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Vinylbenzyl Ethers of Cellulose. Preparation and Polymerization*

H. STEVE KOENIG and CARLETON W. ROBERTS, *Textile Department, Clemson University, Clemson, South Carolina 29631*

Synopsis

Grafting of chain-growth polymerizable monomers onto cellulose has been a thoroughly investigated area. Introduction of polymerizable monomeric species chemically bound to cellulose has been less fruitful. Crotonate esters, methacrylate esters, and allyl and vinyl derivatives are examples where subsequent polymerization to crosslinked species has been described. Reported are the reactions of vinylbenzyl chloride with causticized cotton fabric to give a series of vinylbenzylated celluloses with degrees of substitution from 0.05 to 0.26. Homopolymerization of these or copolymerization with maleic anhydride or dimethyl maleate gave little or no crosslinking under the conditions employed. Vinylbenzyl cellulose acetate proved to be a polymerizable "prepolymer" with diethyl maleate.

INTRODUCTION

Formation of radical sites on the cellulose chain by homolytic bond fission (radical abstraction of a hydrogen from carbon or oxygen) often leads to chain scission and does not necessarily leave the substrate polymer intact. Chain-growth polymerization initiated by the cellulose radical leads to "graft copolymers" in the case of a single monomer or more complex polymeric chains (linear or crosslinked) if mixtures of copolymerizable monomers are present.[1] An added complication arises if the original initiation mechanism also initiates mono- or copolymerization of the added monomer(s). Contamination of the grafted cellulose copolymeric species requires separation of homo- or copolymers from the grafted material.

Several attempts have been made to overcome the disadvantages of initiation processes requiring bond fission in the cellulosic by chemically modifying the cellulose with a potentially more active initiating site. Many of these modifications are reviewed.[2] Particular examples of the introduction of vinyl moieties on cellulose are: the formation of ethylvinyl cellulose[3] (grafting by subsequent polymerization with maleate esters); the formation of crotonate esters[4] and subsequent crosslinking by "Michael additions" of hexamethylenediamine; formation of methacrylate esters of cellulose acetate[5] and subsequent graft (linear and crosslinking) poly-

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merizations with methyl methacrylate and ethylene dimethacrylate; formation of crotonate and maleate esters of cellulose acetate and grafting of styrene[6] to give a 6–8% graft; introduction of a methacrylamide moiety, by way of a $-OCH_2CH_2-$ bridge, onto cellulose acetate and subsequent graft polymerization using styrene[6]; introduction of an acrylamide linked through a $-OCH_2NH-$ bridge to cellulose and direct crosslinking of the substituted cellulose.

The controlled introduction of a styryl moiety onto cellulose through a benzyl ether linkage offered an excellent opportunity to study the copolymerization behavior of styrene on a polymeric substrate. Especially of interest is the possibility for directed copolymerization of the styryl moiety with comonomers having strong alternating tendencies. This paper reports preliminary results on the vinylbenzylation of cellulose and cellulose acetate and attempted copolymerization of each with maleic anhydride and diethyl maleate.

EXPERIMENTAL

Materials and Analyses. Infrared analyses were obtained from a Perkin-Elmer Model 237B spectrophotometer. Infrared analyses of the cellulosics were obtained using the KBr sampling method described by O'Connor et al.[8] except where noted. Hydrolyzed cellulosics were prepared by dissolving the appropriate samples in copper ethylenediamine (CUEN) and precipitating the cellulosics with 10% H_2SO_4 as described by McCaffery.[9] NMR spectra were obtained from a Varian 60 MHz spectrophotometer. Ultraviolet reflectance spectra were obtained from a Zeiss-DMC-25 spectrophotometer. Ultraviolet fluorescence analyses were performed using a hand-held UVSL-25 Minerallight.

Reagent-grade cyclohexanol, pyridine, acetic anhydride, maleic anhydride (MA), diethyl maleate (DEM), chloroform, and dimethyl sulfoxide (DMSO) were used directly. Reagent-grade benzyl chloride was distilled before use. Sodium methoxide solutions were prepared by dissolving the required amounts of either sodium methoxide or sodium in synthetic-grade anhydrous methanol. Monomer-grade vinylbenzyl chloride (VBC), 60% meta, 40% para, containing 50 ppm *t*-butylcatechol, was obtained from the Dow Chemical Company.

Preparation of Benzylcyclohexyl Ether. Cyclohexanol (318 ml, 3.0 moles) was added to a 1-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, a thermometer, a dropping funnel, a condenser connected to a $CaCl_2$ drying tube, and a Glas-col heating mantle. The alcohol was heated to 150°C, flushed with nitrogen, and 6.9 g (0.30 mole) sodium was added portionwise. Freshly distilled benzyl chloride (50 ml, 0.435 mole) was added dropwise to the sodium cyclohexanate solution and the reaction was allowed to proceed for 2.5 hr at reflux (155°C). The reaction mixture was cooled and filtered by suction to remove NaCl. The filtrant was fractionally distilled at 60°C and 10 mm to remove cyclohexanol. The pressure was reduced to 3 mm and the distillation was continued to give a

60-ml fraction, bp 105–110°C. The distillate was redried over $CaCl_2$, filtered, and vacuum distilled to yield 40 g (70%) product, bp 88–91°C/1.3 mm, n^{20} 1.5178 (lit.[10] n^{20} 1.5178); Beilstein test for halogen negative; IR 1087 (C—O—C); 1439, 1351 (CH_2—O—acyclic); 733, 694 cm^{-1} (C_6H_5).

