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## Biodegradable Cellulose Block Copolymers

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### ABSTRACT

Biodegradable polymers can be prepared by the incorporation of cellulose oligomeric blocks into the polymer backbone. Block copolymers prepared by reacting equimolar amounts of depolymerized cellulose triacetate (CTA) with MDI or TDI and block terpolymers prepared by reacting the CTA oligomer with poly(propylene glycol) capped with MDI or TDI were deacetylated and incubated with cellulysin at pH 5 and 50°C. The intrinsic viscosity of each copolymer decreased substantially even after 10 hr incubation time. There was negligible acid hydrolysis. Cellulose showed a smaller decrease at the same incubation time—probably due to its lower accessibility. Methods for incorporating cellulose oligomeric blocks and other biodegradable blocks into different types of polymers are discussed.

### INTRODUCTION

Most synthetic polymers are resistant to microbiological attack [1, 2]. Indeed, until recently, the paramount feature sought in polymers has been resistance to environmental degradation conditions (UV light, O<sub>2</sub>, fungi, bacteria, etc.).

Possible approaches to biodegradable systems were proposed by Rodriquez [1]. He suggested a search for new organisms for conventional polymers, the introduction of vulnerable units in the polymer chain, or using added nutrients, e.g., cellulose, as reinforcement in polymer composites. Potts et al. [2] suggested block copolymers containing segments of a biodegradable polymer as an approach to the synthesis of biodegradable polymers.

It is the purpose of this paper to demonstrate this latter approach is indeed a feasible procedure for the preparation of biodegradable polymers, that a variety of biodegradable blocks or segments may be employed, and to illustrate a number of synthetic schemes to prepare such polymers. Preliminary results of our work, including synthetic details, have been published elsewhere [3].

## DISCUSSION

The synthetic scheme for the preparation of the block copolymers containing cellulose oligomer blocks is outlined in Figs. 1 and 2. After blocking the 2,3,6-hydroxyls of the anhydroglucose units, the substitute cellulose is degraded using a mixture of acetic acid and water to an oligomer ( $\overline{D.P.}_n \sim 20$  to 30) containing reactive hydroxyl

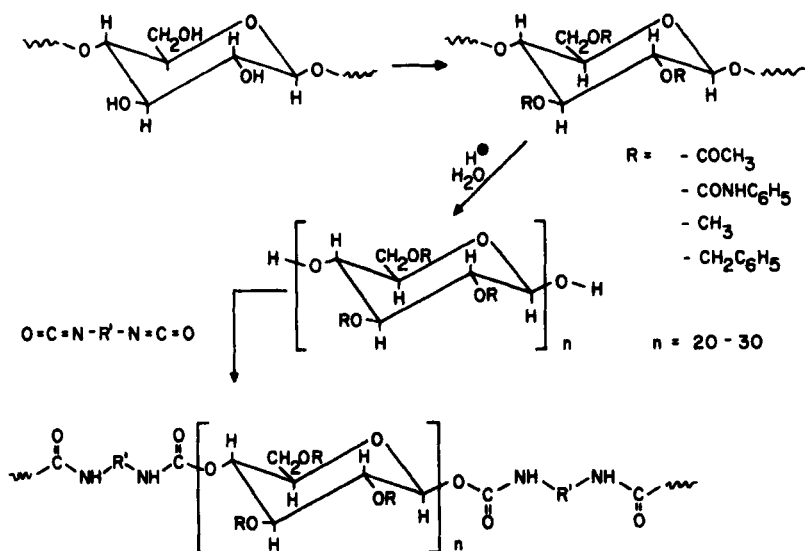
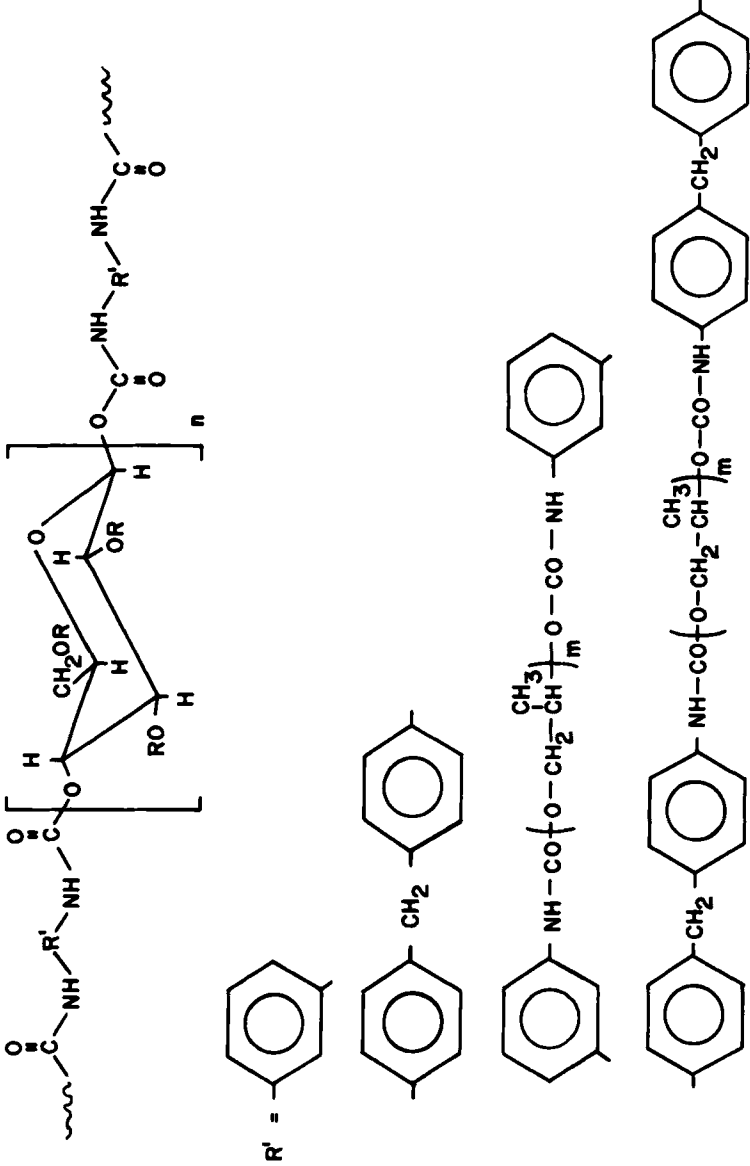


