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Long chain branched celluloses by mild trans-glycosidation

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Cellulose dissolved in anhydrous dimethylacetamide (DMAc)/LiCl solution and treated with dialkylaminosulfur trifluoride (DAST) became highly branched and actually gained in molecular weight. The branching was thought to arise from the action of HF which is generated from the consumption of DAST. Subsequent experiments involving the direct addition of HF to anhydrous cellulose/DMAc/LiCl produced highly branched materials with greater polydispersity and greater molecular weight than the starting cellulose. This branching was likely due to the well known reactivity of glycosyl fluoride endgroups. Although the mechanism is not new, the combination of homogeneous cellulose dissolution and low levels of HF under anhydrous conditions represents a novel method for synthesizing a new class of cellulose derivatives. The potential utility of this method for producing branched cellulose derivatives and blocky cellulosic copolymers is discussed.

INTRODUCTION

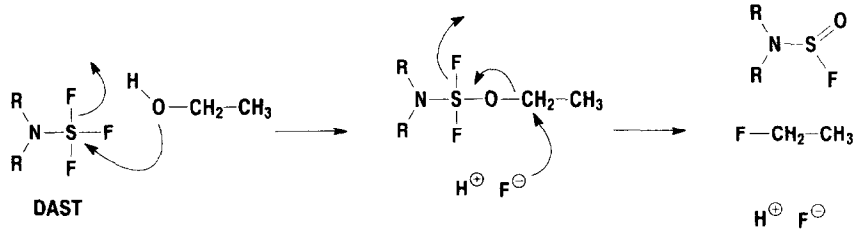
Recent activities in our laboratories have concentrated on the derivatization of cellulose in homogeneous solutions with solvent systems such as dimethylacetamide and lithium chloride, DMAc/LiCl (Glasser & Samaranayake, 1994) and dimethylsulfoxide, SO_2, diethylamine (Frazier & Glasser, 1995). Considerable efforts have also been directed towards the introduction of fluorine directly onto the backbone of cellulose (Frazier & Glasser, 1990), or indirectly with the use of fluorinated derivatizing agents (Frazier & Glasser, 1995). The synthesis of fluorodeoxycellulose by means of direct fluorination has been studied with the use of the very potent fluorinating agent dialkylaminosulfur trifluoride, also known as DAST. Under anhydrous conditions, DAST reacts rapidly with alcohols forming the corresponding alkyl fluoride as well as an equivalent of HF, as shown in Scheme 1 (Hudlicky, 1988). In an effort to combine DAST with homogeneous cellulose solutions, preliminary experiments were undertaken to test the stability of DAST in DMAc/LiCl at room temperature. It was found that DAST is stable in DMAc/LiCl solutions at room temperature for periods of up to 24 h. However, the DAST/DMAc/LiCl solution has no fluorinating capacity, but instead is a potent chlorination reagent for primary and secondary alcohols. This combination also will effect aromatic substitutions.

It was found that cellulose dissolved in DMAc/LiCl becomes highly chlorinated when treated with DAST under anhydrous conditions. However, there was a clear indication of a side reaction that caused an increase in the molecular weight and an increase in the polydispersity of the polymer. Subsequent experiments indicated that anhydrous HF was the cause of the side reaction. This hypothesis was tested by adding anhydrous HF directly to a dry solution of cellulose dissolved in DMAc/LiCl. The side reaction was duplicated in the absence of DAST; i.e., the cellulose molecular weight and polydispersity increased as a result of adding HF directly. It will be shown that the molecular weight and polydispersity of these celluloses rise as a result of an anhydrous HF-catalyzed branching reaction.

