose of DP = 40 in NaOH/D₂O

Derivatization of the cellulose molecule at the C-2, C-3 or C-6 position can lead to pronounced changes in the chemical shift for the C-atoms. Partial substitution is

observed often occurring at all the reaction sites (C-2, C-3 and C-6) to different partial degree of substitution, DS, Values. Thus results in at least a doubling of the number of signals, i.e., one signal each for the substituted and non-substituted site and also for the neighboring C-atoms in the C-1, C-4 and C-5 position, secondarily influenced by the substitution.

Based on experiments with well-defined model compounds, the effect of substitution by different functional groups can be assessed quantitatively, thus enabling the calculation of chemical shifts for the C-atoms of the anhydroglucose (AGU) unit.

In recent years the question of a simultaneous esterification has remained open. Augustine described trifluoroacetic acid as a non-derivatizing cellulose solvent, while Hawkinson assumed a small particle derivatization in the same system. This question was resolved by ^{13}C -NMR spectroscopic investigation. According to the spectra shown in Fig. 6, derivatization to cellulose trifluoroacetate $[\text{Cell-O-C(O)-CF}_3]$ definitely occurs, but the reaction proceeds rather slowly at room temperature. At the beginning the mixture remained turbid, but after 10 hours, a clear solution was obtained and a predominant substitution at C-6 (additional signal at 66 ppm) was detectable. After a reaction time of 2 days, a complete substitution at C-6 and some splitting of the C-1 signal was observed. After a total reaction time of 28 days, the additional C-1 signal at 101 ppm and the original one at 103 ppm are of equal height, indicating further progress of substitution at the C-2 position.

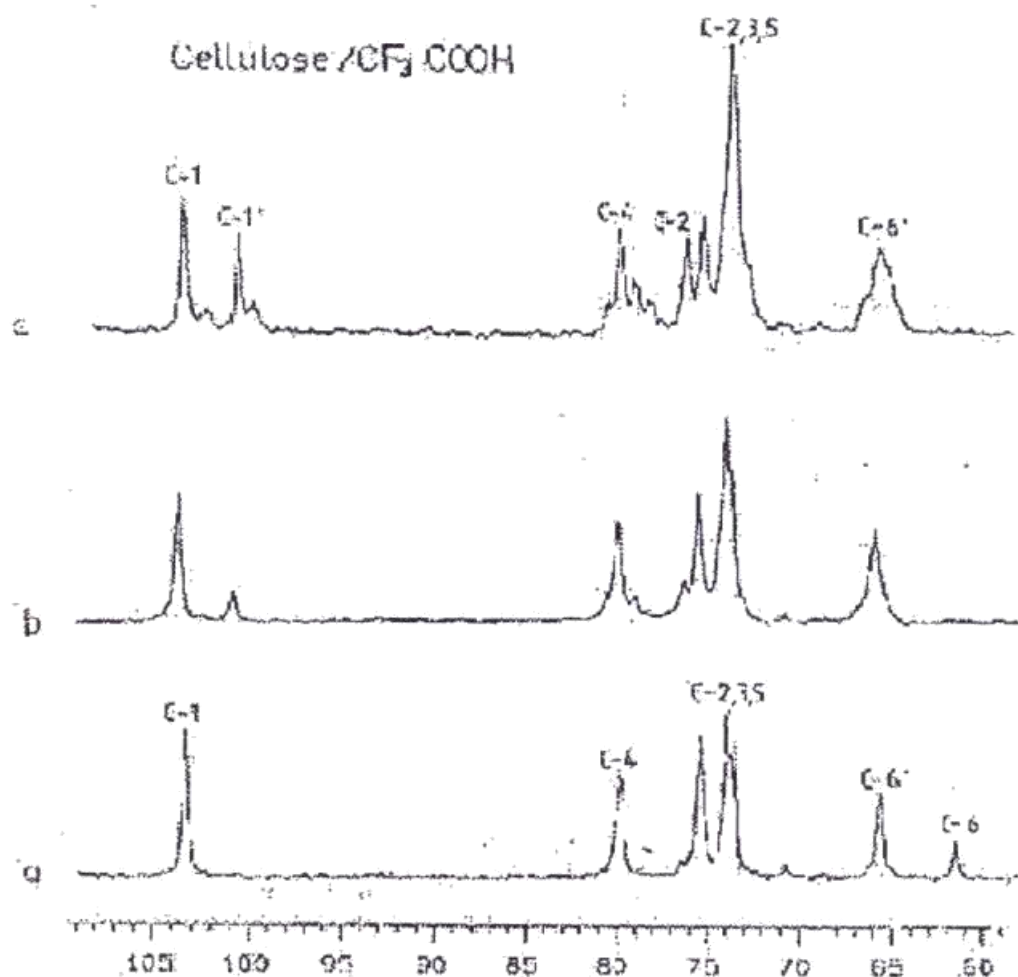


Fig. 6: Comparison of ^{13}C -NMR spectrum of cellulose dissolved in TFA as a function of the time of residence. (a) After 10 hours; (b) After 2 days and (c) After 28 days

1.2. 2. Infra-Red Spectroscopy

Application of this technique is perfectly suited to the chemical identification and characterization of fibrous material such as cellulose. Furthermore by this technique, the quantification of chemical changes is possible such as the determination of the DS. The small area which can be measured allow the evaluation of variations in the derivatization of even individual fibres and thus enhance the knowledge on the influence of the fine structure of cellulose or its derivatives.

IR analyses of cellulose films cast from its TFA-acetic acid solutions showed that partly trifluoroacetylated cellulose in the solution state turns to partly acetylated cellulose in the solid state during evaporation of the solvents in air by the ester interchange on TFA.

Fig. 7 shows the IR spectrum of cellulose prepared from its TFA solutions, with and without 1N NaOH treatment.

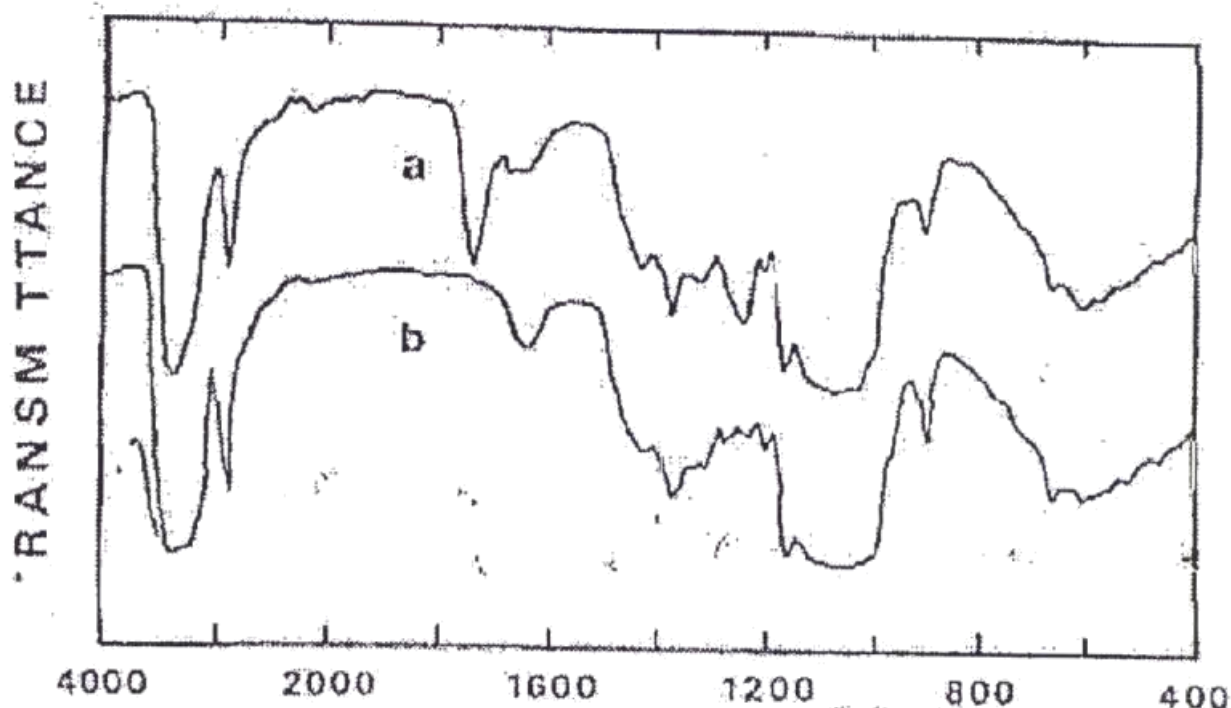


Fig. 7: IR spectra of cellulose from its trifluoroacetic acid solution, with and without 1N NaOH treatment: (a) cellulose film without alkali treatment; (b) cellulose film with alkali treatment.

The IR spectrum of the cellulose film with the alkali treatment (b in fig. 7) showed a typical pattern of cellulose. In contrast, the IR spectrum of the cellulose film without the alkali treatment (a in fig. 7) had an absorption band in the carbonyl region around 1745 cm^{-1} . This absorption was ascribed to C=O stretching vibrations of acetyl ester groups, and no absorption bands due to carbonyls of trifluoroacetyl ester groups 1790 cm^{-1} were detected. Furthermore, if trifluoroacetyl groups were present in the cellulose film (a), three absorption bands due to the stretching vibrations of C-F should appear around $840\text{--}720\text{ cm}^{-1}$. Thus the cellulose without the alkali treatment contained acetyl ester groups, which originated from the acetic acid added to the cellulose solution in TFA for controlling the viscosity.

These observations together with those by ^{13}C -NMR analyses support the idea that the hydroxyl groups of C-6 in cellulose dissolved in TFA are selectively esterified by TFA then the trifluoroacetyl ester groups are partly converted to acetyl groups by the ester interchange in the TFA-acetic acid mixture during evaporation in air. Trifluoroacetyl

ester groups in cellulose are unstable in air and are hydrolyzed with moisture, whereas acetyl ester groups once formed in cellulose are stable to moisture in air.

1.2.3. X-Ray Diffraction

Cellulose has a strong tendency to form highly crystalline fibres. This makes it accessible to x-ray diffraction. The most detailed information on the structures on the structure of cellulose I and II came from x-ray diffraction. Although structures could already be given, details of the molecular structure and hydrogen bonding were not known. In 1970s renewed x-ray crystallographic investigations were carried out. A final settlement of some controversies could not be given. The main reason for this lack of detailed information is that x-ray diffraction on fibres does not go beyond a resolution of about 2.5 Å, which is not enough to determine the position of hydrogen atoms and not even to discriminate between parallel or antiparallel packing.

1.3. CELLULOSE DERIVATIVES

The uniform structure of cellulose, combined with its hydrophobicity, biocompatibility, chirality and structure-forming capacity, as well as its broad synthetic potential, make the design of cellulose-based advanced materials a challenge for polysaccharide research.

Novel cellulose derivatives can exhibit interesting properties, which provide abundant scope for industrial applications. The current applications for cellulose derivatives are diverse with cellulose esters and ethers in highest demand. The esters are typically used as fibres, films and coatings whereas cellulose ethers are most commonly employed as water-soluble viscofiers for aqueous media. Other derivatives such as carbamates, silyl ethers, and halodeoxy compounds are produced on a limited scale and are typically used as aids in structure elucidation. Cellulose is usually derivatized to the corresponding ester, or carbamate by reacting the hydroxyl groups on the anhydryglucose rings under heterogeneous reaction conditions.

A list of a few commercial derivatives of cellulose is given below:

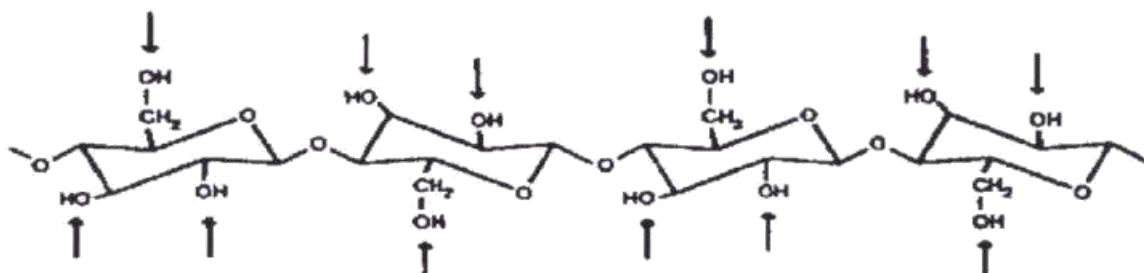
- regenerated cellulose (viscose rayon, cellophane)
- cellulose nitrate or celluloid (Akzo Nobel, BASF, ICI, Nippon Paint)
- cellulose acetate, cellulose propionate/butyrate (Hoechst, Eastman Chemical)

- carboxymethylcellulose, hydroxyethylcellulose, methylcellulose (Metsa-Serla), Akzo, Aqualon/Hercules)

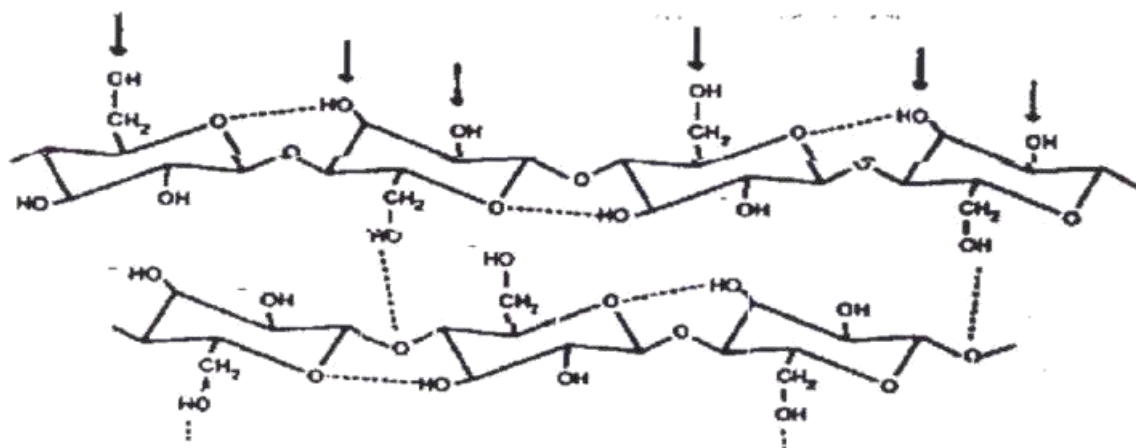
1.3.1. Heterogeneous and homogeneous reactions conditions

In heterogeneous reaction conditions, cellulose typically remains suspended in solution and the reaction proceeds from the surface to the amorphous regions. After sufficient reaction or substitution, the crystalline portions gradually become exposed for reaction. Heterogeneous reactions at low degree of substitution (DS) lead to compositional and structural inhomogenities, including poor uniformity along the cellulosic backbone and extensive by-product formation. Cellulose derivatives with high DS values normally improved solubility in solvents and thermal processibility. Under heterogeneous conditions, uniform products are not obtained.

Homogeneous reaction conditions provide uniform substituent distribution and controlled degree of substitution in cellulose derivatives. This is very important when cellulose derivatives of low DS are desirable. Uniformly substituted cellulose derivatives should exhibit predictable product properties and enhanced resistance to enzymatic properties. Under homogeneous conditions, products with homogeneous chemical structures, which have properties that are independent of the origin of the initial cellulose (morphology and chain packing) are obtained. For homogeneous derivatives, the physical properties should be predicted more directly and related only to the nature of substituent, average degree of substitution (DS) and molecular weight distribution.



Homogeneous System: reaction sites (\rightarrow) are uniform and fully accessible.



Heterogeneous System: reaction sites (\rightarrow) are non-uniform and only on the surface.

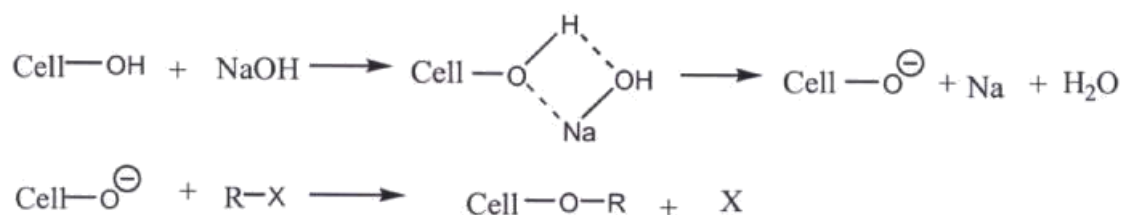
1.3.2. Cellulose Ethers

Cellulose ethers are high-molecular-weight compounds produced by replacing the hydrogen atoms of hydroxyl groups in the anhydroglucose units of cellulose ethers are sodium-carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC) and methylcellulose (MC) derivatives.

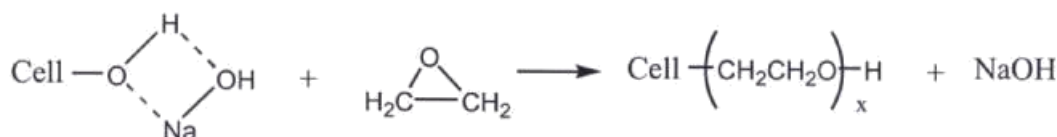
Cellulose ethers are commonly used as thickeners, viscosifiers, binders, film formers, water-retention aids and protective colloids. The principal applications are in the building products, surface coatings, foods, pharmaceuticals and toiletries, oil field chemicals and polymerisation. The cellulose ethers market is truly global in nature, characterized by significant trade. For many applications it is undesirable to disrupt or shorten the cellulose fibres and hence there is a special interest in mild conditions, which results in low degrees of substitution (DS). Long chain alkyl substituents can bring about marked changes in the physical properties of cellulose, even at low DS, and ethers are of special interest because their stability in alkali and good stability in acid.

In recent years there has been emphasis on the development of milder and simpler methods for preparing cellulose ethers (Kondo and Gray, 1992), the control of substituent distribution in these products (Kondo and Gray, 1991), novel reagents and reaction conditions [Isogai *et al.*, J. Appl. Polym. Sci., 29, 2097-2109 (1984)]; and new analytical methods (Fyfe *et al.*, J. Macromol. Sci. Rev. Macromol. Chem. Phys., C23, 187-216 (1983); Isogai *et al.*, J. Appl. Polym. Sci., 31, 341-52 (1986); Carbohydrate Polymers, 21, 277-81 (1993).

Cellulose ethers are usually prepared by the reaction of alkali cellulose with alkyl halides or epoxides (scheme 2 and 3 below).



Scheme 2



Scheme 3

Most typical bases (NaOH and KOH) used are insoluble in LiCl/DMAc, which is a very good solvent for cellulose. DMAc/LiCl, enables reaction to be carried out under mild conditions (McCormick and Callais, 1987) and such a homogeneous procedure ensures a more uniform distribution of the substituents due to a greater accessibility of the -OH sites.

It is very difficult to obtain the alkali cellulose needed to initiate the reaction. M. Hirrien *et al.* [Carbohydrate Polymers, 31, 243-252, (1991)] used dimethyl sodium solution as activator in a new homogeneous reaction with DMAc/LiCl as solvent. They synthesised water-soluble methyl cellulose (MC) using DMAc/LiCl as solvent, a dimethyl sodium solution as activator and CH₃I as alkylating reagent. During this reaction different degrees of substitution were obtained (0.9 < DS < 2.2).

The cellulose was stirred in water for 30 minutes and centrifuged at 9000 g for 15 minutes. The supernatant was then discarded. The same procedure was repeated twice

with DMAc. The cellulose after the last solvent-exchange was dissolved in a solution of DMAc (600 ml) containing 6 wt. % LiCl. The mixture was stirred overnight at room temperature until a clear solution was obtained.

The dimethyl sodium solution was added to the cellulose solution and the mixture was stirred at ambient temperature for one night. After cooling the solution to 10°C, iodomethane (30 ml, was added and the mixture was stirred at room temperature for different times to reach different substitution degrees (Table 1). Methyl cellulose (MC) samples were recovered with a yield of about 70% based on initial dried weight of cellulose. The conditions for each methylcellulose prepared are given in Table 1.

Table 1: Experimental conditions for the synthesis of methyl cellulose samples using the homogeneous procedure

Cellulose	Ratio Cell: DMAc	Anion NaH: DMSO	Duration of Synthesis	DS
A	6:700	20:100	8 hrs	0.9
A	7.5:720	20:100	18 hrs	1.5
A	6:550	15:50	7 hrs	1.2
A	6:700	10:50	7 days	2.2
A	6:600	20:100	5 days	1.4
B	10:600	20:100	24 hrs	1.0
B	10:600	20:100	7 days	1.2

A = Cellulose from dissolving wood pulp with $DP_v = 1300$

B = Cellulose Avicel PH-101 with $DP_v = 130$

The methylcellulose samples were characterized by ^{13}C -NMR spectroscopy. The measurements were performed on a Bruker AC 300 spectrometer at 353 K using DMSO- d_6 as solvent. The signals (fig. 8) were attributed based on the assignments by Parfondy and Perlin (1977) and studies of Takahashi *et al.* (1986). The relative degree of substitution value at an individual hydroxyl group was estimated from the ratio between peak areas.

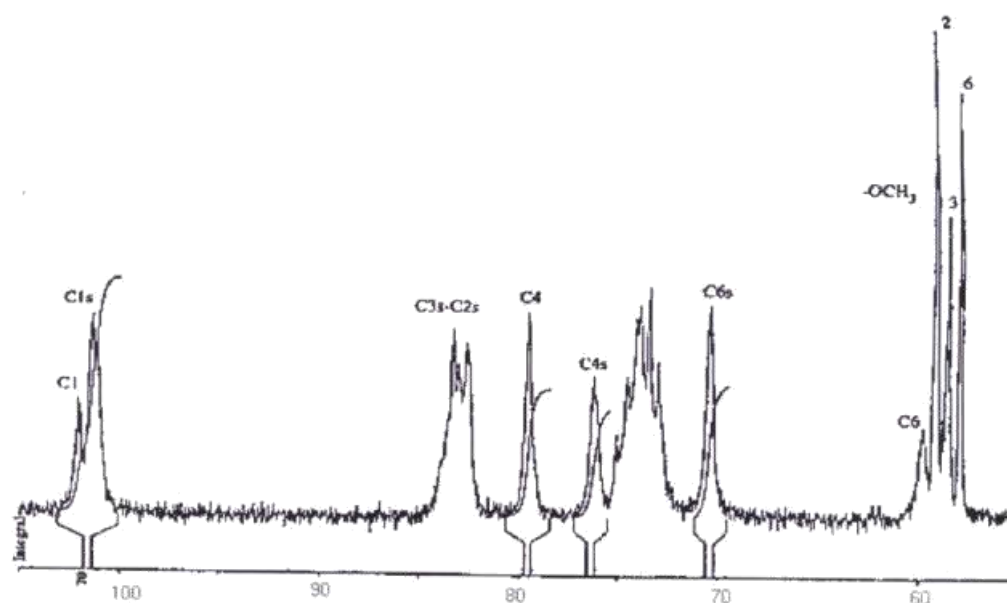


Fig 8: ^{13}C -NMR spectrum recorded at 80°C of a 3% w/v solution in DMSO

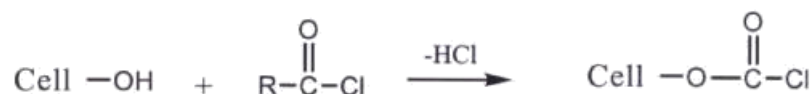
A number of cellulose ether derivatives have been prepared under heterogeneous conditions (Table 2) [C.L. McCormick and P.A. Callais, *Polymer*, **28**, 2317-2323, (1987); S. Takahashi, T. Fujimoto, T. Miyamoto, and H. Inagaki, *J. Polym. Sci. Polym. Chem Ed*, **25**, 987-994, (1987). Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.*, **29**, 2097-2109, (1984)]. The heterogeneous reactions are typically conducted by reacting cellulose with a 3 to 5 molar excess of reagent. KOH or NaOH (as activators is slurried in the reaction mixture at high temperature (60 - 80°C) for 48-72 hrs [C.L. McCormick and P.A. Callais, *Polymer*, **28**, 2317-2323, (1987)].

