Trimethylsilyl Cellulose as Precursor to Regenerated Cellulose Fiber

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Synopsis

Trimethylsilyl cellulose (TMSC) has been found to melt at 320–340°C in the absence of oxygen. When TMSC is prepared from chemical cellulose, using hexamethyldisilazane and a catalytic amount of chlorotrimethylsilane/pyridine in dimethylformamide, a thermoplastic material is obtained which may be melt spun into a fiber. This fiber, when treated with mild aqueous acid, yields regenerated cellulose plus hexamethyldisiloxane. The hexamethyldisiloxane can be converted back to hexamethyldisilazane by known chemistry. The fiber properties of the regenerated cellulose were found to be comparable to commercially available rayons. X-Ray diffraction analyses of the cellulose suggest formation of an unusual polymorphic form.
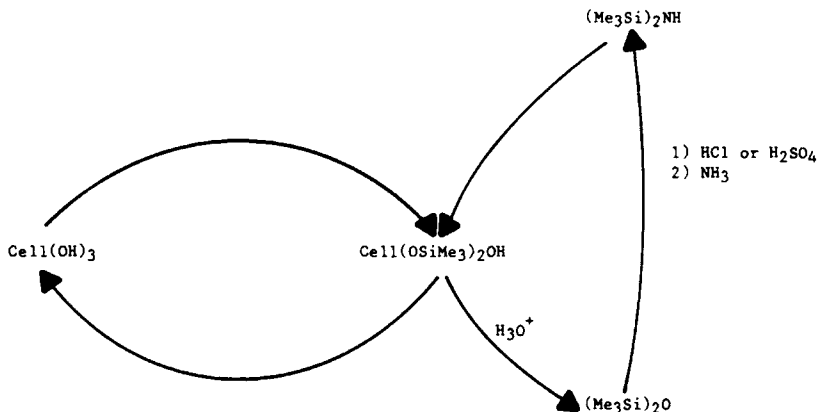
INTRODUCTION

The viscose process for the manufacture of regenerated cellulose (rayon) fiber and film is now used by the majority of producers. However, alternatives to the viscose process are of increasing interest due to the high costs of pollution abatement and the labor requirements for the process.

Two basic approaches to the production of regenerated cellulose are: (1) precipitation from cellulose solutions or dispersions, and (2) chemical reconversion of cellulose derivatives to cellulose. Some examples of the first are use of cellulose solvents such as cuene or cuam, N-methylmorpholine N-oxide, and N,N-dimethylacetamide (DMAc)/lithium chloride. Use of the second approach, other than in the viscose process, has been less explored, with the example of Fortisan (a regenerated cellulose from cellulose acetate) the best known.

We wish to report a new process for producing regenerated cellulose belonging to the second category. This method involves conversion of chemical cellulose (dissolving-grade pulps) to the trimethylsilicon ether of cellulose (trimethylsilyl cellulose, TMSC), followed by melt spinning (or solvent dry spinning) of the thermoplastic TMSC, then cleavage of the silyl ethers in mildly acidic medium to yield cellulose and hexamethyldisiloxane (HDSO). Data concerning fiber properties, X-ray diffraction studies, and reagent recovery and recycling are also presented.

HISTORY

Trimethylsilyl cellulose, a material known for a number of years, has been the subject of several studies.[1–5] First reported in 1951 by H. Schuyten[1] and co-workers, its solubility in organic solvents was noted, but the fact of its melting without substantial decomposition in the absence of oxygen remained unreported until observed by us and concurrently by Shiraishi et al.[6]

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$(Me_3Si)_2NH$

1) HCl or H_2SO_4
2) NH_3

$Cell(OH)_3$

$Cell(OSiMe_3)_2OH$

H_3O^+

$(Me_3Si)_2O$

Scheme I

Klebe and Finkbeiner[2] reported on the synthesis of TMSC and the physical properties of solvent-cast films. TMSC was found to be a structurally weak material, probably due to the lack of hydrogen bonding. It was also stated by these authors that TMSC did not melt.

Cellulose film was prepared by treatment of TMSC film with steam or water vapor at neutral pH. Klebe and Finkbeiner emphasized the high degree of hydrolytic stability of TMSC under neutral conditions, requiring several days in boiling water to achieve 98% removal of the trimethylsilyl groups.