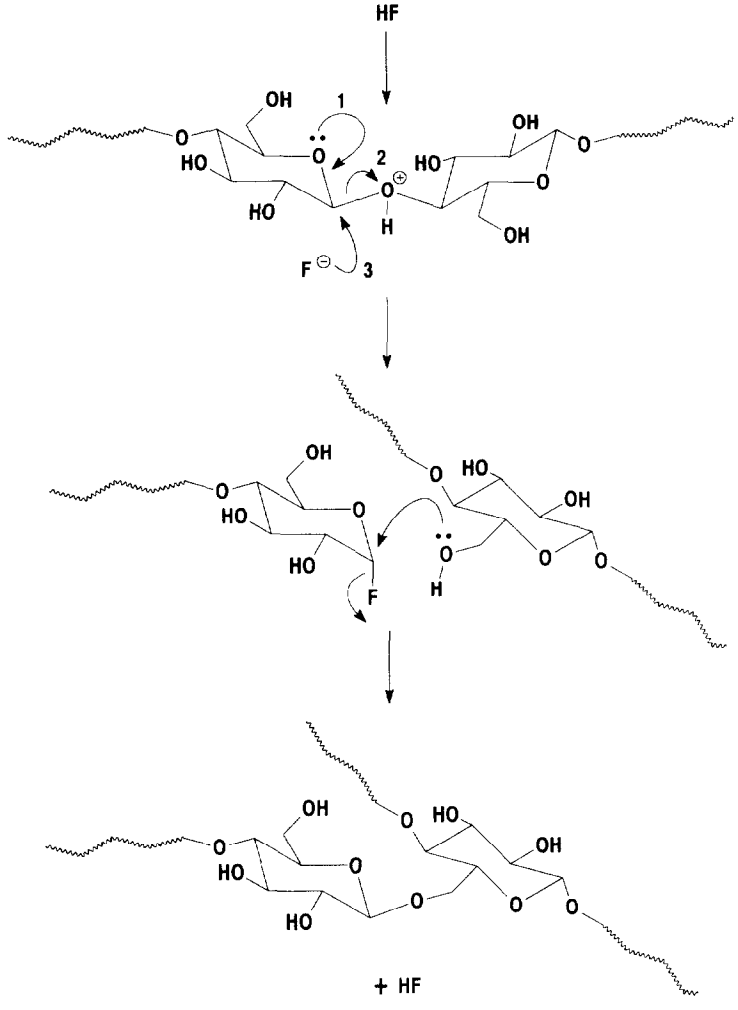
MATERIALS AND METHODS

Materials

Cellulose was Whatman, type CF-11. All reagents were purchased from Aldrich Chemical company and used as received, except for lithium chloride, certified, which was obtained from Fisher Scientific. Solvents were high purity, anhydrous preparations supplied by Aldrich in air tight packaging.



Scheme 1.



Scheme 2.

Analytical

NMR spectra were collected on a Varian, Unity 400 MHz spectrometer. Samples were prepared by dissolving 25–40 mg of material in a 5 mm NMR tube with about 0.7 ml of $CDCl_3$, and tetramethylsilane reference. Polymer molecular weights were obtained using gel permeation chromatography with universal calibration provided by a Viskotek Differential Viscometer, model 100. The system consisted of a Waters 510 pump which passed tetrahydrofuran (THF) to three Ultrastyragel columns in series: 10^3, 10^4, and 10^6 angstroms. The columns were heated at 40°C in an Eldex column heater. A Waters 410 refractive index detector was installed in series, after the viscometer. The viscometer and refractometer were also heated to 40°C. Calibration was performed using narrow dispersity polystyrene standards. Molecular weight of the starting cellulose was determined by synthesizing the cellulose triphenylurethane, CTPU, in dry pyridine and phenylisocyanate as demonstrated by Evans and Wallis (1987). Infrared spectra were obtained using a Nicolet 5SXC FTIR spectrometer. Films were cast from acetone, dried, and analyzed directly. When samples were insoluble, KBr pellets were made and analyzed as such.