Table 2: Cellulose Ether Derivatives Prepared in LiCl/DMAc

Substituent	Ds
$\text{HO}-\text{CH}_2-\text{CH}_2-$	1.3
$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-$ OH	1.7
$-\text{CH}_3$	1.1
$-\text{CH}_3$	2.3
$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-$	2.3
$-\text{CH}_2-$	2.8

1.3.3. Cellulose Esters

The esterification of cellulose was experimentally realized as long as about 150 years ago. It resulted in large-scale industrial processes like cellulose nitrate production and cellulose xanthogenation as a decisive chemical step in artificial fibre production. To date, only a few reports can be found in the literature regarding unsaturated cellulose ester derivatives [K. Rahn, M. Diamantoglou, D. Klemm, H. Berghmans, Th. Heinze, *Angew. Makromol. Chem*, 238, 142 (1996); Th. Heinze, K. Rahn M. Jaspers, H. Berghmans, *J. Appl. Polym. Sci.*, 60, 1891 (1996)]. Cellulose undergoes esterification with acids in the presence of a dehydrating agent or by reaction with acid chlorides. The production of cellulose esters in LiCl/DMAc has been given much interest. A typical reaction pathway is shown in scheme 4.



Scheme 4

Table 3: Cellulose ester derivatives prepared in LiCl/DMAc solutions

Substituent	Ds	Substituent	Ds
$\text{H}_3\text{C}-\text{CCl}_2-\overset{\text{O}}{\parallel}{\text{C}}-$	0.50	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$	2.4
$\text{Cl}-\text{C}_6\text{H}_3(\text{Cl})-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-$	2.7	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-$	2.6
$\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-$	2.8	$\text{H}_3\text{C}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-$	2.7
$\text{C}_6\text{H}_5-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-$	2.8	$\text{H}_3\text{C}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-$	2.8
$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)-\overset{\text{O}}{\parallel}{\text{C}}-$	1.4	$\text{H}_3\text{C}-(\text{CH}_2)_5-\overset{\text{O}}{\parallel}{\text{C}}-$	2.4
$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-$	0.35	$\text{H}_3\text{C}-(\text{CH}_2)_6-\overset{\text{O}}{\parallel}{\text{C}}-$	2.2

The reaction of acid chlorides with cellulose in LiCl/DMAc is facile, especially in the presence of tertiary amines. Table 3 above lists a representative number of cellulose esters produced from their respective acid chlorides.

Reagents other than acid chlorides have been utilized for cellulose esterification. For example, acetic anhydride was utilized to prepare cellulose acetate with DS = 2.2-2.6 (E. Khalik, L. Gal'braith, N. Ilieva, S. Meerson, and Z. Rogovin, *Chem Abs.*, 79 6797w (1973). Similar values (DS = 2.0-2.6) were obtained by utilizing acetic anhydride with pyridine [H. Yabune and M. Uchida, *Chem Abs.*, 98, 12798e (1983)]. Lower values (DS = 1.3) were obtained with H₂SO₄/acetic acid anhydride [Daicel Chemical Ind., Ltd, *Chem Abs.*, 100, 87151e (1984)].

A very common cellulose ester is cellulose trifluoroacetate CTFA. A convenient synthetic method for cellulose trifluoroacetic acid and trifluoroacetic anhydride (33% v/v) at room temperature for 4 hrs and subsequent treatment of the isolated crude polymer at 150°C and 80 pa for 40 min. The preparation of CTFA with DS values up to 2.1 requires the addition of chloroform and 16 hours reaction time. These cellulose trifluoroacetates are soluble in dimethyl sulfoxide, N, N-dimethyl formamide, pyridine, and tetrahydrofuran and thermostable up to 250°C. ¹³C-NMR studies show a complete trifluoroacylation of the primary hydroxy groups of the cellulose.

Acylation with organic acids as well as isocyanates under homogeneous conditions leads to esterification of the free OH groups only [D. Klemm, Th. Heinze, A. Stern, T. Liebert, *Macromol. Symp.*, 99, 129, (1995)].

1.4. APPLICATIONS OF CELLULOSE AND ITS DERIVATIVES

1.4.1. Uses of cellulose (bagasse)

1.4.1.1. Production of Paper Pulp from Sugar Mill Bagasse

Cellulose derivatives have found wide applications in industries but cellulose itself is underused. Cellulose, from either wood or bagasse, can be used in the production of paper pulp for commercial uses. Paper pulp from wood is already being produced on a commercial basis (Atchison, *Paper Trade Journal*, 1952). Bagasse, a major by-product of the sugar industry, is mostly used for energy production. Use of bagasse for the production of wood pulp could be an alternative way of making profitable use of this by-

product. The major problems encountered in the processing of bagasse for the production of paper pulp are:

- difficulties of extracting residual sugars from bagasse
- difficulties of separating the fibrous material from the soft pith with which it is intimately associated.

1.4.1.2. Production of newsprint paper from bagasse

Krüger *et al.* (US Pat 4,260,452, 1981) first reported the production of newspaper print from 100% bagasse. The process consists of the removal of about 65% of the pith content of bagasse followed by wet bulk storing in the presence of an inorganic (metal carbonate or phosphate) and organic preservative (lactic acid/sodium lactate), then the wet depithing and pulping (sulfite process) and lastly washing, cleaning and dewatering.

1.4.2. Uses of cellulose derivatives

Cellulose derivatives have found a wide range of applications in various industries. Some are given below:

- Textiles: use of natural cellulose fibres (cotton) and artificial cellulose fibres (viscose rayon).
- Food industry: as thickeners, binders
- Pharmaceuticals: use of cellulose as a matrix or excipient in drug formulation.
- Construction materials: in manufacture of hardboard, fibreboard, composite board (combination of epoxy and bagasse).
- Surface coatings: use of synthetic cellulose resins (cellulose esters and ethers). Nitrocellulose accounts for 80% of cellulosic resins in coatings.
- Paper production: cellulose pulp from sugar-cane bagasse.
- Degradable materials (e.g. bottles): hydroxypropylcellulose sandwiched between water-insoluble films.

1.5. CONCLUSION

Although a huge amount of work has been carried out with cellulose and its derivatisation, there are still problems in cellulose functionalisation and dissolution that require research efforts. The research for new and better-adapted routes of cellulose activation prior to chemical processing needs close consideration to meet present ecological and economic requirements. Currently, more and more attention is being given to the enzymatically catalyzed regioselective functionalisation (esterification, etherification) of cellulose as already experimentally realized by the lipase-catalysed acylation of low molar mass saccharides. Concerning the chemical modification of cellulose by polymer analogous reactions, the regioselective introduction of two or three different groups and the search for new protective groups are promising goals of future experimental studies.

CHAPTER 2

Results and Discussion

2. DERIVATISATION OF CELLULOSE INTO CELLULOSE ETHERS AND ESTERS

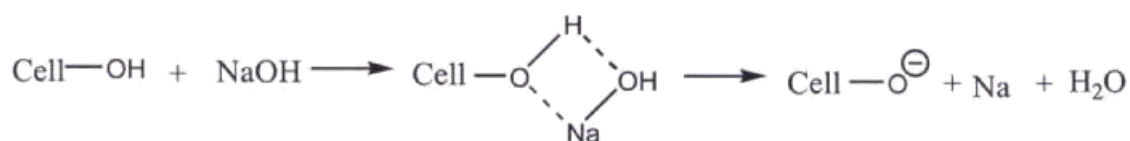
In the first part, the etherification of cellulose in heterogeneous conditions is presented and analysed.

The second part deals with the esterification of cellulose with acids in the presence of dehydrating agent and by reacting with acid chlorides.

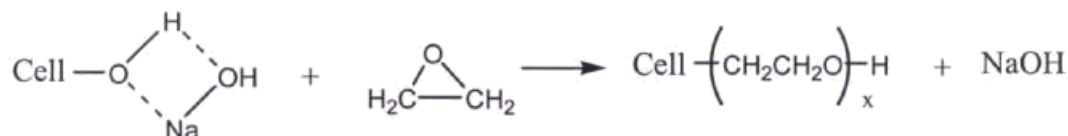
Lastly, the reactions of cellulose with cyclic esters, mainly D,L-lactide, are discussed.

2.1 CELLULOSE ETHERS

Cellulose ethers are typically prepared by the reaction of alkali cellulose with alkyl halides or epoxides (Schemes 5 and 6).



Scheme 5



Scheme 6

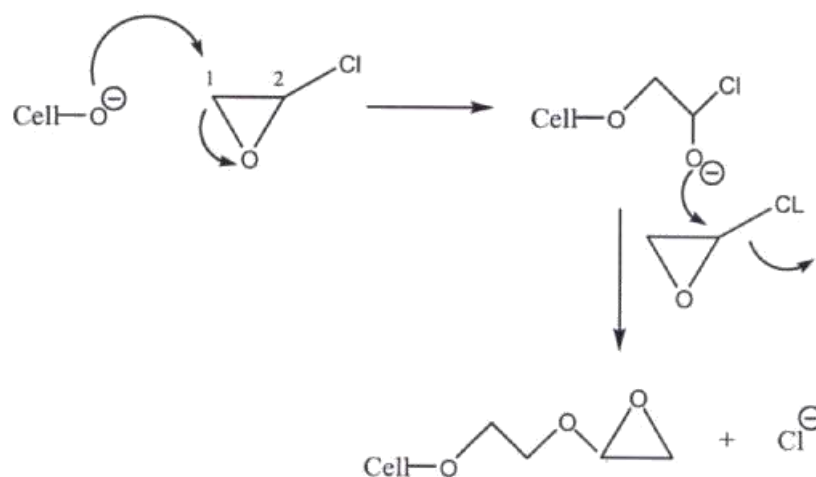
Since most typical bases (NaOH, KOH) are insoluble in LiCl/DMAc, it is difficult to obtain alkali cellulose to initiate the reaction. Efforts to synthesis cellulose ethers in the absence of base have been unsuccessful. Despite these difficulties, a number of cellulose ether derivatives have been prepared under heterogeneous conditions. The reactions are typically conducted by reacting cellulose with a 3 to 5 molar excess of reagent. A base, usually KOH or NaOH powder, is slurried in the reaction mixture at elevated temperatures (60-80°C) for 48-72 hours. Degrees of substitution are low¹.

Blasutto *et al.* (1995) reported the preparation and analysis of 20 derivatives obtained by reacting cellulose with alkyl halides and 1,2-epoxyalkanes at low temperatures and in the presence of swelling agents. The alkylating reagents were 1-bromo-, 1-iodo-, or 1,2-epoxy-derivatives of alkanes. The results showed that cellulose ether derivatives of low DS were obtained. There is a strong dependence of DS upon reaction time, but the kinetics is complex. The rate of substitution varied for the different reagents used. Smaller alkyl groups substituted more readily and alkyl iodide were found to be excellent alkylating agents. The ethers obtained are described as hydrophobic, those with $DS > 0.2$ floated on water and swelled up in organic solvents, in which a few of them partly dissolved².

Further studies were carried out by Hirrien *et al.* (1996) on the synthesis of cellulose ether, namely methyl cellulose, by homogeneous reaction using DMAc/LiCl as solvent, a dimethyl sodium solution as activator and iodomethane as alkylating reagent. Methyl cellulose of various DS were prepared under different experimental conditions; highest DS values were achieved at longer reaction time and using higher concentrations of base, NaH. All the methyl celluloses were soluble in water. Some evidences also showed that the range of DS values of water-soluble methyl cellulose depended strongly on reaction conditions³.

2.1.1 Reaction of cellulose with epichlorohydrin

In this report, we aimed at the synthesis of cellulose ether using epichlorohydrin, using different procedures, in both homogeneous and heterogeneous conditions. ECH has two sites (C1 and C2) where reaction with alkaline cellulose can occur. Scheme 7 shows one possible reaction of cellulose with ECH.



Scheme 7

Typically, under heterogeneous conditions, cellulose was slurried in a mixture of an organic solvent, DMSO and a base NaOH, for a period of time, at room temperature and then, ECH was added to this mixture. The reactions were carried out at room temperature to avoid the degradation of cellulose in the alkaline medium.

Etherification was also carried out in homogeneous conditions, such procedures ensuring a more uniform distribution of the substituents due to a greater accessibility of the –OH sites. The reaction of cellulose in LiCl/DMAc with ECH, using NaH as base was carried out. The highly reactive dimethyl sodium was used. Here the base was stirred with DMSO at 60°C for one hour and this mixture was added to cellulose in LiCl/DMAc and stirred overnight. The epoxide was then reacted with the alkali cellulose, the reaction was carried out at RT for 48 hours.

2.1.1.1. Results of cellulose etherification

The results of cellulose reaction with epichlorohydrin (ECH) with the different conditions of synthesis are summarized in Table 4 below. The different methods of reactions used are given in the experimental section.

Table 4: Conditions of synthesis and results of cellulose etherification with ECH

Sample code	Method used	Base (mol)	ECH (mol)	Mass of product/g of cellulose used
CE B1	B1	0.055	0.01	0.76
CE B2	B2	0.054	0.01	0.69
CE 02	C	0.030	0.05	0.83
SM 09	C	0.030	0.05	0.81

The solubility of the derivatives was carried out in different solvents: DMSO, DMAc, methanol and chloroform.

All the ethers were insoluble in the organic solvents, only a slight swelling in DMSO was observed for SM 09. Since the derivatives were insoluble in the conventional organic solvents, no NMR spectroscopy was carried out.

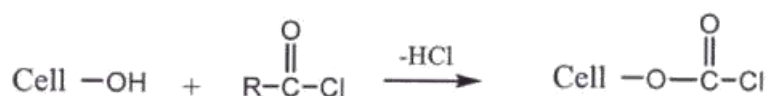
The samples were analysed by IR spectroscopy. The spectra of the derivatives were then compared with that of untreated cellulose (Annexe 3 and 4). The spectra of the derivative were almost similar to that of cellulose, no additional bands could be seen.

It is hard to substitute cellulose with large alkyl groups and hence the DS of the derivatives synthesis were very low, too low to impart solubility in the organic solvents tested.

The conditions of the heterogeneous reactions were to probably too mild and NaOH as a base was not effective to deprotonate cellulose. The reaction carried out in homogeneous condition using dimethyl sodium as activator lead to a derivative (SM 09) which swells in DMSO. Such a reaction could be pursued using higher concentrations of NaH in DMSO, for more effective activation of cellulose. Longer reaction time could lead to derivatives with higher DS.

2.2. CELLULOSE ESTERS

Cellulose undergoes esterification with acids in the presence of a dehydrating agent or by reaction with acid chlorides. A typical reaction pathway is shown in Scheme 8.



Scheme 8

The reaction of acid chlorides with cellulose is carried out in DMAc/LiCl, in the presence of a base, usually a tertiary amine. Other reagents have also been used for cellulose esterifications. Acetic anhydride was used to prepare cellulose acetate. Cyclic anhydride have also been utilised. Cellulose monoesters have been prepared from maleic, succinic, and phthalic anhydride in the presence of potassium acetate at 100°C.

Other ring opening reactions have also yielded cellulose esters. The reaction of lactide with cellulose proceeds at 75°C in the presence of TEA to yield cellulose 2-(2-hydroxyl-1-oxopropoxy) propanoate with DS = 1.4 in 1.5 hours. The product is soluble in water, DMSO, DMAc and NMP. The ring opening of ϵ -caprolactone at 80°C in the presence of TEA results in the formation of cellulose-6-hydroxycaproate, which is soluble in DMSO but water-insoluble.

The esterification of cellulose in LiCl/DMAc by using a dehydrating agent has also been reported. Cellulose acetate was prepared using acetic acid, dimethylaminopyridine (DMAP),

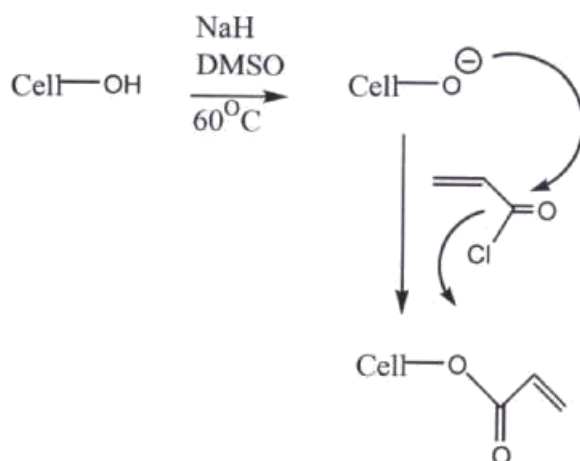
and dicyclohexylcarbodiimide (DCC)⁴. More recently, Zhang *et al.* (1997) have reported acylations reactions of cellulose with a series of unsaturated carboxylic acids or their respective anhydrides including crotonic acid, (CRA), methacrylic acid (MMA), vinyl acetic acid (VAA), fumaric acid monoethyl ester (FAME) and cinnamic acid (CINA) in LiCl/DMAc homogeneous solutions. The acylations reactions were conducted at room temperature using DCC as a condensation agent and DMAP as catalyst. The acylated cellulose derivative, obtained from CRA, MMA, or their anhydrides exhibit poor solubility in organic solvents. However, acylation with VAA, FAME and CINA is facile with derivatives readily soluble in DMSO. These derivatives were characterised with FTIR and ¹H NMR spectroscopy and DS calculated⁴.

2.2.1. REACTION OF CELLULOSE WITH ACIDS AND ACID DERIVATIVES

The esterification of cellulose was carried out in LiCl/DMAc homogeneous solutions with the following acids and acid derivatives: methacrylic acid (MMA), methacryloyl chloride (MMACl), lactic acid (LAc) and oligolactide (OL). MMA and MMACl are unsaturated acid and acid chloride respectively. The oligolactides were synthesised using lactic acid and the molar masses were determined by ¹H NMR spectroscopy.

2.2.1.1. Reaction of cellulose with methacryloyl chloride

Cellulose-methacryloyl chloride derivative was synthesised under homogeneous conditions, using LiCl/DMAc as solvent and dimethyl sodium solution (NaH in DMSO) as activator (Scheme 9). First, NaH was stirred in DMSO at 60°C for one hour. The cooled mixture was added to cellulose in LiCl/DMAc solution and stirred overnight. MMACl was then added and the reaction was carried out under different conditions of time and temperature.



Scheme 9

The results obtained for the reaction of cellulose in LiCl/DMAc with methacryloyl chloride are summarised in Table 5. The different conditions of the reactions are also reported.

Table 5: Conditions of synthesis and results of reactions of cellulose with methacryloyl chloride using NaH as base

Sample code	NaH (mol)	MMACl (mol)	Temp (°C), time (h)	Mass of product/g of cellulose
CE 06	0.042	0.021	RT, 48	0.87
CE 015	0.050	0.050	40, 48	0.78
CE 033	0.10	0.050	60, 120	0.83

The reaction was first carried out at room temperature, methacryloyl chloride being a reactive reagent and NaH, a powerful base. As shown on the table, the molar ration of NaH:MMACl is 2:1. The product, CE 06, obtained was found to be insoluble in the common organic solvents. IR spectroscopy (Annexe 4) showed some modification in the structure of the initial product, cellulose. A slight peak appeared in the region 1700 cm⁻¹ due to the presence of carbonyl group¹. A prominent band appears at 1662 cm⁻¹ due to the presence of C-C double bond. In cellulose this band is short. But the DS of the product is too low to impart any solubility in the usual organic solvents.

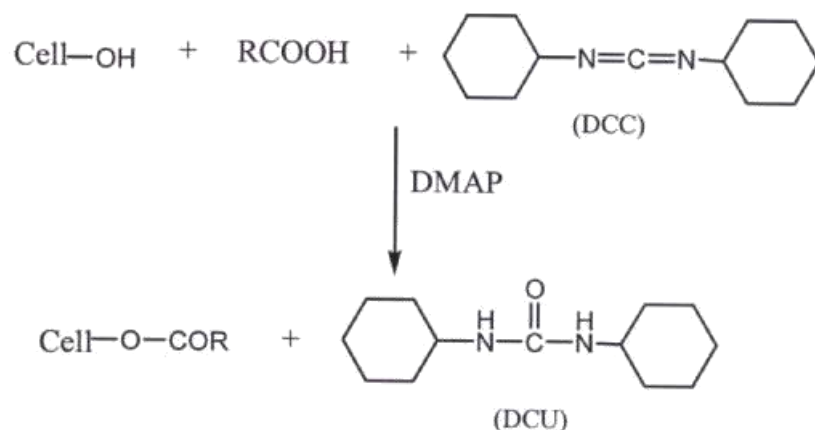
The reaction was carried out using a molar ratio NaH : MMACl of 1:1 at 40°C for 48 hours. Under these conditions, IR spectroscopic analysis (Annexe 5) showed that a higher proportion of hydroxyl groups of cellulose are substituted by the acid chloride. A medium band due to

carbonyl stretching appears at 1720 cm^{-1} . But the DS of CE 015 is still too low and it is insoluble in organic solvents. However a slight swelling in DMSO is observed.

To maximise the reaction of cellulose with MMACl, the next synthesis is carried under more drastic conditions. The molar ratio of NaH : MMACl is 2:1, the reaction is carried out at 60°C for 120 hours. The IR spectrum of the cellulose-acid derivative (Annexe 6) shows a peak at 1718 cm^{-1} , indicating the presence of carbonyl groups. But the derivative is insoluble in DMSO, indicating that the degree of substitution of methacryloyl chloride on the cellulose is low, not sufficient to impart solubility.

2.2.1.2. Reaction of cellulose with acids using a dehydrating agent

The esterification of cellulose was carried out with acid and acid derivatives in LiCl/DMAc using dicyclohexylcarbodiimide as a dehydrating agent and 4-N,N-dimethylaminopyridine as catalyst. This approach is suitable for the esterification of sterically hindered alcohols.



Scheme 10

2.2.1.3. Reaction of cellulose with methacryloyl chloride using dehydrating agent

Cellulose solutions in LiCl/DMAc were reacted with DCC, DMAP and methacryloyl chloride. The reactions were carried out at room temperatures for 24 hours. Table 6 shows the results obtained.

Table 6: Conditions of synthesis and results of reaction of cellulose with MMACl

Sample code	Molar ratio	Temp (°C), Time (h)	Mass collected per gram of cellulose (g)
CE 02	MMACl (1.0), DCC (1.0), DMAP (0.1)	RT, 24	0.85
CE 023	MMACl (2.0), DCC (1.0), DMAP (0.1)		

Both reactions were carried under similar conditions, except that a higher concentration of reagent MMACl is used for the synthesis of CE 023.