Preparation of ar-Vinylbenzyl cyclohexyl Ether. Cyclohexanol (318 ml, 3.0 moles) was added to a 1-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, a thermometer, a condenser connected to a $CaCl_2$ drying tube, a dropping funnel, and a Glas-col heating mantle. The alcohol was heated to 150°C, flushed with nitrogen, and 6.9 g (0.30 mole) sodium was added portionwise during 15 min. Vinylbenzyl chloride (66 ml, 0.44 mole) was added dropwise during 5 min, and the reaction was allowed to proceed at 150°C for 2 hr. The reaction was cooled to room temperature (23°C), and 300 ml of anhydrous ether was added to the flask. The ether solution was separated and washed with six 100-ml portions of water. The organic layer was transferred to a flash evaporator, and the ether and the excess cyclohexanol were evaporated under reduced pressure (2.5 mm) at 60°C. The residue was dissolved in 100 ml anhydrous ether, dried over anhydrous $MgSO_4$ (0.1 g hydroquinone added), and the mixture was filtered. The ether was evaporated under reduced pressure, and the residue was vacuum distilled between 40–60°C and 0.05 mm to remove cyclohexanol and unreacted VBC. The distillation was continued, and 14 g (22%) colorless product was collected, bp 92–94°C/0.01 mm. The residue polymerized during the final distillation. No efforts were made to optimize the yield: n^{25} 1.5368; IR 1087 (C—O—C); 1629, 1605, 1585 (C═C—C_6H_4); 826, 794, 714 cm^{-1} (C_6H_4 meta, para isomers); NMR (neat, TMS) δ 7.0 (mult, AR, 4H), 6.45 (two quartets, meta, para isomers, AR—CH═C, 1H), 5.50 (two quartets, meta, para isomers, AR—C═CH (trans), 1H), 4.96 (two quartets, meta, para isomers, AR—C═CH (cis), 1H), 4.25 (sgl, O—CH_2—AR, 2H), 3.3–2.9 (broad mult, C_5CH—O—, 1H), 2.0–1.0 (broad mult, cyclohexane, 10H).

ANAL. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32; O, 7.40. Found: C, 82.63; H, 9.12; O (diff), 7.69; Cl, 0.54. Chlorine impurity based on VBC is 2.32%.

Formation of Sodium Cellulosate. Bleached and desized 80 × 80 cotton print cloth was used. The fabric samples were dried at 60°C for 15 min in a vacuum desiccator prior to use. A dry, 3.5-g fabric sample was preswollen at room temperature in approximately 100 ml of 20% NaOH for 15 min and was washed with stirring during 15 min with four changes (150 ml each) of dry methanol.[11] The sample was added to 300 ml of 1.65N sodium methoxide in methanol contained in a 1-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, a $CaCl_2$ drying tube, and a magnetic stirrer. The reaction was allowed to proceed at room temperature under anhydrous conditions and mild agitation for 15 min.[11] The sample was removed and the excess sodium methoxide solution on the fabric was extracted by washing the sample, with stirring during 20 min, with four changes (150 ml each) of dry DMSO at room temperature. The degree of substitution (D.S.) of the sodium cellulosate was determined in a separate experiment by soaking the sample in excess 0.10*N* HCl for 1 hr and then back-titrating with 0.10*N* NaOH.[11] The sodium cellulosate D.S. was found to be 0.55.

Preparation of Benzyl Cellulose. A 3.5-g fabric sample of sodium cellulosate was added to a solution of 10 ml of excess benzyl chloride in 250 ml DMSO[12] contained in a 1-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, a condenser connected to a $CaCl_2$ drying tube, a thermometer, a Glas-col heating mantle, and a magnetic stirrer. The reaction was allowed to proceed under anhydrous conditions and mild agitation at 110°C for 3 hr or until the fabric dissolved. The reaction mixture was poured into 1 liter of vigorously stirred water, and the precipitated benzyl cellulose was collected on a sintered glass funnel. The precipitate was washed with 1 liter boiling water and 500 ml 95% ethanol until the filtrants were clear. The product was dried in an oven at 80°C and was weighed to yield 4.4 g (90%) of an off-white powder: benzylation D.S. = 0.50 based on per cent weight increase; IR 1639, 741, 699 cm^{-1} (C_6H_5).

Preparation of Vinylbenzyl Cellulose. Five 3.5-g fabric samples of sodium cellulosate were added to separate solutions of 30 ml excess VBC in 250 ml dry DMSO contained in 1-liter, three-necked, round-bottomed flasks each equipped with a thermometer, a nitrogen inlet and outlet, a Glas-col heating mantle, and a magnetic stirrer. The reactions were allowed to proceed for 1 hr at various temperatures between 23°C and 80°C. The samples were removed from their reaction flasks and were washed with vigorous stirring with four changes of methanol (150 ml each), four changes of water (150 ml each), and two changes of acetone (150 ml each). The samples were dried at 60°C in a vacuum desiccator and then weighed. The washing process was repeated until constant weights were obtained. The etherification D.S. was determined by weight difference: UV max (reflectance) 355, 295–230 nm; IR (hydrolyzed cellulose) 1626, 1600, 1575 ($C{=}C{-}C_6H_4$); 826, 794, 714 cm^{-1} (C_6H_4 meta, para isomers).

ANAL. Calcd for $C_{57}H_{88}O_{40}$ (D.S. 0.13): C, 48.44; H, 6.28; O, 45.29. Found: C, 48.10; H, 6.29; O, 45.62.

Ultraviolet Fluorescence of Vinylbenzyl Cellulose. Ultraviolet fluorescent analysis of vinylbenzyl cellulose was obtained using a hand-held ultraviolet light source capable of emitting long or short wavelength radiation. Vinylbenzyl cellulose (D.S. 0.16), regenerated cellulose, and Whatman #1 filter paper with monomeric VBC added directly and air dried were examined.

