

The Preparation and Properties of Vinyl Cellulose

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Synopsis

The vinylation of cellulose by acetylene under alkaline conditions was optimized with respect to both DS and DP. Shortening the reaction time reduced the harmful alkaline depolymerization of cellulose during the reaction and gave products with higher DP values. Thus cellulose, activated by KOH, was vinylated for 180 min at 431K and 5.5 MPa to yield 72.1% of a product with DS 1.46 and \overline{DP}_w 175. Results of vinyl cellulose analysis by new and old methods were in good agreement with each other. Trimethylsilylated vinyl cellulose was prepared for proton NMR and GPC measurements. It was found that vinyl cellulose slowly loses its vinyl groups when stored in light and air.

INTRODUCTION

The preparation of vinyl ethers by nucleophilic addition of alcohols to acetylene is a well-known, industrially utilized reaction. The vinylation of polysaccharides has also been investigated. After two deficiently documented^{1,2} and one unsuccessful vinylation work³ cellulose was first vinylated by Shostakovskii et al.⁴ Later, the vinylation of sulfite cellulose,^{5,6} cotton,⁷⁻⁹ cellulose derivatives,^{6,10} and other polysaccharides^{11,12} have been investigated. Three patents have been granted.^{1,6,9}

The best vinylation catalyst for polysaccharides, as for alcohols in general, is KOH. In cellulose vinylation, the amount of KOH has been optimized by a preceding activation procedure,⁴ or in connection with the actual vinylation reaction.⁵ The former method, which produces potassium cellulose II¹³ as an intermediate, gives a higher degree of substitution (DS 2.1 vs. 1.16) at otherwise similar reaction conditions, which were 4.5–5 h at 410–450 K in dioxane. In order to preserve the fiber structure of cotton slivers and cloth, Chiddix et al. have used 6 h and 390 K giving only DS 0.03–0.74.^{8,9} The DS grows with acetylene pressure, indicating that the vinylation rate is proportional to the acetylene concentration. Adding more water has been assumed to facilitate the vinylation of mono-^{12,14} and polysaccharides^{5,6} by reducing intermolecular H-bonding,¹⁵ but, in the vinylation of cellulose, water gives smaller DS values.^{4 vs 5,8} This is partly because it forms a separate phase with KOH in some solvents thus disturbing the reaction.

Cellulose has been vinylated in aprotic, non- or dipolar solvents. The largest DS values have been achieved with dioxane, in which the product dissolves, also.⁴⁻⁶ The fiber structure of cotton is preserved, when dibutyl acetal or diisobutyl acetal are used.^{8,9} Starch¹¹ and partly substituted methyl cellulose⁶ have been vinylated in tetrahydrofuran, and cellulose acetate in cellosolve.¹⁰ The most harmful side reactions are the alkaline hydrolysis and peeling reactions of cellulose at temperatures over 430 K.¹⁶ NaOH as a catalyst degrades cellulose more than KOH.^{4,8} The presence of dioxane

also increases degradation.⁴ Some formation of intermolecular acetals has been indicated.¹⁶

The product has been neutralized and isolated from homogenous^{4-6,11,12} or heterogenous^{2,3,8,9} reaction mixtures. As neutralization of the homogeneous mixture with HCl³ may hydrolyze the vinyl group (see below), the use of CO₂⁵ is more convenient. Precipitation of the product with petroleum ether⁵ is more complete and selective than with water,⁴ which, however, makes neutralization unnecessary. The vinyl group has been identified with bromine,³ iodine,⁴ and by IR spectroscopy.³ X-ray diffraction of vinylated cotton showed that the crystallinity disappeared at DS > 0.05–0.08.¹⁶ Elementary analysis^{2-4,6} acid catalysed hydrolysis^{2-5,8,9,11} and iodometry^{4,5,8,9,11} have been used to determine the DS. Elementary analysis and hydrolysis cannot distinguish between the isomers vinyl cellulose and its acetal, which both are hydrolyzed to acetaldehyde and alcohol, while iodometry seems more reliable. The iodometric and hydrolytic values of earlier methods did not agree⁴ while those of later methods did.^{5,8,9,11} The degree of polymerization (DP) has been approximated by a method including hydrolysis with HCl and cellulose viscometry,⁴ or by cellulose viscometry of products with very low DS.¹⁶ The distribution of substituents in vinyl amylose and vinyl amylopectin has been determined by a sequence of catalytic hydrogenation, methanolysis, and chromatographic techniques, giving hydroxyl activities OH-2 > OH-6 >> OH-3.¹⁷

