Chemical Modification OF Cellulose Via Reaction With Polyfunctional Compounds

Thesis

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By

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Reaction With Polyfunctional Compounds.

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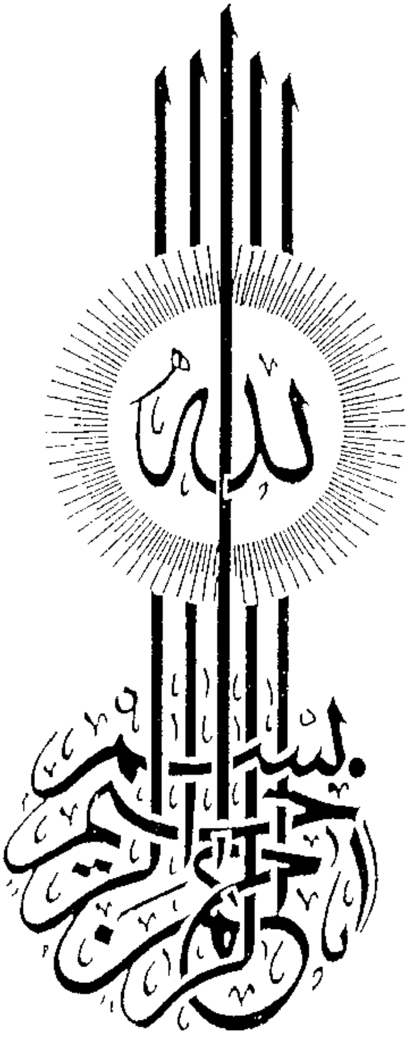
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SUMMARY

PART I

Mechanism Of Reaction of Alkoxy Adducts Of Acrylamide and Hexahydro-1,3,5-Triacryloyl-S-Triazine With Cotton Cellulose In Non-aqueous Medium.

Reaction of alcohols with acrylamide:

The addition of methyl alcohol on the double bond of acrylamide requires a very strong base as a catalyst. Sodium methoxide proved its efficiency in catalyzing this addition reaction in comparison to sodium hydroxide, triethylamine and triethanolamine. It was shown that the degree of conversion of acrylamide increases Significantly by increasing sodium methoxide concentration up to 0.05% . A further increase in sodium methoxide concentration causes a decrease in the degree of conversion, reflecting the reversibility of the reaction. At higher sodium methoxide concentration, splitting of the ether adduct takes place via E_2 β-elimination mechanism.

$$\mathrm{CH_3OH} + \mathrm{CH_2=CH\text{-}CO\text{-}NH_2} \xrightleftharpoons[\bar{\mathrm{O}}\mathrm{CH_3}]{\mathrm{NaOCH_3}} \mathrm{CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}NH_2}$$

It can be shown that the dgree of conversion of acrylamide to β-methoxypropionamide increases rapidly by (a) raising the reaction temperature from -3°C to +40°C, (b) by prolonging the duration of the reaction time to 180 minutes and (c) by increasing the concentration of acrylamide (ca 20%) .

Replacement of methyl alcohol with ethyl alcohol in the nonaqueous preparation of the acrylamide adduct yields β-ethoxyproionamide. On the other hand, replacement of methyl alcohol with isopropyl alcohol in the nonaqueous preparation of acrylamide adducts failed to produce β-(dimethyl)-methoxy propionamide.

Reaction of β-methoxypropionamide with cotton cellulose

Nitrogen analysis showed that the reaction between cotton cellulose and β-methoxypropionamide is dependent upon the type of catalyst and also upon the applied reaction conditions. Significant enhancement in the extent of reaction could be achieved when free acids namely hydrochloric and phosphoric acids were independently used as catalysts. The extent of reaction observed with phosphoric acid is higher than that of the hydrochloric acid particularly when the pad-dry-baking technique was used. When the latter technique was applied, the extent of the reaction obtained was greater in comparison with the pad-batch technique. In addition, the time of baking has a noticeable influence on the extent of the reaction. When sodium hydroxide was used as a catalyst instead of the acidic catalysts, no reaction occured between β-methoxypropionamide and cotton cellulose.

Acid catalyzed reaction of β-methoxypropionamide with cotton cellulose in nonaqueous medium seems to proceed via substitution reaction to yield carbamoylethylated cellulose. The reaction may be represented as follows:

$$\text{Cell-OH} + CH_3\text{-O-}CH_2\text{-}CH_2\text{-CO-}NH_2 \xrightarrow{H^+} \text{Cell-O-}CH_2\text{-}CH_2\text{-CO-}NH_2 + CH_3OH$$

In support of this reaction are the following:

a) Alkaline catalyst failed to expedite the reaction between β-methoxypropionamide and cotton cellulose.

