Carbohydrate Research, 153 (1986) C1–C3
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Preliminary communication

Triflates of cellulose acetate and *O*-methylcellulose: occurrence of crosslinking

CHRISTOPHER J. BIERMANN and RAMANI NARAYAN

Laboratory of Renewable Resources Engineering, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

(Received June 6th, 1986; accepted for publication, June 13th, 1986)

In our work on grafting such synthetic polymers as polystyrene onto cellulose, we have been interested in cellulose derivatives having substituents, such as the tosyl group, that can function as good leaving groups in nucleophilic-displacement reactions with polymeric ions[1]. Cellulose acetate and *O*-methylcellulose have been used, as they are solubl in suitable solvents for homogeneous reaction with the polymeric ions.

The trifluoromethanesulfonate (triflate) group is a very good leaving-group, over 10,000 times more reactive than the *p*-toluenesulfonate group in solvolysis[2,3]. With the assumption that the introduction of triflate groups onto cellulose derivatives may speed the grafting reaction and increase the yield of products, we prepared triflates of cellulose acetate (Kodak, Rochester, NY; viscosity (ASTM-A): 25 s; 40.0% acetyl, d.s. 2.5) and *O*-methylcellulose (Sigma, St. Louis, MO, product M7140; d.s. 1.7; mol. wt. 15,000) in the usual manner[3,4] as for the methanesulfonylation of cellulose derivatives[5]. Thus, 5 g of cellulose acetate (19.0 mmol) or *O*-methylcellulose (26.9 mmol) was dissolved in 100 mL of pyridine (freshly distilled from sodium hydroxide pellets), cooled to 5°, and treated with 6.5 mL (38.6 mmol) of trifluoromethanesulfonic (triflic) anhydride with stirring in a dry nitrogen atmosphere. In both cases the solution quickly turned deep red and began warming up within a matter of seconds to ~30°. The viscosity increased noticeably as well. The mixtures were allowed to react overnight at 5°.

After 12 h the solutions had formed solid gels, indicating crosslinking of the cellulose chains. This behavior has not been observed for mesylation of cellulose acetate in the literature[5] or in our laboratory. Evidently, some of the introduced triflate groups had been displaced by nucleophilic reaction with free hydroxyl groups of another cellulose chain, resulting in methylene ether crosslinks. The triflates are powerful alkylating agents[2]. In this case the alkyl group is a cellulose acetate molecule.

$$\text{Cell–CH}_2\ddot{\text{O}}\text{H} + \text{Cell–CH}_2\text{–OSO}_2\text{CF}_3 \rightarrow \text{Cell–CH}_2\text{OCH}_2\text{–Cell}$$

The presence of methylene ether crosslinks is nicely corroborated by the i.r. spectra of the products. The i.r. spectra of the triflates of both cellulose acetate and *O*-methylcellulose show well defined C–H stretching vibrations above 3000 cm^{-1} (Fig. 1).

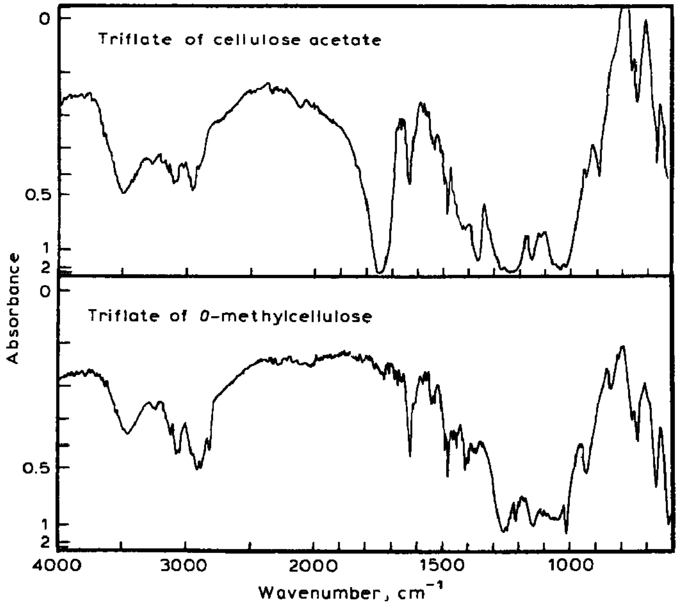

Fig. 1. I.r. spectra of the triflated products.

This is rather unusual for cellulose derivatives which do not contain aromatic or unsaturated groups; however, methylene ($-CH_2-$) groups present as a part of a rigid system do show absorptions above 3000 cm^{-1} due to C–H vibrations[6]. Consequently, the C–H stretching vibrations above 3000 cm^{-1} in these cellulose products are attributed to methylene groups that are part of the rigid, crosslinked system.

The high reactivity of the triflate group may preclude its use in the intended reactions; however, triflic anhydride is a useful crosslinking agent. Crosslinking of cellulose acetate may be useful for such applications as changing the properties of semipermeable membranes and plastics made from cellulose acetate. The products were washed with 500 mL of 5:1 water–acetone, filtered, and dried. The yield of triflated *O*-methylcellulose was 170% (theoretical yield, 192%); the yield of triflated cellulose acetate was 123% (theoretical, 125%). The triflate of *O*-methylcellulose was insoluble in toluene, was very slightly swelled by ethanol, tetrahydrofuran, and CH_2Cl_2, and swelled by $HCONMe_2$, Me_2SO, and acetone after being stirred with each solvent for 24 h. The triflate of cellulose acetate was insoluble in toluene, ethanol, and tetrahydrofuran, and was swelled by $HCONMe_2$, CH_2Cl_2, Me_2SO, and acetone.

Table I gives the elemental analysis of the products and the theoretical elemental analysis of the products, assuming that all available ROH groups had been derivatized. From Table I it appears, based on the presence of nitrogen, that some pyridine was incorporated into the products, either by reaction or by physical inclusion.

The low fluorine content of the products (compared to the theoretical pertriflated derivatives) indicates that derivatization was not complete. This is expected if a significant proportion of ether linkages is formed. The i.r. spectra also show a fairly large OH peak at 3500 cm^{-1}, indicating that many ROH groups were neither crosslinked nor triflated.

TABLE 1

ELEMENTAL ANALYSIS OF THE PRODUCTS

Element	*Actual triflate product*		*Theoretical triflate product*	
	Acetate	*Methyl*	*Acetate*	*Methyl*
C	42.55	39.51	40.0	30.22
H	4.99	4.59	4.15	3.39
F	7.22	13.48	10.0	20.73
S	5.79	9.43	5.61	11.64
N	1.09	2.88	0.00	0.00
O[a]	38.35	30.11	40.23	34.02

[a] Determined by difference.

ACKNOWLEDGMENT

This work was supported by a grant (85-CSRS-2-2554) from the United States Department of Agriculture (USDA) to the Wood Utilization Research Program (WURP) at Purdue.

REFERENCES

1 R. Narayan and G. T. Tsao, *Am. Chem. Soc., Div. Polymer, Preprints*, 25 (2) (1984) 29–30.
2 R. L. Hansen, *J. Org. Chem.*, 30 (1965) 4322–4324.
3 T. M. Su, W. F. Sliwinski, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 91 (1969) 5386–5388.
4 L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, NY, 1967, p. 1180.
5 M. L. Wolfrom, J. C. Sowden, and E. A. Metcalf, *J. Am. Chem. Soc.*, 63 (1941) 1688–1691.
6 K. Nakanishi and P. H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, 1977, pp. 16, 114.