The IR spectra of both products (Annexe 7 and 8) showed the C = O stretching of the ester at 1712 and 1715 cm^{-1} respectively.

This band appears as a slight shoulder. No such band is observed in the IR spectrum of cellulose. Neither derivative is soluble in the organic acid solvents, showing that DS is low. Use of higher temperatures and longer reaction time can lead to an increase in the DS of derivatives.

The IR spectra of CE 020 and CE 023 were compared with those obtained for cellulose-methacryloyl chloride derivatives obtained using dimethyl sodium. Only in the case of CE 015, the band due to the carbonyl stretching was more prominent. The products had the same appearance.

2.2.1.4. Reaction of cellulose with methacrylic acid

Methacrylic acid is less reactive than its derivative, methacryloyl chloride. The cellulose methacrylic acid derivatives were prepared in the presence of DC and DMAP, under varied reaction conditions. The results of these reactions are given in Table 7.

Table 7: Conditions of synthesis and results of reaction of cellulose with MMA

Sample code	Molar ratio	Temp (°C), Time (h)	Mass collected per gram of cellulose (g)
CE 025	MMA (2.0), DCC (1.0), DMAP (0.1)	RT, 24	0.79
CE 026	MMA (2.0), DCC (1.0), DMAP (0.1)	40, 120	0.72
CE 034	MMA (2.0), DCC (1.0), DMAP (0.1)	60, 120	0.84

All the three products were insoluble in the organic solvents tested.

The IR spectra of the products (Annexe 9, 10, 11) showed the slight shoulder in the region $1710\text{--}1720\text{ cm}^{-1}$ for the carbonyl stretching of the ester. The medium absorption band in the region $1635\text{--}1645\text{ cm}^{-1}$ is characteristic of $\text{C}=\text{C}$ stretching of alkenyl groups.

Increasing the reaction time and temperature did not lead to derivatives with DS high enough to impart insolubility.

2.2.1.5. Reaction of cellulose with oligo-D,L-lactide (OL)

oligolactide samples were prepared in the laboratory using microwaves from lactic acid. The molar masses were determined by ^1H NMR spectroscopy.

The results of the reaction using oligolactide of molar mass 1512 are presented in Table 8.

The reaction of cellulose using oligolactide of lower molar mass is more facile, as shorter oligolactide chains can react more easily with the hydroxyl functionality of cellulose.

Table 8: Conditions of synthesis and results of reaction of cellulose with OL

Sample code	Molar ratio	Temp (°C), Time (h)	Mass collected per gram of cellulose (g)
CE 014	OL (1.0), DCC (1.0), DMAP (1.0)	RT, 24	0.701
CE 016	OL (1.0), DCC (1.0), DMAP (0.1)	RT, 48	0.670
CE 028	OL (1.0), DCC (1.0), DMAP (0.1)	60, 120	0.513

The reaction carried out with the oligolactide of molar mass 1224 at room temperature for 24 hours gave a product insoluble in the organic solvents. The IR spectra (Annexe 12) showed the presence of carbonyl group of the ester, a slight band is observed at 1751 cm^{-1} . Increasing the reaction time yields a product that is still insoluble.

The reaction with the oligolactide was next carried out at 60°C for 120 hours. The derivative obtained is found to be insoluble in the organic solvents. The $\text{C}=\text{O}$ stretching (Annexe 14) of the ester can be observed in the IR spectra at 1743 cm^{-1} .

The insolubility of the derivatives is due to their low DS. The oligo-D,L-lactides consist of random coiled chains and hence the end groups functionality are now easily accessible for reaction with the cellulose hydroxyl functionalities.

2.2.1.6. Reaction of cellulose with lactic acid (LAc)

The results obtained for the reaction of lactic acid with cellulose is given in Table 9.

Table 9: Conditions of synthesis and results of reaction of cellulose with LAc

Sample code	Molar ratio	Temp ($^{\circ}\text{C}$), Time (h)	Mass collected per gram of cellulose (g)
CE 024	LAc (1.0), DCC (1.0), DMAP (0.1)	60, 120	0.800
CE 031	LAc (2.0), DCC (1.0), DMAP (1.0)	60, 120	0.85

The lactic acid-cellulose derivatives were both insoluble in the solvents.

The conditions of the reactions were drastic to promote the substitution of hydroxyl groups of cellulose. The IR spectra of cellulose-lactic acid derivatives (Annexe 15 and 16) showed a significant difference compared to that of cellulose. The broad, strong band in the region $3200\text{-}3600\text{ cm}^{-1}$ due to O-H stretching of hydroxyl bonds, have decreased to a large extent, indicating that a proportion of the hydroxyl functionalities have reacted with the lactic acid. Carbonyl stretching in the region 1700 cm^{-1} indicate that esterification has occurred. In the case of CE 024, this band had merged with the neighbouring one of the alkenyl group appearing at 1627 cm^{-1} .

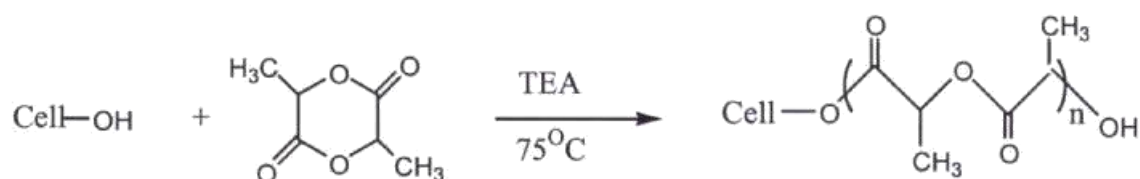
2.2.1.7. Reaction of cellulose with cyclic esters

The ring opening reactions was carried out using D,L-lactide, ϵ -caprolactone and δ -gluconolactone with cellulose in the presence of a base, triethylamine, yielding cellulose esters. The reactions were carried out under homogeneous conditions using cellulose solutions in DMAc/LiCl.

The cyclic esters used were miscible with the cellulose solutions.

2.2.1.8. Reaction of cellulose with D,L-lactide

The reaction of lactide (3,6-dimethyl-1,4-dioxane-2,5-one) with cellulose proceeds at 75°C in the presence of TEA to yield cellulose-lactide ester. The reactions were carried out for 120 hours. It is assumed that the molar mass, M_n , of cellulose used is 10 000.



Scheme 11

The reactions were carried using varying amounts of D,L-lactide.

The results of the reactions are given in Table 10.

Table 10: Conditions of synthesis and results of reaction of D,L-lactide with cellulose

Sample code	Molar ratio Cell-OH : D,L,lactide
CE 037	1:70
CE 041	1:140
CE 042	1:35

The products were obtained by precipitating the cellulose/DMAc/Lactide solution in acetate to remove DMAc. The polymer was washed twice in ethyl acetate for further purification and

was then dried under vacuum at 50°C for 48 hours. The product was not completely dried as DMAc has a high boiling point and cannot be easily extracted from the polymer.

It was observed that the final mixture in DMAc/LiCl containing the cellulose ester was perfectly miscible with DMSO. But as the polymer was dried, dissolution in DMSO is more difficult.

The ^1H and ^{13}C -NMR of the products obtained were carried out in DMSO.

The spectra of CE 037 (Annexe 17 and 18) showed the presence of many signals also merge with the DMSO signals. The interpretation of such a spectrum is difficult.

The ^{13}C NMR shows the presence of many signals, indicating the different carbon present in the polymer. A few of these signals indicate the presence of remaining solvent, DMAc, in the polymer. The presence of a signal in the region 169 ppm indicate presence of the carbonyl C of lactide, which usually appears in this region. Two more signals appear in the same region, showing the presence of other carbonyl carbons. One of these can be attributed to the carbonyl C of DMAc.

Not all the carbons present in cellulose appear in the spectrum.

The cellulose derivative was further washed with ethyl acetate to eliminate DMAc then dried under vacuum. The product obtained did not easily dissolve in DMSO. It was left to swell in the solvent overnight, and was then stirred at 50°C to allow maximum dissolution. ^1H and ^{13}C -NMR spectra were run. The ^1H NMR spectra shows an intense signal due to DMSO, while the signals due to the polymer were barely visible. This is due to the slight solubility of the polymer. ^1H spectrum of CE042 (Annexe 19) is also complex, and is of no help in the characterisation of the derivative.

The reactions with gluconolactone and caprolactone was carried out under similar conditions as with D,L-lactide, with the molar ratio of cellulose to cyclic ester being 1:70. The reactions yielded derivatives which were insoluble in DMSO and were hence not characterised.

CHAPTER 3

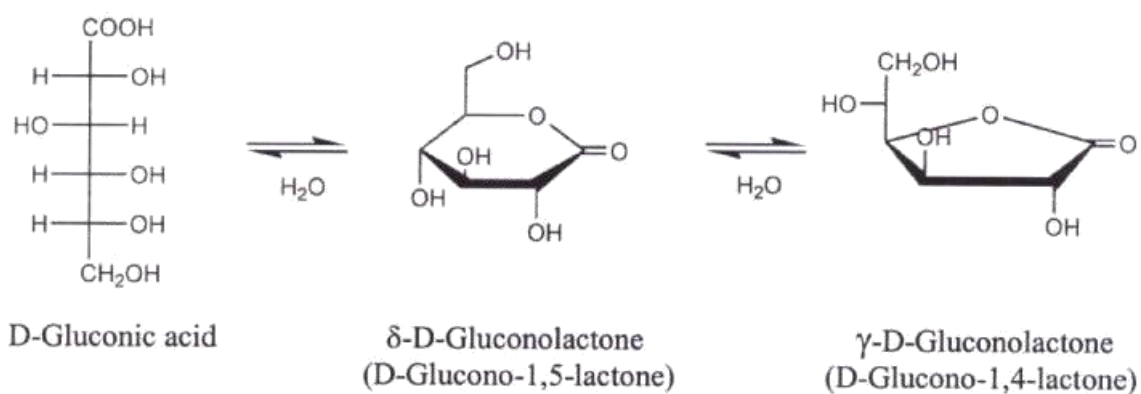
3.0 INTRODUCTION

The ^1H and ^{13}C NMR spectra of gluconolactone are presented in Figure 9 (a, b). When gluconolactone is stirred in water, part of it isomerises into gluconic acid. This is revealed by ^{13}C NMR analysis in Figure 9 (c), which shows the presence of a signal at 176.5 ppm in addition to the carbonyl signal of gluconolactone at 173.4 ppm.

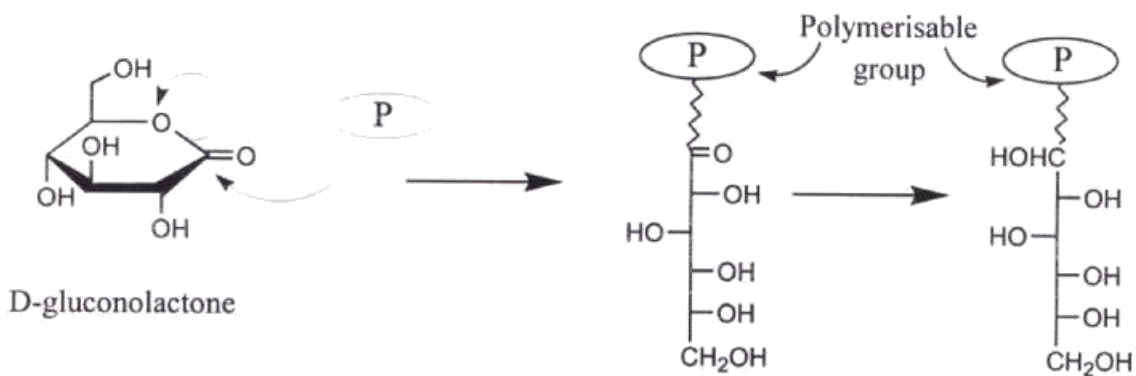
D-Glucose D-Gluconolactone

32

Isomerisation of D-gluconic acid to D-gluconolactone



Scheme 13. Isomerisation of D-Gluconolactone to D-Gluconic acid and γ -D-gluconolactone in water



Scheme 14. Anchoring a polymerizable group on gluconolactone

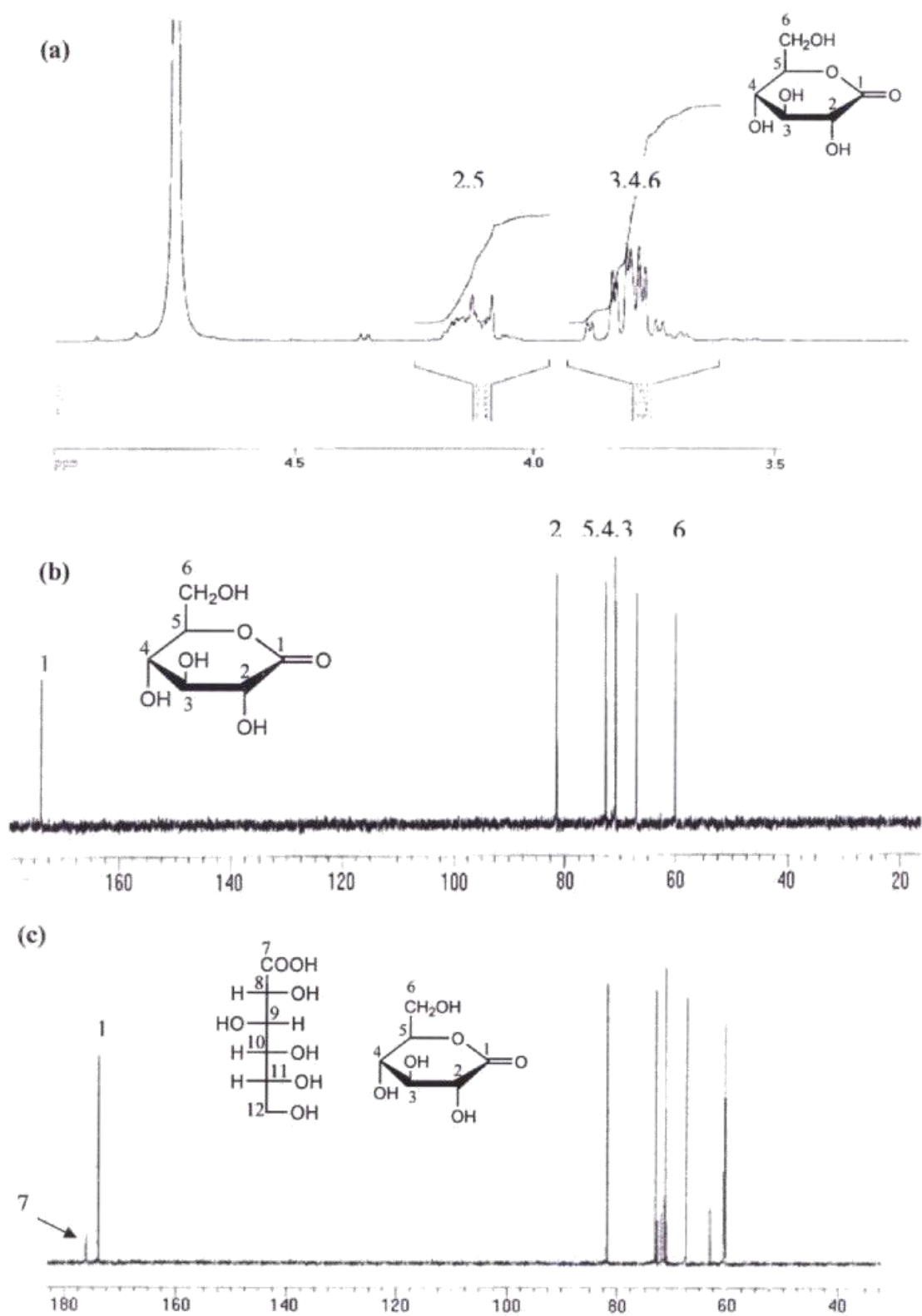
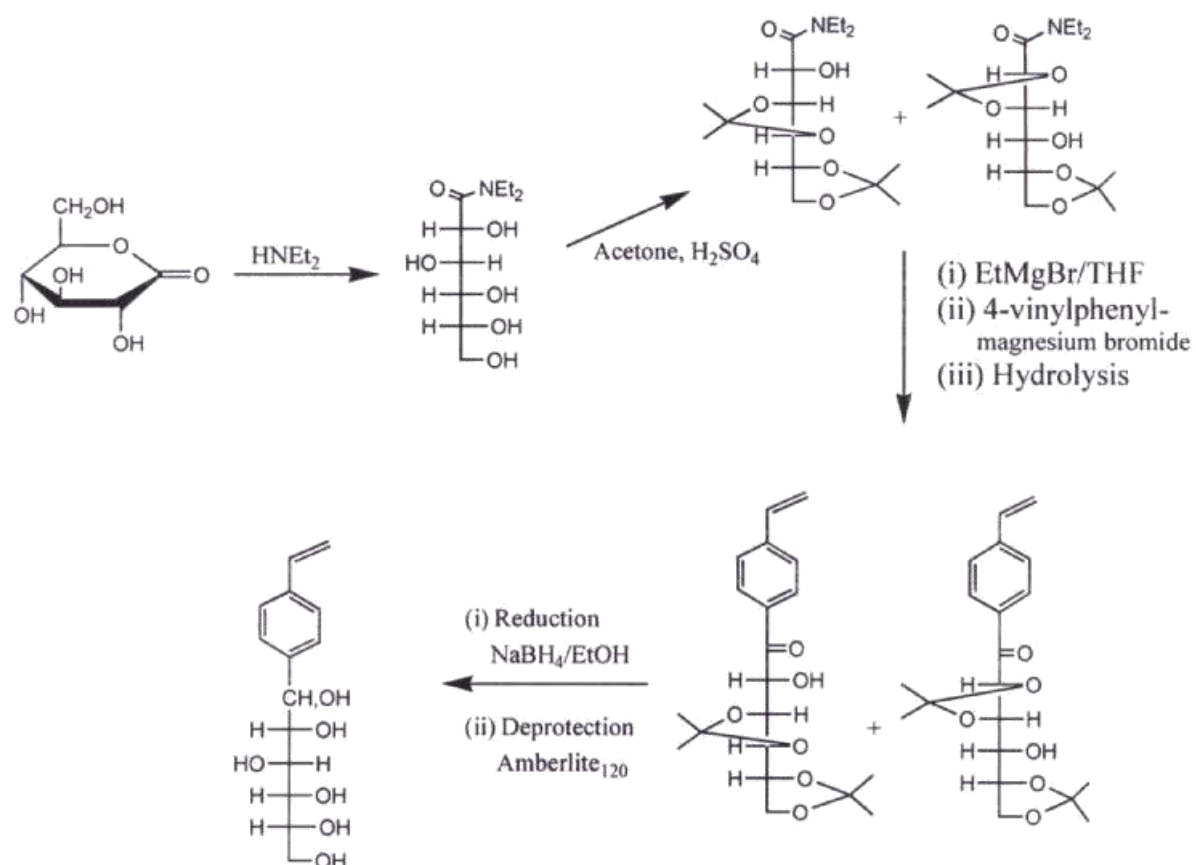


Fig. 9. ^1H and ^{13}C NMR (D_2O) spectra of D-gluconolactone

This chapter will focus on polymers containing sugar units linked to the main chain via C-C linkage. Vinyl sugars containing a C-C linkage were first described by Wulff *et al.* The interesting characteristic of such monomers is that they are quite stable under both acidic and basic conditions. The synthesis of 4-vinylphenyl-D-gluco(D-manno) hexitol is here described. The homopolymerization behaviour of this monomer has been examined.

3.1 SYNTHESIS OF 4-VINYLPHENYL-D-GLUCO(D-MANNO)-HEXITOL

Gluconolactone was first reacted with diethylamine followed by protection with acetone to give the 2,3,5,6 and 3,4,5,6-di-O-isopropylidene-D-gluconic acid diethylamide. The isomers were successively reacted with ethylmagnesium bromide and vinylphenylmagnesium bromide in THF under an inert atmosphere to yield a mixture of two 4-vinylphenyl ketone isomers. After reduction of the latter derivatives with NaBH₄ and subsequent deprotection, monomer is obtained in 75 % yield (Scheme 15). HPLC analysis of the product showed the presence of a single signal, thus confirming the very high purity of the monomer (Figure 10). ¹H and ¹³C NMR spectra are also illustrated in Figure 11.