Homogenously vinylated cellulose is a light yellow, very light, infusible powder, which starts to decompose in air at 490 K.^{4,5} It is soluble in some organic solvents^{2,4,5} but not in common cellulose solvents.^{2,3,4,16} Because of slow hydrolysis or crosslinking, the solubility decreases with time.^{4,16} The cationic polymerization of vinyl cellulose to a gel-like product has been reported,⁴ but, in this case, intermolecular acetal formation and/or hydrolysis seem more likely. The only uses of vinyl cellulose have been in the synthesis of incombustible cellulose ethers¹⁸ and cellulosic organotin derivatives.¹⁹

EXPERIMENTAL

About 20 g of sulphite cellulose (Rauma RRF, $\overline{DP}_v = 700$) was activated by a steeping and pressing technique of Sihtola et al.²⁰ No tearing or ageing was performed between the steeping operations. For safety reasons, the vinylation was carried out in a bunker. Activated and torn cellulose in 300 mL of purified²¹ dioxane (Merck, zur Analyse) was poured into a 1 L autoclave equipped with an external stirring device (Ernst Haage, n:o 75.12.484/1), and washed three times with N₂ and twice with C₂H₂ (Aga Ab, welding grade) before filling with C₂H₂. The right reaction pressure was obtained by means of the system's $p = f(T)$ curve of heating, which had been determined earlier. Heating took about 0.5 h. After the reaction the autoclave was allowed to cool and the pressure was released. The reaction mixture was poured into 3 L of distilled water for precipitation (precipitation into petroleum ether failed) after which the precipitate or the heterogenous reaction product (VIII, X, and XIV) was Soxhlet-extracted with ether, dried, and weighed.

The DS was determined iodometrically,^{22,5} and the DP either by vaporsmometry (\overline{DP}_n , dimethyl formamide solution, Mechrolab 301 A), or by cellulose viscometry (heterogenous products, \overline{DP}_v , SCAN-C 15:62) preceded by hydrolysis of vinyl cellulose to cellulose (1*N* HCl, 10 h, 293 K). The \overline{DP}_n values of the heterogenous vinylations (Table I, in parentheses) were approximated by making following assumptions: As the parameter *a* of the Mark-Houwink equation is near 1 (SCAN-C 15:62), we can assume that $\overline{DP}_v \approx \overline{DP}_w$.²³ By using the mean polydispersity of the GPC measurements, 5.23 (see below), we can write $\overline{DP}_n \approx \overline{DP}_v/5.23$.

Perkin-Elmer 257 was used for IR spectroscopy, and JEOL PMX-60 and JEOL FX 60 for proton and ¹³C NMR spectrometry, respectively. Vinyl cellulose was trimethyl silylated according to Sweeley et al.²⁴ and Borbély-Kuszmán et al.²⁵ for better solubility in GPC analysis (Waters 200, styrogel, PS calibration, tetrahydrofurane solvent), and for better solubility, resolution, and accuracy [OH → OSi(CH₃)₃ in proton NMR analysis].

RESULTS AND DISCUSSION

Preparation

The goal was to obtain soluble vinyl cellulose with as high DS and DP values as possible. Improving the activation method of cellulose increases its accessibility and reduces alkali-catalyzed side reactions. Such an improvement has been introduced into the viscose process, where an additional steeping operation has reduced side reactions between CS₂ and alkali, and increased cellulose accessibility by swelling (the so-called SINI method; Refs. 26–31). Preliminary vinylation experiments with cellulose steeped first by 27% aqueous KOH for activation,¹³ then by 10% aqueous NaOH for swelling and reduction of free alkali content, justified an optimization of this method.

The optimization was made in three series of experiments, where the influence of the reaction parameters on anhydroglucose based yield (*Y*), acetylene consumption (Δp), amount of ether soluble byproduct, DS, and DP (number average value, \overline{DP}_n) was measured in four experiments per series (see Table I). Figures 1–6 show the influence of reaction pressure, time, and temperature on DS, \overline{DP}_n , *Y*, Δp , and fraction of byproduct.

The graphs show that:

—At pressures below 5.5 MPa, the DS increases with pressure. Raising the pressure further improves the result very little.

—At $t < 240$ min the DS rises to a maximal 1.5 and \overline{DP}_n drops to a minimal 10 with time. At $t > 240$ min the DS decreases, probably due to loss of high DS, low DP product in the isolation procedure. If both DS and DP are to be considered, 180 min is the most favorable reaction time.