Preparation of Vinylbenzyl Cellulose Acetate. A dry, 0.5-g fabric sample of vinylbenzyl cellulose (D.S. 0.16) was added to 40 ml dry pyridine and 40 ml acetic anhydride contained in a 250-ml Erlenmeyer flask that was previously dried and flushed with nitrogen. The acetylation was allowed to proceed at room temperature with vigorous agitation for four days or until complete solution was effected. The reaction mixture was poured into 400 ml vigorously stirred cold water and the precipitated product collected on a sintered glass funnel. The product was washed with water until neutral to pH paper and then dried to give 0.9 g (82%) of a white fibrous solid. Acetylation D.S. was 2.5 based on weight difference. A 0.20-g sample of the vinylbenzyl cellulose acetate was dissolved in 100 ml $CHCl_3$, and a film was cast by pouring the solution into a clean Pyrex dish and evaporating the solvent in an oven at 80°C: IR 1754 (C=O); 1227 (C—O); 3448 (O—H); 826, 800, 719 cm^{-1} (C_6H_5 meta, para isomers).

Copolymerization of Vinylbenzyl Cellulose Acetate with Diethyl Maleate. Dry vinylbenzyl cellulose acetate fiber (0.50 g, 2.34 moles) was suspended in a solution of 30 ml DEM in 300 ml $CHCl_3$ contained in a 1-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, a thermometer, a condenser connected to a $CaCl_2$ drying tube, and a Glas-col heating mantle. The system was flushed with nitrogen, and 0.40 g benzoyl peroxide (Bz_2O_2) was added and the reaction was allowed to proceed at reflux (64°C) overnight. The reaction mixture was cooled to room temperature, and the precipitated product was collected on a sintered glass funnel, was washed with four 100-ml portions of acetone, and then dried in an oven at 80°C to yield 0.5 g (71%) of a white fibrous product: IR 1754 (C=O); 775, 758, 699 cm^{-1} (C_6H_4 meta, para isomers).

Reactions of Vinylbenzyl Cellulose with DEM. (1) A dry, 4.1-g fabric sample of vinylbenzyl cellulose (D.S. 0.16) was added to a solution of 0.5-g Bz_2O_2 in 200 ml DEM contained in a 1-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet and outlet, a thermometer, a Glas-col heating mantle, and an air stirrer. The reaction was allowed to proceed under anhydrous conditions and vigorous agitation for 10 hr at 100°C. The reaction was cooled to room temperature, the sample was removed from the reaction flask, and washed following the procedures outlined above and then dried in a vacuum desiccator at 60°C and weighed. The washing procedure was repeated and the sample was dried to yield a 0.2-g weight increase: IR 1733 (C=O); 1639 (C=C), 826, 800, 714 cm^{-1} (C_6H_4 meta, para isomers).

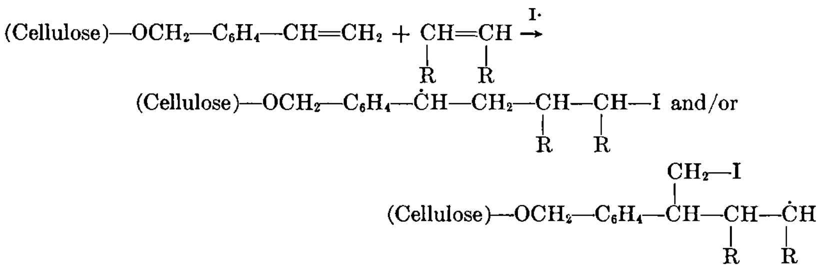
(2) In a similar way, 4.1 g dry vinylbenzyl cellulose (D.S. 0.16) was allowed to react with 30 ml DEM dissolved in 250 ml DMSO, 90 ml benzene, and 0.1 g Bz_2O_2. The reaction was allowed to proceed for 10 hr at 105°C to yield a 0.2-g weight increase of the vinylbenzyl cellulose: IR 1733 (C=O); 1639 (C=C); 826, 800, 714 cm^{-1} (C_6H_4 meta, para isomers).

Reactions of Vinylbenzyl Cellulose with MA. A dry, 4.5-g fabric sample of vinylbenzyl cellulose (D.S. 0.26) was added to a solution of 7.85-g (0.08 mole) MA and 78.5 mg Bz_2O_2 in 300 ml benzene contained in a 1-liter, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen inlet, a condenser connected to a $CaCl_2$ drying tube, a Glas-col heating mantle, and magnetic stirrer. The reaction was allowed to proceed under anhydrous conditions and mild agitation for 5 hr at 85°C. The reaction was cooled to room temperature, the sample was removed and washed, dried, and weighed following the procedures outlined above to yield a 0.2-g weight increase: IR 1724 (C=O); 826, 800, 714 cm^{-1} (C_6H_4 meta, para isomers).

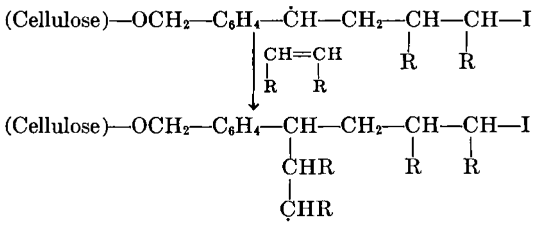
Physical Properties of Vinylbenzyl Cellulose. The mechanical properties of the vinylbenzyl celluloses and the control fabrics (untreated fabric, regenerated fabric, and regenerated fabric subjected to the vinylbenzylation reaction conditions) were determined using a Scott-Bendix tensile tester according to the ASTM-D1682-64 ravel strip method. Each sample was ravelled to 65 threads. The jaws of the tensile tester were set 3 in apart, and the rate of extension was 10 in per min. Flexing and abrasion tests were performed according to ASTM procedure D1175-64T. The head load was 0.5 lb, and the bar load was 2 lb. One-inch ravelled strips were used. Wrinkle recovery was determined using a Monsanto crease recovery angle tester according to ASTM procedure D1295-67. All samples used for the physical testing were conditioned for at least 12 hr at 70°F and 65% relative humidity.