FIGURE 1.



Removal of R Group  $\longrightarrow$  CELLULOSE BLOCK COPOLYMERS

FIGURE 2.

end groups. As noted, a variety of blocking groups for the 2,3,6-hydroxyls may be employed.

The substituted cellulose oligomer blocks may be reacted with other difunctional blocks or with difunctional monomers to give a wide variety of block copolymers. For example, they can be coupled with diisocyanates or with polyethers (Fig. 2), polyesters, etc. capped with diisocyanates. Steinmann [4, 5] has prepared elastomeric fibers using cellulose triacetate oligomers and the same general reaction scheme.

Removal of the hydroxyl blocking groups will give rise to another group of block copolymers with a wide variety of properties depending upon the composition of the blocks.

Of the various possible blocking groups for the 2,3,6-hydroxyls of the anhydroglucose unit, the acetyl groups is obviously the one of choice as regards ease of removal. However, it is important that the blocking groups are not inadvertently removed during the degradation and chain-extension steps. Otherwise branching and cross-linking can result. Nevertheless, the acetyl group was selected for the present work. The resulting block copolymers are shown in Fig. 3.

They were deacetylated with sodium methoxide. The properties of the copolymers are given in Table 1. No attempt was made to determine their molecular weights, but their intrinsic viscosity values were considered to be adequately high. The degree of acetylation of the deacetylated copolymers is sufficiently low that enzymatic attack should not be impeded.

Each deacetylated copolymer was incubated with cellulysin at 50°C and pH 5, and the enzymatic hydrolysis monitored by intrinsic viscosity measurements. The results are summarized in Table 2 and Fig. 4. In each case, a control was run in the absence of the cellulysin. The acid hydrolysis of the copolymers was negligible.

However, there was a significant decrease in the intrinsic viscosity for each of the copolymers, even at 10 hr incubation time. Cellulose showed a smaller decrease—15% vs 26 to 54% for the block copolymers, undoubtedly due to the lower accessibility of the cellulose.

It is apparent the incorporation of cellulose blocks in a polymer will result in biodegradability and, gratifyingly, the block copolymers degrade more rapidly than cellulose itself.