—At $T < 430$ K the DS rises and the DP drops very strongly with temperature. At $T > 430$ K and DS does not rise, but the yield still drops and the amount of byproduct increases. When both DS and DP are considered, 5.5 MPa, 180 min, and 430 K seem to be the best reaction conditions. They gave a soluble product with DS=1.38 and $\overline{DP}_n=20.6$, which formed by comparison the strongest film on evaporation. The conditions were then

TABLE I
Vinylation Conditions and Results of Sulfite Cellulose Activated by Double Steeping

Experiment	<i>t</i> (min)	<i>T</i> (K)	<i>p</i> (MPa)	Δp (MPa)	<i>Y</i> (mol %)	Byproduct (wt %)	DS	\overline{DP}_n
I	300	435	4.5	0.4	61.6	17.2	1.16	
II	300	431	5.1	1.1	63.7	24.8	1.30	
III	300	431	5.7	1.3	59.9	20.9	1.32	
IV	300	431	5.8	1.3	45.9	22.8	1.36	10.7
V	180	431	5.8	1.0	57.2	16.3	1.38	20.6
VI	120	431	5.5	0.8	56.5	16.7	1.16	31.9
VII	240	431	5.5	1.0	63.4	18.1	1.49	10.3
VIII	180	413	5.6	0.5	90.5	3.0	0.79	(38)
IX	180	445	5.3	1.1	42.5	31.3	1.43	14.5
X	180	421	5.6	0.5	62.2	3.9	1.21	(17)

*The titrated catalyst amount was 29 wt % based on cellulose. In experiment IV, part of the product was lost. The \overline{DP}_n values in parenthesis were approximations (see Experimental).

tried on other cellulose activation methods (Table II). It is clear that, although double steeping reduces acetylene side reactions as measured by amount of ether soluble byproduct, both DS and DP are reduced. In this respect, the effect of double steeping seems to be reduced by the severe reaction conditions needed for vinylation. However, shortening the reaction time of single steeped cellulose vinylation to 180 min gave $\overline{DP}_w = 175$ (experiment XI, $\overline{DP}_n = 23.6$ and $\overline{DP}_w / n = 7.40$), which is 2–4 times the values of Shostakovskii et al.⁴ and near the values of commercial cellulose ethers. The presence of NaOH very strongly degrades cellulose and reduces the yield. The "blind" experiment (XIV) shows that DP and yield are practically independent of the presence of acetylene.

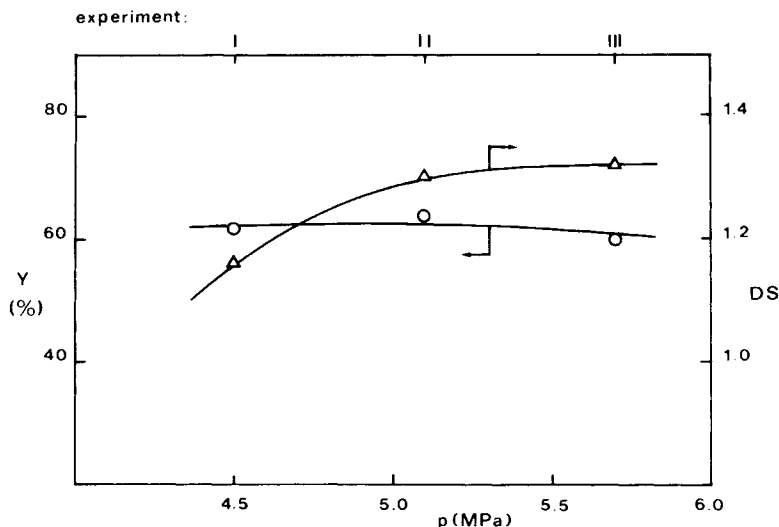


Fig. 1. The influence of reaction pressure *p* on yield *Y*(○) and degree of substitution DS (△).