RESULTS AND DISCUSSION

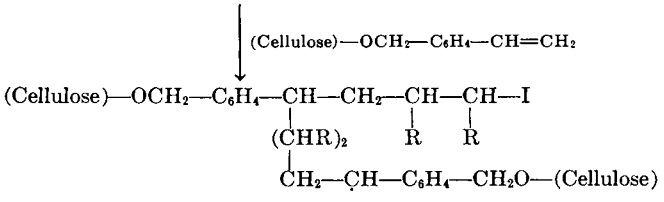
In this research, investigations of crosslinking cellulose by the graft polymerization of a vinyl cellulose derivative with a comonomer were undertaken. Vinylbenzyl cellulose was prepared as the precursor for subsequent crosslinking by free-radical addition polymerization with either DEM or MA. The choice of comonomers was restricted to those that would not readily homopolymerize and to those that possessed reactivity ratios less than unity (relative to styrene). In this way, the styrene moieties of the vinylbenzyl cellulose would form an alternating copolymer with DEM or MA resulting in the crosslinking of the cellulose, reactions (1), (2), and (3):



$$\mathrm{(Cellulose)—OCH_2—C_6H_4—CH{=}CH_2} + \underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}{=}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}} \xrightarrow{\mathrm{I}\cdot}$$
$$\mathrm{(Cellulose)—OCH_2—C_6H_4—\dot{C}H—CH_2—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—I}\ \text{and/or}$$
$$\mathrm{(Cellulose)—OCH_2—C_6H_4—}\overset{\mathrm{CH_2—I}}{\overset{|}{\mathrm{CH}}}\mathrm{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{\dot{C}H}}} \qquad (1)$$



$$\mathrm{(Cellulose)—OCH_2—C_6H_4—\dot{C}H—CH_2—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—I}$$
$$\Big\downarrow\ \underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}{=}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}$$
$$\mathrm{(Cellulose)—OCH_2—C_6H_4—}\underset{\underset{\mathrm{\dot{C}HR}}{|}}{\underset{|}{\underset{\mathrm{CHR}}{\underset{|}{\mathrm{CH}}}}}\mathrm{—CH_2—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—I} \qquad (2)$$



$$\Big\downarrow\ \mathrm{(Cellulose)—OCH_2—C_6H_4—CH{=}CH_2}$$
$$\mathrm{(Cellulose)—OCH_2—C_6H_4—}\underset{\underset{\mathrm{CH_2—\dot{C}H—C_6H_4—CH_2O—(Cellulose)}}{|}}{\underset{\mathrm{(CHR)_2}}{\underset{|}{\mathrm{CH}}}}\mathrm{—CH_2—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\mathrm{—I} \qquad (3)$$

The propagation of the alternating copolymer, reaction (3), may be terminated after the addition of one comonomer molecule or after the addition of the comonomer across two of the styrene groups. The latter case would yield a highly crosslinked system. However, this is dependent upon the availability of the styrene moieties during the addition polymerization.

Model Compounds

Benzyl cyclohexyl ether, vinylbenzyl cyclohexyl ether, and benzyl cellulose were prepared as model compounds of vinylbenzyl cellulose. Vinylbenzyl cellulose acetate was prepared in order to study the copolymerization of the cellulosic styrene groups with DEM.

The preparation of benzyl cyclohexyl ether was studied in order to test the synthetic route for the preparation of vinylbenzyl cyclohexyl ether. If the vinylbenzyl cyclohexyl ether could be synthesized, then the preparation of the cellulose analog seemed feasible. Figure 1 displays the infrared spectra of vinylbenzyl cyclohexyl ether. The broad C—O—C stretching absorption centered at 1097 cm^{-1}, and the C=C stretching absorptions at 1629, 1605, and 1585 cm^{-1} of a vinyl group conjugated with benzene are supportive evidence that the desired ether was isolated. The aromatic C—H out-of-plane beinding at 826 cm^{-1} (para subst.), 794 cm^{-1} (meta subst.), and 714 cm^{-1} (meta subst.) indicate that the product was a mixture of the meta and para isomers. The NMR spectrum confirmed that the desired product was isolated. The appearance of the three vinyl proton absorptions exhibiting the expected coupling constants (17 cps for trans vicinal, 10 cps for cis vicinal, 1.5 cps for geminal) and the appearance of a cyclohexyl ethereal proton substantiated the structure of the ether (see Fig. 2). Comparison of the vinylbenzyl cyclohexyl ether spectrum with the spectrum of VBC, a 60% meta, 40% para mixture, revealed that the ether was also a mixture of the meta and para isomers, with an isomer ratio (determined by the absorption intensities) comparable to VBC.

Benzyl cellulose was prepared as a model system of vinylbenzyl cellulose. Benzyl cellulose is a known cellulose derivative, and its physical characteristics are available. However, the accepted procedure for its preparation, as given by Klein and co-workers,[13] was not amenable to vinylbenzylation.

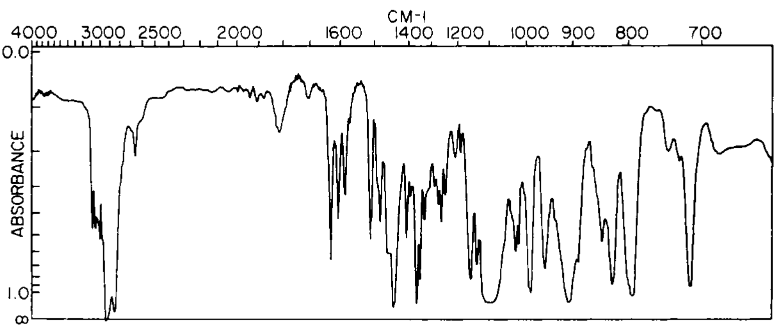


Fig. 1. Infrared spectrum of vinylbenzyl cyclohexyl ether.