These authors also mentioned that TMSC film was found to have a very high dielectric constant, making the material useful for electric insulation.

EXPERIMENTAL

From the literature observation of the slow hydrolytic regeneration of cellulose from TMSC at neutral pH, and from knowledge of the facile hydrolysis catalyzed by acid[7,8] often used in the cleavage of trimethylsilyl ethers of low molecular weight alcohols, we reasoned that addition of mineral acid would markedly enhance the rate of cellulose regeneration. Also, it was thought that addition of a water-miscible organic cosolvent such as ethanol or isopropanol to the regeneration medium would improve wetting and thus reaction of the hydrophobic TMSC. Both theories were substantiated by the fact that the time required to bring about better than 98% removal of the trimethylsilyl groups is cut from days to minutes using the modified procedures.

The two key observations of the melting property of TMSC and the facile cellulose regeneration in weak acid solutions then led us to propose a process for production of regenerated cellulose fiber or film via melt spinning of TMSC and regeneration of cellulose under acidic conditions.

Several literature procedures for the synthesis of TMSC were applied; however, it was found that modification of a method devised by Nagy et al.[3] gave the best results in terms of melting properties. A representative procedure is given below.

For regeneration of cellulose, a variety of conditions, outlined in Table I, were applied. It was found that the fastest regeneration consistent with the least degree of polymerization (DP) loss and the best removal of silicon took place in

TABLE I
Cuene Intrinsic Viscosity (I.V.) and Residual Silicon Content of Regenerated Cellulose as a
Function of Regeneration Conditions

Isopropanol/ water, v:v	HCl, %	Time, min at 75°C	Cuene I.V., dL/g	Residual Si, %[a]
30:70	0.37	10	1.44	—
30:70	0.97	5	insol.	6.88
40:60	0.37	5	1.67	3.13
40:60	1.85	1	1.74	1.12
50:50	0.37	5	insol.	—
50:50	1.85	1	1.69	0.48
60:40	0.37	5	1.62	—
60:40	1.85	1	1.53	0.32
b			1.96	

[a] Starting TMSC = 19.40% Si.
[b] $NaBH_4/CH_3OH$, three days 22°C.

a solution consisting of 1–2.5% HCl in water with 30–60% isopropanol added as a cosolvent.

Melt spinning of the TMSC was carried out using a home-built bench scale ram-type melt extruder with an electrically heated platen/spinneret. Oxygen was excluded by use of a nitrogen flush, and an extrusion temperature of 320–340°C was maintained.

Differential thermal analysis (DTA) of the TMSC indicated that as little as 2% O_2 in N_2 caused decomposition with loss of gaseous products at temperatures below 320°C, see Figures 1(a) and 1(b).

Fiber strength analyses (see Table II) were obtained using standard procedures. Raman and X-ray analyses and interpretations were performed by Professor Rajai Atalla of the Institute of Paper Chemistry, Appleton, Wisconsin. Fiber X-ray diffraction data were also obtained by Walter M. McCrone Laboratories, Incorporated, of Chicago, Illinois.

Combustion analyses of TMSC for determination of silicon content were carried out by Galbraith Laboratories, Knoxville, Tenn.

Preparation of TMSC

Hexamethyldisilazane (HMDS, 65 g, 85 ml, 400 mmol) was stirred at 20°C as dry HCl gas was bubbled through for about 20 s. The resulting ammonium chloride precipitate was filtered, dried, and weighed, and the amount of trimethylchlorosilane generated in HMDS solution was calculated according to the formula $(Me_3Si)_2NH + 3 HCl \rightarrow 2 Me_3SiCl + NH_4Cl$. A molar concentration of about 15% trimethylchlorosilane in HMDS was used. Pyridine was added in an amount equal to twice the molar quantity of trimethylchlorosilane.