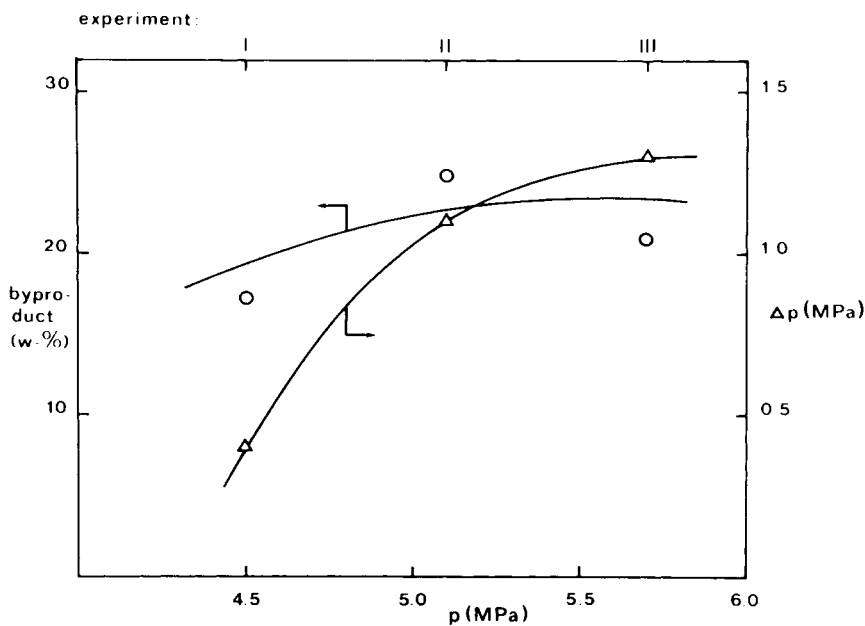


Fig. 2. The influence of reaction pressure p on fraction of byproduct (○) and pressure drop during reaction, Δp (Δ).

Analysis

The IR spectrum of vinyl cellulose is shown in Figure 7. Characteristic are the bands at 3110 cm^{-1} ($=\text{CH}_2$, C—H stretching), 3020 cm^{-1} ($=\text{CH}$, C—H stretching), 1640 cm^{-1} (C=C stretching), 1200 cm^{-1} (C=O stretching), 960 , 945 , and 830 cm^{-1} ($=\text{CH}$ deformation out of plane). These inten-

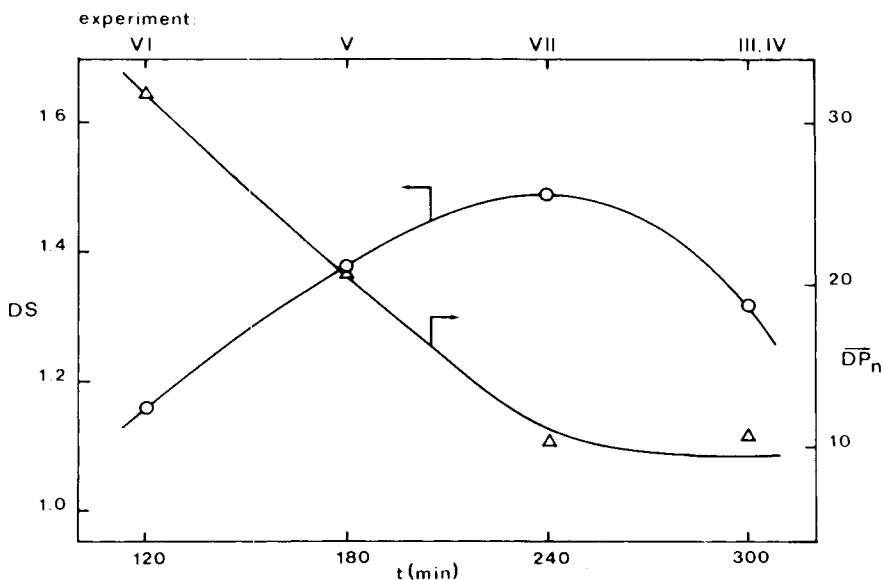


Fig. 3. The influence of reaction time t on degree of substitution, DS (○), and degree of polymerization, \overline{DP}_n (Δ).

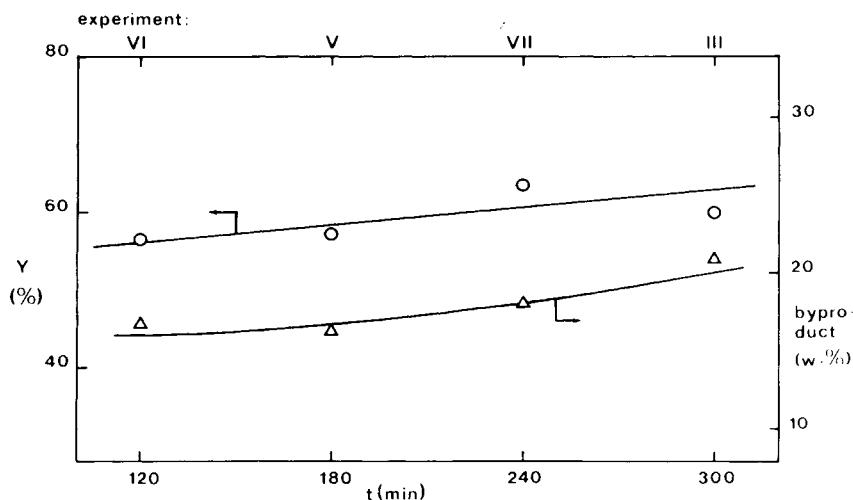


Fig. 4. The influence of reaction time t on yield Y (○) and fraction of byproduct (△).

sities were proportional to the iodometric DS values. In addition to the vinyl cellulose absorptions, the ether soluble byproduct showed absorptions at 3010, 2960, 2450, and 1380 cm^{-1} (CH_3), and at 1710 and 1660 cm^{-1} (conjugated $\text{C}=\text{O}$), indicating the formation of acetaldehyde and its aldol condensation products. Trimethyl silylated vinyl cellulose was also identified by IR.

