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Biodegradable Cellulose Graft Copolymers.
II. Vinyl Addition-Type Graft Reactions

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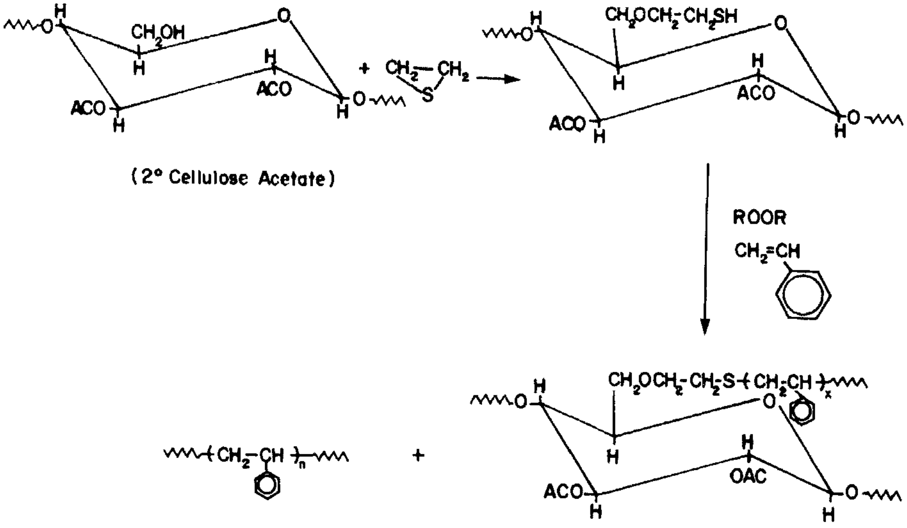
ABSTRACT

The synthesis of cellulose graft copolymers using a vinyl addition type graft reaction procedure is described. Cellulose acetate (D.S. 2.37) was first mercaptoethylated and then reacted with styrene in the presence of benzoyl peroxide. The degree of grafting was varied. Grafting was confirmed by IR spectroscopy. The copolymers were smoothly deacetylated with NaOMe. The deacetylated products were readily degraded by cellulysin.

INTRODUCTION

In Part I the synthesis of cellulose graft copolymers using a condensation type grafting reaction was described. The synthesis of graft copolymers employing an addition-type grafting step is presented here. The synthetic scheme is outlined below. It is essentially the procedure of Hermans and Chaudhuri [1, 2]. However, in one case BF_3-trietherate was used as a catalyst for the mercaptoethylation step. Deacetylation would give a cellulose graft copolymer that should be degraded by enzymes that attack cellulose.



EXPERIMENTAL

Materials

Cellulose acetate (CA) was supplied by Tennessee Eastman Co., styrene and boron trifluoride/trietherate were obtained from Eastman Chemical Co., and ethylene sulfide from ICN Pharmaceuticals.

Mercaptoethylation of Secondary Cellulose Acetate

CA (D.S. 2.37, 0.13 mmol) was dissolved in dioxane (250 mL) in a 3-neck, 500-mL flasked equipped with a heating mantle, magnetic stirrer, thermometer, and N_2 inlet and outlet tubes. The flask and contents were heated to 75° under N_2, ethylene sulfide (8 g, 0.13 mmol) was added, and the mixture heated for 12 h, then poured into isoProH to precipitate a white product (I) which was washed several times with isoProH and then dried under vacuum. The yield was 8.2 g.

The reaction was repeated but BF_3-etherate (0.3 mL) was added to the CA solution and the mixture stirred at 65° for 1 h under N_2 prior to the addition of the ethylene sulfide. Heating was then continued at 65° for an additional 12 h. The yield of Product (II) was 8.5 g.

TABLE 1. Sulfur Analyses

Mercaptoethylated polymer	Sulfur (%)	D.S.[a]
I	1.58	0.08
II	5.08	0.25

[a] Assuming $-OCH_2CH_2SH$ as substituent

Chemical Grafting onto Mercaptoethylated Cellulose Acetate

A slight modification of the procedure of Hermans and Chaudhuri [1, 2] was employed.

Product I was dissolved in acetone and a film was solvent cast. A portion of the film was analyzed for sulfur (Table 1). Analysis was by Schwarzkopf Microanalytical Laboratory.

Styrene was freed of inhibitor by distillation under vacuum. Benzene was refluxed and distilled over Na. The film of I was cut into small pieces (1.1 g) and placed in a tube along with benzoyl peroxide (0.011 g), benzene (15 mL), and styrene (4.4 g). The tube was connected to a high vacuum line and frozen and thawed three times under vacuum. Then the evacuated tube was sealed and placed in a constant temperature bath at 65° for 24.5 h. The film was removed and extracted for 4 d with toluene in a Soxhlet extractor. The weight of film after extraction and drying was 1.18 g. It was coded III.

The procedure was repeated with II. It was not completely soluble in acetone and the insoluble portion was removed by centrifugation. A film was cast from the acetone-soluble portion. A portion of the film was analyzed for sulfur (Table 1). The yield of product (IV) after reaction with styrene was 1.26 g.

IR spectra of films of III and IV were obtained with a P.E. 337 Grating Spectrometer at R.T. The IR data are summarized in Table 2.

The intrinsic viscosities of III, IV, and the original cellulose acetate were determined at 30 ± 0.02° employing a Ubelholde viscometer with dioxane as solvent. The results are in Table 4.