Scheme 15. Synthesis of 4-vinylphenyl-D-gluco(D-manno) hexitol (38)

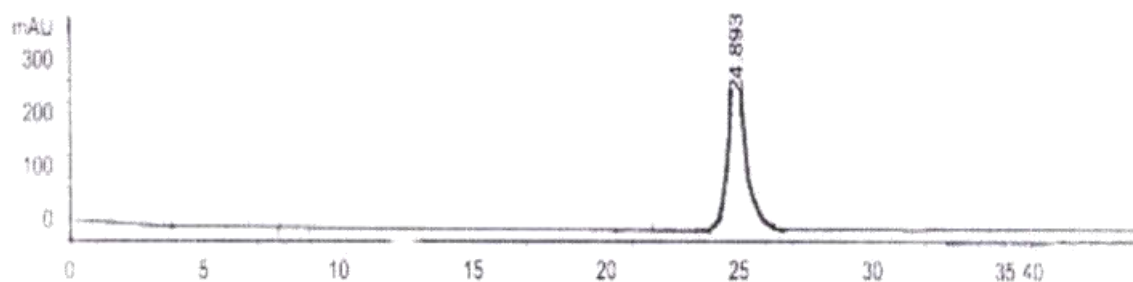


Fig. 10. HPLC of monomer 38 (eluent: acetonitrile-water, UV detector)

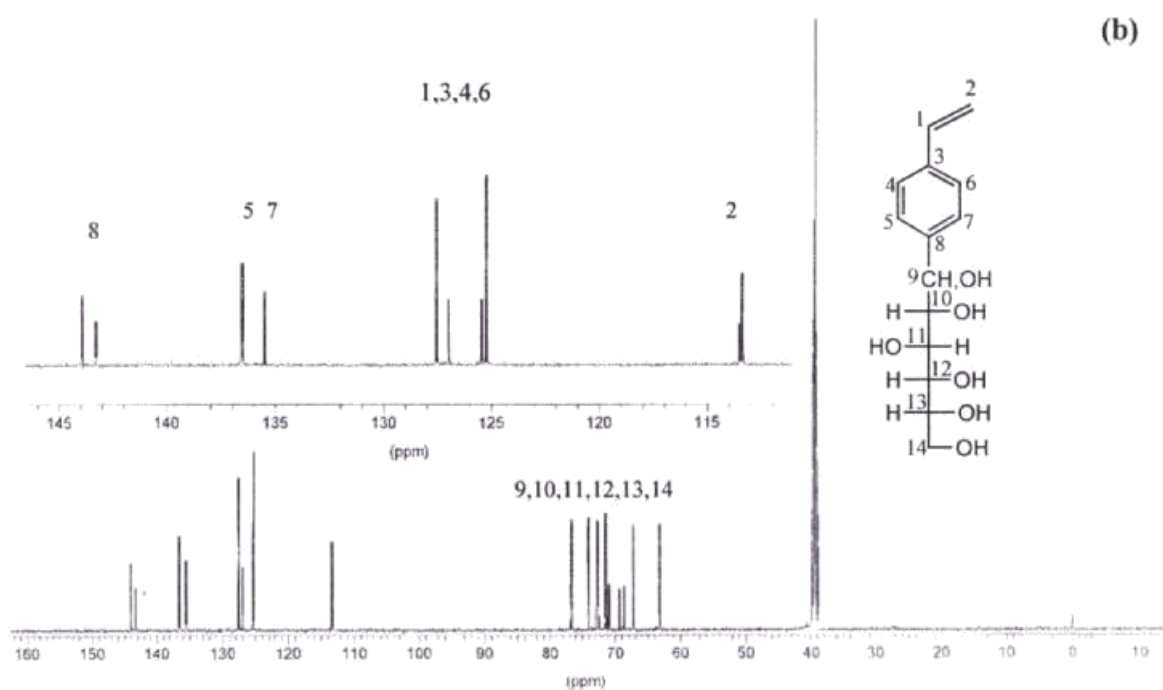
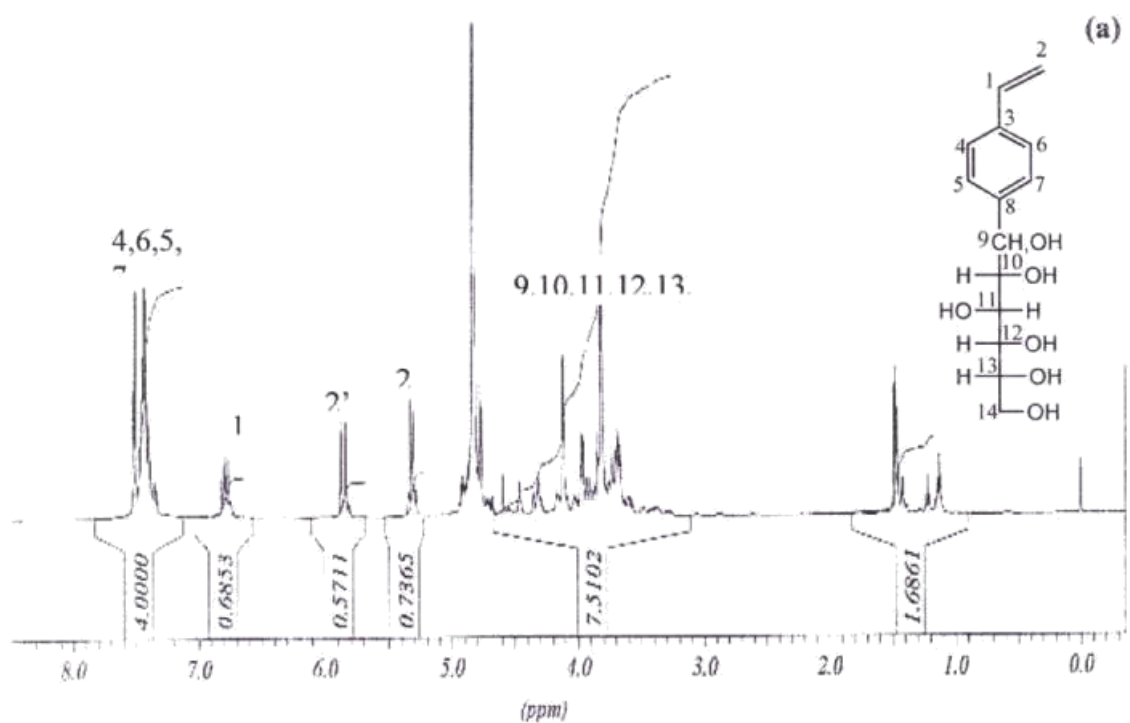
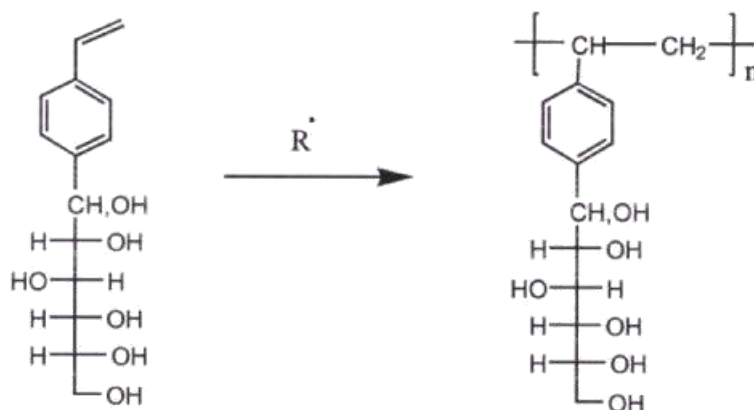


Fig. 11. (a) ^1H (D_2O) & (b) ^{13}C NMR (DMSO-d_6) spectra of 38

The ^1H NMR spectrum indicates clearly the presence of signals corresponding to the styryl (5.0-8.0 ppm) and sugar protons (3.0-4.7 ppm). The ^{13}C NMR spectrum further confirms the formation of the monomer by the presence of signals corresponding to the sugar carbon atoms (60-80 ppm) and those due to the styryl unit (110-150 ppm).

3.2 HOMOPOLYMERIZATION OF MONOMER

The homopolymerization of monomer, which contains free hydroxyl groups, has been examined in both aqueous and organic media, with various free radical initiators such as ammonium persulphate/tetramethylethylenediamine, azobis-(2-amidinopropan) dihydrochloride and 2,2'-azobis(isobutyronitrile) (scheme 16). The latter was added as a solution in acetone since it is insoluble in water.



Scheme 16. Homopolymerization of vinylhexitol

Table 11

Homopolymerization of monomer (38) in the presence of various free radical initiators ([I]=1 mol%; Temp. = 70°C; reaction time = 24 h).

Polymer	Initiator	Solvent	Yield %	M_n^b	M_w^b	M_w/M_n
P1	TMEDA ^a / (NH ₄) ₂ S ₂ O ₈	H ₂ O	78	150,000	185,000	1.2
P2	2,2'- azobis(isobutyronitrile)	H ₂ O	80	200,000	240,000	1.2
P3	Azobis-(2-amidinopropan) dihydrochloride	H ₂ O	75	1,100,000	1,200,000	1.1
P4	2,2'- azobis(isobutyronitrile)	DMF	80	- ^c	- ^c	- ^c

^aTMEDA – N,N,N',N'-tetramethylethylenediamine.

^b M_n and M_w determined by SEC using 0.1 M Na₂SO₄ as eluent.

^cNot determined – bimodal distribution.

The yields of the polymers were calculated after several precipitations in ethanol and drying in vacuo. As can be seen in Table 11, the polymers were obtained in reasonably good yield after 24 h reaction time. It is probable that a fraction of the crude sample consisting of oligomers might have been lost during precipitation in ethanol. SEC analysis of the precipitated polymers were performed using a multi-angle light scattering detector. It was observed that the polymers, prepared in water as solvent, showed monomodal distributions, corresponding to quite high molar masses as indicated in Figure 12. Moreover, the molar mass distribution (M_w/M_n) was remarkably narrow for a conventional radical polymerization. This probably results from the fractionation of the polymer sample during precipitation and it also indicates that transfer reactions are minimized. These results are concordant with those reported previously in the case of 1-(4-vinylphenyl)-D-glucopentitol⁷¹ ($M_n = 380,000$, $M_w/M_n = 1.7$) and methacryloyl sucrose²⁸ ($M_n > 10^6$).

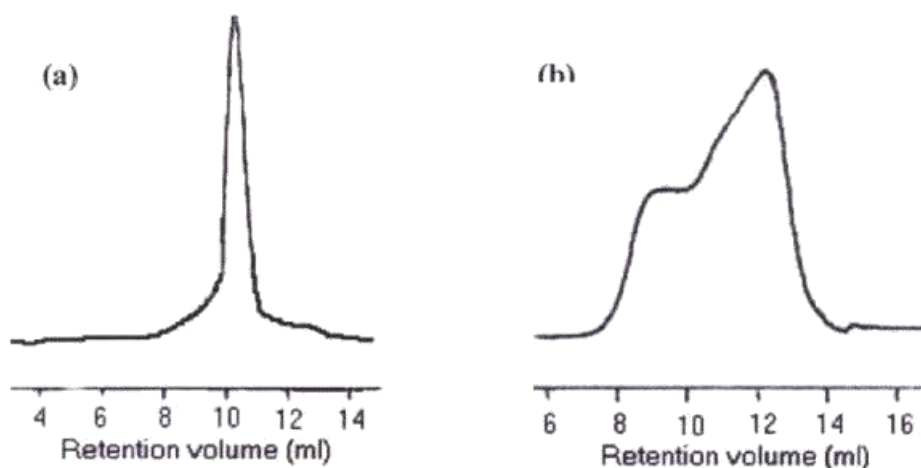


Fig. 12. SEC chromatograms of (a) polymer (P1) obtained in water and (b) polymer (P4) obtained in DMF (eluent – water)

However, when DMF was used as solvent, the SEC chromatogram exhibited a bimodal distribution with a smaller fraction corresponding to high molar masses.

All the polymers, including P3 obtained in the presence of AADPH with a molar mass of about 10^6 , were completely soluble in water. This is in favour of a linear structure and the absence of crosslinked fractions confirms that the monofunctionalization of the sugar derivative was quite effective.

NMR Characterization

The polymer structure was confirmed by ^1H and ^{13}C NMR, as presented in Figure 13. The absence of signals in the ^1H and ^{13}C NMR spectra due to vinyl double bond and the broadening of the signals confirmed the formation of polymers.

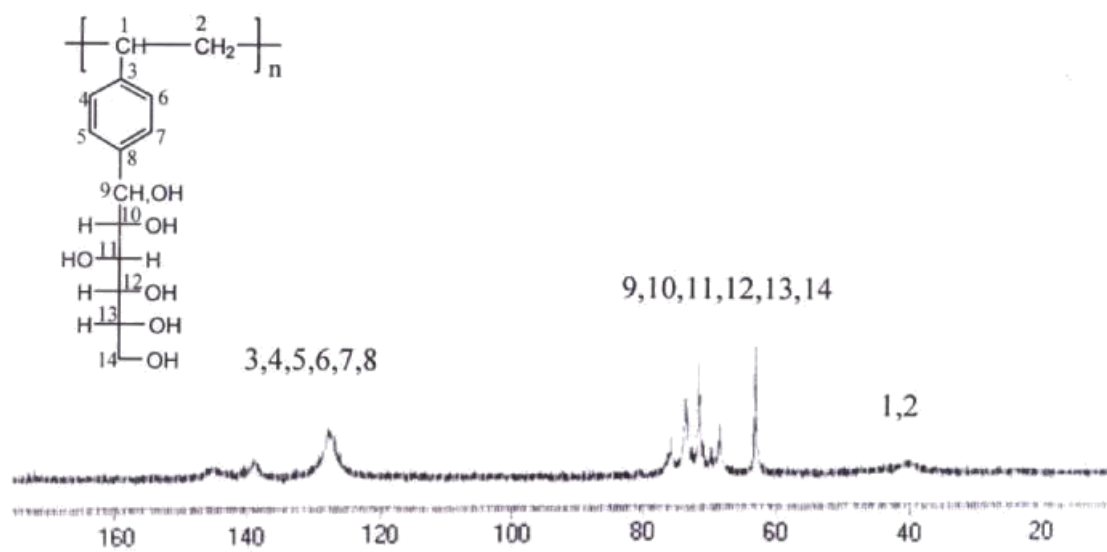
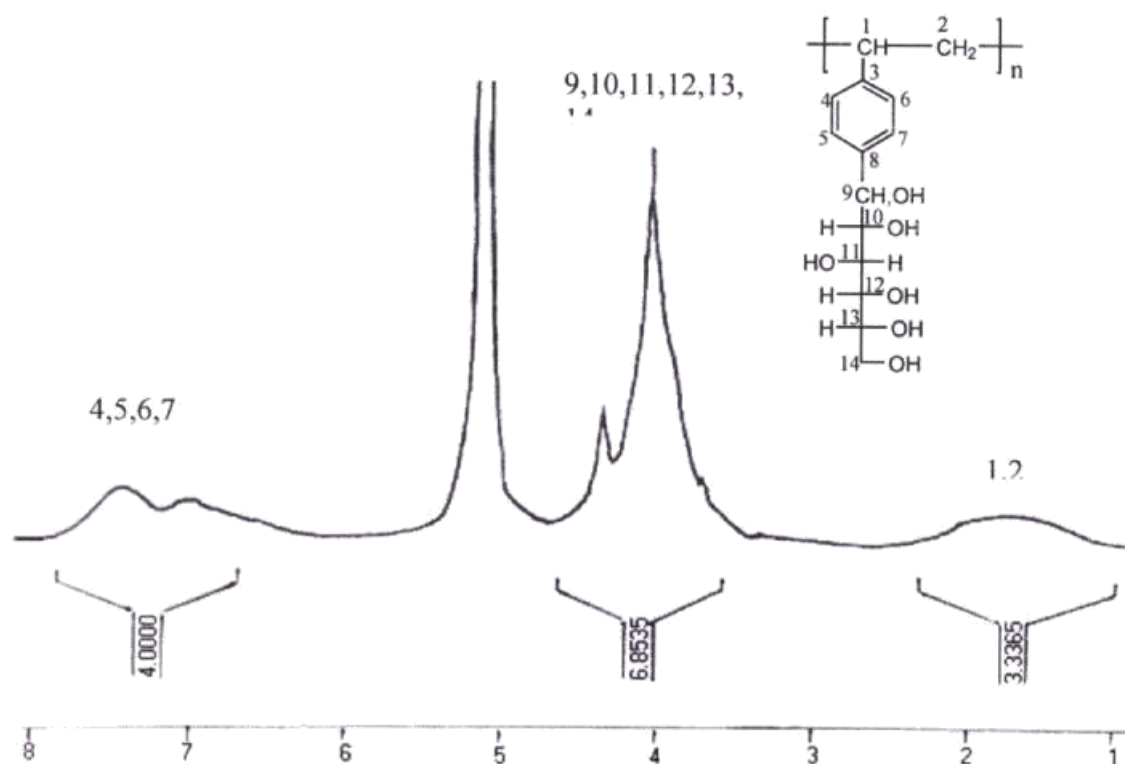


Fig. 13. ¹H and ¹³C NMR (D₂O) spectra of polymer P2

DSC Characterization

The homopolymers were analyzed by differential scanning calorimetry. As shown in Figure 14, the polymer P2 exhibits a glass transition temperature at about 60°C and a melting transition at 144°C. The latter is a sign of an ordered structure and close packing of chains.

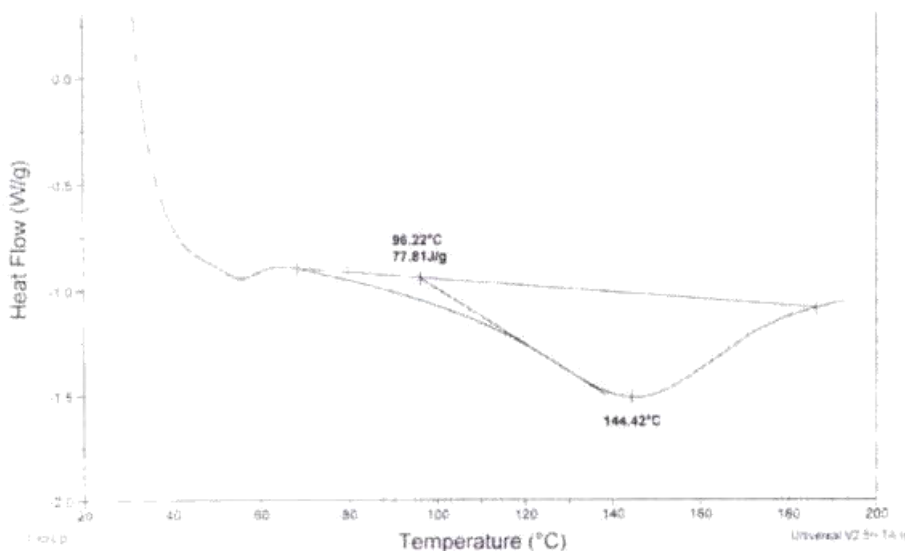


Fig. 14. DSC thermogram of polymer P2

3.3 SYNTHESIS OF AMINOALKYLAMMONIUM METHACRYLATES

The synthesis of gluconamidoalkyl ammonium methacrylates is carried out according to Scheme 17. The first step involves a reaction between methacrylic acid and a diamine, such as 1,2-diaminoethane or 1,5-diaminopentane or 1,8-diaminooctane, in water at room temperature. The experimental conditions are chosen such that the acid-base reaction occurs selectively at only one amino group to give the corresponding aminoalkyl ammonium methacrylate salts (**a-c**). The latter were isolated and their structures were confirmed by ^{13}C NMR. The presence of the carboxylate signal appearing downfield at about 177.5 ppm confirms the existence of a salt. When the reaction is conducted in an

100

Fig. 15. ^1H NMR spectrum of ethyldiammonium methacrylate

Amidation of D-gluconolactone is then achieved *in situ* at ambient temperature with the remaining amino group yielding the water-soluble gluconamidoalkyl ammonium methacrylates (**d-f**). Excellent yields (>90%) were obtained and the compounds present a high degree of purity, as confirmed by HPLC (Figure 16) and NMR (Figures 17, 18, 19) characterization. The presence of signals in ^{13}C NMR spectra at higher field ($\delta_{\text{CONH}} = 174.2$ or 175.5 ppm) confirms the formation of an amide bond, and not an ammonium carboxylate.

It is important to note that amidation of gluconolactone is commonly carried out in organic solvents such as methanol but proves here to be effective also in water. The sequence of addition of the reactants is an important parameter for the amidation to take place. The amide bond formation, under our experimental conditions, suggests that the nucleophilic attack of the amino group onto the lactone is faster than its hydrolysis into gluconic acid and subsequent acid-base reaction. The formation of an ionic bond ($\delta_{\text{COO}^-} = 180.5$ ppm) results upon reaction of (**d**) with gluconic acid in place of gluconolactone. Indeed, reacting first the diamine with gluconolactone does not lead to the formation of the monosubstituted derivative under the above conditions and hence this strategy cannot be envisaged for the synthesis of the gluconamidoalkyl ammonium methacrylates.

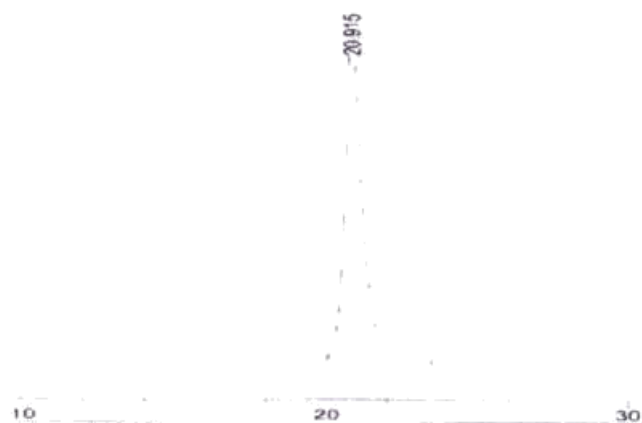
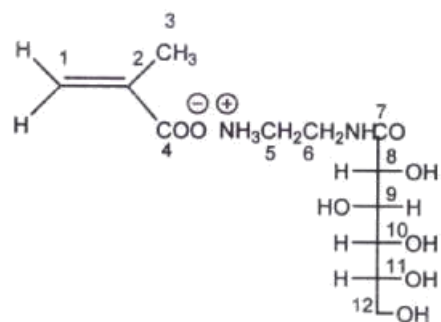
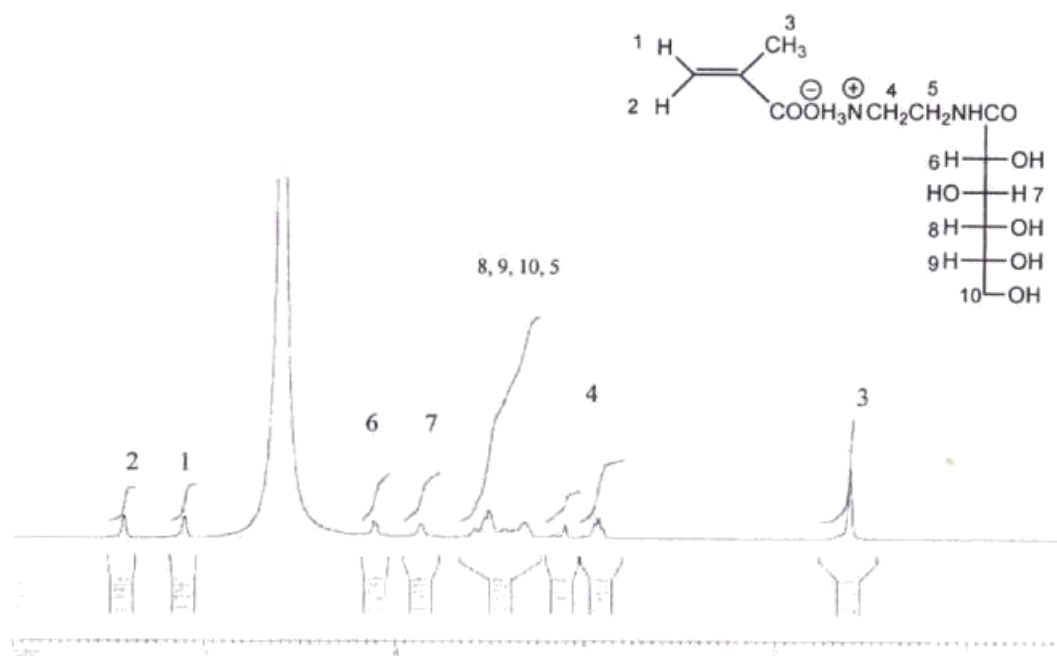


Fig. 16. HPLC of monomer (e)



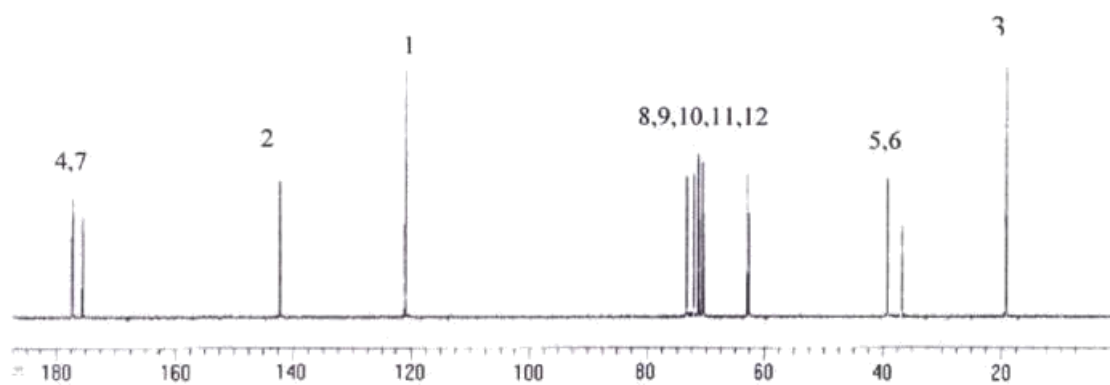


Fig. 17. ^1H and ^{13}C NMR (D_2O) spectra of monomer (d)

