Note

Synthesis of nitrogenous derivatives of cellulose–poly(methyl vinyl ketone) copolymers. Oximes, semicarbazones, and hydantoins

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(Received April 7th, 1972)

The preparation of nitrogenous derivatives of cellulose is of particular interest in modifying the mechanism and rate of oxidation of cotton[1] We have recently reported the preparation of fibrous cellulose-poly(methyl vinyl ketone)** copolymers[2]; a graft copolymer with a covalent linkage between cellulose and poly(methyl vinyl ketone) is formed We have now extended these investigations to obtain nitrogenous derivatives by the reaction of the ketone groups of the copolymers with hydroxylamine hydrochloride (**1**), semicarbazide hydrochloride (**2**), and potassium cyanide (**3**) plus ammonium carbonate

EXPERIMENTAL

Materials — Deltapine cotton in the form of 7s/3 yarn was purified to yield cellulose[3] (mol wt [4] 700,000) The ethanol, pyridine, sodium acetate, ammonium carbonate, hydroxylamine hydrochloride (**1**), semicarbazide hydrochloride (**2**), and potassium cyanide (**3**) used, were of analytical grade Distilled water was used to prepare the solutions The samples of fibrous cellulose–poly(methyl vinyl ketone) were prepared by the methods described by Reine and Arthur[2].

Methods — Physical tests were performed by ASTM methods[5]. I.r. spectra of materials in potassium bromide discs (sample KBr $= 1$ 300) were recorded with a Perkin–Elmer***, double-beam, i r spectrophotometer Nitrogen analyses were made by the Kjeldahl method[6]

Reaction conditions — The solution was placed in a test tube ($\sim 3 \times 20$ cm) which had a standard-tapered end, and the fibrous cellulose–poly(methyl vinyl ketone) copolymer was added. The tube was fitted with a condenser, and the contents were

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**Poly(3-buten-2-one)

***Trade names are given as part of the exact experimental conditions, and not as an endorsement of the products over those of other manufacturers heated for the desired time in an oil bath at the desired temperature After completion of the reaction, the treated, fibrous copolymer was removed from the solution, washed several times with distilled water, and dried for 1 h in an air stream at 60° The extent of reaction was ascertained by determining the nitrogen content and recording the i r. spectrum of the sample

Reaction with **1** Fibrous cellulose–poly(methyl vinyl ketone) copolymer (2 g), ethanol (20 ml), pyridine (5 ml), and compound **1** (2 6 molecular proportions per ketone group contained in the copolymer) were refluxed for 2 h in[7] an oil bath at 82° Then, the reacted, fibrous copolymer was washed with water, and dried in an air stream for 1 h at 60° Quantitative reactions of the ketone groups of the copolymer with compound **1** were observed as follows· reacted copolymer having 7 4% poly-(methyl vinyl ketone) "add-on" (increase in weight) contained N 1.49% (calc 1 37%); having 18% add-on, N 3 15% (calc 3 08%), having 30% add-on, N 4 20% (calc 4 46%), and having 45% add-on, N 5 79% (calc. 5 92%)

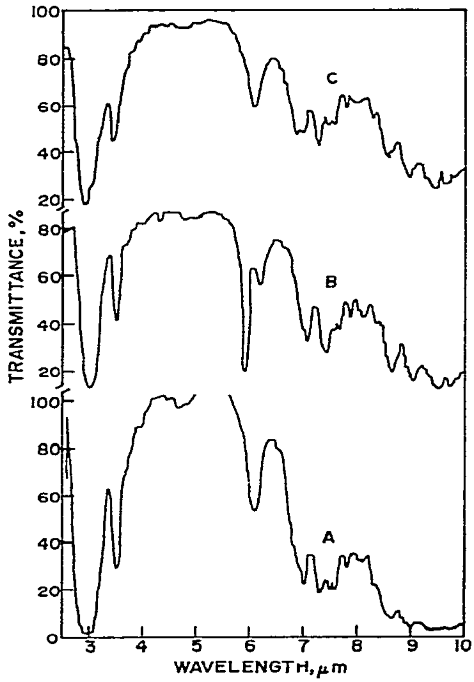

Fig 1. Infrared spectra A, purified cotton cellulose, B, cellulose–poly(methyl vinyl ketone) copolymer, C, product from reaction of hydroxylamine hydrochloride (1) with cellulose–poly(methyl vinyl ketone) copolymer