Vinyl cellulose [Exp. VII] was trimethyl silylated by a convenient carbohydrate silylation method^{24,25} for easier and more accurate proton NMR

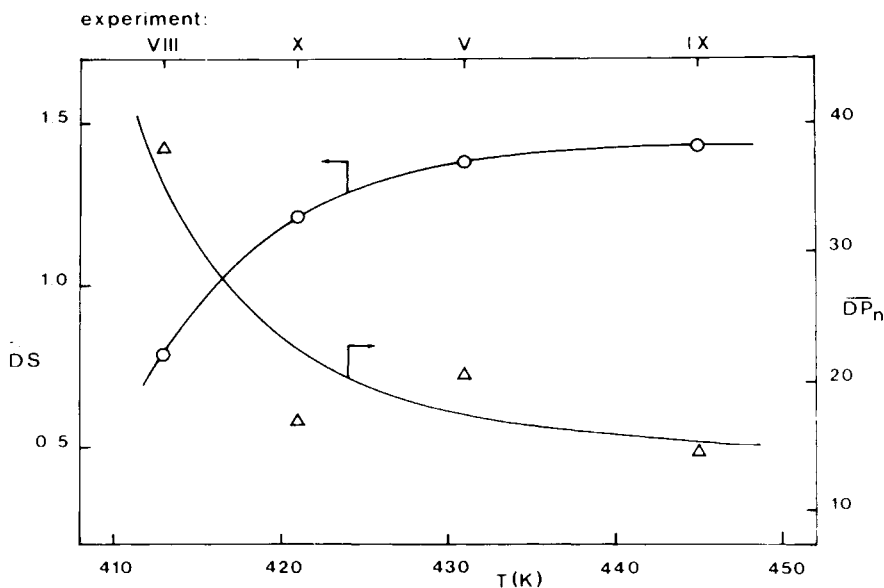


Fig. 5. The influence of reaction temperature T on degree of substitution, DS (○), and degree of polymerization, DP_n (△).

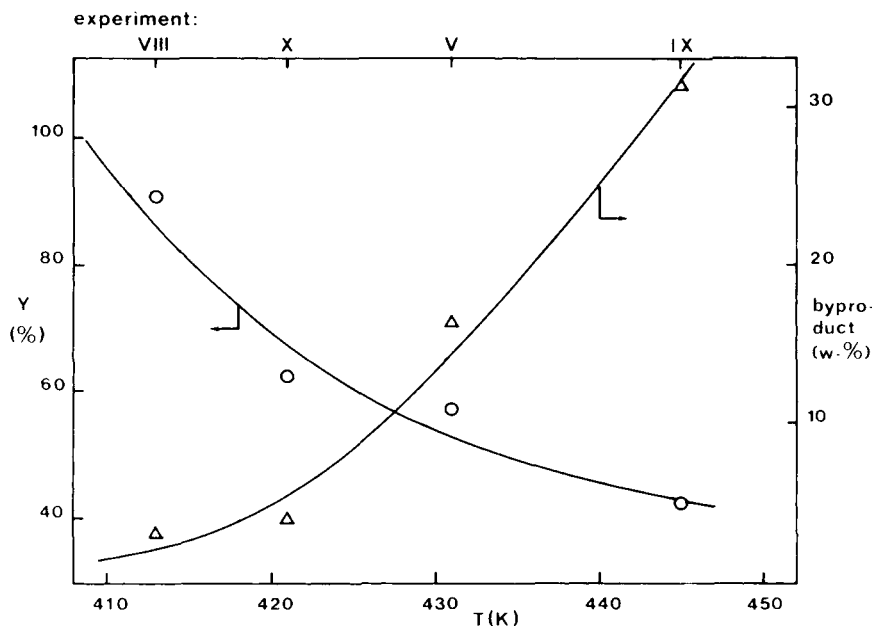


Fig. 6. The influence of reaction temperature T on yield Y (○) and fraction of byproduct (△).