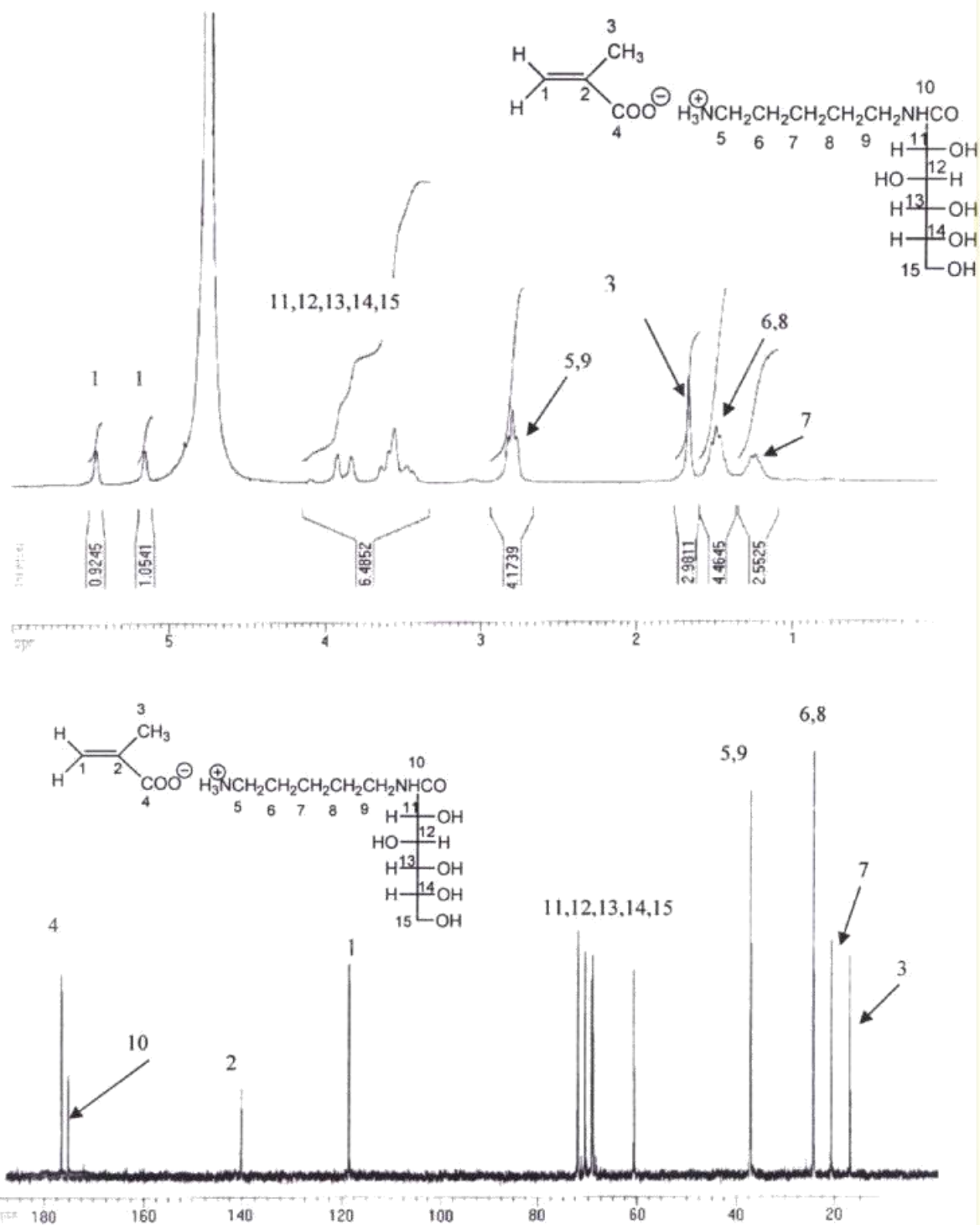


Fig. 18. ¹H and ¹³C NMR (D₂O) spectra of monomer (e)

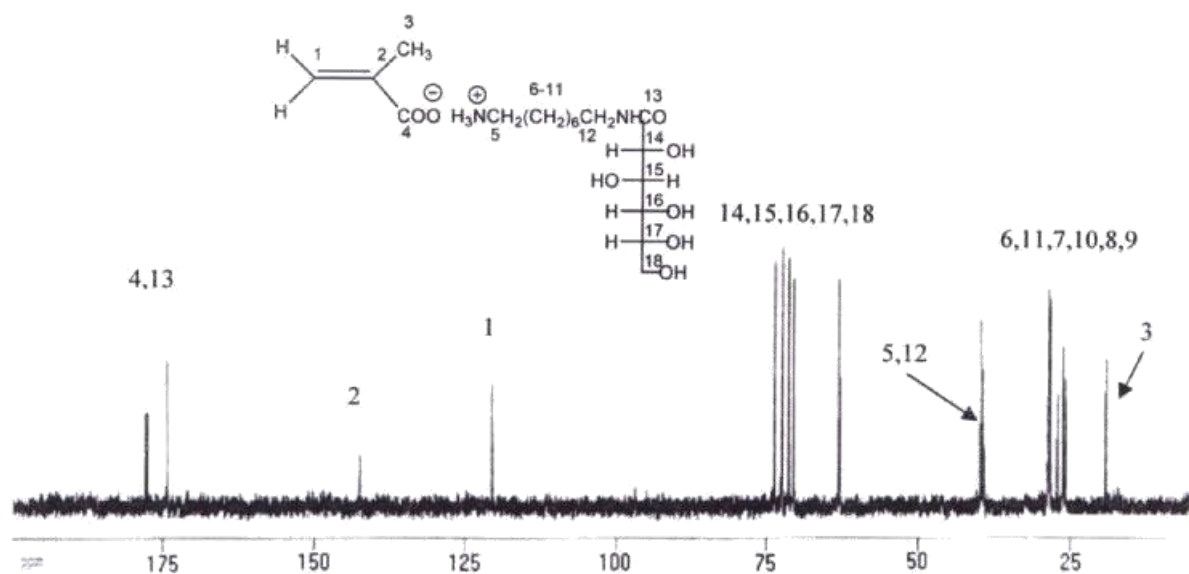
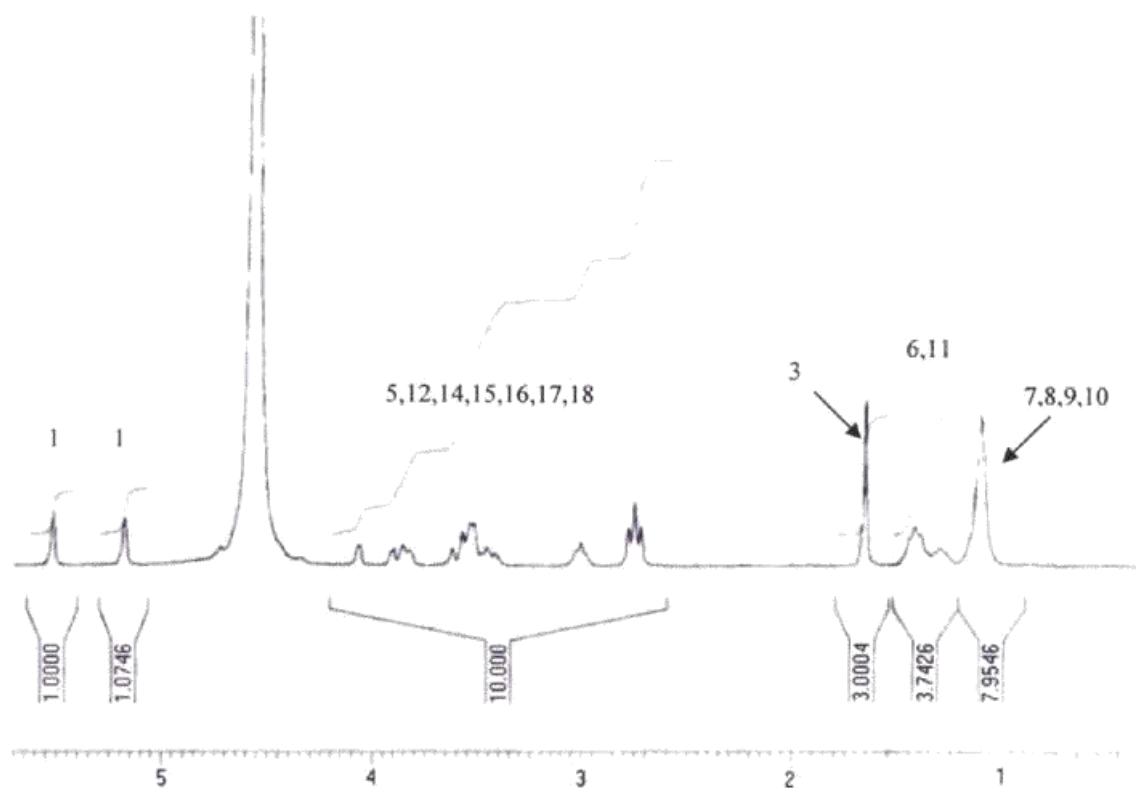
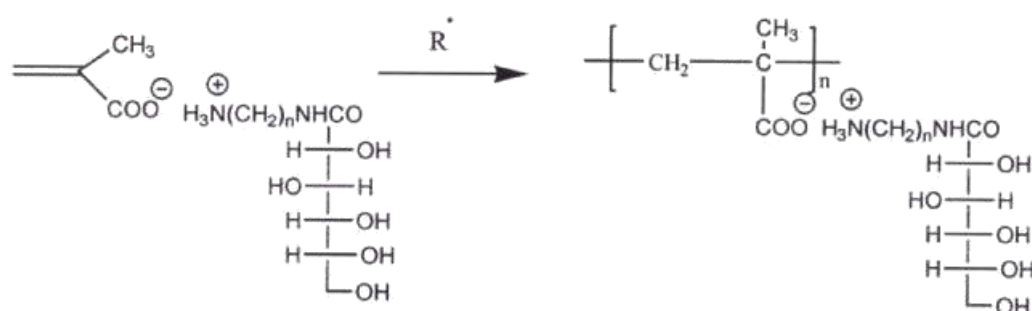


Fig. 19. ^1H and ^{13}C NMR (D_2O) spectra of monomer (f)

3.5 SYNTHESIS AND CHARACTERIZATION OF HOMOPOLYMERS

The homopolymerization of monomers (**d-f**) were carried out in water at 70 °C with free-radical initiators such as 2,2'-azobis-(2-amidinopropan) dihydrochloride and 2,2'-azobis(isobutyronitrile) and at 25 °C with tetramethylethylenediamine (TMEDA)/(NH₄)₂S₂O₈ (scheme 18).



Scheme 18. Homopolymerization of monomers (40b-42b)

Table 12

Homopolymerization of gluconamidoalkyl ammonium methacrylates (**d-f**) using different free-radical initiators in water at 70 °C^a. [M] = 1.45 mol/L; t = 24h

Polymer	Initiator	Initiator (mol-%)	Yield ^{d)} (%)	$\eta_{red}^{c)}$ (dL/g)
P(40b)	TMEDA ^{b)} /(NH ₄) ₂ S ₂ O ₈	1.0	92	0.36
P(40b)	2,2'-azobis(isobutyronitrile)	1.0	90	0.38
P(40b)		1.0	90	0.34
P(40b)		0.75	85	0.66
P(40b)	AAPDH ^{c)}	0.50	78	1.05
P(40b)		0.35	80	1.40
P(40b)		0.25	76	1.82
P(41b)	AAPDH	1.0	92	0.32
P(42b)	AAPDH	1.0	89	0.45

^{a)} Except for TMEDA/(NH₄)₂S₂O₈, for which temperature = 25 °C

^{b)} Tetramethylethylenediamine

^{c)} AAPDH - 2,2'-azobis-(2-amidinopropan) dihydrochloride

^{d)} Calculated after isolation and drying

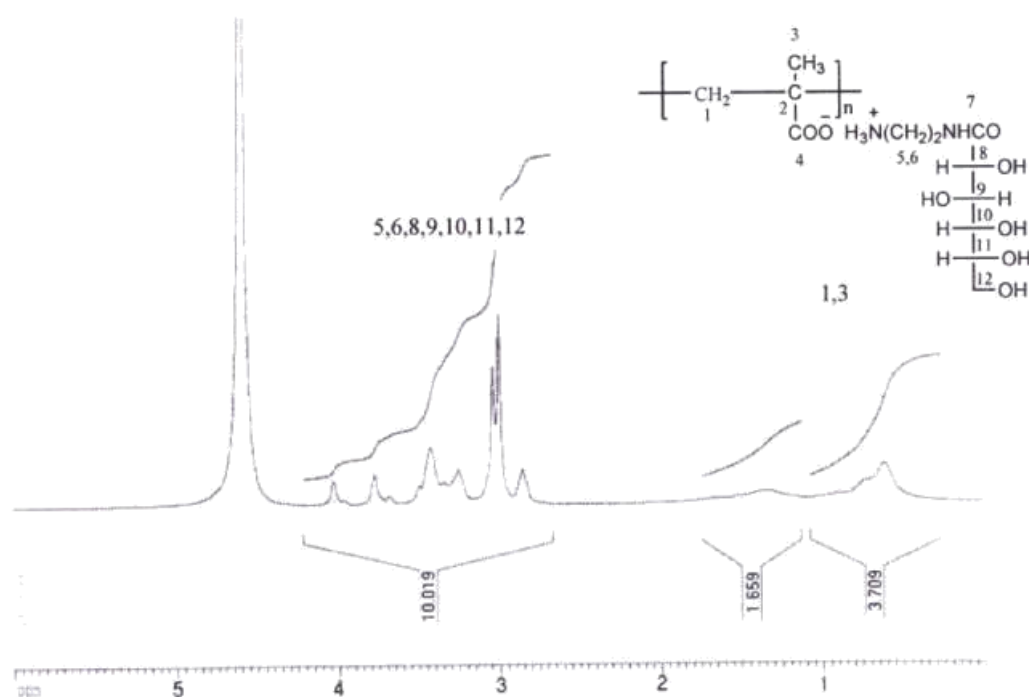
^{e)} Determined in water with a Ubbelohde tube at 25 °C; concentration = 1.0 g/dL

The polymers were isolated after several precipitations in methanol and dried in vacuo.

Homopolymers, in a range of molar masses, were prepared from monomer (**d**) by varying the initiator concentrations in the range 0.25 – 1 mol%. As can be seen in Table 12, the polymers were obtained in good yields. Their reduced viscosities were also determined in aqueous solution using a Ubbelohde tube.

NMR Characterization and Tacticity

All polymers were characterized by ^1H and ^{13}C NMR in D_2O and were found to be consistent with the expected structures, as illustrated by poly(d) in Fig. (20a, b). The signal due to the carboxylate group adjacent to the polymer backbone was broadened and shifted downfield ($\delta = 187$ ppm) in the ^{13}C NMR spectrum compared to that of the monomer ($\delta=177.5$ ppm).



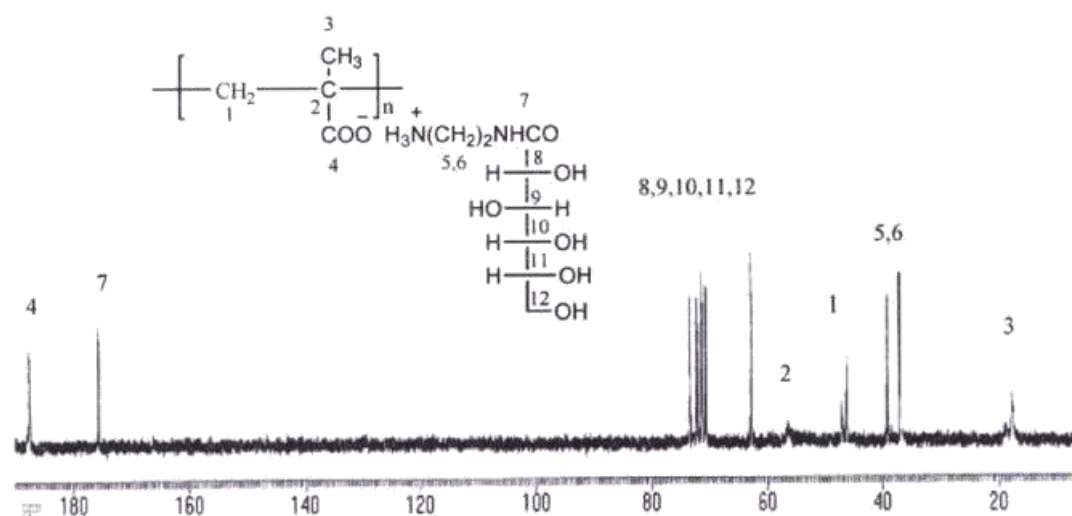


Fig. 20. (a) ^1H and (b) ^{13}C NMR (D_2O) spectra of poly(d)

The stereochemical configuration of monomeric units along the macromolecular chains has been analyzed by ^1H NMR spectroscopy. Figure 21 shows an expansion of signals corresponding to the methyl groups in the range of 0.6-1.1 ppm. The $\alpha\text{-CH}_3$ splits into three peaks, which can be assigned to isotactic- (mm), heterotactic- (mr + rm) and syndiotactic (rr) triads in order of increasing field. Measurements of the intensities of these signals give the relative proportions of triads present. These are listed in Table 13. In all cases, a predominantly syndiotactic structure is obtained, as would have been expected. Moreover, it should be pointed out that no significant difference in syndiotacticity was noted for poly(d) obtained at 70 °C and 25 °C with AAPDH and TMEDA/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ respectively.

Table 13
Relative proportions of triads determined by ^1H NMR for polymers P40-P42

Polymer	rr (%)	rm+mr (%)	mm (%)
P(40a)	62	27	11
P(40b)	68	32	-

P(41a)	61	28	11
P(41b)	64	36	-
P(42a)	66	23	11
P(42b)	63	37	-

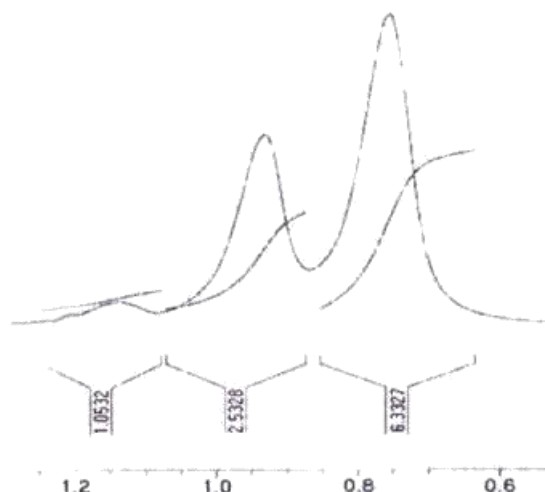


Fig. 21. ^1H NMR spectrum of the methyl groups

Viscosity behaviour

A relative comparison of the dimensions of the polymers prepared under identical conditions was obtained from the measurement of their reduced viscosities in aqueous solution, at a concentration of 1 g/dL (Table 14). Polymer **f** was found to possess a higher reduced viscosity and therefore a higher molar mass than polymers **d** and **e**, in accordance with the kinetic results. Indeed, in the absence of transfer reactions and under constant monomer and initiator concentrations, the kinetic chain length (ν) and the degree of polymerization are directly proportional to the rate constant of propagation.

A more detailed investigation of the viscosity behaviour was obtained by plotting η_{sp}/c against concentration for poly(**c**) and poly(**f**) (see Figure 22). The viscosity plot of poly(methacrylic) acid synthesized under identical conditions is also included for comparison purposes. All polymers exhibit a decrease in viscosity with increasing concentration, thus confirming their polyelectrolyte nature. The plots of poly(methacrylic acid) and poly(**c**) were found to be almost coincident. On the other hand, much higher

viscosity values were obtained for poly(**f**) at comparable concentrations. This can be plausibly explained by the presence of the sugar unit, which leads to enhanced stretching of the polymer chains.

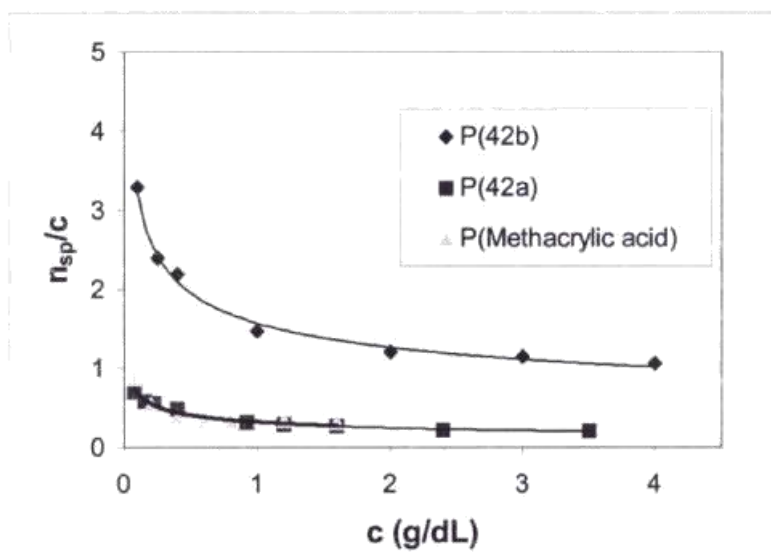


Fig. 22. Plot of η_{sp}/c against concentration

Viscosity behaviour in the presence of salt

It is well established that the viscosity of polyelectrolytes is highly dependent on the ionic strength of the aqueous solution. This has been verified for **P(c)** and **P(f)** whose viscosity increases with increasing concentration in the presence of 0.2 M NaCl (Figure 23).

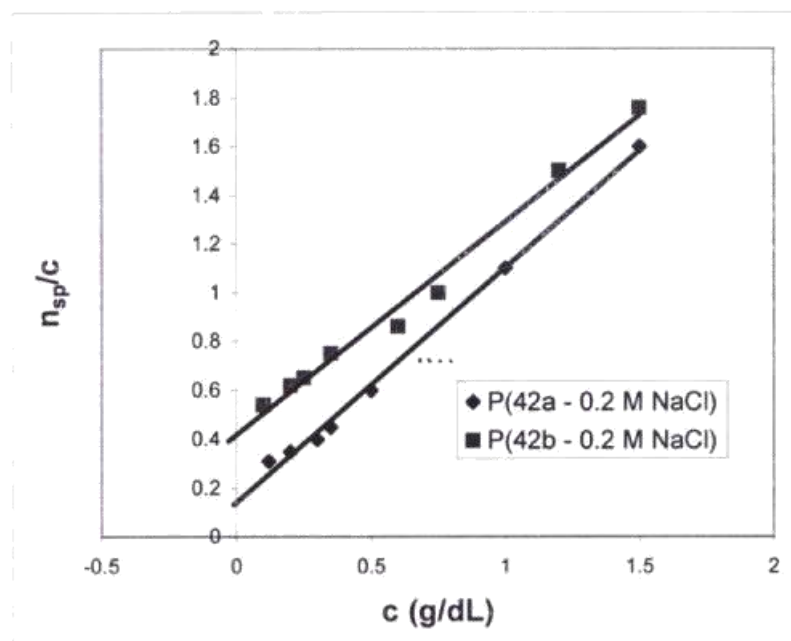


Fig. 23. Plot of η_{sp}/c against concentration for polymers c and f in the presence of NaCl

In the absence of NaCl, the polymer stretches out in aqueous solution due to the large number of negative charges along the polymer chain. This makes the solution more viscous. However, in the presence of NaCl, the negative charges of the polyelectrolyte are cancelled out and the polymer chain collapses to a random coil structure and hence shows similar viscosity behaviour to that of non-ionic polymers (figure 24). Extrapolation of the linear plots to zero concentration gives the intrinsic viscosity of the polymers. Values of 0.142 dL/g and 0.42 dL/g are thus obtained for P(c) and P(f). Here also the viscosity of the polymer containing the sugar residue is higher.