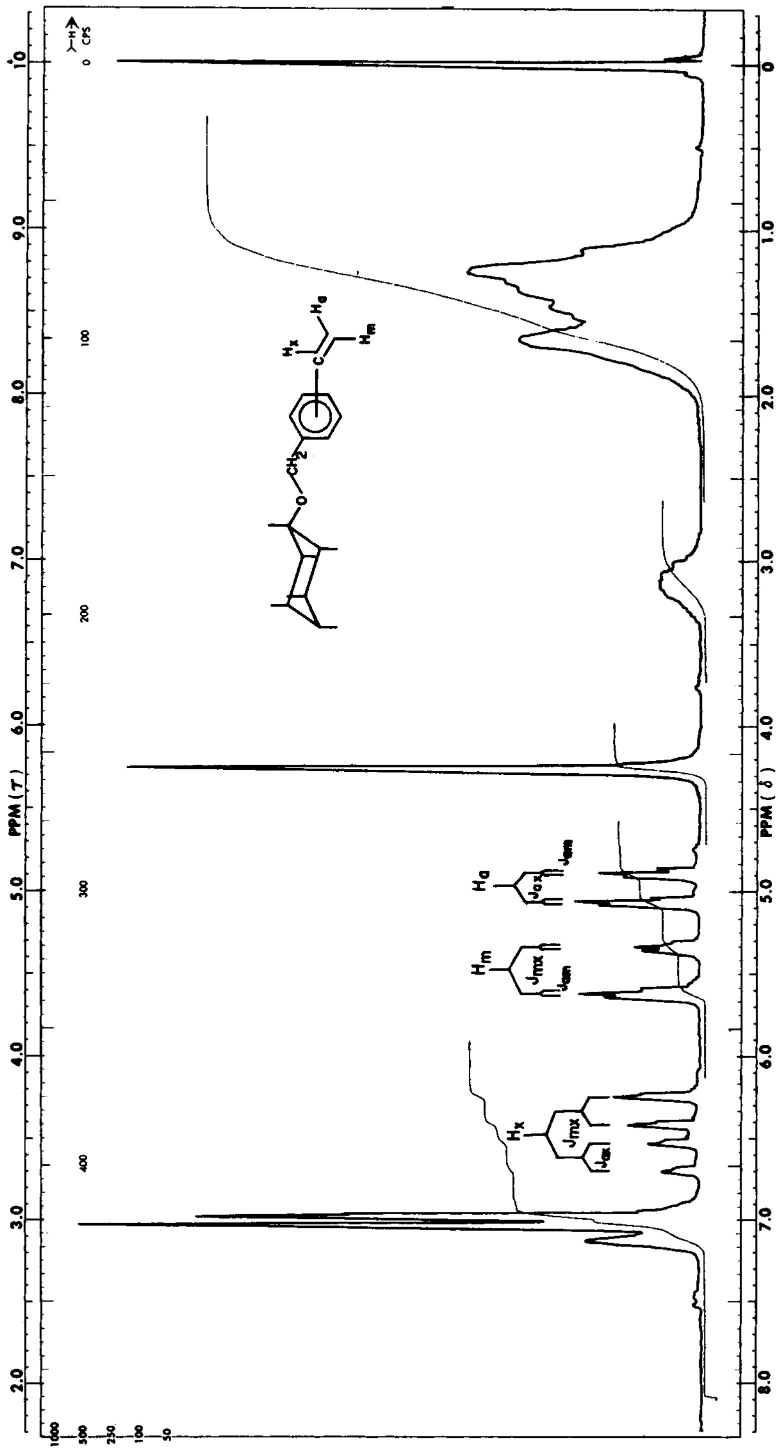


Fig. 2. Nuclear magnetic resonance spectra of vinylbenzyl cyclohexyl ether.

Therefore, the benzylation of cellulose in DMSO was investigated, as reported by Iwashige and Saeki[12] for the benzylation of carbohydrate derivatives. When a fabric sample of sodium cellulosate in DMSO was allowed to react at 110°C with an excess of benzyl chloride, the fabric dissolved—evidence that benzylation occurred. The infrared spectrum of the benzyl cellulose, Figure 3, comports with the spectrum published by Klein and co-workers.[13] The benzyl cellulose spectrum differs from the spectrum of cotton cellulose due to the appearance of the aromatic C=C stretching absorptions at 1490 cm^{-1} and 1456 cm^{-1} and the broad aromatic C—H out-of-plane bending absorptions centered at 741 cm^{-1} and 699 cm^{-1}.

The infrared spectrum of vinylbenzyl cellulose, Figure 4, was obtained using a KBr disk of hydrolyzed vinylbenzyl cellulose (D.S. 0.24) in the sample beam and a KBr disk of hydrolyzed cotton in the reference beam The appearance of the C=C stretching absorptions at 1626, 1600, and 1575 cm^{-1} is supportive of vinylbenzylation. The broad aromatic C—H bending absorptions centered at 826, 794, and 714 cm^{-1} indicate that the meta and para isomers of the vinylbenzyl groups are present.

The qualitative ultraviolet analysis of the vinylbenzyl cellulose yielded additional evidence that the cotton cellulose had been chemically modified. Using the short wavelength of the hand-held Minerallight, the vinylbenzyl cellulose (D.S. 0.16) and the Whatman #1 filter paper treated with VBC

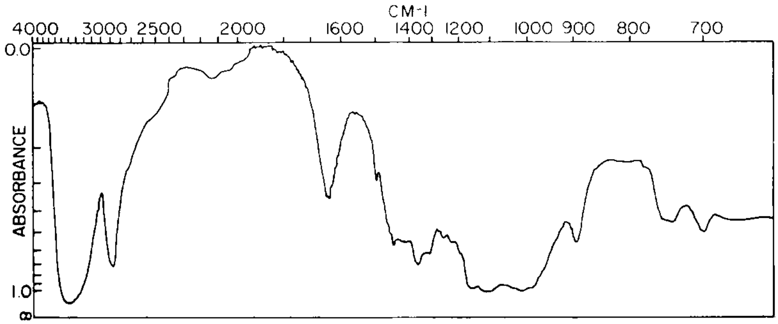


Fig. 3. Infrared spectrum of benzyl cellulose.