analysis. The spectrum, shown in Figure 8, gave the following chemical shifts (δ):

6.0–6.7 ($-\text{CH}=\text{}$), 2.8–5.2 ($-\text{CH}$, $-\text{OH}$, $=\text{CH}$, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{CH}$), 0.5–1.5 ($\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}-\text{CH}$),

and 0.0–0.5 ($\text{Si}-\text{CH}$). Calculations gave the approximate DS values 1.50, 0.25, and 1.07 for vinyl, acetal, and trimethyl silyl substitutions, respectively. As vinyl cellulose solution tends to form a gel, the accumulation of ^{13}C spectra was limited, making a quantitative analysis impossible. Figure 9 shows the ^{13}C chemical shifts (δ) of vinyl cellulose, which were interpreted as (no model compounds or spectra were available): 39.5 [$(\text{CD}_3)_2\text{SO}$ solvent], 66.5 (possibly acetal CH_3), 72.9–82.9 (unsubstituted C-2, C-3, and substituted

TABLE II
Influence of Cellulose Activation Method and the Absence of Acetylene (Exp. XIV) on the Properties of the Product

exp.	Wt % catalyst		Y (%)	Δp	DS	Byproduct (wt %)	$\overline{\text{DP}}_n$
	1. Steeping	2. Steeping					
XI	26% KOH		72.1	1.4	1.46	33.3	23.6
XII	19% NaOH		37.0	0.9	1.37	24.9	10.7
V	26% KOH	10% NaOH	57.2	1.0	1.38	16.3	20.6
XIII	19% NaOH	10% NaOH	50.6	0.7	1.32	9.9	13.3
XIV	26% KOH	10% NaOH	63.6	0.0	0.00	0.0	(19)

*The reaction conditions were 5.5 MPa, 180 min, and 430 K. The $\overline{\text{DP}}_n$ of experiment XIV was approximated (see Experimental).

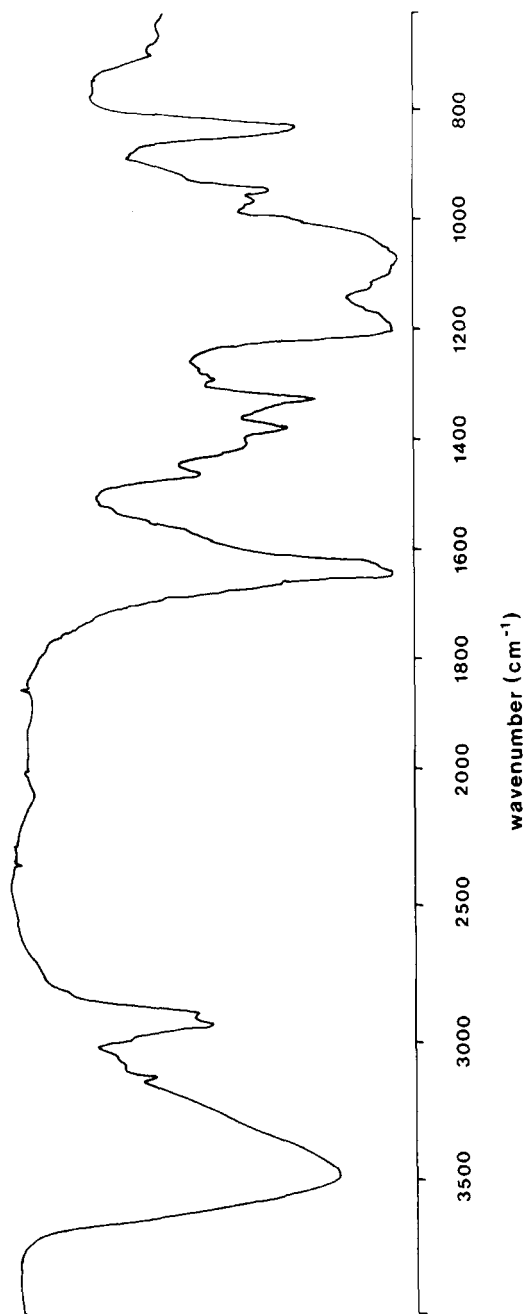


Fig. 7. The IR spectrum of vinyl cellulose (experiment IV, DS = 1.36).