To the best of our knowledge, there is no example in the literature concerning ionic polymers bearing sugar units with which our polymers could be compared. However, it is interesting to note that the non-ionic N-p-vinylbenzyl-D-gluconamide homopolymers described by Kobayashi *et al.*⁵⁷ possess much lower intrinsic viscosity values, typically in the range 0.4-0.5 dL/g.

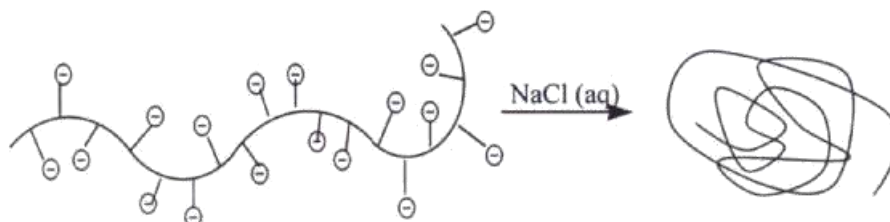


Fig. 24. Structure of polymer in presence of NaCl

CHAPTER 4

Experimental Part

4.1. CHARACTERISATION OF CELLULOSE

The cellulose available for use in this study were of two types: microcrystalline cellulose (Camag) and cellulose powder (Aldrich). The degree of polymerization (DP) of these celluloses was not known. Cellulose is insoluble in most conventional organic solvents (DMSO, CHCl_3 , D_2O) and therefore could not be characterised by ^1H - and ^{13}C -NMR.

4.1.1. IR Spectroscopy

The spectrum of untreated cellulose powder (Annexe 1) showed a characteristic broad, strong absorption band between 3200 and 3600 cm^{-1} representing the O-H stretching of free and bonded hydroxyl groups. The band at 3000-3100 cm^{-1} is attributed to alkyl, -C-H, stretching frequency, and the other bands are due to -C-O- and -C-C-bonds, in the lower wavenumber regions.

4.2. PRETREATMENT OF CELLULOSE

Reagents

Cellulose powder, methanol (distilled over iodine and magnesium), distilled water, 4,4-dimethylacetamide (DMAc), stored under nitrogen.

Procedure

Cellulose (10.0 g) was slurried in water (100 ml) overnight and then filtered. To the swollen cellulose, methanol (50 ml) was added, stirred for 1 hour and then filtered. This procedure was repeated twice more with 50 ml portions of DMAc to complete the solvent – exchange swelling process. The cellulose was filtered each time.

The amount of cellulose per gram of swollen material was determined by weighing samples after drying for 48 hours under vacuum.

4.2.1. DISSOLUTION OF CELLULOSE IN DMAc/LiCl

A typical preparation of cellulose (5.0 w/w%) in DMAc/LiCl (9 w/w%) system is described below.

Reagents

Pretreated cellulose, DMAc, LiCl (dried under vacuum for 48 hours).

Procedure

LiCl (1.80 g) was added to DMAc (20.05 g) and the mixture was stirred under N₂ at 70°C until complete dissolution of LiCl.

This binary solvent system was cooled to 40-50°C and the pretreated cellulose (1.0 g of cellulose) was added. The mixture was stirred until a clear solution was obtained.

4.3. SYNTHESIS OF CELLULOSE DERIVATIVES

A broad range of cellulose derivatives, esters, ethers and carbamates, have been prepared in LiCl/DMAc solvent, which allows the preparation in homogeneous conditions¹.

Cellulose derivatives are also prepared in heterogeneous a condition, which involves use of slurry of cellulose in a solvent which swells but does not dissolve the polymer.

In this study, cellulose-ether (ECH) and cellulose-carboxylic compounds derivatives were prepared in both homogeneous and heterogeneous conditions.

4.3.1. GENERAL CHARACTERISATION OF DERIVATISED CELLULOSE

Solubility in organic solvents

Qualitative tests were carried out to evaluate the solubilities of the cellulose derivatives in methanol, DMAc and DMSO. Portions of the derivatives were suspended in the solvent and stirred overnight. The appearance of the undissolved fibres was compared with that of untreated fibres.

Furthermore, the derivatives were heated to $\sim 60^{\circ}\text{C}$ in the solvent to test the solubility in hot solvent. The mixture was filtered and the fibres were left to dry. The mass after solubility treatment was compared with the initial mass used.

Infra Red Spectroscopy

The measurements were performed with a Mattson 1000 FTIR spectrometer in the range 4000 to 500 cm^{-1} . Portions of cellulose derivatives were mixed with portions of dry potassium bromide. The mixtures were converted into pellets with a 10-ton press.

The spectra of the derivatives were compared to that of untreated cellulose.

NMR Spectroscopy

^1H and ^{13}C NMR were recorded on a 250 MHz Bruker Electrospin spectrometer, for those derivatives which were soluble in dimethyl sulphoxide.

4.3.2. SYNTHESIS OF ETHERS

Cellulose ethers are prepared by the reaction of alkali cellulose with alkyl halides or epoxides. Since most typical bases (NaOH and KOH) are insoluble in organic solvents used, the ethers prepared have low degree of substitution (DS).

Reactions are typically conducted by reacting cellulose with an excess of the reagent in the presence of base.

Typical preparations of cellulose ether using epichlorohydrin with NaOH and NaH as bases are described below. Different procedures were followed.

4.3.2.1. Method B1

Reagents

Cellulose, ECH, NaOH pellets, DMSO were used without further purification.

Procedure

Cellulose was mixed by grinding in a mortar and pestle with a mixture of DMSO and epichlorohydrin was added. The mixture was maintained for 3 hours at RT to allow maximum of reagent into the fibres. Finely ground NaOH was added as a suspension in DMSO with vigorous grinding.

The mixture was then retained at RT for 3 days.

The product was collected on a sintered glass filter, and washed successively with DMSO, water, dilute acetic acid, water and finally ethanol. The product was air-dried.

4.3.2.2. Method B2

The procedure was similar to B1, except that the cellulose was first fully swollen by grinding with DMSO and NaOH, after which epichlorohydrin was added with thorough mixing.

4.3.2.3. Method C

Reagents

Cellulose solution in DMAc/LiCl, NaH, DMSO, ECH

Procedure

Sodium hydride was carefully added to DMSO in a 250 ml RB and the solution was stirred at 50-60°C until the end of gaseous emission. This dimethyl sodium solution was added to cellulose in DMAc/LiCl solvent and the mixture was stirred at RT overnight. The solution became white in colour. The cellulose solution was then cooled to ~10°C and epichlorohydrin was added and the mixture was stirred at RT for 48 hours. Acetic acid (5.0 ml) and distilled water (5.0 ml) were added for neutralization. The mixture obtained was dialysed against water for 3 days and was then freeze dried. A white product was collected.

4.3.3. SYNTHESIS OF ESTERS

The reaction of cellulose, in LiCl/DMAc solvent, was carried out with a series of carboxylic acid compounds, namely methacrylic acid (MMA), methacryloyl chloride (NMACl), oligolactide (OL) and lactide acid (LAc) and cyclic ester, D,L-lactide, gluconolactone and caprolactone.

4.3.3.1. REACTION OF CELLULOSE WITH METHACRYLOYL CHLORIDE

A typical reaction of cellulose with methacryloyl chloride using NaH as base is described below.

Reagents

Cellulose in DMAc/LiCl, DMSO, NaH, methacryloyl chloride. The reagents were used without prior purification.

Procedure

Sodium hydride was carefully added to DMSO in a 250 ml RB and the solution was stirred at 50-60°C until the end of gaseous emission. This dimethyl sodium solution was added to

cellulose in DMAc/LiCl solvent and the mixture was stirred at RT overnight. The solution became white in colour.

The cellulose solution was then cooled to $\sim 10^{\circ}\text{C}$ and methacryloyl chloride was added and the mixture was stirred at RT for t hours. Acetic acid (5.0 ml) and distilled water (5.0 ml) were added for neutralisation. The mixture obtained was dialysed against water for 3 days and was then freeze dried. A white product was collected.

4.3.3.2. SYNTHESIS OF CELLULOSE-CARBOXYLIC COMPOUND DERIVATIVES USING A DEHYDRATING AGENT (DCC)

Cellulose was reacted with different carboxylic acid derivatives, using dicyclohexylcarbodiimide (DCC) as a condensation agent and 4-dimethylaminopyridine (DMAP) as catalyst.

A typical synthesis of cellulose carboxylic acid derivative, using methacryloyl chloride is described below.

Reagents

Cellulose in DMAc/LiCl, MMACl, DMAP

Procedure

DCC was added to cellulose in DMAc/LiCl solvent and the mixture was well stirred. DMAP was then added, with continuous stirring. Methacryloyl chloride was added and the reaction was stirred at $T^{\circ}\text{C}$ for t hours.

The cellulose product was separated by first precipitating the reaction solution into water to remove the LiCl, DMAc and most of the unreacted carboxylic compound. The precipitate was then filtered, washed with several aliquots of water, then washed with methanol to completely remove hydrated DCC. The cellulose derivative was then dried under vacuum at 40°C for 48 hours.

4.3.3.3. REACTION OF CELLULOSE WITH CYCLIC ESTERS

A typical reaction of cellulose with D,L-lactide is described below.

Reagents

Cellulose solution in DMAc/LiCl. Triethylamine and D,L-lactide were used without prior purification.

Procedure

Triethylamine (1.0 ml, 7 mmol) was added to cellulose (1.0 g) solution in DMAc/LiCl and the reaction mixture was stirred at room temperature for 10 minutes. D,L-lactide (1.0 g, 7 mmol) was added and the mixture was stirred at 75°C for 120 hours. The reaction was carried out under nitrogen for the first 24 hours.

The resulting mixture was precipitated in ethyl acetate. The cellulose-ester derivative precipitated out as a white, sticky product. It was washed twice with portions of ethyl acetate to remove DMAc and other unreacted reagents and was then dried under vacuum for 48 hours.

CONCLUSION

We have presented in this project the main applications of non modified cellulose which could find potential development in Mauritius, in particular in the food industry or in the making of paper pulp. It is good to point out though that the technology transfer seems to be feasible on scientific terms but the economics of the processes need to be studied in depth before any commercial applications are envisaged.

We have outlined our main findings concerning the synthesis of polymers based on both non modified cellulose and enzymatically degraded cellulose. The results as regards the direct chemical modification of cellulose are not quite promising although this strategy would have been more viable industrially. The second approach has proved to be very successful. A variety of novel monomers and in particular the ionic gluconamidoalkylmethacrylates were synthesized in water. The monomers can thus be obtained on large scale at low cost and at the same time they do stand as a threat to the environment. They can be transformed to polymers in a one step reaction still using water as solvent. The resulting polymers present special properties which would certainly be of interest in the Mauritian context – in water treatment and as viscosifying agents in the food industry. Laboratory tests concerning the decolourization of water showed that the polymer samples used were particularly efficient at low concentrations.

This project has given us the possibility to develop expertise in this important field of biopolymers and has lead to a number of publications in internationally refereed journals.

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MRC-Seminar

12 December 2001

MATERIALS DERIVED FROM CELLULOSE

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Faculty of Science

University of Mauritius

Leading Sectors in Mauritius

- Sugar
 - Textile
 - Manufacturing (EPZ)
 - Tourism
 - Financial
- Chemists
can play a
leading role
- Forthcoming... ICT

Sugar Industry

- Lomé conventions
- Cotonou agreement (valid up to 2007)
- Possible extension to be discussed in 2002

→ Major challenges

- Restructuring the sugar sector :
*enhanced productivity,
focus on use of bagasse for
energy production,
valorization of by-products*

RENEWABLE RESOURCES

SUGAR CANE

Bagasse, Molasses

Natural
polymers

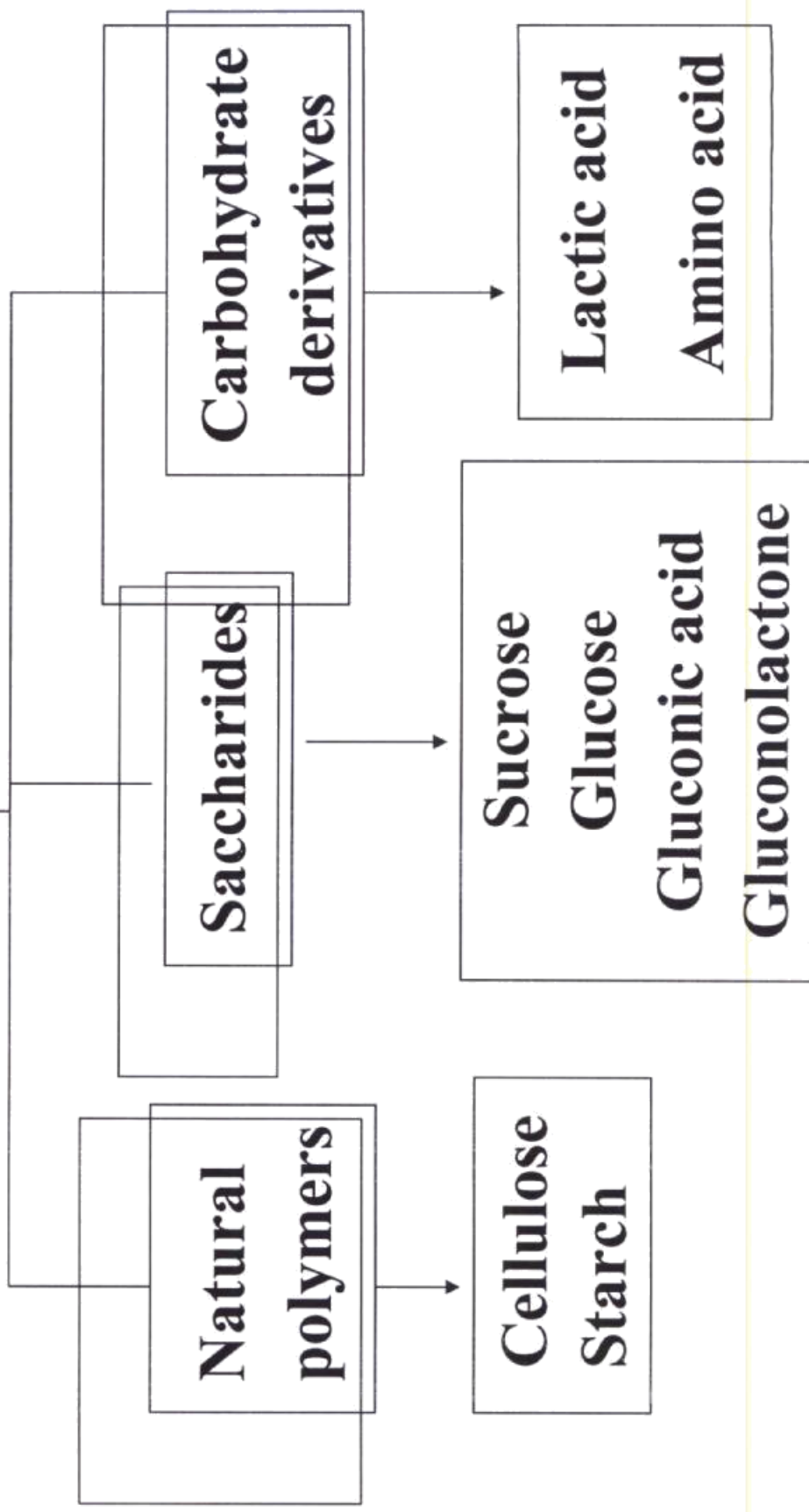
Saccharides

Carbohydrate
derivatives

Cellulose
Starch

Sucrose
Glucose
Gluconic acid
Gluconolactone

Lactic acid
Amino acid



FOOD INDUSTRY

POLYMERS

**RENEWABLE RESOURCES
AS
RAW MATERIALS**

DETERGENTS

FINE CHEMICALS

CARBOHYDRATE DERIVED POLYMERS

Type I



Type II



Type III



POLYSACCHARIDES

Type I

Biosynthetic Pathway

- Cellulose : β -1,4-linked glucose units
- Dextrans : (from sucrose)

Mainly α -1,6-linked glucose units

- Polyfructose : (from sucrose and sugar molasses)

Mainly β -1,2-linked fructose units

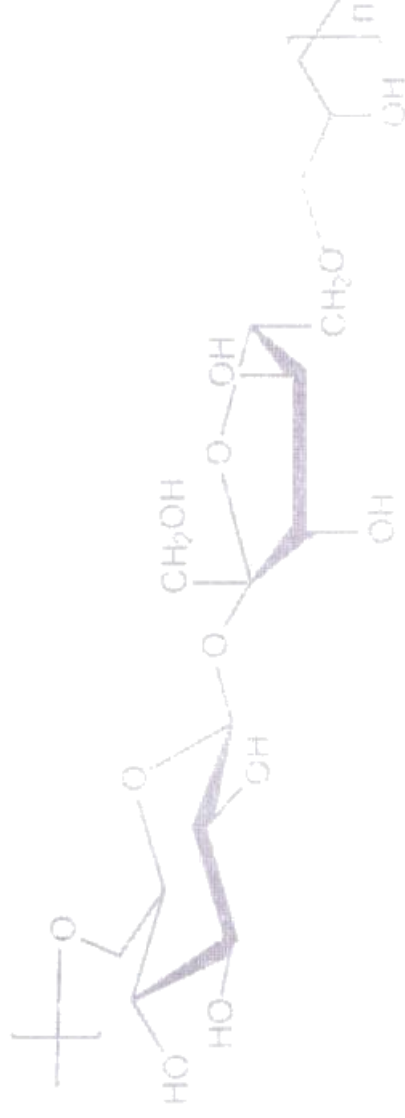
Chemical Pathway

- Polydextrose: *highly branched polymer of glucose*

POLYMERS WITH SUGAR UNITS IN THE MAIN CHAIN

TYPE II

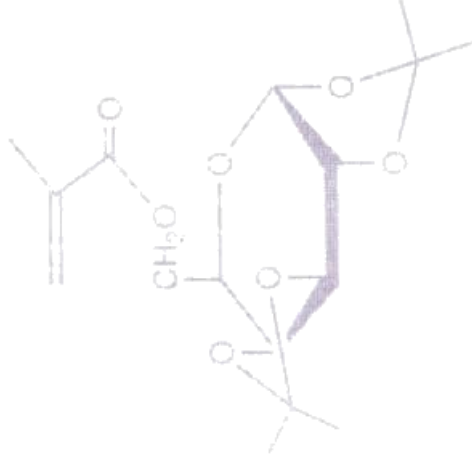
Sucrose-Epichlorhydrin Polycondensate (Ficoll®)



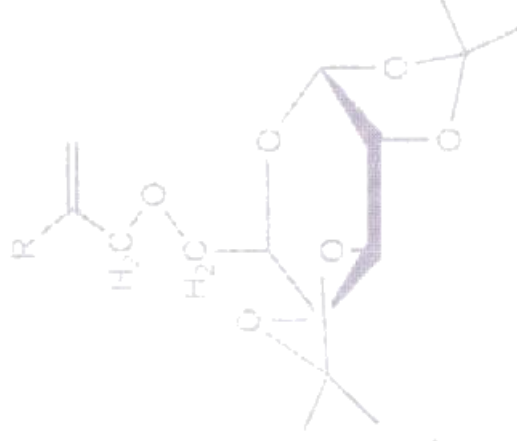
POLYMERS WITH SUGAR UNITS AS PENDANT GROUPS

TYPE III

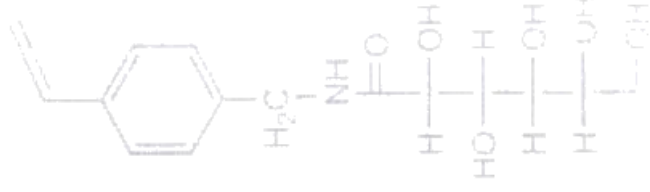
Based on monosaccharides



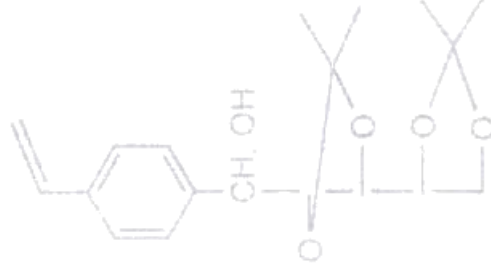
Black *et al.*
(1960)



Klein *et al.*
(1987)



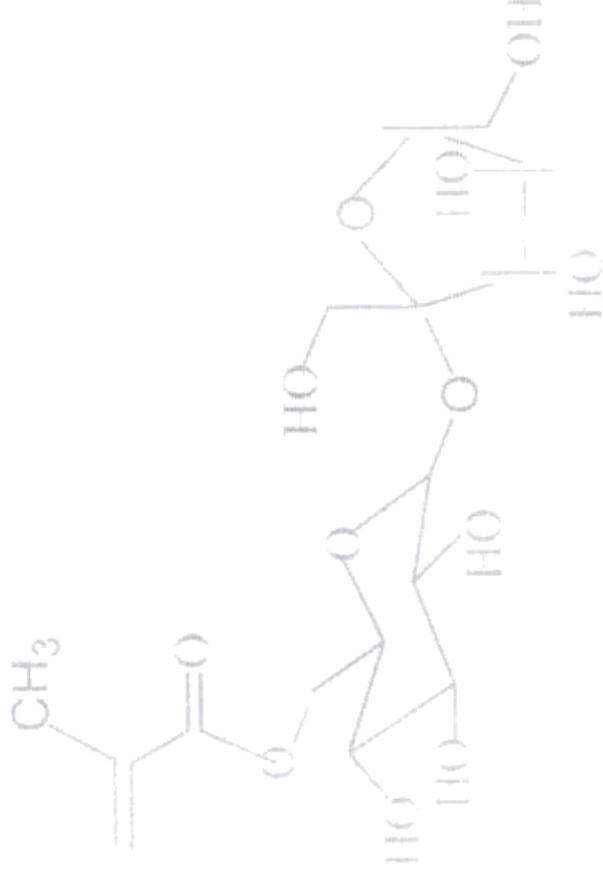
Kobayashi *et al.*
(1985)



Wulff *et al.*
(1997)