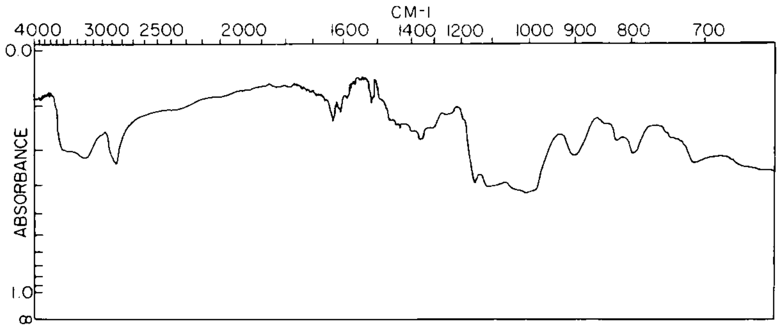


Fig. 4. Infrared spectrum of vinylbenzyl cellulose.

absorbed more radiation, as observed visually, than the regenerated cellulose. The fluorescence of the vinylbenzyl cellulose was uniform over the entire sample, indicating uniform vinylbenzylation.

The reflectance ultraviolet analysis of vinylbenzyl cellulose and regenerated cellulose displayed a marked difference in the region between 230 and 650 nm. The reflectance ultraviolet spectrum of the regenerated cellulose, Figure 5,a, did not exhibit a maximum absorption in the wavelength region studied. The reflectance spectrum of the vinylbenzyl cellulose, Figure 5,b, displayed absorptions at 355 and 295–230 nm. These absorptions are attributed to the $\Pi \rightarrow \Pi^*$ transition of the conjugated vinylbenzyl group.

The dependence of vinylbenzylation D.S. upon temperature is shown in Figure 6; the extent of reaction increases with increasing temperature up to 65°C and decreases above 65°C. The observed decrease in D.S. at higher temperatures may be a function of the diffusion reaction kinetics and/or a function of the swelling effects of DMSO upon cellulose.

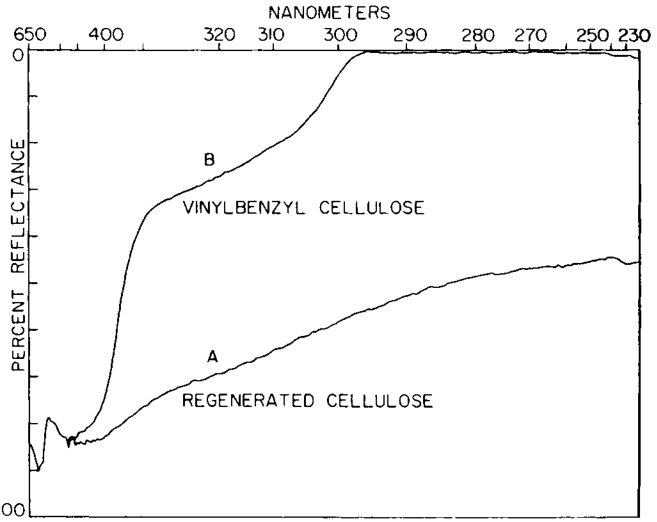


Fig. 5. Reflectance ultraviolet spectra: (a) regenerated cellulose; (b) vinylbenzyl cellulose.

Vinylbenzyl Cellulose Reacted with DEM

The copolymerization of vinylbenzyl cellulose with DEM was investigated as a possible method for crosslinking cellulose. The infrared spectrum of the vinylbenzyl cellulose reacted with DEM, Figure 7, displays a carbonyl stretching absorption at 1733 cm^{-1}. This ester absorption can be attributed to either the maleate ester or the ester which would result from a transesterification between DEM and cellulose. The C=C stretching bands at 1639, 1612, and 1588 cm^{-1} and the aromatic C—H out-of-plane bending absorptions at 826, 800, and 714 cm^{-1} indicate that the conjugated

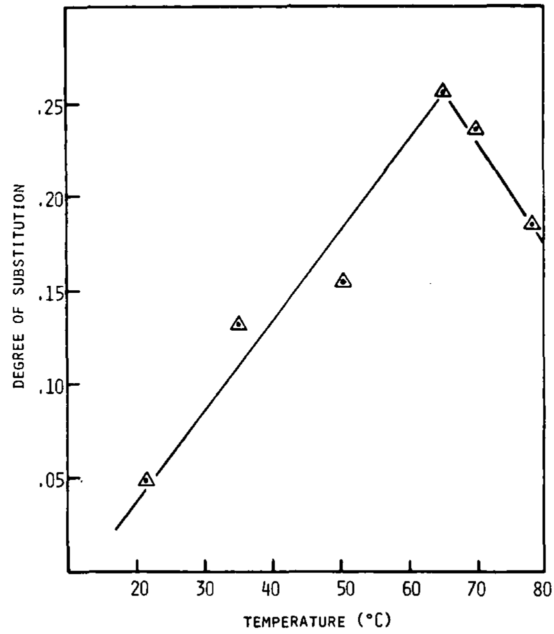


Fig. 6. Dependence of vinylbenzylation upon temperature.

vinylbenzyl groups did not react with DEM. The sample fluoresced upon exposure to ultraviolet light, verifying that the reaction conditions favored the transesterification over the copolymerization.

Vinylbenzyl Cellulose Reacted with MA

The reaction of vinylbenzyl cellulose with MA was investigated as a possible method for crosslinking cellulose. The infrared spectrum of the product, Figure 8, displays two carbonyl absorptions at 1770 cm^{-1} and 1724 cm^{-1}. The lower intensity band at 1770 cm^{-1} is attributed to a carboxylic acid carbonyl, and the absorption at 1724 cm^{-1} is due to an ester

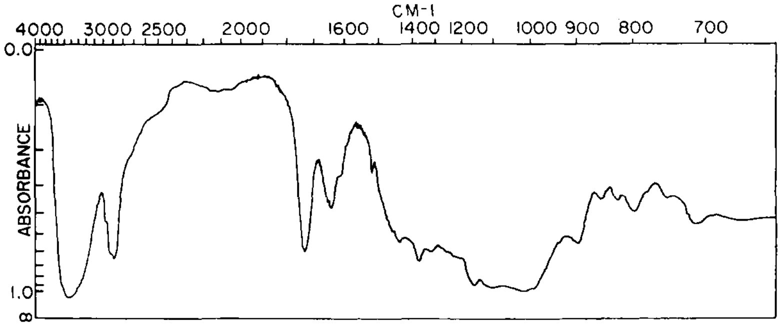


Fig. 7. Infrared spectrum of vinylbenzyl cellulose reacted with diethyl maleate.