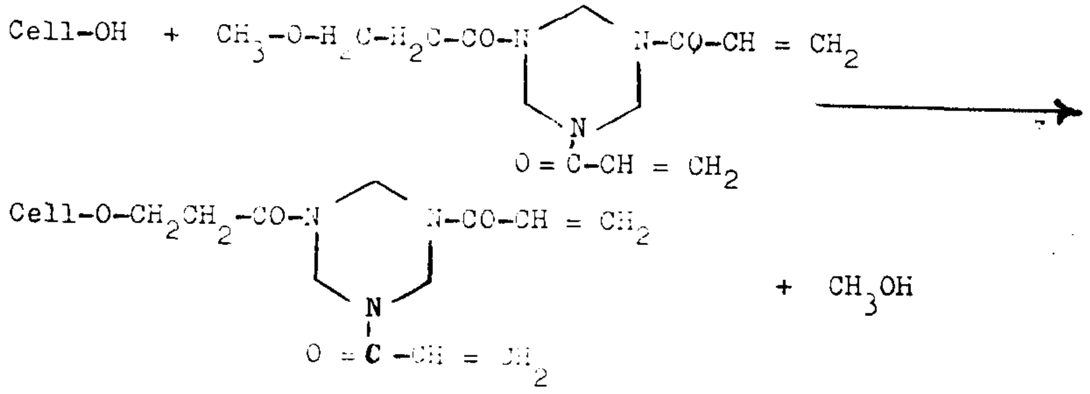
b) Alkaline hydrolysis of the modified cotton showed substantial amount of carboxyl groups, indicating hydrolysis of the carbamoylethyl groups to carboxyethyl groups.

Reaction of methyl alcohol with Hexahydro-1,3,5-triacryloyl-s-triazine (I):

The reaction of methyl alcohol with I in presence of sodium methoxide (0.05%) at 40°C for varying lengths of time (5-180 minutes) yields a number of reaction products as shown by thin-layer chromatography. This could be associated with hygroscopic character of methyl alcohol, since presence of water causes decomposition of sodium methoxide to yield sodium hydroxyde and the latter splitts the ring of I into simpler compounds. Also, it is likely that the methoxy-propionyl adduct of I (if it is present in this mixture) decomposes under the influence of the methoxide anion to give rise to I and methyl alcohol. In order to avoid these effects, the reaction between I and methyl alcohol was catalyzed by triethanolamine and was carried out in chloroform as solvent. Under these conditions only one acryloyl group of I could be saturated with methyl alcohol.

Reaction of the Hexahydro-1,3,5-mono (β-alkoxypropionyl)-diacryloyl-s-triazine with cotton cellulose:

Reaction of the adduct of I and methyl alcohol with cotton cellulose may occur via a substitution reaction or an addition reaction or both under certain conditions. According to detailed investigation concerning factors affecting this reaction, it is probably correct to say that reaction of hexahydro-1,3,5-mono(β-methoxypropionyl) diacryloyl-s-triazine (mono adduct of I) with cotton cellulose in nonaqueous medium proceeds essentially via a substitution reaction with elimination of methyl alcohol as shown by the mechanism suggested by the following equation.



Involvement of the double bonds in addition or polymerization reaction or both occurs if the reaction (shown in the above equation) is performed at higher temperature, i.e. above 130°C, or for longer duration, i.e. more than 10 minutes at 150°C, or using higher concentration of the mono-adduct (above 8%) at 150°C for 10 minutes.

PART II

Grafting Of Acrylonitrile and Methylmethacrylate Onto Methylolated Carbamoylethylated Cellulose Using Ceric Ammonium Sulphate As Initiator.

Ceric initiated graft copohymerization of acrylonitrile and methylmethacrylate onto methylolated carbamoylethyl cellulose was investigated. Regardless of the grafting conditions used this modified cotton showed lower graft yield and higher homopolymer content as compared with the nonmodified cotton cellulose. Furthermore ceric consumption during grafting of methylol carbamoylethyl cellulose is higher than during grafting of the nonmodified cotton. The opposite holds true for Ce (IV) consumption during oxidation. It is believed that in the acidic polymerization medium crosslinking occured via condensation of the methylol groups of the modified cellulose and adjacent cellulose hydroxyls.

$$\mathrm{Cell{-}O{-}CH_2{-}CH_2{-}CO{-}NH{-}CH_2OH} \xrightarrow{H^+} \mathrm{Cell{-}O{-}CH_2{-}CH_2{-}CO{-}NH{-}CH_2^+} + \mathrm{H_2O}$$

$$\mathrm{Cell{-}O{-}CH_2{-}CH_2{-}CO{-}NH{-}CH_2^+} + \mathrm{Cell{-}OH} \longrightarrow \mathrm{Cell{-}O{-}CH_2{-}CH_2{-}CO{-}NH{-}CH_2{-}O{-}Cell} + \mathrm{H^+}$$

Formation of crosslinked cellulose seems to be responsible for lower grafting as well as for the lower susceptibility to oxidation with ceric ions.