A slurry of chemical cellulose (Acetanier-P acetate grade, 16.2 g, 100 mmol anhydroglucose, cuene intrinsic viscosity ~9 dl/g, DP ~ 2600) in N,N-dimethylformamide (160 ml) was heated under a nitrogen stream at 150°C for 1 h and then cooled to 100°C, and silating reagent (90 ml) was added. Vigorous ammonia gas evolution occurred, and the reaction was stirred until no more ammonia was formed (1–3 h). The suspension of TMSC was then filtered out of the reaction medium, washed with acetone, and dried under vacuum to yield 30–32 g TMSC
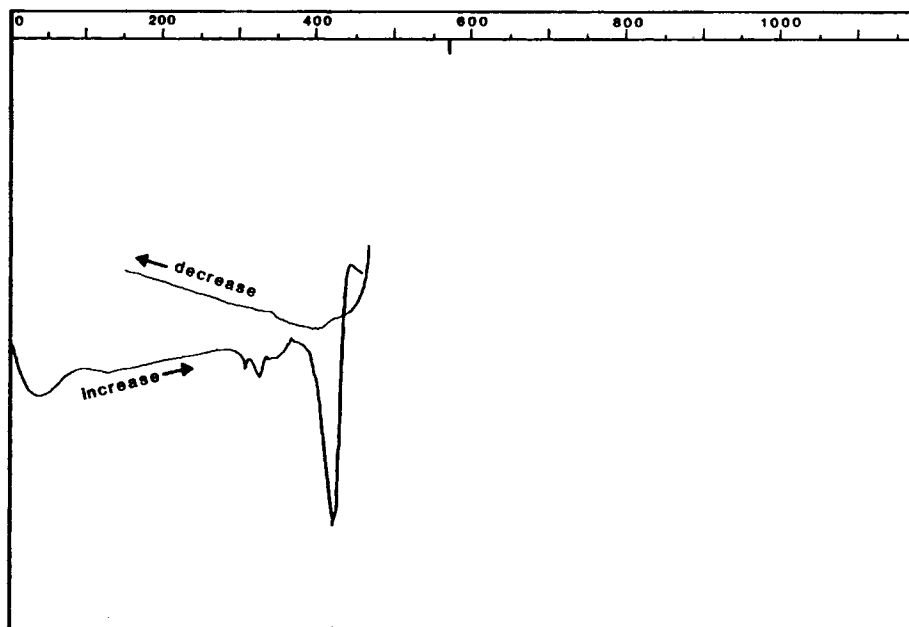
(a)
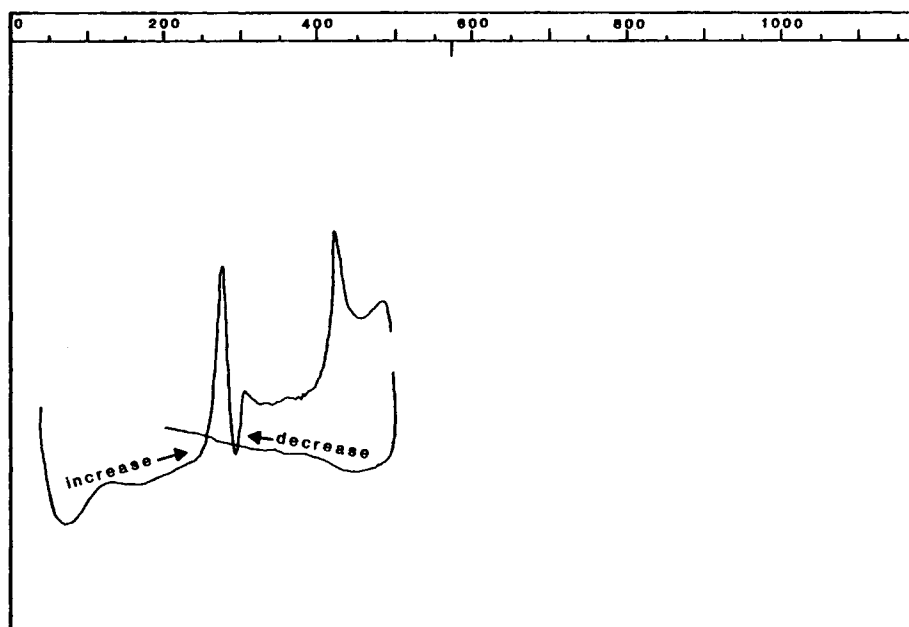
(b)

Fig. 1. (a) Differential thermal analysis of TMSC with 0% O_2 in N_2. (b) Differential thermal analysis of TMSC with 1.8% O_2 in N_2.