POLYMERS WITH SUCROSE UNITS AS PENDANT GROUPS

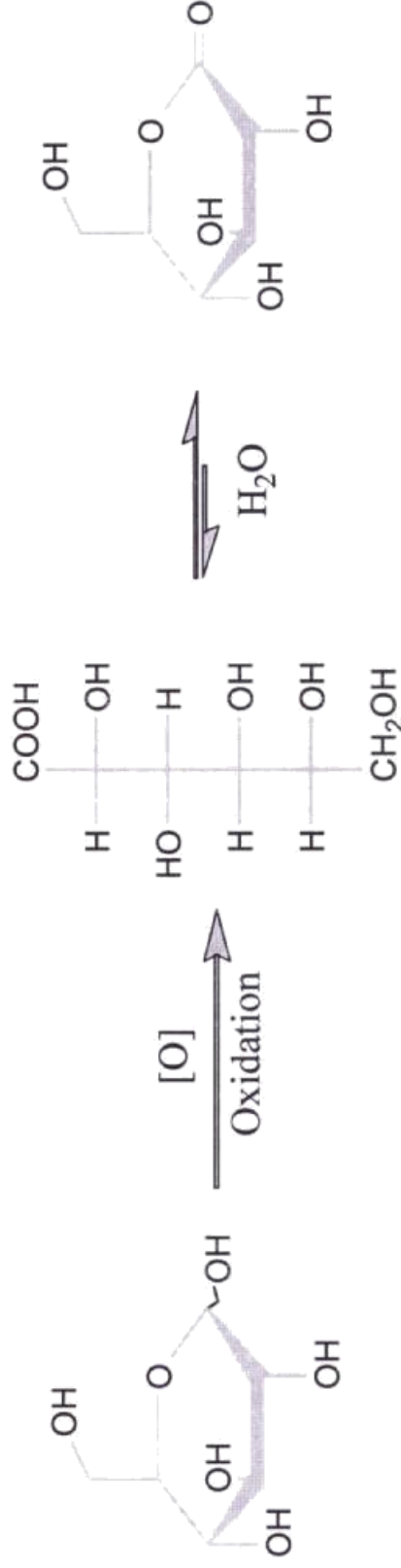
Based on disaccharide (Sucrose)



Jhurry et al. (1992)

- Water-soluble polymers
- Wide range of applications by modulating the hydrophilic/hydrophobic balance:
thickeners, flocculants, detergents, hydrogels, surface modification of polymers, waste water treatment, biological systems

GLUCONOLACTONE AS RAW MATERIAL



D-Glucose

D-Gluconic acid

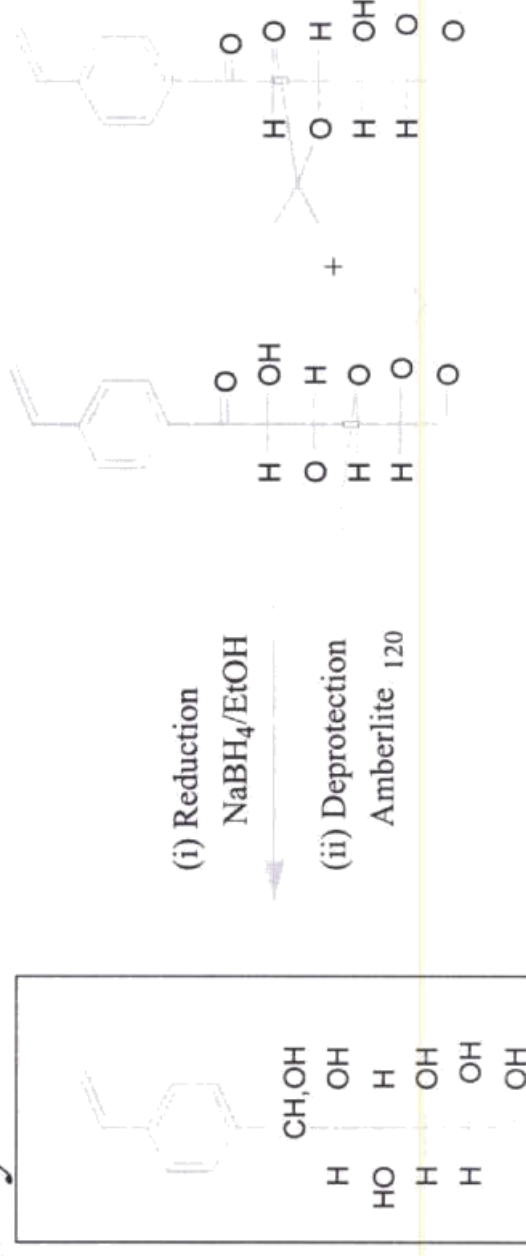
D-Gluconolactone

World production: 70,000 tonnes

Innovations

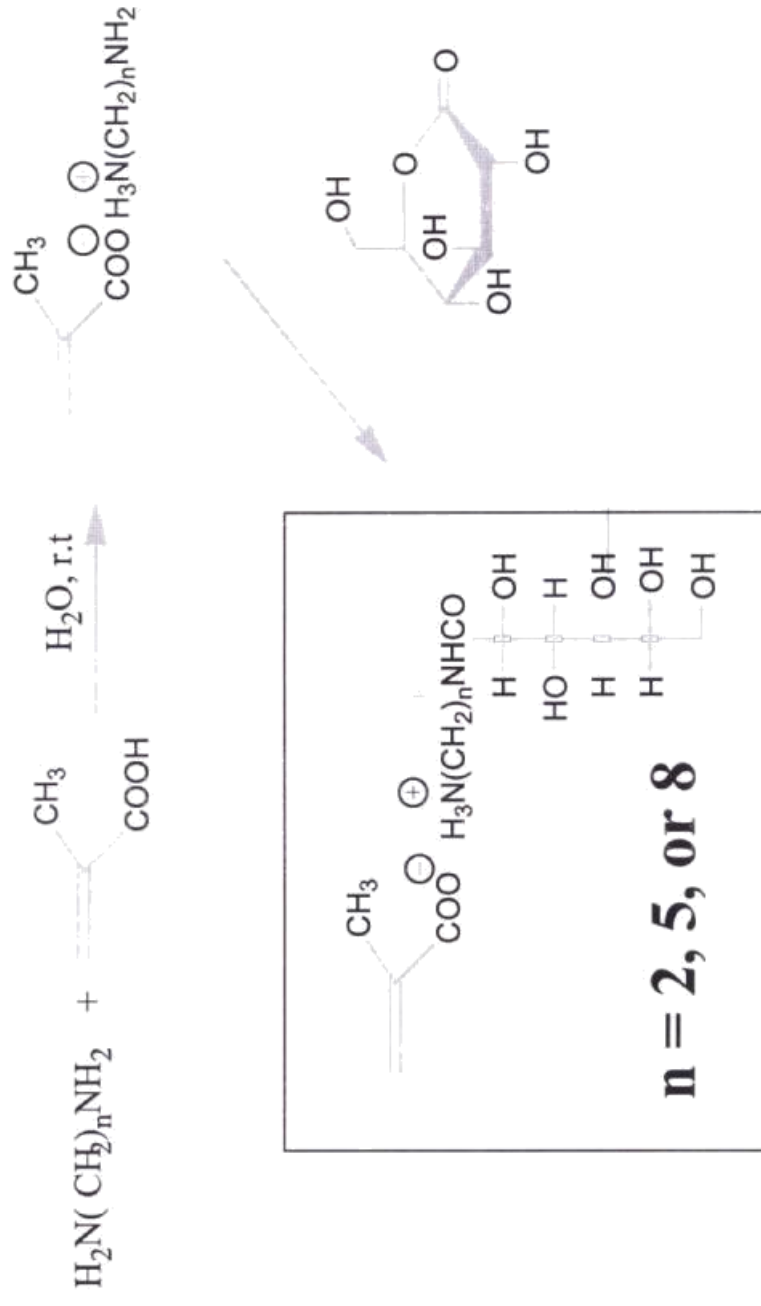
Eur. Polym. J.

(2001) 38/2, 273



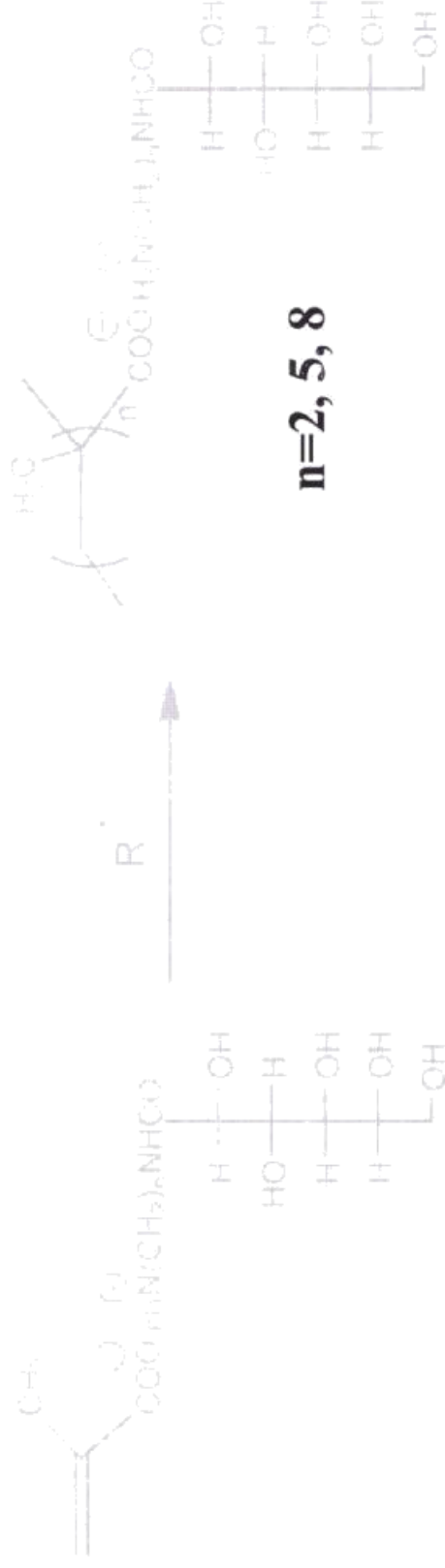
Innovations

Ammonium methacrylates



- One-step synthesis
- Water as solvent (environmentally friendly and economical)

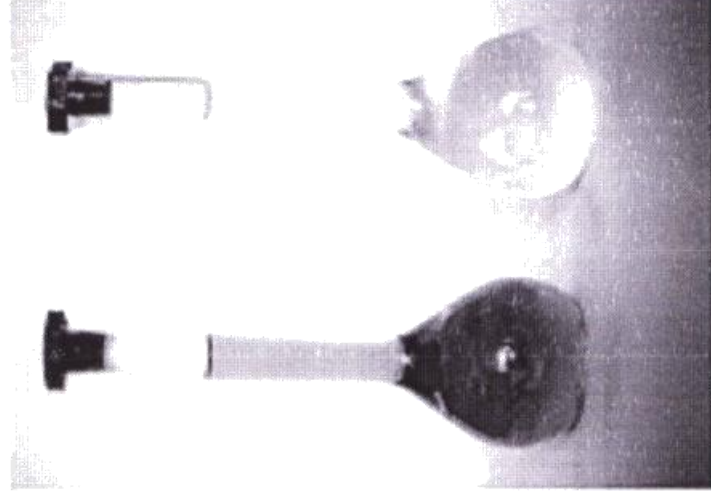
POLY(AMMONIUM METHACRYLATES)



- Polymerization in H_2O
- Formation of a Polyelectrolyte

*R. Narain, D. Jhurry,
Polymer Int. (2002) 51, 1-7*

BINDING OF METHYL ORANGE



METHYL ORANGE

MO + POLYMER

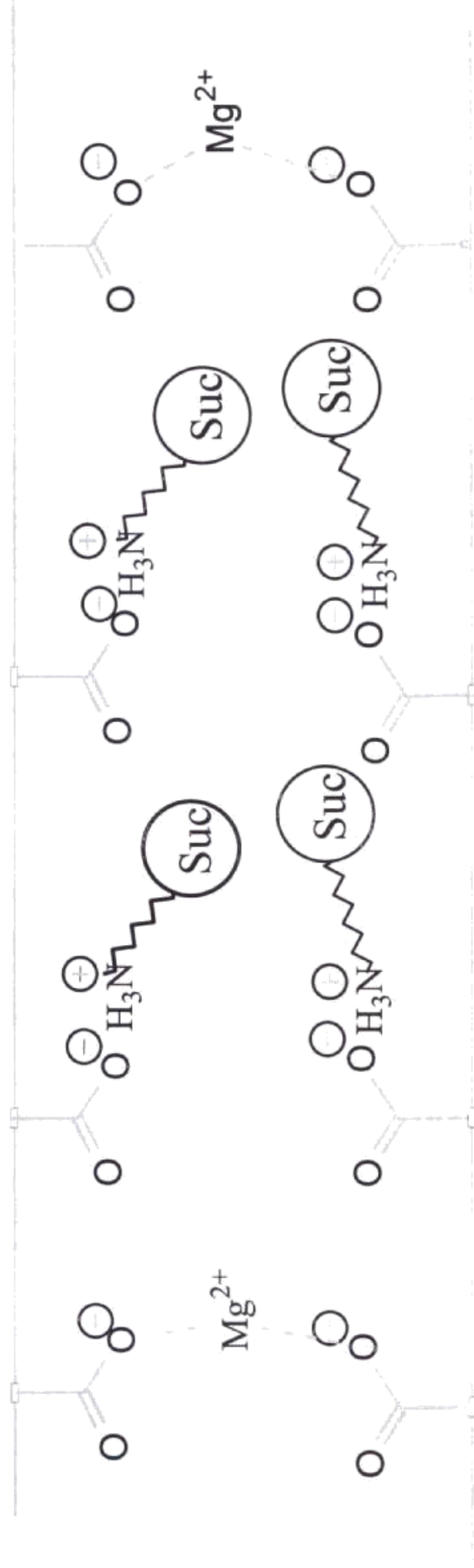
No change in colour in presence of monomer

*R. Narain, D. Jhurry,
Journal de la Nature, in press (2001)*

Binding of metal ions

- Precipitation of polymer with divalent metal ions
- No precipitation with monovalent ions
- No precipitation with monomer

Crosslinking of Polymer Chains



POLYLACTIDES



- Biodegradable / Bioresorbable polymers

Various applications :

- Suture materials, prostheses, screws for the biomedical field
- Controlled release devices for the medical and pharmaceutical sectors (eg controlled drug release)
- Plastic materials for commodity applications

Innovations

- Design of a new family of initiators used to synthesize the polylactides: Al-Schiff's base complexes
- Introduction of a novel anionic initiator: Lithium diisopropylamide
- Controlled Ring-Opening polymerization (access to tailor-made polymers)
- Synthesis of stereoregular biodegradable polymers

Recent Contributions

Cameron PA, Jhurry D, Gibson V, White AJP, Williams DJ, Williams S.; *Macromol Rapid Commun* (1999) 20, 616-618

Controlled polymerization of lactides at ambient temperature
Bhaw-Luximon A, Jhurry D, Spassky N.; *Polym Bull* (2000) 44, 31-38
Using 15-crown-5-ether
Controlled Polymerization of DL-lactide using a Schiff's base Al-alkoxide initiator derived from 2-hydroxyacetophenone.

Jhurry D, Bhaw-Luximon A, Spassky N.;
Macromol Symp (2001) 175, 67
Synthesis of polylactides by new Al-Schiff's base complexes

Bhaw-Luximon A, Jhurry D, Spassky N, Pensec S, Belleney J.;
Polymer (2001) 42, 9651

Anionic polymerization of D,L-lactide initiated by
lithium diisopropylamide

POLYPEPTIDES



- Biodegradable polymers

*Applications in the biomedical field:
e.g. Wound dressings*

Innovations

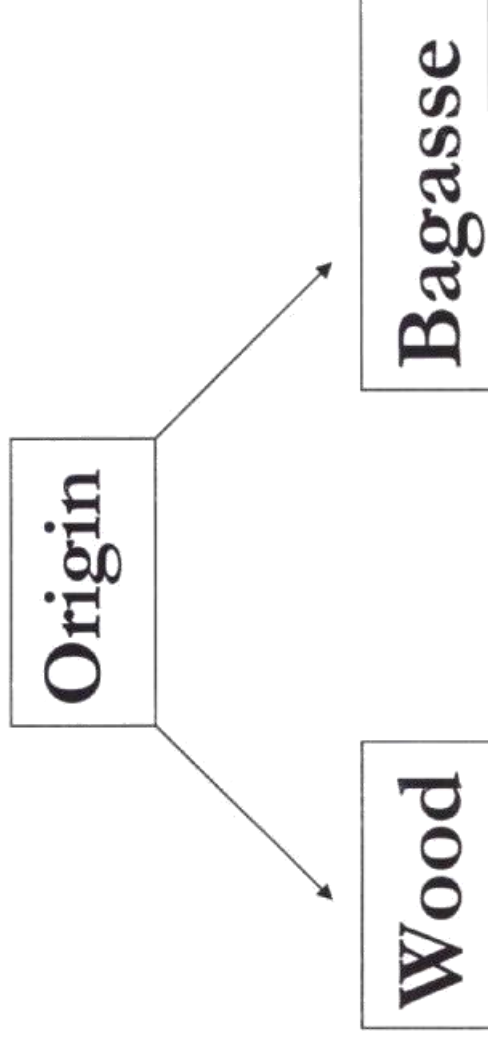
Bhaw-Luximon A, Jhurry D, Belleney J.;

Macromolecules, submitted (2001)

Polymerization of NCA- γ -methylglutamate using Al-Schiff's base complexes as initiators. Application to the synthesis of block copolymers containing ester and peptide units.

CELLULOSE

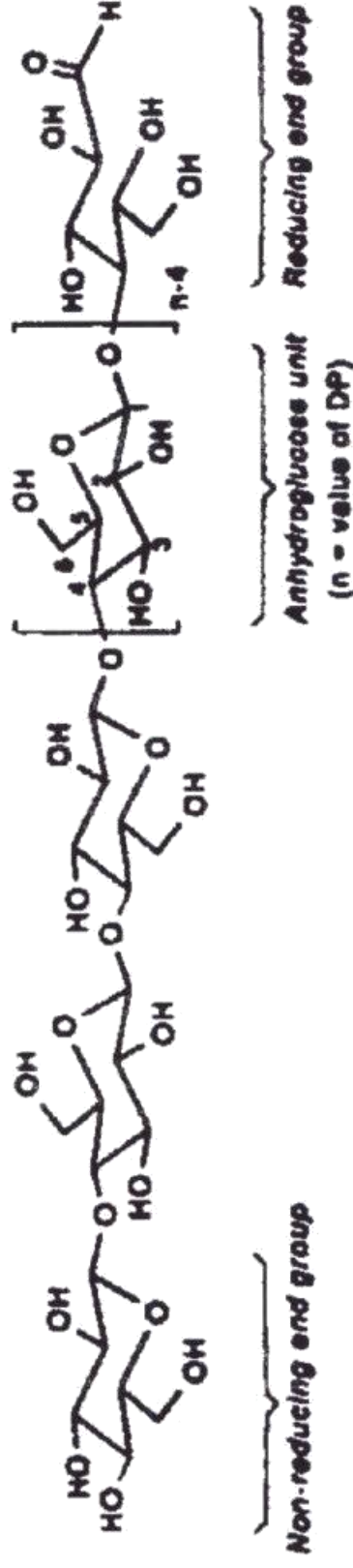
- Main constituent of the cell wall of woody plant
 - Oldest raw material of the chemical industry.
- Important renewable polymeric resource.
- Hydrophilic, biocompatible, chiral.



Molecular Structure

Highly uniform (1,4)- β -glucan

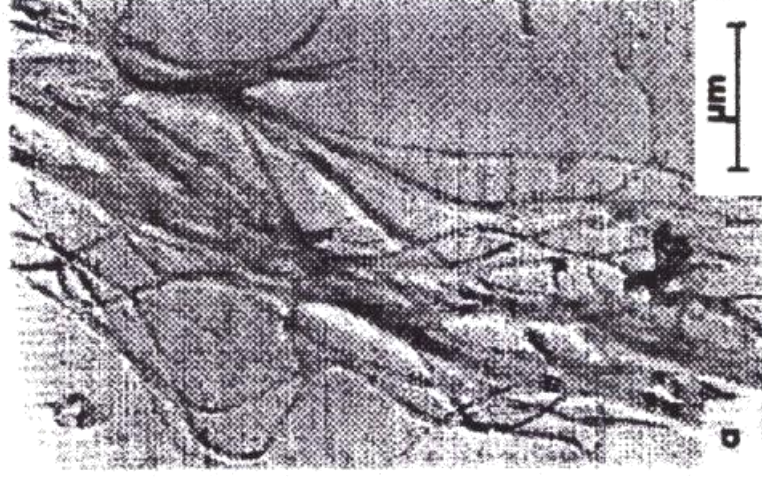
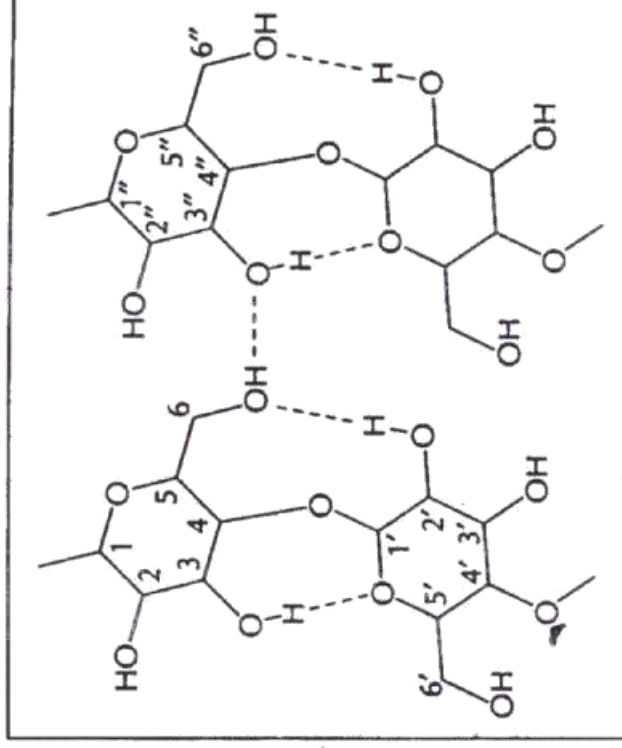
Best described as a polycellobiose (2 glucose units)



3 reactive hydroxyl groups per anhydroglucose unit

Network of Intra- and Intermolecular H- bonds

Fibrillar morphology



Highly crystalline and insoluble in almost all organic solvents

Commercial derivatives of Cellulose

- Regenerated Cellulose (viscose rayon, cellophane)
- Cellulose nitrate or celluloid (Akzo Nobel, BASF, ICI, Nippon Paint)
- Cellulose acetate, cellulose propionate/butyrate (Hoechst, Eastman Chemical)
- Carboxymethylcellulose, hydroxyethylcellulose, methylcellulose (water soluble) (Metsa-Serla, Akzo, Aqualon/Hercules)

Applications of Cellulose and derivatives

- Textiles: use of natural cellulose fibres (cotton) and artificial cellulose fibres (viscose rayon).
- Food industry: as thickeners, binders
- Pharmaceuticals: use of cellulose as a matrix or excipient in drug formulation.
- Construction materials: in manufacture of hardboard, fibre board, composite board (combination of epoxy and bagasse).
- Surface coatings: use of synthetic cellulose resins (cellulose esters and ethers). Nitrocellulose accounts for 80% of cellulosic resins in coatings.
- Paper production: cellulose pulp from sugar-cane bagasse.
- Degradable materials (e.g bottles): hydroxypropylcellulose sandwiched between water-insoluble films.