The i r spectrum of purified cotton cellulose is shown in Fig 1A, and that of cellulose–poly(methyl vinyl ketone) having 45% add-on in Fig 1B, 5 87 μm (C=O)[8] In Fig 1C is shown the i r spectrum of the product from reaction of **1** with cellulose–poly(methyl vinyl ketone) copolymer having 45% add-on Comparison of spectrum 1B with spectrum 1C indicated that quantitative oximation of the copolymer at the ketone group (5 87 µm) had occurred The properties of the oximated, fibrous cellulose–poly(methyl vinyl ketone) copolymers are shown in Table I The oximated copolymers had properties satisfactory for most textile uses

TABLE I

PROPERTIES OF OXIMATED, FIBROUS COTTON CELLULOSE–POLY(METHYL VINYL KETONE) COPOLYMERS

Polymer content of copolymer, % "add-on"	*Breaking strength* $\times 10^{-3}$ *(g)*	*Elongation-at-break (%)*	*Tenacity (g/tex)*	*Breaking toughness (g/tex)*	*Average stiffness (g/tex)*
Control[a]	4 13	16	16	0 72	99
Control[b]	4 17	15	17	0 74	111
Control[c]	4 45	14	18	0 82	130
7 5	3 13	13	11	0 50	84
34	3 54	13	9 8	0 39	73

[a] Purified, fibrous cotton cellulose, 7 s/3 yarn [b] Purified yarn irradiated to a dosage of 520 GeV/g [c] Purified yarn (2 g) heated under reflux with pyridine (5 ml), ethanol (20 ml), and hydroxylamine hydrochloride (**1**, 1 g) for 2 h at 82°

Reaction with **2** — Fibrous cellulose–poly(methyl vinyl ketone) copolymer (2 g), sodium acetate (1 g), water (25 ml), and compound **2** (2 6 molar proportions per ketone group contained in the copolymer) were heated for[9] 30 min at 60° Then the reacted, fibrous copolymers were washed with water, and dried in an air stream for 1 h at 60° For products from reaction of **2** with cellulose–poly(methyl vinyl ketone) copolymer, both the i r spectra and the nitrogen analyses indicated that less than quantitative reaction of the ketone groups had occurred Reacted copolymer having 15% poly(methyl vinyl ketone) add-on contained N 5 89% (calc for quantitative reaction, N 7 15%), having 27% add-on, N 8 22% (calc 10 94%), and having 35% add-on, N 10 14% (calc 12 94%)

Reaction with **3** — Fibrous cellulose–poly(methyl vinyl ketone) copolymer (2 g), compound **3** (2 molecular proportions per ketone group contained in the copolymer), ammonium carbonate (4 molecular proportions), and 50% aqueous ethanol (40 ml) were heated[10] for 3 h at 80°; then the reacted, fibrous copolymers were washed with water, and dried for 1 h in an air stream at 60° For products from reaction of **3** and ammonium carbonate with cellulose–poly(methyl vinyl ketone) copolymer, both the i r spectra and the nitrogen analyses indicated that less than quantitative reaction of the ketone groups had occurred. Reacted copolymer having 6 3% poly(methyl vinyl ketone) add-on contained N 1 08% (calc for quantitative reaction, assuming hydantoin formation, 2 35%), having 16% add-on, N 2 73% (calc 5 40%), and having 27% add-on, N 3 76% (calc 8 00%) If formation of cyanohydrin derivatives of the copolymers is assumed, based on nitrogen analyses, occurrence of quantitative reaction was indicated However, the formation of these derivatives is unlikely, because presence of unreacted ketone groups was indicated by the i r spectra, and there was no CN stretching absorption near[8] 4 5 μm in the spectra

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