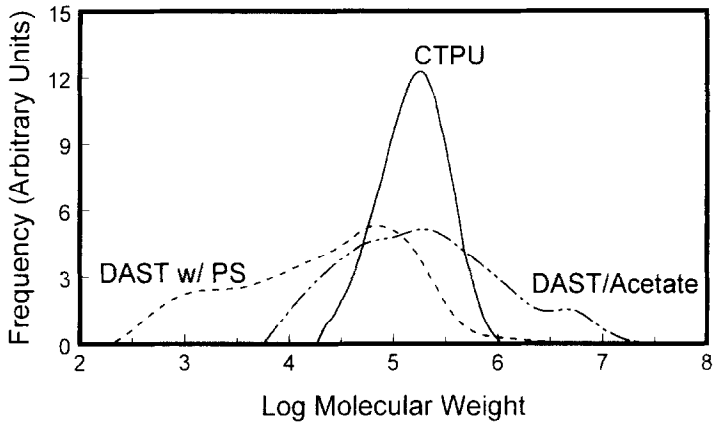


Fig. 1. Molecular weight distributions for celluloses treated with DAST alone (DAST/acetate), with DAST in the presence of a non-nucleophilic base (DAST w/PS) and also of the triphenylurethane of the starting cellulose (CTPU).

Dilute solution viscometry

Two different glass viscometers were used for this investigation: a size 25 Cannon-Fenske capillary viscometer, and a size 100 Cannon-Ubbelohde viscometer. Measurements were made in a constant temperature bath maintained at 40 ± 0.2°C. For each of samples 1–4, four solutions were prepared in DMAc at concentrations (w/w) of 0.13%, 0.11%, 0.08%, and 0.05%; these samples were tested in the size 25 Cannon-Fenske viscometer. Samples 5–10 were tested in the size 100 Cannon-Ubellohde viscometer. Samples 5–10 were each prepared at an initial concentration (w/w) of 0.13% in DMAc. These samples were then diluted to concentrations of 0.11%, 0.08%, 0.05%, and 0.03%. The control sample was analyzed with both viscometers. Measured intrinsic viscosities for the control were identical with both viscometers.

Differential scanning calorimetry

Cellulose triacetates, linear and branched, were analyzed on a Perkin Elmer DSC-4 using a TADS data station. The calorimeter was calibrated in the usual fashion with indium standards. Sample sizes ranged from 10 to 19 mg. Samples were heated at 20°C/min and cooled at 30°C/min under a dry nitrogen gas purge. Linear cellulose triacetate was analyzed as a powder. All branched samples were first hotpressed into films at 200°C under 60 psi of pressure for less than 2 min. The resulting films were not discolored or otherwise affected by hotpressing. DSC samples were then cut from these films.

Cellulose activation

Cellulose was dried for at least 24 h at 100°C, 5 mm Hg vacuum. After drying, the cellulose was activated by soaking in anhydrous DMAc in a sealed flask which was placed in a desiccator with fresh, anhydrous calcium chloride. The cellulose was soaked in DMAc until swelling was completed, about 1 wk. After activation, the cellulose slurry was filtered through a sintered glass buchner funnel under a blanket of dry N_2. The activated cellulose (solids content 34.5%) was stored in an air-tight container under dry N_2. DAST reactions were all performed by dissolving the appropriate amount of activated cellulose in the reaction flask in DMAc/LiCl (see below). HF/pyridine reactions were performed upon a stock solution of 0.5% cellulose dissolved in DMAc/LiCl (8–9% LiCl w/w) which was prepared by vacuum distilling a dilute solution of cellulose in DMAc/LiCl, thereby leaving an anhydrous solution in the distillation bottom. This distillation was performed at sufficient vacuum so that DMAc distilled at 40°C. A similar procedure was used to make an anhydrous cellulose solution with a concentration of 1.33%.