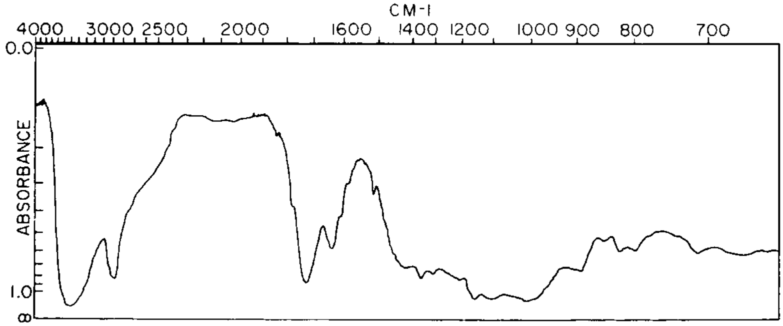


Fig. 8. Infrared spectrum of vinylbenzyl cellulose reacted with maleic anhydride.

C=O stretching, indicating that the MA reacted with the cellulose hydroxyl groups instead of copolymerizing with the vinylbenzyl groups. The presence of the C=C stretching absorptions at 1639, 1612, and 1588 cm^{-1} and the aromatic C—H bending bands at 826, 800, and 714 cm^{-1} also indicate that the conjugated vinylbenzyl groups failed to react with MA. The sample fluoresced upon exposure to ultraviolet light, verifying that the reaction conditions favored the esterification over the copolymerization.

Vinylbenzyl Cellulose Acetate

Vinylbenzyl cellulose acetate was prepared in order to study its copolymerization with DEM. The infrared spectrum of the vinylbenzyl cellulose acetate, Figure 9, displayed the characteristic carbonyl stretching band at 1754 cm^{-1}. The acetylation was not complete as evidenced by the small O—H stretching absorption at 3448 cm^{-1}. The vinylbenzyl aromatic C—H bending absorptions centered at 826, 800, and 719 cm^{-1} and the C=C stretching bands at 1620, 1612, and 1588 cm^{-1} indicate that the vinylbenzyl groups were not affected by the acetylation procedure.

Copolymerization of Vinylbenzyl Cellulose Acetate with DEM

If the copolymerization between vinylbenzyl cellulose and DEM is feasible, then the vinylbenzyl cellulose acetate should prevent the possible

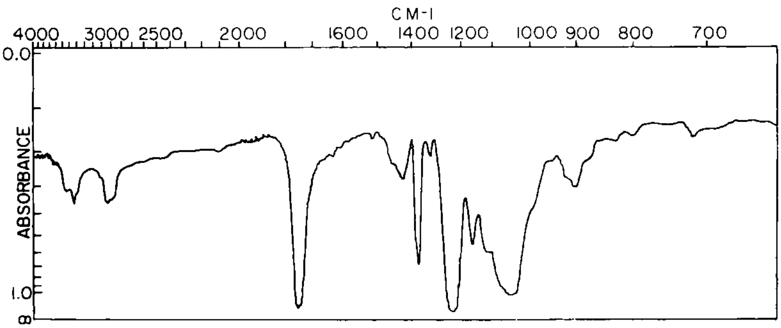


Fig. 9. Infrared spectrum of vinylbenzyl cellulose acetate.

transesterification between DEM and cellulose and direct the reaction in favor of the copolymerization. The infrared spectrum of the product from the copolymerization of vinylbenzyl cellulose acetate with DEM, Figure 10, displays a carbonyl absorption centered at 1754 cm^{-1}. This C=O stretching mode is characteristic of the acetate, and it cannot be used to identify the ethyl ester of the comonomer. However, the long wavelength absorptions of the vinylbenzyl aromatic C—H bending display a marked change. The loss of the bands at 826, 800, and 719 cm^{-1} and the appearance of the bands at 775, 758, and 699 cm^{-1} indicate that the vinylbenzyl moieties have undergone a change in chemical structure. The aromatic region of the spectrum of the copolymerized vinylbenzyl cellulose acetate is similar to the aromatic region of benzyl cellulose, Figure 3, indicating the loss of conjugation of the vinylbenzyl groups. The product also failed to fluoresce in the presence of ultraviolet light. Solubility tests (in CUEN) of the controls and the copolymerized product indicated a marked decrease in the product's solubility.

Physical Properties of Vinylbenzyl Cellulose

The mechanical properties of the cotton fabrics were determined before and after vinylbenzylation. Table I shows the mechanical properties of the controls and the vinylbenzylated fabrics. The variation of the tensile properties with D.S. are given in Figures 11 and 12. The load at break in the warp and filling direction of the vinylbenzylated fabrics decreased with increasing vinylbenzylation. The per cent extension at break in the warp and filling directions of the vinylbenzylated fabrics were greater than those of the untreated fabric and similar to those of the control fabrics. The per cent extension of the vinylbenzylated fabrics increased with increasing substitution. This effect is expected since the chemical modification of cotton cellulose results in a decrease in the crystallinity creating a more extensible fiber. The crease recovery data for the vinylbenzylated fabrics, the control fabrics, and the untreated fabric were similar. The flexing and abrasion resistances of the vinylbenzylated fabrics are greater than the untreated fabric and similar to the controls.