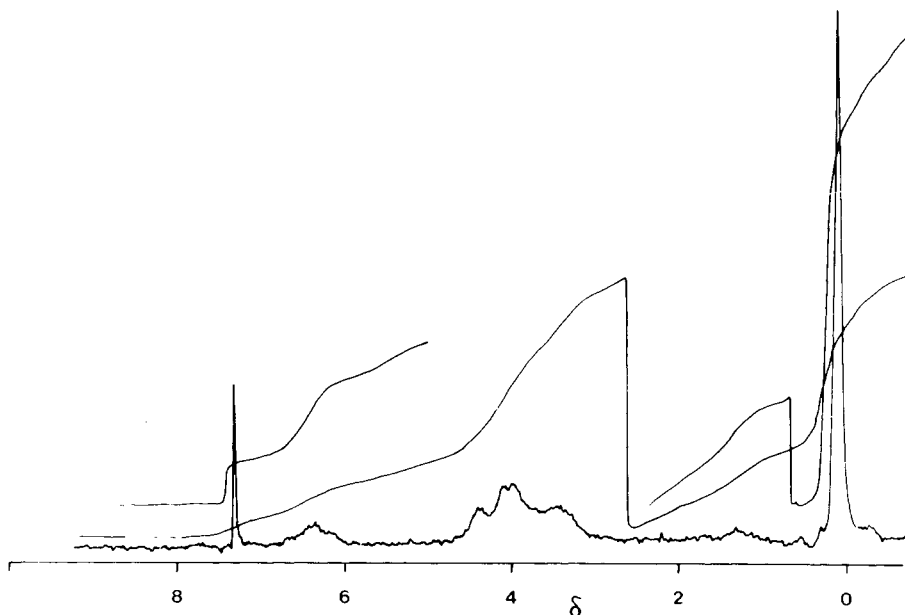


Fig. 8. The proton NMR pectrum of trimethylsilylated vinyl cellulose (DS = 1.49).

C-2, C-3, and C-6), 87.5 ($=\text{CH}_2$), 100.2–102.4 (C-1 and formed $\begin{array}{c} \text{O} \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{O} \end{array}$), 151.8–152.3 (O—CH= at C-2), and 153.2–153.7 (O—CH= at C-6). Both the proton chemical shift at $\delta = 1.2$ and the ^{13}C chemical shift at $\delta = 66.5$ indicate some formation of acetal. The two shifts at $\delta = 151.8$ –153.7 indicate slightly more substitution at C-2 than at C-6.

The viscometric $\overline{\text{DP}}_v$ values of α -cellulose was 700 and, for the products

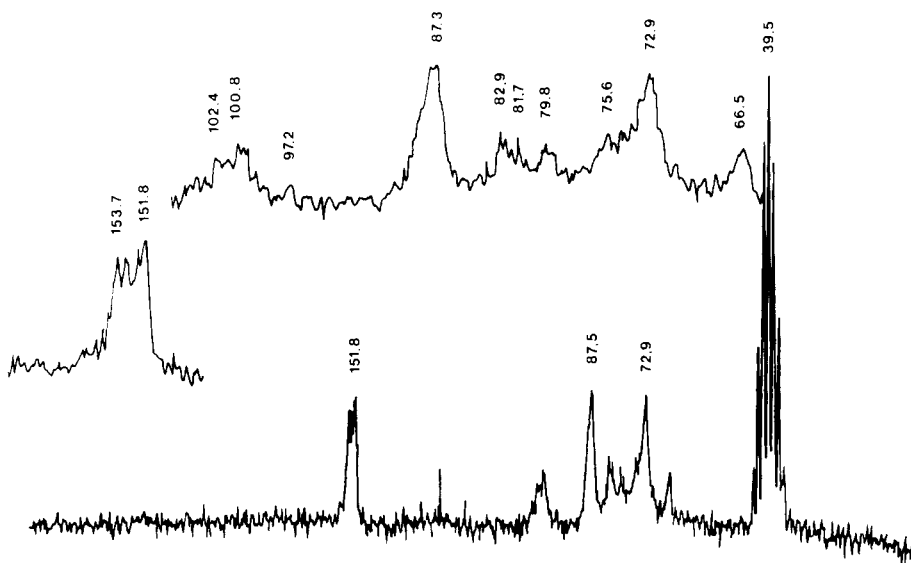


Fig. 9. The ^{13}C NMR spectrum of vinyl cellulose. $\delta_{(\text{CD}_3)_2\text{SO}} = 39.5$.