Homogeneous cellulose – DAST reaction

Where possible, all precautions were taken to ensure the exclusion of moisture. For example, all liquid transfers were performed using syringe or cannula techniques under dry N_2. An 8% solution of LiCl in anhydrous DMAc was made by quickly transferring 8 g of LiCl to a dry, 250 ml triple-neck flask. The flask with LiCl, and magnetic stir bar, was flamed thoroughly under dry N_2 purge. Anhydrous DMAc (100 ml) was added to the flask, and LiCl dissolution was hastened by heating to 80°C with magnetic stirring. After complete salt dissolution, 2.9 g of activated cellulose (1 g dry cellulose) was quickly added to the flask and the mixture was stirred at room temperature, under dry N_2, until dissolution of cellulose was complete (4–12 h). After cellulose dissolution, the reaction flask was fitted with a dry 50 ml addition funnel. A solution of 1.8 ml of dimethylaminosulfur trifluoride (18 mmoles, 1:1 ratio of DAST to OH) in 25 ml of DMAc was transferred to the addition funnel and slowly added to the reaction flask with stirring over a period of 60 min. After approximately 45 min, the solution gelled. This gel was broken with careful atten-

tion to stirring and by continued addition of the DAST solution. Eventually, free, unassisted stirring was resumed, and the solution was allowed to react at room temperature for 20 h. After all DAST was added, the solution was an opaque neon yellow, which gradually became orange in color overnight. Besides the initial gelation, this solution seemed to be nearly completely homogeneous at all times. The reaction was ended by carefully pouring the solution into about 400 ml ice water with excess $NaHCO_3$. The precipitate was filtered and washed with distilled water and methanol. The yellowish-white powder was extracted with methanol in a soxhlet apparatus for 48 h, and then dried under vacuum (5 mm Hg) at 50°C overnight. A light yellow powder (2.72 g) was recovered. This material was acetylated by treating with 90 ml of anhydrous pyridine–acetic anhydride (1:1, v/v) under dry N_2 at 60°C for 24 h, and then heated to 100°C for 4 h. The brown solution was cooled and poured into 300 ml of methanol. Brown product was filtered and extracted with ethanol in a soxhlet apparatus for 24 h. The sample was dried, dissolved in chloroform, and then centrifuged. The supernatant was concentrated and the viscous solution was poured into methanol. After vacuum drying, 1.16 g of brown precipitate was recovered. The brown color of the product may have arisen from sulfur impurities introduced by the action of DAST.

Another DAST reaction was carried out in the same manner except for the following: 1,8-bis(dimethylamino)naphthalene and proton sponge (1.95 g, approximately 1 equivalent per anhydroglucose unit), which were dissolved in 15 ml of dry DMAc and added prior to the addition of DAST. Thereafter, the reaction proceeded as above. This product was not acetylated, but instead was reacted with phenylisocyanate in dry pyridine as described above in the analytical section.

Homogeneous cellulose–hydrogen fluoride/pyridine reaction

Anhydrous cellulose (100 ml) solution was transferred to a dry 125 ml erlenmeyer flask equipped with magnetic stir bar and sealed with a septum under dry N_2. HF/pyridine (70% HF) was transferred directly to the cellulose solution dropwise with a syringe. With the addition of each drop of HF/pyridine, a small drop of cellulose precipitated from the homogeneous solution. After the addition of all the HF/pyridine there was a finite amount of precipitated cellulose. After 5 min of stirring, the precipitated cellulose had redissolved. After 10 min, the solution was opaque, but appeared homogeneous. For three of the experiments a 5% (v/v) solution of HF/pyridine dissolved in anhydrous DMAc was used instead of pure HF/pyridine. See Table 1 for the amounts of applied HF. Reactions were run at room temperature for periods of 15, 25, and 40 min and were ended by pouring the cellulose solution into water (400 ml) containing excess Na_2CO_3 or $NaHCO_3$. The products were filtered and washed thoroughly with distilled water, and then with acetone. After soxhlet extraction in water for 24 h, the sample was dried under vacuum (2 mm Hg) at 60°C.