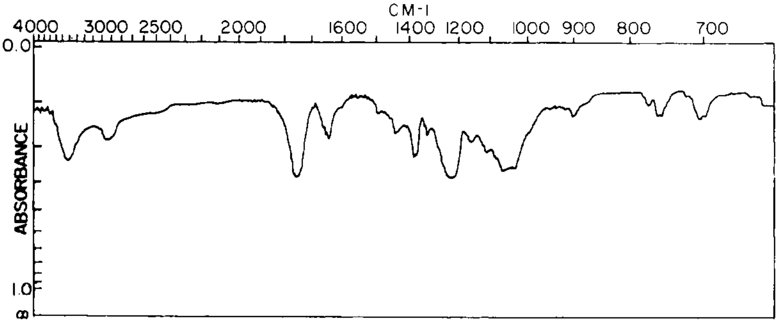


Fig. 10. Infrared spectrum of vinylbenzyl cellulose acetate copolymerized with diethyl maleate.

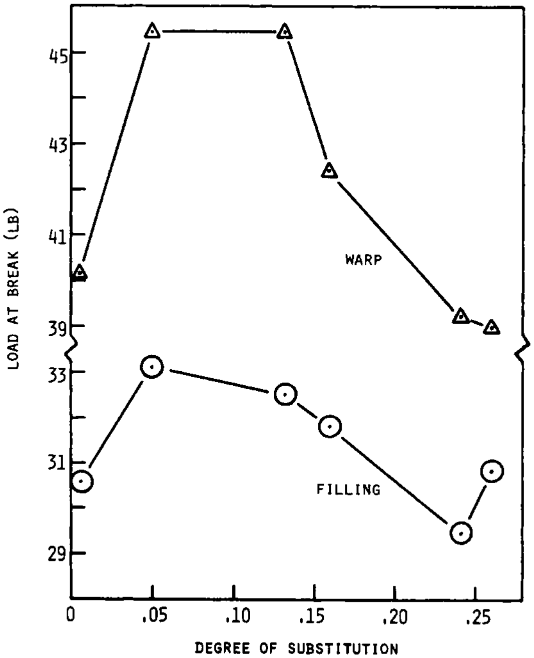


Fig. 11. Effect of vinylbenzylation upon strength of cotton fabric.

The vinylbenzylated fabrics of D.S. 0.05 and D.S. 0.13 possess the more favorable mechanical properties. The reaction conditions for the preparation of these lower-D.S. fabrics do not adversely affect the mechanical behavior of the cellulose. In all cases, the control fabrics and the least-

TABLE I
Physical Properties of Vinylbenzylated Fabrics

	Load (lb)/% extension		Wrinkle recovery			Abrasion	
Fabric sample	Warp	Filling	W	F	W + F	W	F
Untreated	40.2/10	30.6/23	77	78	155	211	207
Control #1 regenerated[a]	44.6/23	33.6/30	75	78	153	311	306
Control #2 Cell—OH/ DMSO[b]	45.6/27	33.8/33	76	83	159	317	326
Control #3 Cell—ONa/ DMSO[c]	45.5/27	35.5/33	75	72	147	288	276
D.S. 0.05	45.4/23	33.1/27	70	73	143	374	352
D.S. 0.13	45.4/23	32.3/27	75	77	152	293	253
D.S. 0.16	42.7/23	31.7/30	77	78	155	233	245
D.S. 0.24	39.2/27	29.5/33	75	76	151	275	261
D.S. 0.26	39.0/27	31.1/33	74	77	151	241	263

[a] Acidified sodium cellulosate.

[b] Fabric subjected to total reaction sequence *except* for conversion to sodium salt.

[c] Sodium cellulosate subjected to total process *except* no VBC added.

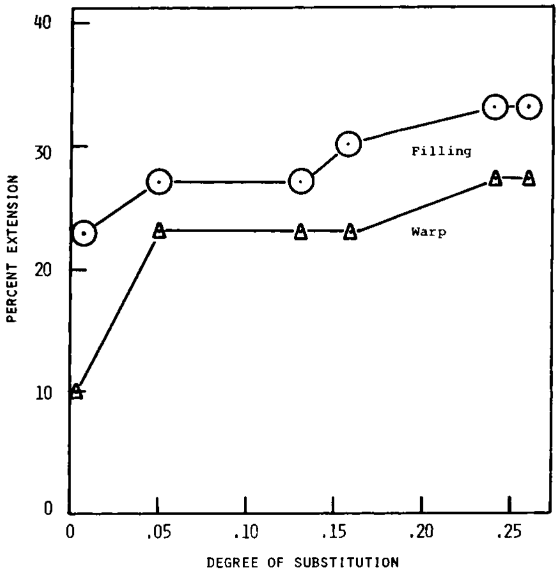


Fig. 12. Effect of vinylbenzylation upon per cent extension of cotton fabric.

substituted fabrics performed similarly suggesting that the combined effects of vinylbenzylation and swelling are no more adverse than the causticization of the cellulose fabric (control #3).

SUMMARY

Mild causticization of 80 × 80 cotton print cloth in methanolic sodium methylate yielded an intermediate which was caused to react with ar-vinylbenzyl chloride to produce ar-vinylbenzylated cellulose. The physical properties of the cloth having degrees of substitution of less than 0.30 were not materially affected. Attempts to form copolymeric crosslinked systems by use of maleic anhydride or diethyl maleate as comonomers were unsuccessful, as shown by preferential reaction of the maleyl moieties with the residual hydroxylic groups in the cellulose. Diethyl maleate does react in a copolymerizing fashion with vinylbenzylated cellulose acetate at the expense of the integrity of the cloth structure.

Conceptually, it has been shown that a styryl moiety on cellulose (vinylbenzylated cellulose) will copolymerize with monomers having strong tendencies for alternation (favorable r_1r_2 values). Further work is underway to determine monomers and methods suitable for effecting crosslinking of cellulose by this process with emphasis on comonomers reluctant to homopolymerize under the conditions employed.

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