Deacetylation of Graft Copolymers

III and IV (0.19 g) were placed in screw-cap bottles containing CH_3OH (60 mL) and sodium (0.26 g). The bottles were tightly capped, allowed to stand for 24 h, the films collected, washed with isoProH, and dried under vacuum. Their acetyl values were determined by

TABLE 2. Infrared Absorption Peaks Graft Copolymers III and IV

Group	Assignment (cm^{-1})
$-COCH_3$	1760
$-OH$	3430
Aromatic C–H out-of-plane bending	690, 850
C–C ring stretching	1400-1500
C=C stretching	1450-1650

the method of Eberstadt [3] and are listed in Table 2. Deacetylated Copolymer III formed clear, flexible, and strong films; Copolymer IV formed slightly opaque but strong films.

Enzymatic Hydrolysis

The deacetylated copolymers (III, 0.0307 g; IV, 0.0421 g) were dissolved in tetrahydrofuran and films solvent cast. The dried films were placed in screw-cap bottles containing 10 mL of 0.5% Cellulysin solution buffered to pH 5 with 0.05 M Na acetate and HOAC and incubated at 50° for 4 d. Controls (III, 0.0249 g; IV, 0.0120 g) were run in the absence of Cellulysin. The films were collected, washed with water dried under vacuum at 60°, and reweighed. A white friable powder was present in the sample bottles containing Cellulysin.

RESULTS AND DISCUSSION

Secondary cellulose acetate was selected as the graft substrate to permit some control of the degree and location of the polystyrene graft side-chains. The mercaptoethylation of the cellulose acetate was carried out both in the presence and absence of BF_3 as a catalyst. Higher levels of mercaptoethylation were obtained in the presence of BF_3 as shown by the sulfur analyses in Table 1. Whether a greater number of individual mercaptoethyl groups were added to the cellulose backbone or a number of vinyl sulfide units added at one site on the cellulose acetate in the presence of BF_3 cannot be decided. The latter is unlikely, however, since no special drying precautions were taken. However, in the case of II there was an acetone-insoluble portion. As polyethylene sulfide is insoluble in any solvent at room temperature, it is always possible that several CH_2CH_2S groups reacted at an OH group on the cellulose acetate. Another possibility is that some cross-linking occurred by mutual termination of mercaptoethylated side groups on different cellulose chains.

TABLE 3. Weight Increases after Grafting and Toluene Extraction

Sample	Original weight (g)	Weight increases (g)	Weight increases (%)
III	1.1	0.08	7.2
IV	1.1	0.16	14.5

TABLE 4. Intrinsic Viscosity Data

Polymer	Solvent	$[\eta]$ (dL/g)
III	Dioxane	1.58
IV	Dioxane	0.50
Cellulose acetate (D.S. 2.37)	Dioxane	1.38
Polystyrene homopolymer:		
1. From III	$CHCl_3$	1.8
2. From IV	$CHCl_3$	0.9

The IR spectrum of III and IV indicated that the mercaptoethylation and styrene grafting steps were successful. The IR data are summarized in Table 2. A strong carbonyl absorption at 1760 cm^{-1} and an OH absorption peak at 3430 cm^{-1} confirm the presence of partially acetylated cellulose acetate. Evidence for the presence of styrene side-chains is the aromatic out-of-plane bending at 690 and 850 cm^{-1}, skeletal vibrations for C–C stretching within the ring at 1400-1500 cm^{-1}, and aromatic C=C bonds at 1450-1650 cm^{-1}.

Further evidence that the grafting was successful are the weight gains of III and IV after reaction with styrene and extraction with toluene, viz., 7.2 and 14.5%, respectively (Table 3). Hermans and Chaudhuri [2] state that when the percent grafting is high, quantitative homopolymer removal is not possible. However, the weight increases are unlikely to be due solely to polystyrene at the low degrees of grafting which were achieved.

The intrinsic viscosity of III was 1.58 dL/g (Table 4), which is significantly higher than that of the starting material, cellulose acetate (1.38 dL/g). The intrinsic viscosity of IV (0.50 dL/g) was lower than that of the cellulose acetate. However, IV was prepared from only the acetone-soluble portion of the cellulose acetate mercaptoethylated with BF_3. The BF_3 probably caused high mercaptoethylation to occur, resulting in a decrease in solubility as the degree of mercaptoethylation increased, particularly for the high molecular weight cellulose acetate fractions. This most likely resulted in

TABLE 5. Acetyl and D.S. Values

Polymer	Acetyl values	D.S.
III	9.0	0.37
IV	11.9	0.50

TABLE 6. Enzymatic Degradation Data Deacetylated Polymers

Polymer	Weight loss (mg)[a]	Weight loss (%)
III	3.5	11.4
IV	17.0	40.0
Control III[b]	0.4	1.6
Control IV[b]	0	0

[a] After 4 d in 0.5% Cellulysin solution, pH 5.
[b] In absence of Cellulysin.

extraction of only low molecular weight and least substituted polymer. In addition, as noted above, cross-linking probably occurred preferentially, insolubilizing the high molecular weight species. The polystyrene side-chains were probably shorter on IV than on III judging from the recovered polystyrene intrinsic viscosity data. This may have influenced the intrinsic viscosity values of the grafted copolymers.

Copolymers III and IV deacetylated smoothly using NaOMe. Acetyl and D.S. values after deacetylation are in Table 5. The D.S. values are sufficiently low to permit enzymatic attack. Enzymatic degradation data are summarized in Table 6. Weight loss measurements were used because the deacetylated copolymers were insoluble in common solvents. A white friable powder was also evident in the tube containing IV and Cellulysin. The control samples had insignificant weight losses. It is evident that these graft copolymers are biodegradable.

REFERENCES

[1] D. Chaudhuri and J. J. Hermans, J. Polym. Sci., 48, 159 (1960).
[2] D. Chaudhuri and J. J. Hermans, Ibid., 51, 373 (1961).
[3] L. J. Tanghe, L. B. Genung, and J. W. Mench, Methods in Carbohydrate Chemistry, Vol. 3, Academic, New York, 1963, p. 201.

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