Acetylation of HF treated cellulose

The recovered, dried, cellulose samples were each suspended in 30 ml of anhydrous dimethylformamide in a 100 ml 3-neck flask equipped with magnetic stir bar,

Table 1. Solubility, viscosity, and molecular weight information for peracetylated cellulose derivatives with varying degrees of branching

Sample #	Cellulose solution conc. % (wt/vol)	Applied HF (ml)	Reaction time (min)	% soluble of acetate	Intrinsic viscosity (dl/gm)[a]	DP_n	DP_w/DP_n	DP_z/DP_n
	Cellulose triacetate control	—	—	100	1.62	170[b]	1.8	9.2
1	0.5	0.5	15	92	0.78	225	5.1	56.4
2	0.5	0.5	25	0	—	—	—	—
3	0.5	0.5	40	0	—	—	—	—
4	0.5	0.25	15	100	1.08	—[c]	—	—
5	1.0	0.25	15	0	—	—	—	—
6	1.0	0.25	25	39	0.88	179	3.0	10.5
7	1.0	0.25	40	45	0.47	180	4.0	23.7
8	1.0	2[d]	15	55	1.05	147	3.8	23.1
9	1.0	2[d]	25	39	0.70	203	6.3	58.3
10	1.0	2[d]	40	27	0.85	60	3.3	23.7

[a]In anhydrous DMAc, at 40°C.
[b]Molecular weight information for the control was obtained from the triphenyl urethane derivative of the cellulose starting material.
[c]No GPC data available as this sample was not THF soluble.
[d]This is 2 ml of a 5% (vol/vol) solution of HF/pyridine in anhydrous DMAc.

septum, and dry N_2. Glacial acetic acid (4 moles per mole of cellulose OH) was added followed by the same molar amount of benzene sulfonyl chloride. The temperature was raised to 55°C and held there for 7 h. Then the solution was poured into distilled water, filtered and the precipitate was washed with water, and then with methanol. The acetylated samples were then extracted with methanol in a soxhlet apparatus for 24 h. Finally the samples were dried under vacuum (2 mm Hg) at 60°C. The dried samples were then placed in an excess of DMAc and stirred for several hours. These DMAc suspensions were filtered and the soluble portion was collected for intrinsic viscosity and gel permeation experiments. The cellulose triacetate control sample was prepared by acetylating amorphous Whatman, type CF-11, cellulose. The sample was made amorphous by precipitation from DMAc/LiCl solution, whereupon it was washed with methanol and dried. The acetylation of the control was carried out as above.

RESULTS AND DISCUSSION

The initial treatment of an anhydrous solution of cellulose dissolved in DMAc/LiCl with DAST resulted in a temporary gelation of the reaction medium. The solution was a soft, gelatinous mass that was visually homogenous and transparent, indicative of a lightly crosslinked network. The addition of more DAST combined with assisted stirring broke the gel and normal magnetic stirring was resumed. The recovered product was apparently crosslinked to some degree because unusually harsh conditions were required to acetylate the material in pyridine/acetic anhydride. Furthermore, after acetylation some of the sample remained insoluble. Figure 1 shows the molecular weight distribution of the cellulose sample treated with DAST in DMAc/LiCl and then subsequently peracetylated (DAST/acetate). It is compared to the starting cellulose which has been treated with phenyl isocyanate to form cellulose triphenylurethane (CTPU). Also shown is the molecular weight distribution of the phenyl urethane derivative of cellulose treated with DAST in DMAc/LiCl in the presence of a non-nucleophilic base, 1,8-bis(dimethylamino)naphthalene, commonly known as proton sponge (DAST w/PS). The increases in molecular weight and polydispersity of the acetate are clearly evident in Fig. 1. It is also apparent that proton sponge retards the effects of the DAST treatment but does not prevent the increase in polydispersity. Proton sponge did prevent the occurrence of gelation. The effects of the added base suggest a reaction caused by HF generated from DAST.