The synthetic approach outlined above is quite simple and straightforward. Other biodegradable oligomeric blocks, e.g., starch and proteins (casein, gelatin), could be used to replace the cellulose blocks. It is important, as noted above, that the D.S. of the substituted oligomeric blocks be as close to 3 as possible and that no desubstitution occurs during the degradation or chain-extension steps. Otherwise, the degree of functionality of the oligomeric block quickly

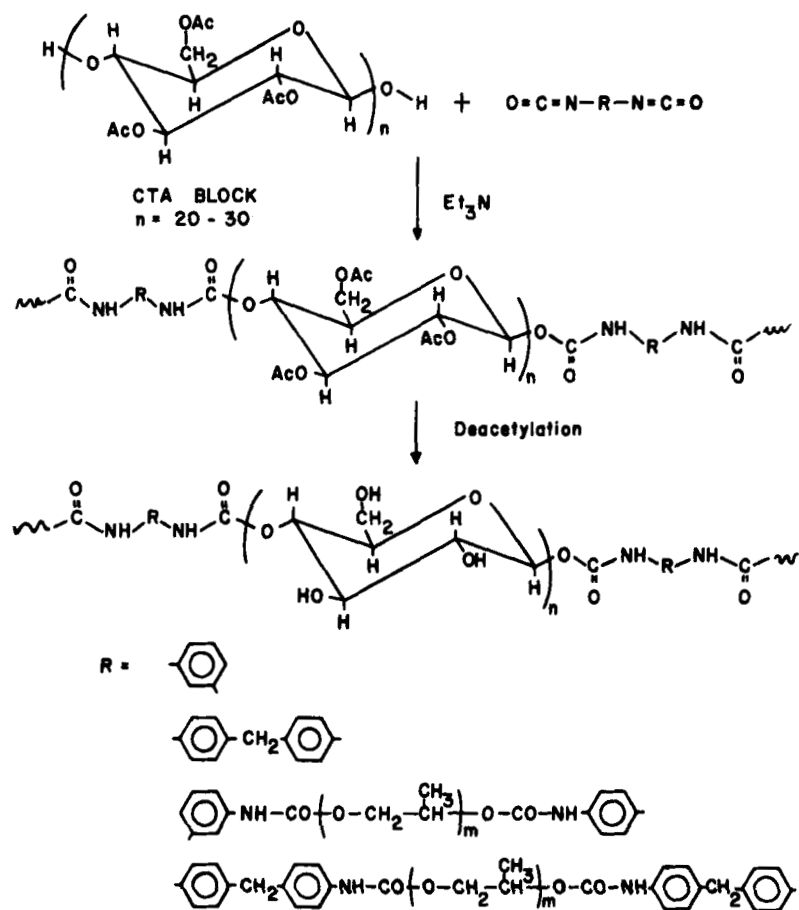


FIGURE 3.

increases, causing a rapid increase in the onset of gelation, or conversely, a rapid decrease in the maximum obtainable D.P. of the block copolymer before the onset of gelation. The above synthetic procedure is also limited to condensation type polymers.

Outlined below are two reaction schemes to circumvent these difficulties and extend the concept of introducing a biodegradable block into addition-type polymers.

TABLE 1. Summary of Copolymer Properties<sup>a</sup>

Copolymer	Original			Deacetylated	
	Yield (%)	$[\eta]^b$	Softening range (°C)	$[\eta]^c$	Acetyl valued
CTA-MDI	70	0.37	180-240	0.35	9.0
CTA-TDI	90	0.41	245-260	0.36	9.8
PPG-MDI-CTA	85	0.33	300-310	0.43	10.3
PPG-TDI-CTA	89	0.64	315-330	0.52	10.7
CTA (depolymerized)	93	0.16	210-222 <sup>e</sup>		10.6

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<sup>b</sup>In  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (9/1) solution at 25°C.

<sup>c</sup>In DMSO solution at 30°C.

<sup>d</sup>Average of two determinations. Acetyl value of 10% corresponds to a D.S. = 0.42.

<sup>e</sup>Melting range.

TABLE 2. Enzymatic Degradation Results<sup>a</sup>

Polymer	% Decrease in $[\eta]$						
	2 hr	5 hr	9 hr	10 hr	24 hr	48 hr	72 hr
CTA-MDI	6.1	31.4	-	54.3	61.4	71.4	-
CTA-TDI	14.7	20.8	-	36.1	55.6	69.4	-
CTA-MDI-PPG	25.6	33.0	-	40.0	68.6	74.4	-
CTA-TDI-PPG	14.9	21.4	-	26.2	49.9	62.1	65.0
Cellulose			15.4				

