Crosslinking of Cellulose Acetate with Phosphorus Pentoxide

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In previous work in our laboratory, it was shown that trifluoromethanesulfonate (triflate) esters of cellulose acetate and methyl cellulose undergo crosslinking to form solid gels in pyridine solution. The crosslinking process, summarized by eqs. (1) and (2), occurred at 5°C overnight. We hypothesized that if trifluoromethanesulfonic (triflic) anhydride could be formed in situ from triflic acid in the pyridine reaction mixture, only catalytic amounts of triflic acid would be required to form crosslinks. Triflic anhydride is produced from triflic acid in the presence of P_2O_5 at ambient temperature? Furthermore, triflic anhydride will form triflates from alcohol groups in pyridine? In turn, triflates are sufficiently reactive to alkylate alcohols. Thus, crosslinking is predicted to occur by the following reactions, with the overall reaction written as eq. (4).

\[ \text{ROH} + \text{Tf}_2\text{O} \rightleftharpoons \text{ROTf} + \text{TfOH} \]  
\[ \text{ROH} + \text{ROTf} = \text{R'OR} + \text{TfOH} \]  
\[ 2\text{TfOH} = \text{Tf}_2\text{O} + \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \]  
\[ \text{ROH} + \text{ROH} = \text{R'OR} + \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \]  

**EXPERIMENTAL**

Cellulose acetate [Eastman Kodak, Rochester, NY; viscosity (ASTM-A): 25 s; 40% acetyl] was dried overnight in a vacuum oven over phosphorus pentoxide at 50°C. Five grams of cellulose acetate was first added to each of two flasks, followed by 100 mL of dry pyridine freshly distilled over NaOH pellets. After the cellulose acetate dissolved, 2 g of P_2O_5 powder was added with stirring. 200 μL of triflic anhydride was added, under nitrogen, to one flask, while the other flask was used as a control. After 48 h, the contents of both flasks had formed firm gels. The gels were mixed with 1 L of 70:30 water:acetone and stirred for 24 h. The gels were filtered and washed twice more with water:acetone as above. Finally the gels were filtered, dried, and dried over P_2O_5 in a desiccator. Infrared (IR) analysis, elemental analysis, and thermomechanical analysis were used to characterize the products. Thermomechanical analysis was carried out on a model TMS-2 (Perkin Elmer) from 50°C to 240°C (190°C for the crosslinked products) at 10°C/min.

**RESULTS AND DISCUSSION**

Reaction of cellulose acetate with phosphorus pentoxide in pyridine with or without, catalytic amounts of triflic anhydride led to the formation of a gel. The formation of a
gel is indicative of crosslinking because cellulose acetate does not normally gel in pyridine. Since both samples formed gels it is apparent that triflic anhydride is not needed as a catalyst in the reaction. Indeed, its presence causes larger amounts of phosphorus and nitrogen to be retained in the product (Table I). Thus, phosphorus pentoxide by itself is sufficient to promote crosslinking in cellulose acetate under anhydrous conditions. Characterization of the sample was necessary to determine if the cellulose acetate was significantly altered beyond crosslinking. The color of the solutions remained almost clear during the course of the reaction, except in the case of the sample where triflic anhydride was added which turned slightly red, a color characteristic of the triflate derivative. Both products were found to be insoluble in all solvents tested, but were swelled by dimethyl formamide, dimethyl sulfoxide, acetone, methylene chloride, pyridine, and tetrahydrofuran, which are all solvents for cellulose acetate. In all cases the gel was translucent.

The results of the elemental analysis (Table I) show that the carbon and hydrogen contents of the crosslinked products are comparable to cellulose acetate; the slight lowering of the carbon content is due to simple displacement by nitrogen, phosphorus, and, in the case where triflic anhydride was added, fluorine. The fact that nitrogen and phosphorus are present is due to entrapment of pyridine and phosphorus compounds or actual chemical linkage. The amount of these substances is relatively small, though the presence of the triflate groups apparently increases their presence.

The IR spectra of the products (Fig. 1) are very similar to the original cellulose acetate. The small amount of triflic anhydride reacted with the cellulose acetate is not enough to significantly alter the IR spectrum. Furthermore, the small amounts of pyridine and phosphorus which remained in the samples also did not alter the IR spectra significantly. In all of the materials, the carbonyl peak at 1750 cm\(^{-1}\) is strong; consequently, hydrolysis of the acetyl group did not occur to an appreciable extent.

As indicated by eq. (4), the crosslinks are predicted to be ether linkages. Due to steric considerations, and the fact that primary hydroxyl groups outnumber secondary hydroxyl groups in cellulose acetate, crosslinking will principally involve the C-6 primary hydroxyl groups with the formation of methylene ether linkages. The presence of methylene ether crosslinks is corroborated by the IR spectra of the products. The IR spectra of the products show well-defined C—H stretching vibrations slightly above 3000 cm\(^{-1}\). Although it is unusual for cellulose derivatives to have absorbances in the region of 3100 cm\(^{-1}\), methylene (—CH\(_2\)—) groups present as part of a rigid system do show absorptions slightly above 3000 cm\(^{-1}\). This same phenomenon was observed to a more pronounced degree for crosslinked triflates of cellulose acetate and O-methylcellulose.

Characterization of the cellulose acetate and the products by thermal mechanical analysis showed that the original cellulose acetate had a coefficient of thermal expan-

### Table I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>P</th>
<th>O&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose (theoretical)</td>
<td></td>
<td>44.44</td>
<td>6.17</td>
<td>0.00</td>
<td>0.00</td>
<td>49.38</td>
</tr>
<tr>
<td>Cellulose acetate (theor.)</td>
<td></td>
<td>49.44</td>
<td>5.62</td>
<td>0.00</td>
<td>0.00</td>
<td>44.94</td>
</tr>
<tr>
<td>Cellulose acetate (actual)</td>
<td></td>
<td>49.41</td>
<td>5.63</td>
<td>0.00</td>
<td>0.00</td>
<td>44.96</td>
</tr>
<tr>
<td>Cellulose acetate, P(_2)O(_6)</td>
<td></td>
<td>47.18</td>
<td>5.72</td>
<td>0.56</td>
<td>1.86</td>
<td>44.68</td>
</tr>
<tr>
<td>Cellulose acetate, P(_2)O(_6), Tf(_2)O(^b)</td>
<td></td>
<td>43.96</td>
<td>5.63</td>
<td>0.85</td>
<td>3.76</td>
<td>—</td>
</tr>
</tbody>
</table>

"Oxygen determined by difference.

\(^b\)Tf denotes the triflic group.
sion of \(8.21 \times 10^{-5}/^\circ\text{C}\) below the glass transition temperature of 190°C and \(26.6 \times 10^{-5}/^\circ\text{C}\) above the glass transition temperature. The crosslinked products had thermal expansions of \(1.28 \times 10^{-4}/^\circ\text{C}\) without triflic anhydride and \(1.15 \times 10^{-4}/^\circ\text{C}\) with triflic anhydride. The crosslinked products are particularly susceptible to decomposition above 190°C, although cellulose acetate has little decomposition below 240°C. This is probably due to the presence of phosphorus which acts as a fire retarder by lowering the decomposition temperature. For this reason, the thermal mechanical analysis had to be carried out below 190°C in the case of the crosslinked products. The reason that the products may have a slightly higher thermal expansion is that they shrank considerably when drying from their swollen gel states.

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References


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