The DEPT (Distortionless Enhancement Polarization Transfer) ^{13}C solution state NMR spectrum of the DAST/acetate in Fig. 2 displays multiple C1 resonances in the 100 ppm region. There are also at least four methylene signals corresponding to the C6 carbon, one of which occurs at about 62 ppm and is similar in chemical shift to an acetylated C6 carbon (Buchanan *et al.*, 1987). The remaining methylene carbons at 42–44 ppm are probably chlorodeoxy carbons (Ishizu *et al.*, 1987). As mentioned previously, the DMAc/LiCl/DAST combination is a strong chlorinating medium; elemental

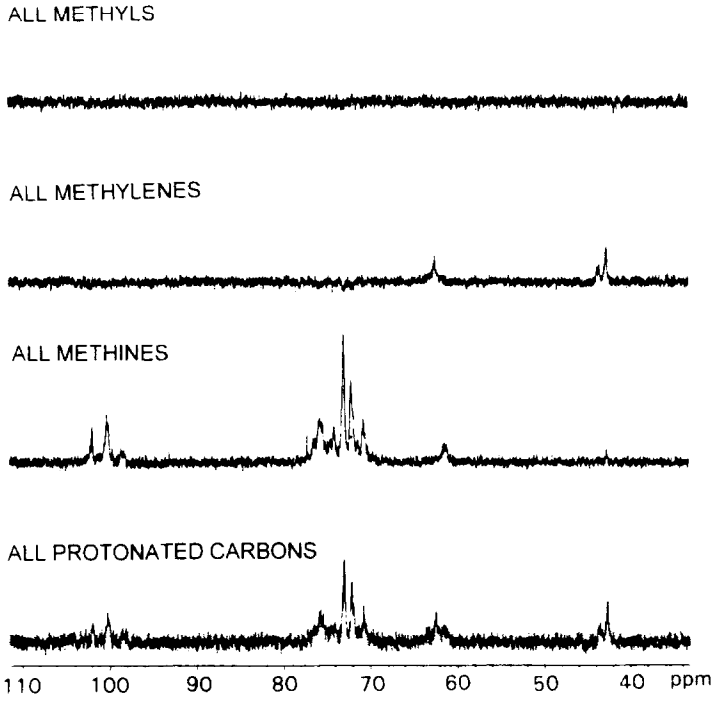


Fig. 2. DEPT ^{13}C NMR solution state spectrum of DAST/acetate referenced at 0 ppm with tetramethylsilane.

analysis of the DAST/acetate revealed a high chlorine content corresponding to a DS of about 1.0. Apparently, DAST activates hydroxyl groups for rapid displacement by the abundant free chloride. This is a similar activation to that previously described by Ishizu *et al.* (1987) for cellulose dissolved in DMAc/LiCl and treated with sulfuryl chloride. However, chlorination by DAST is less effective because of a competing HF-catalyzed branching reaction.

The suspicion that HF is the cause of the gelation is reasonable because it is well established that anhydrous HF readily dissolves cellulose by depolymerization into α-D-glucosyl fluoride (Defaye *et al.*, 1982; Hardt & Lamport, 1982; Franz *et al.*, 1987). Glucosyl fluoride is highly susceptible to attack by any nucleophile. Evaporation of HF drives the coupling of the glucosyl fluoride with any available hydroxyl group, which leads to a highly branched oligomeric product (Scheme 2). Under this scenario, multiple C1 resonances are expected in the ^{13}C spectrum as is shown in Fig. 2. Some of these C1 signals may be due to the effects of chlorination. It is reasonable to assume that chlorination by DAST is very rapid and that HF-catalyzed branching occurs afterwards. The question remains as to the location of the branch points. As mentioned, the methylene signals near 44 ppm are assigned as chlorinated and the remaining methylene signal near 62 ppm is similar in chemical shift to the C6 carbon of cellulose triacetate, which implies branching at secondary positions in cellulose. Alternatively, C6 branching sites are similar in chemical shift to the above mentioned methylene carbons. Figure 2 shows what may be considered as an unusual chemical shift for a methine carbon at 62 ppm. It may be that this methine carbon corresponds to the branch points within the sample, but no verification for this possibility is presented here. While the configurations of the branch points are not clear from this NMR spectrum, the multiplicity of the C1 signal is consistent with a redistribution of C1 linkages.