TABLE II
Fiber Properties of Cellulose Fiber from TMSC Versus Commercial Rayons

Sample		Conditioned tenacity, g/denier	Elongation, %	Wet tenacity, g/denier	Elongation, %	Wet modulus
TMSC batch A	2 min regen.	0.86	15.6	0.35	20.9	0.10
	4 min regen.	0.75	12.6	0.38	18.3	0.11
TMSC batch B	2 min regen.	1.60	10.9	0.90	16.2	0.30
	4 min regen.	1.81	9.1	0.85	9.2	0.47
Regular rayon[a] (continuous fiber)		2.0	20	1.0	26	0.2
High wet-modulus fiber[a]		4.5	13	2.9	12	0.5
Tire cord[a]		5.5	13	3.5	19	0.6

[a] Source: H. Steinman, *Viscose Rayon Technology*, private communication.

as a white to pale pink powder. The silicon content was in the 18–20% range (DS = 2.2–2.6). The material was completely soluble in methylene chloride, yielding an extremely viscous solution exhibiting anisotropic flow at 2% solids, with gelation occurring at around 5% solids. Differential thermal analysis under nitrogen showed the presence of a melt at 320–340°C.

Melt Spinning of TMSC

For melt spinning, the TMSC powder was Wiley milled, passed through a 20-mesh screen, baked 1 h at 110°C to remove residual solvent, and then pressed into pellets using a hydraulic press. The pellets were placed in the barrel of the melt extruder against the heated platen under nitrogen, and then a pressure of 2.0–4.0 kg/cm^2 was applied with a weighted piston. When the platen temperature reached about 320°C, a filament emerged from the spinneret and was attached to a take-up reel. The fiber was drawn at 3–10 m/min. The degree of stretch (fiber orientation) could not be controlled on this machine. The TMSC fiber was moderately weak and brittle but strong enough to take up, and ranged in color from clear to a platinum blonde. In contrast to that with cellulose acetate, extrusion from the jet was very smooth.

Regeneration of Cellulose

For cellulose regeneration, a 1-g skein of the TMSC fiber was immersed in isopropanol/water/hydrochloric acid (for example, 1:1 IPA/water with 1.8–2.4% hydrogen chloride) at 75°C for 2–4 min, then removed, washed with dilute aqueous sodium bicarbonate solution and water, and then air dried.

The fiber was tested for solubility in cuene solution (cupriethylene diamine, 1 molar in H_2O) as a rough indicator of the extent of silicon removal. Solubility in cuene occurred when silicon content was less than 6%, corresponding roughly to a 70% removal of the trimethylsilyl groups. Soluble samples were analyzed for silicon content by elemental analysis.

Recovery of the Organosilicon By-Product

A mixture of isopropanol (50 ml), deionized water (50 ml), concentrated aqueous hydrochloric acid (5 ml, corresponding to 1.85% hydrogen chloride), and hexamethyldisiloxane (HDSO, 10 ml) was made up and refluxed overnight, and all excess undissolved HDSO was removed (upper phase, 8.5 ml).

Trimethylsilyl cellulose powder (30.6 g containing 20% Si) was added, and the mixture was stirred at 75°C under N_2 for 19 h. The cellulose powder was allowed to settle, and the upper liquid phase was drawn off with a pipette, yielding 23 ml (17.6 g) HDSO that was 99% pure (by vapor-phase chromatography). The amount of HDSO obtained corresponds to a quantitative recovery of silicon from TMSC.

Conversion of Hexamethyldisiloxane to Hexamethyldisilazane

Literature procedures exist for conversion of HDSO back to the silating reagent, HMDS, using either H_2SO_4 or HCl followed by ammonia gas.[9,10] Water and ammonium sulfate or chloride are the only by-products of these reactions, and yields are reported to be good to quantitative.

Hexamethyldisiloxane (99 g, 0.61 mol) was stirred in a three-neck round bottom flask fitted with a condenser, thermometer, and addition funnel as sulfuric acid (a mixture of 55 ml 95% H_2SO_4 and 42 ml 30% fuming H_2SO_4) was added dropwise. The temperature rose to 80°C, and the mixture was stirred without further heating until the solution was homogeneous. Then, methylene chloride (250 ml, dried over P_2O_5) was added. The excess H_2SO_4 formed a separate (lower) phase and was drawn off. Then anhydrous ammonia was bubbled through the solution for 4 h with stirring to break up the ammonium sulfate precipitate. The entire mixture was then placed under vacuum and distilled. After a forerun of methylene chloride, a yield of 75 g (76% of theoretical) HMDS was obtained, along with some methylene chloride. The product was analyzed by vapor-phase chromatography.