Production of Paper Pulp from Sugar Mill Bagasse

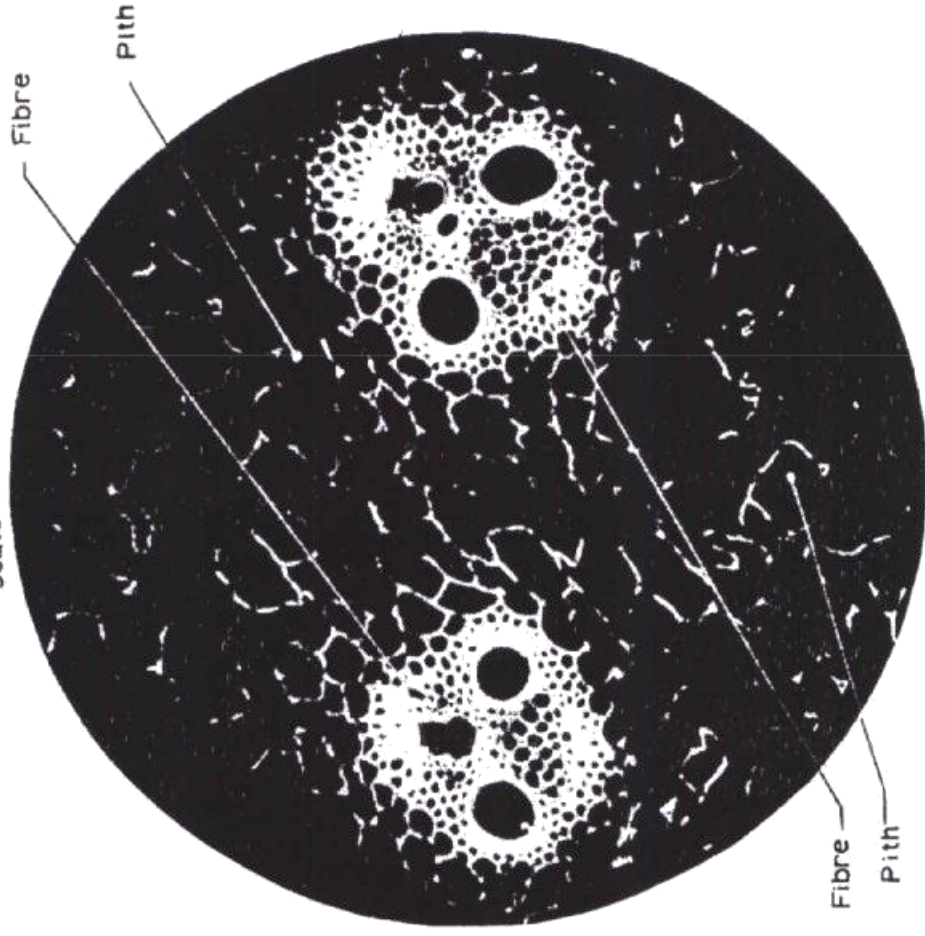
- Production of paper pulp from wood on a commercial basis :
Atchison; Paper Trade Journal 36-42 (1952)

Major problems encountered with bagasse :

- difficulty of extracting residual sugars from bagasse.
- difficulty of separating the fibrous material from the soft pith with which it is intimately associated

Cane Section

Two vascular bundles
scale x 108



**Production of newsprint paper from
100% bagasse**

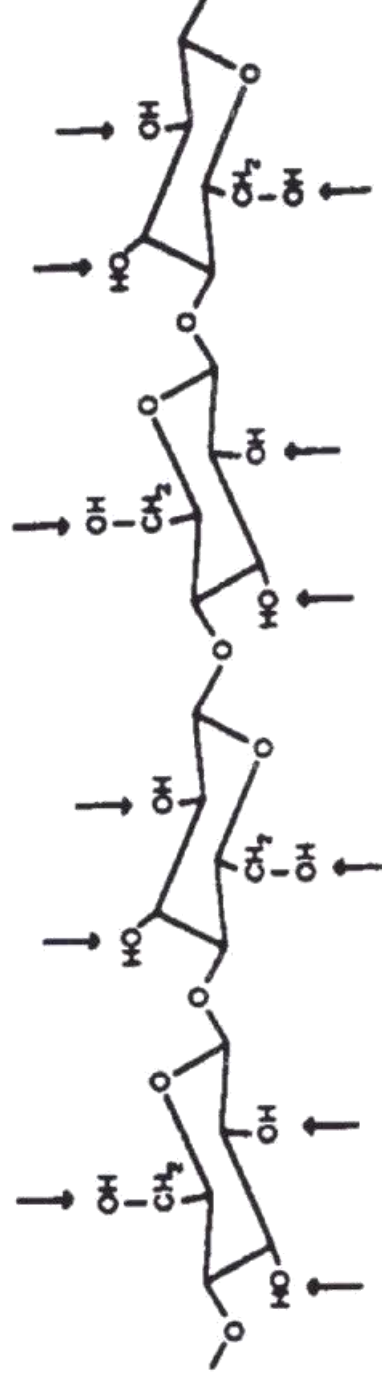
Krüger et al.; US Pat 4,260,452 (1981)

Removal of about 65% of the pith content of bagasse; wet bulk storing in the presence of an inorganic (metal carbonate or phosphate) and organic preservative (lactic acid/sodium lactate); wet depithing; pulping (sulfite process); washing, cleaning and dewatering.

→ Possibility for technology transfer

Derivatization of cellulose under homogeneous conditions

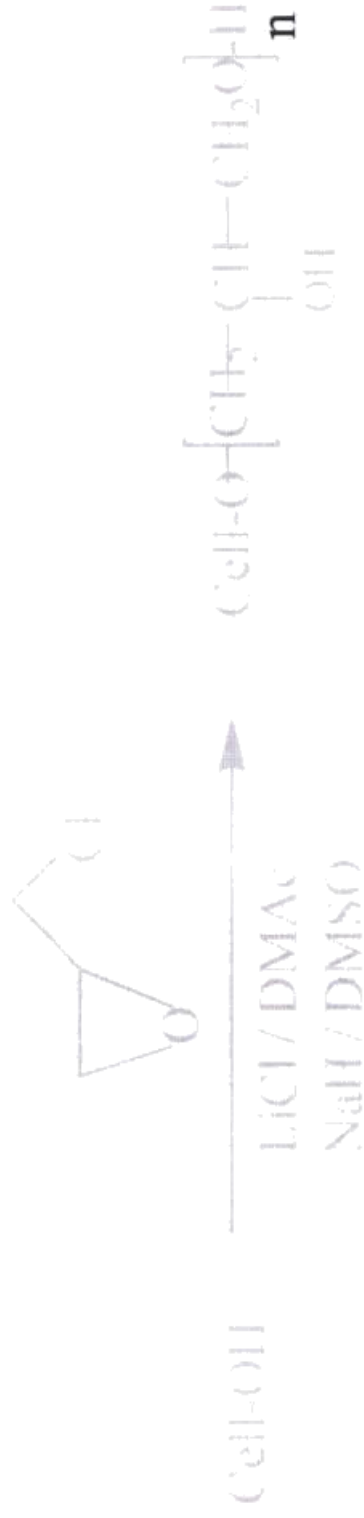
Solvent system: LiCl (9 w/w%) dimethyl acetamide



Reaction sites are uniform and fully accessible

Synthesis of Cellulose Ethers

With epichlorhydrin :

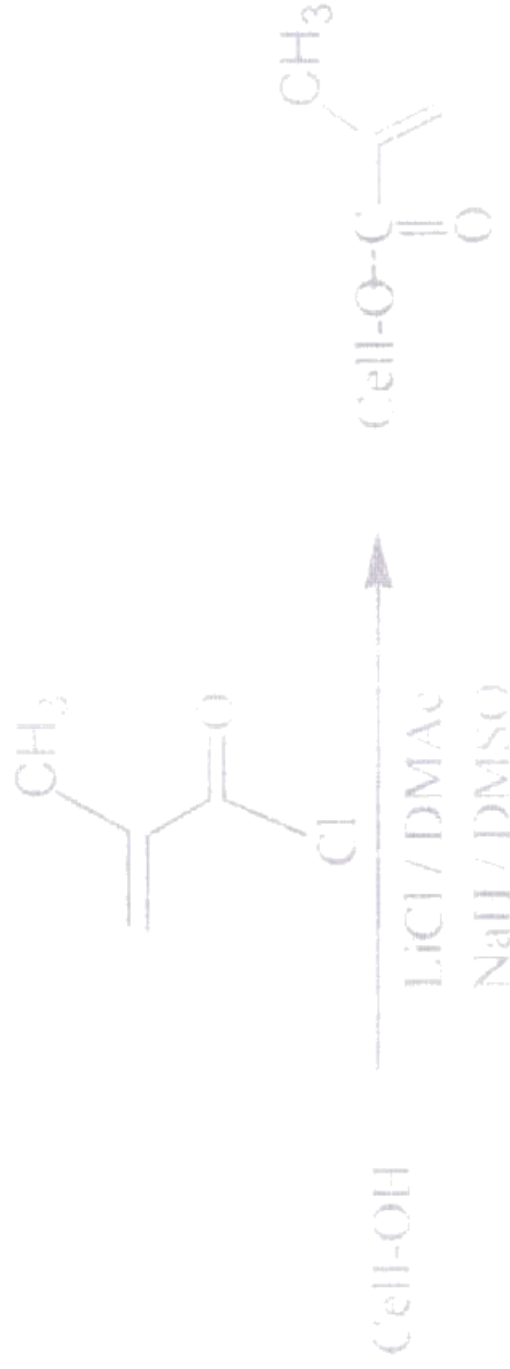


Swells in DMSO

→ **Close in structure to Ethyllose®**
(polymer of ethylene oxide and cellulose)

Synthesis of Cellulose Esters

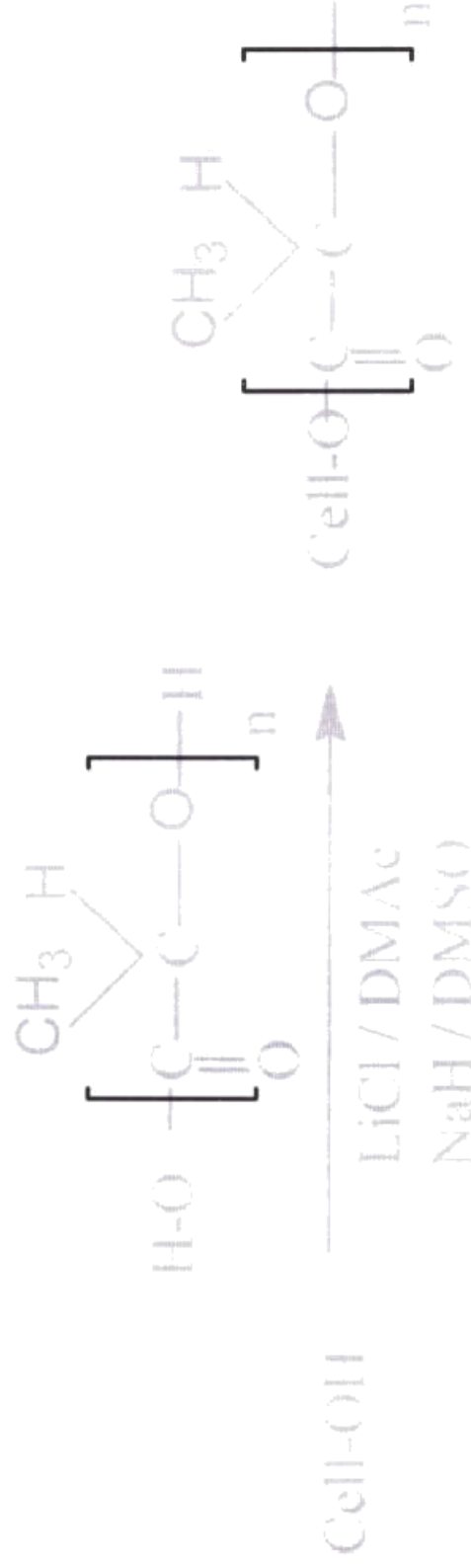
With methacryloyl chloride :



IR: $\nu_{\text{C=O}} = 1718 \text{ cm}^{-1}$

...Synthesis of Cellulose Esters

With oligolactic acid :



IR: $\nu_{\text{C=O}} = 1743 \text{ cm}^{-1}$

Innovations

- Access to various novel cellulose derivatives (ethers and esters)
- Limited possibility for development

Waste-water Treatment

- Use of rice husk (Prabhu and Thangavelu; 1995)
- Use of bagasse fly-ash (Allybokus and Horan; 1998)
- Use of cellulose modified with acrylamide and methylamine (Mandal *et al*; 2000)

Investigation of the efficiency of cellulose for colour removal of textile waste water

- Quite low % colour removal : 10%
- High concentrations of cellulose required : 60 g/L (Freundlich adsorption isotherm)

Compared to :

- Activated charcoal : 95% decolourization at 2 g/L
- Locally available charcoal : about 60% colour removal at 40 g/L

In both cases Langmuir adsorption isotherms

Efficiency of Sawdust for colour removal

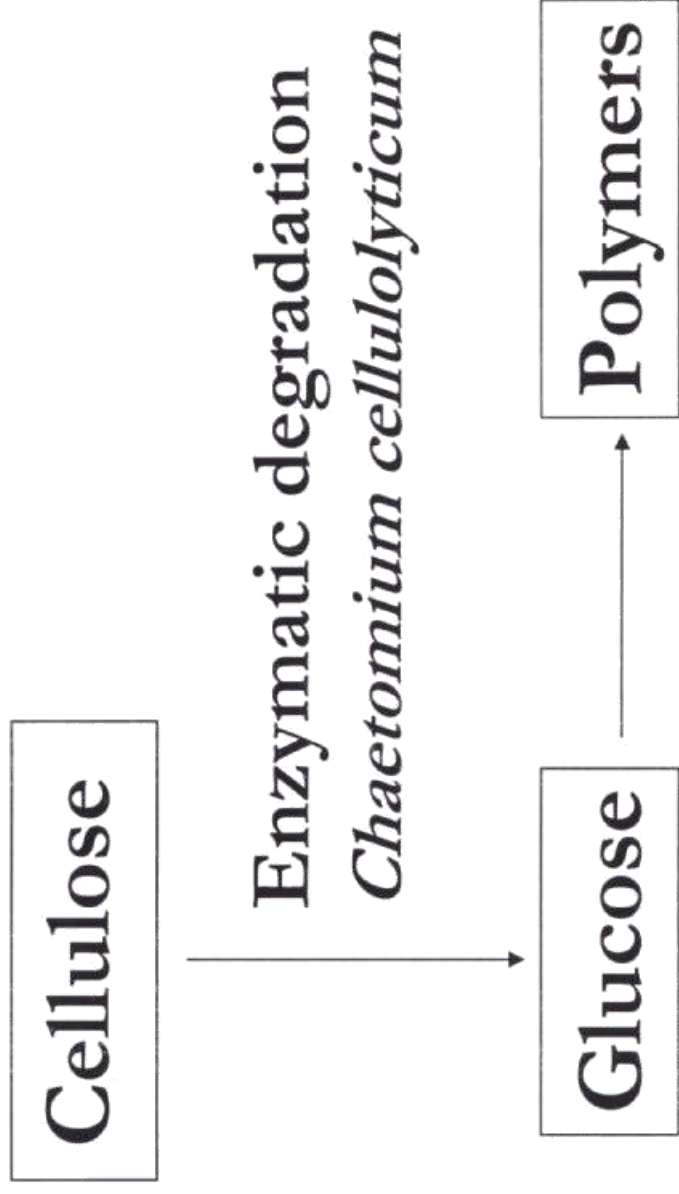
- Attractive as % colour removal : 70%
- Concentration of sawdust: 20 g/L
(Freundlich adsorption isotherm)

Heavily dependent upon :

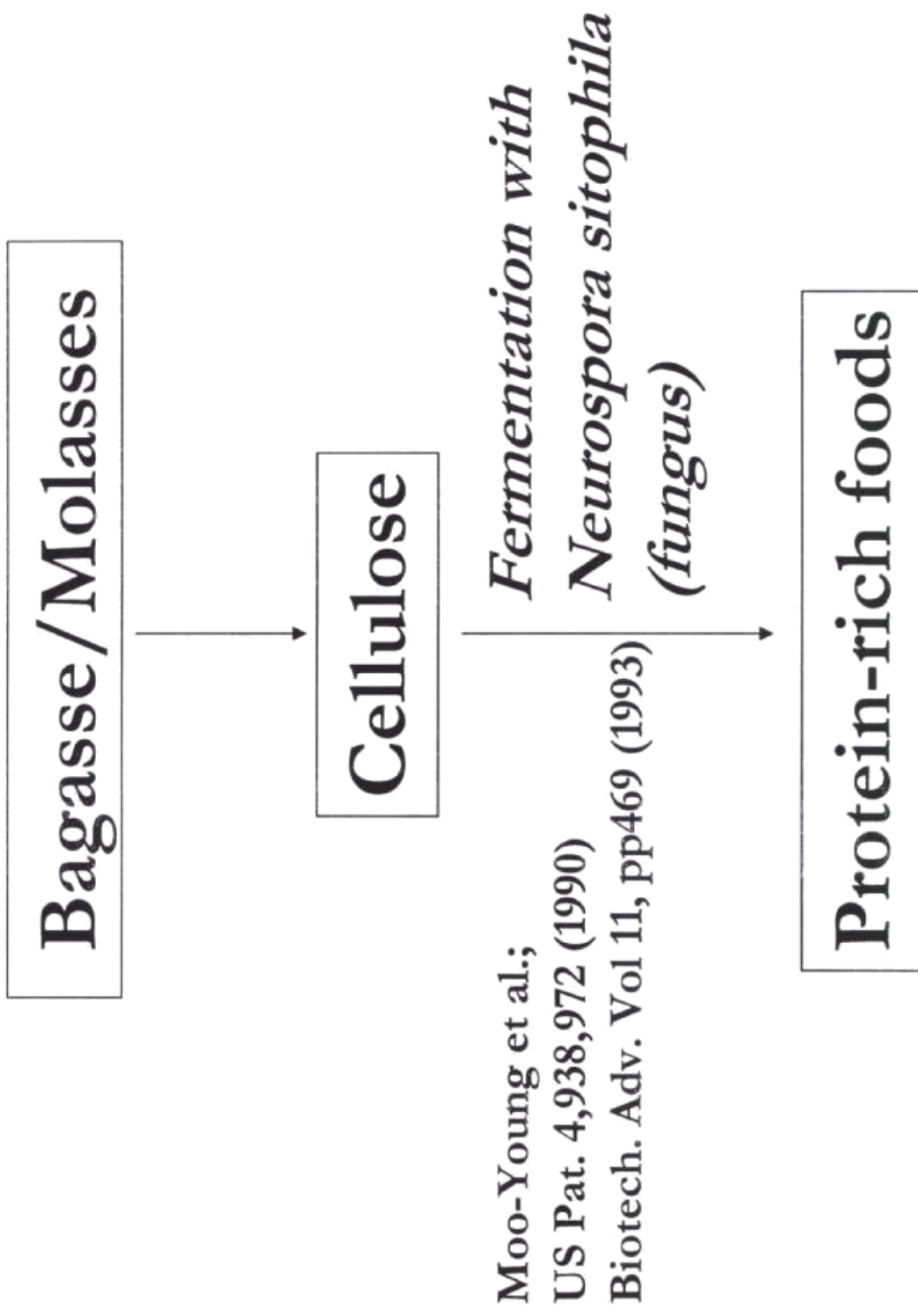
- Type of sawdust (nature of wood)
- Size of particles
- Mass of sawdust used
- Stirring time

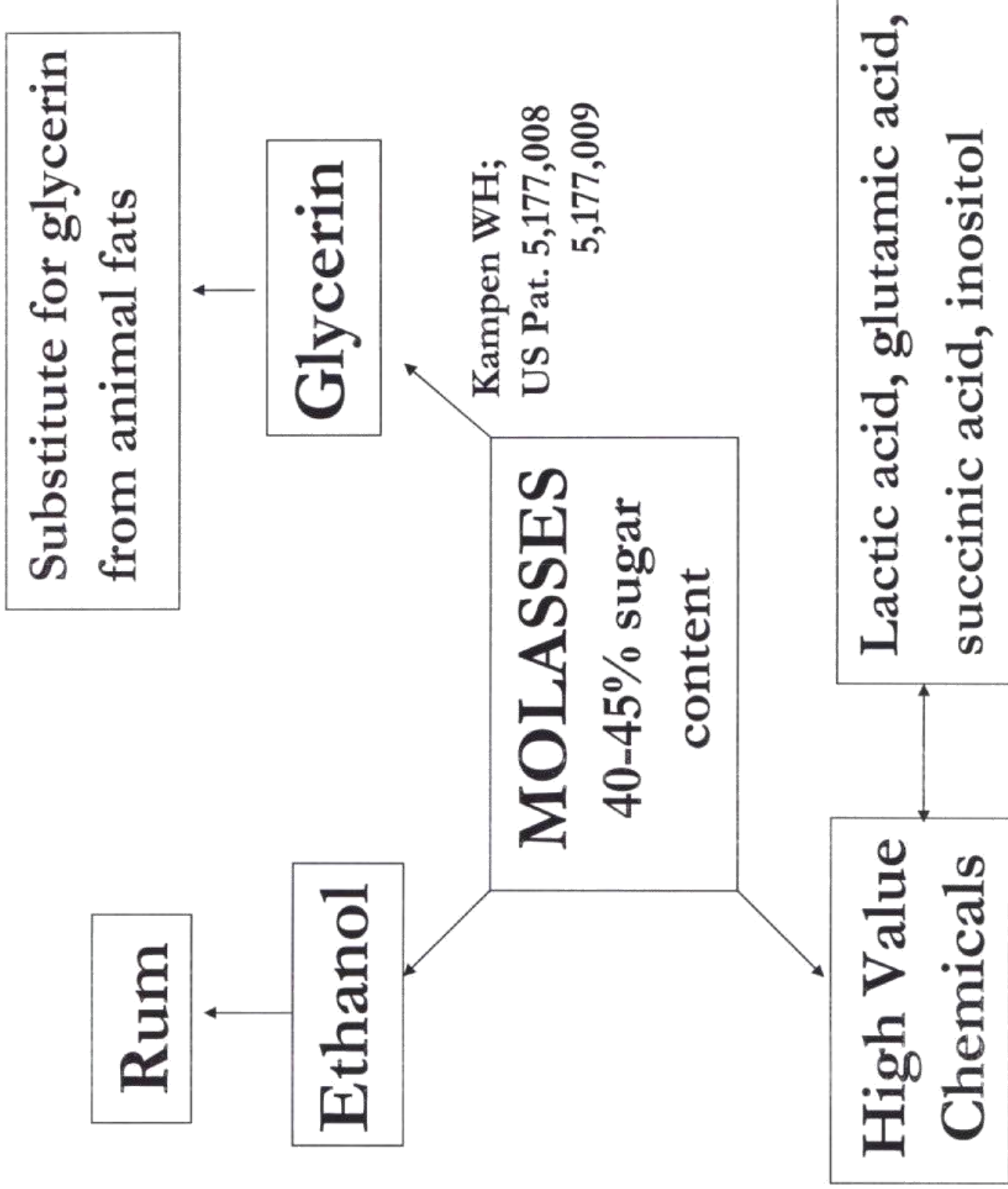
PROSPECTS:

Frontiers of Chemistry and Biology



Biochemical conversion





Acknowledgements

- Co-workers :

Dr (Mrs) A. Bhaw-Luximon (PhD, UoM)

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et Marie Curie

Prof H. Cramail, Univ of Bordeaux-1

Prof G. Wulff, Univ. of Dusseldorf

Merry Christmas

&

Happy New Year 2002