Additional support for branching via formation of reactive glucosyl fluoride endgroups was sought through independent experiments wherein anhydrous HF was added directly to dry solutions of cellulose dissolved in DMAc/LiCl. HF/pyridine was selected as the source of anhydrous HF because of its ease in handling. Two sets of experiments were performed; one set of four experiments with 0.5% cellulose solutions in DMAc/LiCl, and a second set of six experiments with 1% cellulose solutions. Various concentrations of HF/pyridine were employed and reaction times were set at 15, 25, and 40 min. The recovered cellulose samples were purified and then peracetylated. After peracetylation some of the samples were soluble, partially soluble, or insoluble in DMAc. The soluble portions of the peracetylated samples were recovered and analyzed. Infrared spectroscopy showed that the acetylations were complete in that only a very minor or no hydroxyl signal was observed.

Table 1 shows solubility, intrinsic viscosity, and gel permeation chromatography results for celluloses that had been treated with HF. Sample 1 has a lower intrinsic viscosity and a higher number average molecular weight than the linear cellulose triacetate control. Also note the extreme increase in molecular polydispersity, a clear indication that HF treatment has caused a high degree of branching and molecular weight gain in sample 1. Samples 2 and 3 were completely insoluble in DMAc, presumably because of excessive branching or network formation. The remaining samples, 4–10, resulted from variations in the reaction with changes in cellulose solution concentration and/or the amount of applied HF. Most samples show significant decreases in intrinsic viscosity with attendant increases in number average molecular weight, and polydispersity. Sample number 10 underwent branching but also a net depolymerization.

This compilation of data strongly suggests that these samples are branching and advancing in molecular weight from the effects of anhydrous HF, likely due to the generation of highly reactive glucosyl fluoride endgroups. Given this scenario, one may envisage the manipulation of this reaction for the production of novel cellulose derivatives. Of course, the method is not limited to the use of DMAc/LiCl as solvent. The basic requirements would be: a homogeneous solution of cellulose or cellulose derivative in an HF compatible solvent, an appropriate nucleophile, and anhydrous conditions. An abundance of water (or any other terminating nucleophile that does not promote chain branching) will result in a net depolymerization. (Indeed, the free chloride in the DMAc/LiCl system may have caused the net depolymerization of sample 10 shown in Table 1.) Franz *et al.* (1987) have previously discussed the same transformation when they studied the synthesis of various O-glycosides by simply mixing glucose with HF and nucleophiles such as methanol, octanol, or sorbitol. They found that these added nucleophiles were less effective in glycosylation than the hydroxyl groups of glucose, meaning that oligomeric and polymeric reversion products were often favored. Nonetheless, the work of Franz *et al.* demonstrates the general feasibility of manipulating the trans-glycosidation for synthesizing new cellulose derivatives, and opens possibilities for making branched versions of traditional cellulose derivatives. It may also be possible to synthesize blocky cellulosic copolymers by adding HF to anhydrous solutions of protected, trisubstituted cellulose derivatives in the presence of any number of hydroxy terminal polymers.

HF-catalyzed transglycosidation offers a route to new cellulosic materials with novel properties. For example, consider the thermal properties of the branched cellulose triacetates prepared in this work. The difficulty in determining a clear and unambiguous glass transition