Physical Properties

Cellulose fibers prepared from TMSC using the regeneration conditions described above were tested for strength and elongation using standard equipment. Both conditioned and wet tenacities and elongations and wet moduli (wet tenacity at 5% extension) were measured. Results are summarized in Table II. Clearly, a substantial degree of variation was observed. Both batches A and B were obtained from the same sample of TMSC powder, but under different spinning conditions. There was substantially less difference brought about by residence time in the regeneration bath. As might be expected, the degree of fiber stretch during spinning (which was not controllable on our apparatus) is crucial in determining fiber strength. For the better of the two spin batches (B), the tenacities approach those of commercial rayon, and the wet moduli are substantially better than those of regular rayon putting the fiber in the high wet-modulus class. However, the high tenacities could be due to a high degree of crystallinity induced by the spinning technique. These fiber properties may be regarded as minima, as careful regulation of spinning parameters could probably yield a cellulose fiber of superior properties.

X-Ray diffraction patterns and Raman spectra were obtained in the hope of determining the polymorphic form of the cellulose obtained. An X-ray fiber diffraction (obtained by R. Hinch of Walter C. McCrone Laboratories, Incorporated of Chicago, Illinois) of regenerated cellulose, Figure 2(a), shows a substantially different pattern from two diffractograms [Figs. 2(b) and 2(c)] taken by Dr. Atalla on regenerated cellulose in powder form. The two powder diffraction patterns are also different from each other despite the fact that the only difference in their preparation was time spent in the regeneration medium (2 h vs. 20 h). Apparently, the polymorphic form obtained is an unusual one for regenerated cellulose, but it is difficult to draw any concrete conclusions from the data. Raman spectra, Figure 2(d), of the two powder samples are also given.

DISCUSSION

This process for producing good-quality regenerated cellulose fiber is clearly feasible in a technical sense. Trimethylsilyl cellulose of sufficient silicon content (18–20%) prepared by any method which avoids crosslinking from highly refined pulp (>95% α-cellulose) should undergo melting in the absence of oxygen. The conditions of the actual melt spinning are crucial. The degree of stretch imposed during spinning apparently plays a strong role in establishing fiber strength properties, as might be expected. The necessity of rigorous oxygen exclusion while the TMSC is hot, and the rather poor tensile strength of the TMSC, would require consideration in the design of a commercial-scale extruder if large-scale production were contemplated. The fact that the largest amount of polymer chain length degradation occurs in the melt (see Table III) also emphasizes that a short residence time of TMSC in the melt phase is desirable. Contrary to expectation, the acidic cellulose regeneration conditions brought about very little cellulose chain degradation when an organic cosolvent such as isopropanol was present to enhance fiber wetting. Upon increasing residence time of a given spin batch of TMSC in the regeneration bath from 2 to 4 min, very little change in fiber properties was noted. Much longer bath residence times would presumably degrade the polymer.

For the process to be economical, very good efficiency of silicon recovery and recycle is imperative due to the high cost of the reagent (December 1980: $6.32/lb HMDS, Dow Corning). In our hands, the recovery of HDSO from the regeneration bath was very good, as previously described, but the conversion of HDSO to HMDS via bistrimethylsilyl sulfate using sulfuric acid in methylene chloride, followed by ammonia gas, gave only a 75% yield of HMDS. However, this yield could probably be increased substantially through development of techniques, as the reactions appear to be quite clean, and the literature reports[9,10] good yields for these conversions.

Also, the excess silating reagent used in the initial formation of TMSC must be recovered to give overall high efficiency to the process.