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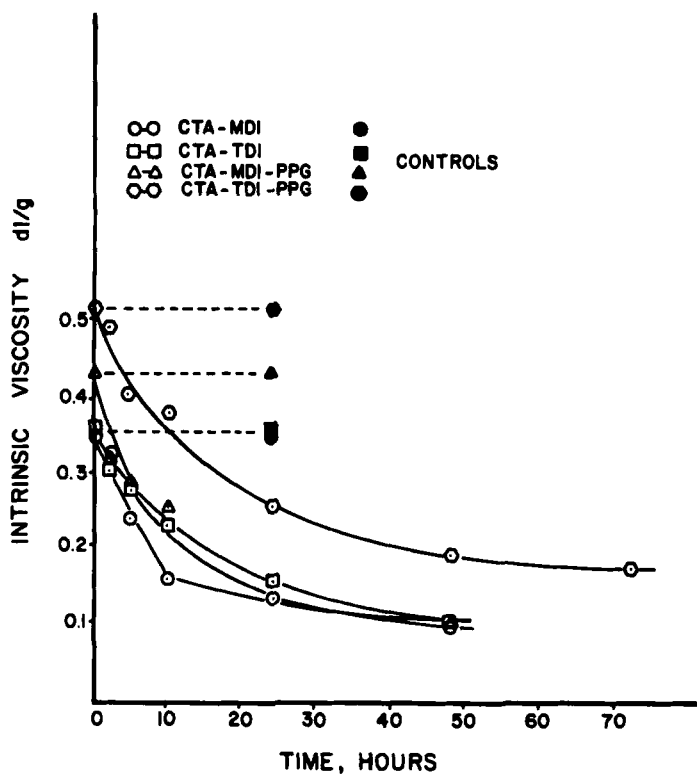
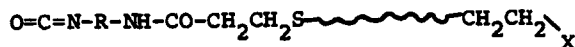
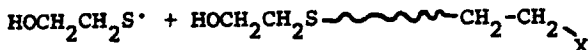
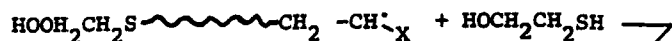
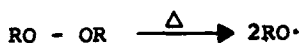


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+ CTA Block, Deacetylation



FIGURE 5.

In the first scheme, Fig. 5, a hydroxyl group is attached to a vinyl polymer and then capped with an isocyanate group and a block copolymer formed by reaction with a cellulose triacetate oligomeric block. Deacetylation would yield a block copolymer with a biodegradable cellulose block.

Another route is outlined in Fig. 6. By proper control of the degree of substitution in the ethylene sulfide grafting step, a grafted polymer of the hypothetical structure I would be formed containing a biodegradable cellulose block between the vinyl chains. Of course, cellulose of low D.P. could be used for the graft substrate.

Again, these schemes could be extended to starch and protein like materials.

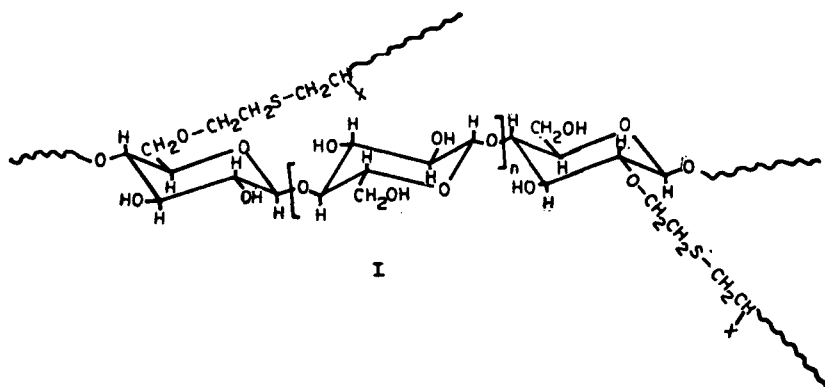
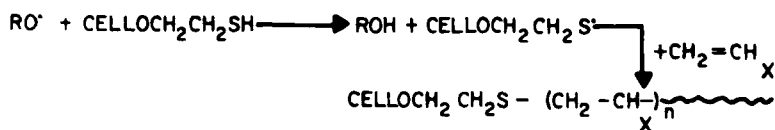
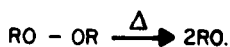
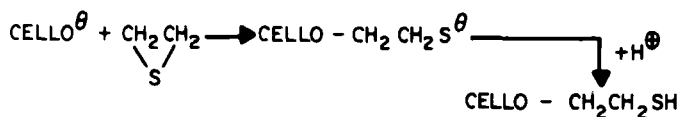


FIGURE 6.

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