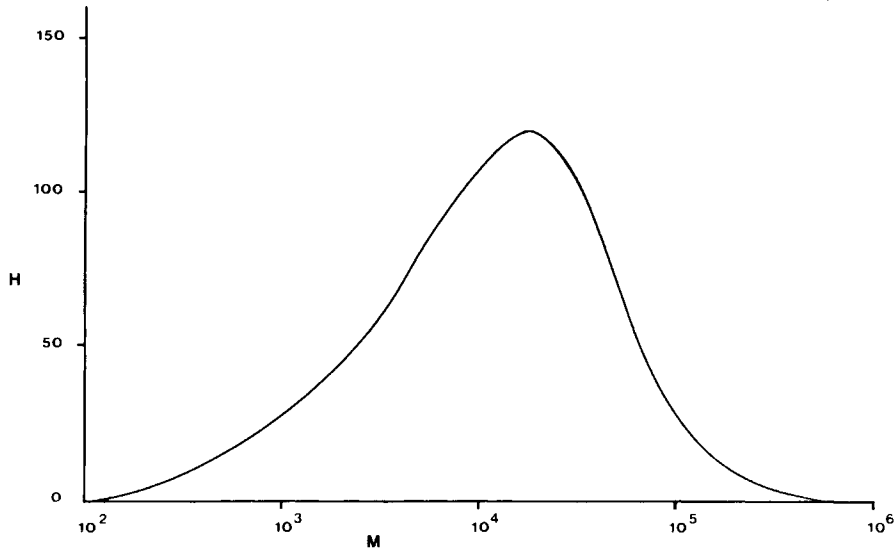


Fig. 10. The molecular weight distribution of trimethylsilylated vinyl cellulose (exp. II) measured by GPC. The M values are from PS calibration. H is equivalent to the mass of the fractions ($M \cdot N$).

of experiments VIII, X, and XIV, 200, 90, and 100, respectively. Figure 10 shows the molecular weight distribution of experiment II, from which the polydispersity 5.4 was calculated. Experiments VII and XI had similar distributions and the polydispersities 2.9 and 7.4, respectively.

The reaction gas, analysed by gas chromatography, contained only 0.46% other hydrocarbons and 0.39% hydrogen.

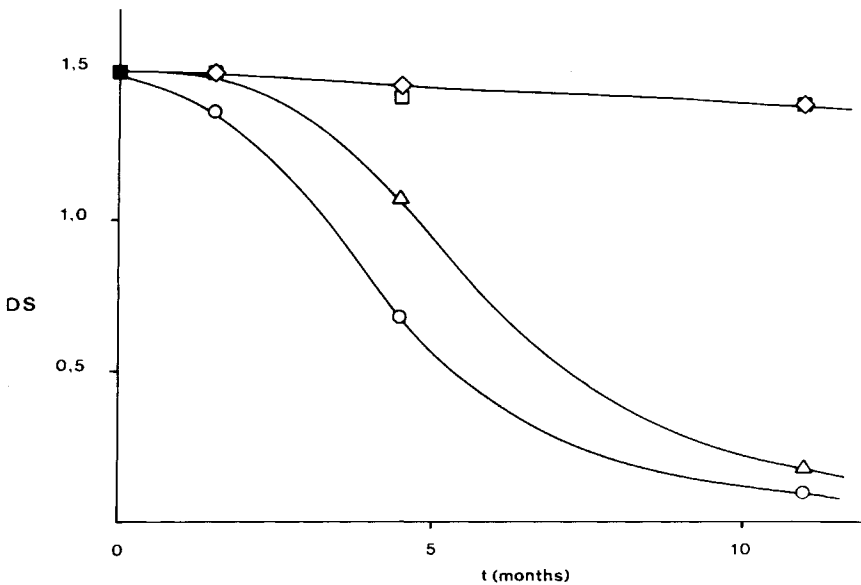


Fig. 11. The degree of substitution DS of vinyl cellulose (exp. VII) as a function of time under different storage conditions: (O) light and air; (□) air without light; (△) nitrogen and light; (◇) nitrogen without light.

Properties

Vinyl cellulose is a yellow, very light (0.12 g/cm^3) powder. Film made by evaporation from 1,3-dioxolane is dark yellow and becomes brittle and insoluble on storage. Objects made by evaporation are very light and hard, infusible materials. Vinyl cellulose is soluble in typical cellulose ether solvents including strongly polar solvents, 8:2 mixtures of chlorinated hydrocarbons and alcohols, and cyclic ethers.³² It is alkali resistant but decomposes in acids such as formic acid, trifluoroacetic acid, concentrated sulfuric, hydrochloric, and nitric acids. Vinyl cellulose is decomposed by heat at 500–550 K and loses its vinyl groups when exposed to light in air at room temperature (Fig. 11). This slow decomposition is accompanied by a decrease of the characteristic vinyl IR band intensities and, an increase of the hydroxyl band intensity, and a new carbonyl band at 1730 cm^{-1} . Simultaneously there is a decrease in solubility.

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