The unexpected results of the X-ray diffraction experiments, while offering no clear-cut answer to the question of the polymorphic form, seem to indicate that production of the usual cellulose II from a cellulose regeneration process is not what occurs in this case. Whether cellulose I or cellulose IV is also present is a question that would require further study.
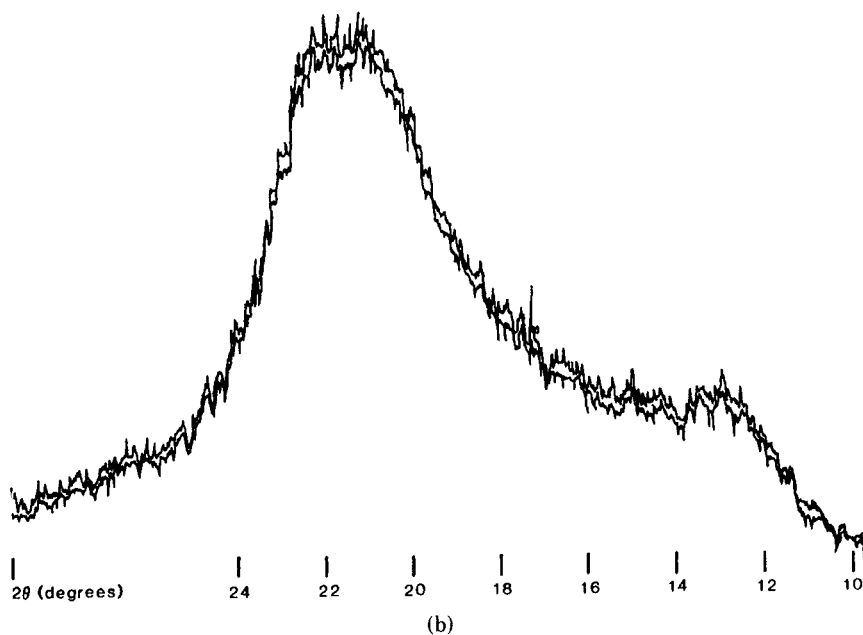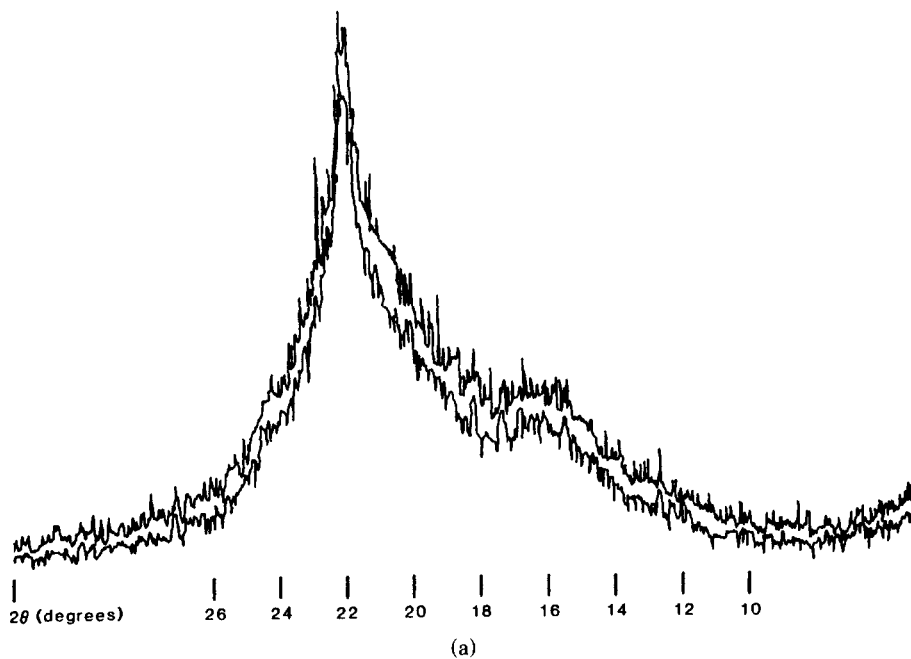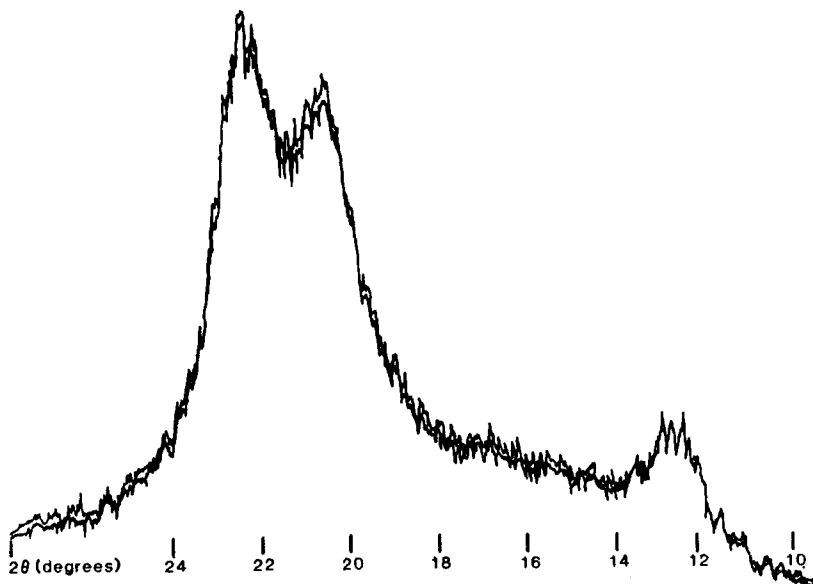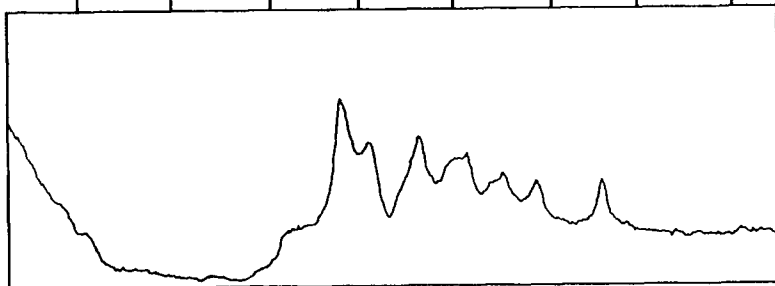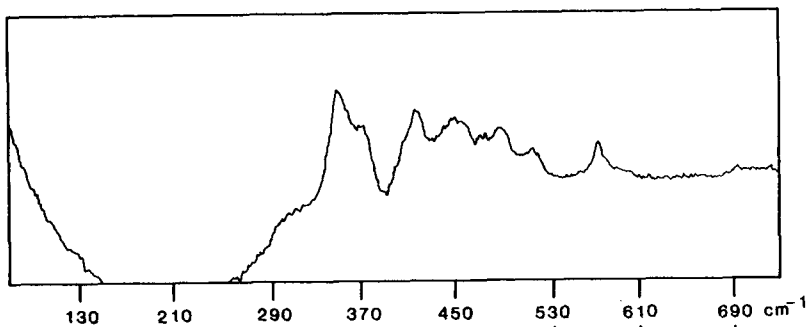
(a)