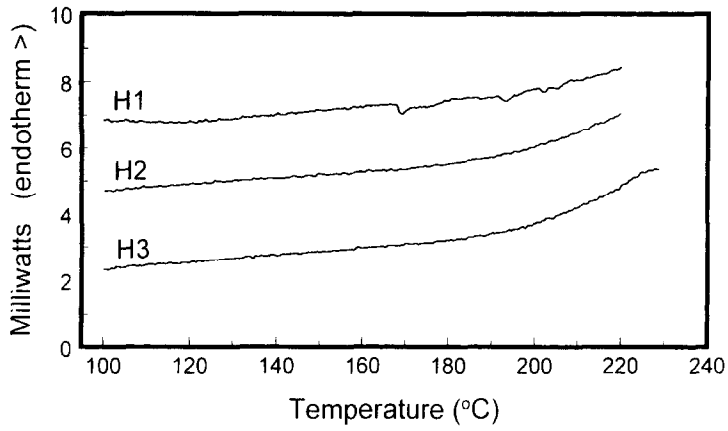


Fig. 3. DSC thermograms of the cellulose triacetate control synthesized for this study. H1, H2, and H3 refer to successive heats, one–three, for the same sample. Sample was heated at 20°C/min and immediately cooled at 30°C/min. Thermograms have been vertically shifted for clarity.

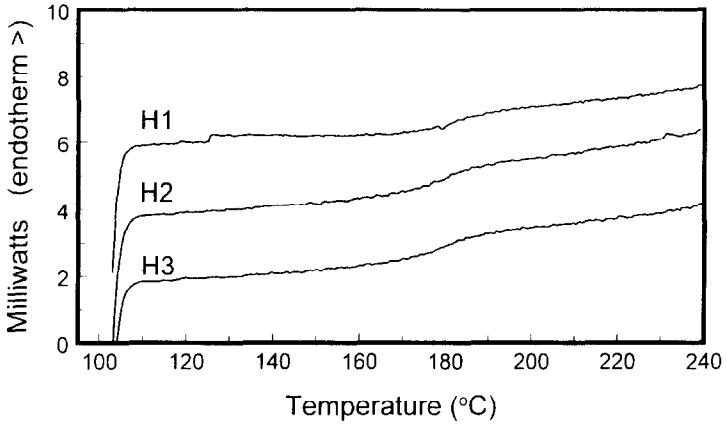


Fig. 4. DSC thermograms of branched cellulose triacetate, sample 9. H1, H2, and H3 refer to successive heats, one–three, for the same sample. Sample was heated at 20°C/min and immediately cooled at 30°C/min. Thermograms have been vertically shifted for clarity. The initial start-up endotherms have not been removed here as they were in Fig. 3.

temperature in linear cellulose triacetate is well known (Brandrup & Immergut, 1989). Figure 3 displays a series of differential scanning calorimetry (DSC) scans of the linear cellulose triacetate listed as the control in Table 1. These scans do not display a clear stepwise endothermal transition that is commonly associated with the glass transition in most synthetic polymers. Scanning to higher temperatures does not reveal a step increase, but instead initiates thermal decomposition. Compare this behavior to the DSC scans of branched cellulose triacetate, sample 9 shown in Fig. 4. Branched cellulose triacetate displays a clean stepwise endothermal transition that is reproducible. The glass transition temperature of this sample is seen at about 176°C. Glass transition temperatures for all of the branched triacetates that were isolated are listed in Table 2. These clear glass transitions likely reflect the reduced crystallinity that must result from chain branching.

Table 2. Glass transition temperatures for peracetylated branched cellulose derivatives from DSC

Sample #	Tg Heat 2	Tg Heat 3
Control	??	??
1	184	186
4	187	182
6	183	183
7	180	—
8	183	182
9	176	178
10	177	177

CONCLUSIONS

The action of HF on cellulose has been known for many years. However, much of the early studies dealt with the saccharification of cellulose where great excesses of HF were applied to cellulose under heterogeneous conditions. The discovery of this trans-glycosidation for making branched cellulose derivatives is rather a rediscovery of the reactivity and utility of glycosyl fluoride. The potential utility of this method comes from the use of: homogeneously dissolved and anhydrous cellulose

solutions, very low levels of HF, and the judicious selection and control of an appropriate nucleophile.

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