(b)

Fig. 2. (a) X-Ray diffraction pattern of cellulose fiber regenerated from melt-spun TMSC. (b) X-Ray diffraction pattern of cellulose powder regenerated from TMSC for 2 h. (c) X-Ray diffraction pattern of cellulose powder regenerated from TMSC for 20 h. (d) Raman spectra of cellulose powder samples regenerated from TMSC.

(c)

(d)

Fig. 2. *(Continued from previous page.)*

Some advantages of this process relative to other methods available for production of regenerated cellulose fiber are:

(1) The high cellulose content (50%) at the spinning stage exceeds that of any cellulose solution or of viscose, allowing more throughput.

(2) The high velocity achievable in melt spinning compared to wet or dry spinning allows greater production of fiber in a given time per spinneret.

TABLE III
Cellulose Cuene Intrinsic Viscosity (I.V.) Versus Process Stage

Sample	Cuene I.V., dL/g	DP
Acetanier-P	9.0	2600
TMSC, NaBH$_4$/CH$_3$OH regeneration	6.6	1750
TMSC melt-spun, NaBH$_4$/CH$_3$OH regeneration	1.7–2.0	290–360
TMSC melt-spun, IPA/H$_2$O/HCl regeneration	1.4–2.0	230–360

(3) The higher degree of fiber stretch (orientation) obtainable in melt spinning compared to wet or dry spinning allows improvement of fiber properties.

(4) The chemically self-contained nature of the process markedly reduces the amount of toxic or undesirable by-products.

Although the viscose process will probably continue to be the method of choice for commercial production of regenerated cellulose, the TMSC method clearly offers an alternative approach.   If the engineering problems associated with the melt spinning and reagent recycle aspects were solved, this process could provide a new and effective method for production of regenerated cellulose.

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