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Grafting of Poly(ethylenimine) onto Mesylated Cellulose Acetate, Poly(methyl methacrylate) and Poly(vinyl chloride)

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ABSTRACT

Work on the formation of graft copolymers of cellulose derivatives has been continued by grafting poly(ethylenimine) (PEI) onto mesylated cellulose acetate (MCA) by second order nucleophilic displacement (SN_2) of mesylate groups by amine groups. Three solutions each containing 5% MCA and 2·5, 5 and 10% PEI, respectively, in dimethylformamide (DMF) were reacted at 80°C. The first solution did not form a gel, while the others formed gels (since cross-linking occurs) in 3 h and 1·5 h, respectively. This indicates aminolysis of acetate groups was taking place preferentially to the SN_2 reaction. Reaction of PEI with poly(methyl methacrylate) (PMMA) led to gelation, indicating that aminolysis of ester groups was occurring even with the 'hindered' esters of PMMA. The nucleophilic reaction leading to grafting was demonstrated by reaction of PEI with poly(vinyl chloride) (PVC), which also led to gelation. These grafting reactions could be used to produce cross-linked resins with high ion-exchange capacity.

INTRODUCTION

Grafting of synthetic polymers onto cellulose fibers and derivatives offers the potential for preparing new classes of materials with the

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advantages of both materials. To date, there are few useful reaction schemes to make these materials. The lack of significant commercialization of materials based on graft copolymers of cellulose is a reflection of this situation. The situation exists because most methods of preparation of cellulose graft copolymers depend on free radical polymerization methods (Hebeish & Guthrie, 1981; McDowall *et al.*, 1984), with their inherent disadvantages of high molecular weight side-chains, low levels of graft substitution and poor reproducibility of results (Stannett, 1982).

The work by the present authors on the formation of graft copolymers of cellulose derivatives is based on synthetic organic chemistry techniques, giving control over the grafting reaction as well as the side-chain to be grafted, using second order nucleophilic displacement reaction of preformed polymers (Biermann & Narayan, 1987*a*, *b*). This work has been continued by grafting poly(ethylenimine) (PEI) (also known as aziridine polymer) onto mesylated cellulose acetate (MCA). The reaction is summarized as

$$RNH_2 + Cell\text{-}CH_2\text{-}OMs \rightarrow Cell\text{-}CH_2NHR$$

EXPERIMENTAL

Mesylated cellulose acetate was prepared as described by Biermann and Narayan (1987*b*) with 0·46 methanesulfonate groups per anhydroglucose unit. Poly(ethylenimine) solution (50%, 10 g, average molecular wt. 50 000; Aldrich Chemical Co., Milwaukee, Wisconsin, USA) was evaporated to about 6 g in a vacuum desiccator over P_2O_5. Dimethylformamide was added to make 50 ml of 10% PEI solution. Mesylated cellulose acetate (1·0 g) was added to each of five 25 ml Erlenmeyer flasks. Poly(ethylenimine) solution was added as follows: Flasks 1 and 2, 5 ml; 3 and 4, 10 ml; 5, 20 ml. Dimethylformamide was added to the first four flasks to make 20 ml, and the contents stirred overnight. The flasks were then heated at 80°C for 20 h.

All of the flasks gave an ammonia smell when opened. The contents of each flask were precipitated in 100 ml of water. The copolymers were mixed with the water for 20 min and filtered. The water was evaporated to recovery homopolymer (ungrafted PEI). Both the homopolymer and graft copolymer samples were dried over P_2O_5. Because PEI absorbs water tenaciously, the entire recovered mass was greater than that of the starting PEI and MCA. The graft yield represents the percentage of PEI covalently linked to MCA compared to the original amount of PEI and assumed that the PEI of the graft copolymer and homopolymer each absorbed the same proportion of water. Infrared analysis of the PEI homopolymer showed the presence of a peak at 1700 cm^{-1} which was not present in the original PEI.

Poly(methyl methacrylate) (1·0 g, average molecular weight 12 000; Aldrich Chemical Co.) and PEI solution (50%, 2·0 g) were dissolved in DMF to make 20 ml and heated at 100°C; after 10 days the contents had formed a gel. The same experiment repeated with PMA solution (2·0 g, 50% solution in toluene, average molecular weight 30 000; Aldrich Chemical Co.) gave a gel after about 4 days.

Poly(vinyl chloride) (2 g, low molecular weight, Aldrich Chemical Co.) and PEI solution (50%, 1·0 g) were dissolved in DMF to make 20 ml and heated at 80°C; after 8 h the contents had formed a gel and were deep red in color.

RESULTS AND DISCUSSION

Table 1 gives the results of the grafting reactions carried out in this study. As the amount of PEI was increased in solution from 2·5 to 10% with 5% MCA, a decrease in gelation time was achieved. PEI is a branched polymer containing primary, secondary, and tertiary amine groups (Tashiro, 1986). Gelation indicates grafting occurs with cross-linking—that is the side chains have more than one reactive species, in this case probably primary amines. This supports the work of Isao *et al.* (1986) who grafted PEI onto tosylated cellulose with products that they hypothesized had cross-linking due to their high thermal stabilities. With large amounts of PEI present, the second order nucleophilic displacement (SN_2) reaction of mesylate groups by primary amine groups becomes favorable, as the amount of acetate groups decrease relative to

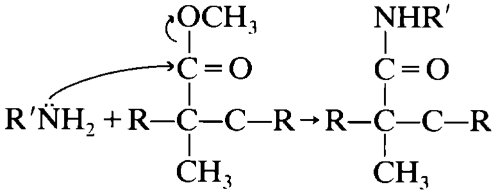
TABLE 1
Summary of Reactions Grafting PEI onto MCA, PMMA, PMA and PVC

Trial	*PEI (%)*	*Other reactant (%)*	*Graft yield (%)*	*Gelation time (h)*
1	2·5	MCA, 5	74	> 20 (80°C)
2	2·5	MCA, 5	78	> 20 (80°C)
3	5·0	MCA, 5	73	3 (80°C)
4	5·0	MCA, 5	73	3 (80°C)
5	10·0	MCA, 5	80	1·5 (80°C)
6	2·5	PMMA, 5	—[a]	240 (100°C)
7	2·5	PMA, 5	—	100 (100°C)
8	2·5	PVC, 10	—	8 (80°C)

[a] Values not determined.

primary amines. We have already shown that carboxylate groups were sufficiently nucleophilic to displace mesylate groups (Biermann & Narayan, 1987*a*,*b*), and primary amines are better nucleophiles than carboxylate groups.

A competing reaction called aminolysis is possible. Here acetyl groups are cleaved from the cellulose backbone by amines. Aminolysis of acetyl groups has been shown by Månsson and Westfelt (1980) to occur in yields above 50% after treatment of cellulose acetate graft copolymers by bulky amines such as pyrrolidine (60–85°C, 15 h). The absorption peak at 1700 cm^{-1} in the IR band of the graft copolymers is indicative of amide groups. The aminolysis reaction can be used, however, as the basis of a grafting reaction of PEI onto poly(methyl methacrylate) (PMMA). Reaction of 2·5% PEI with 5% PMMA in DMF at 100°C led to a gel after 5 days, indicating that aminolysis of ester groups was occurring even in the case of the 'hindered' esters of PMMA. The 'less hindered' ester groups of poly(methacrylate) (PMA) reacted in about half the time. The aminolysis of PMMA by PEI leading to grafting occurs as follows



$$\mathrm{R'NH_2 + R{-}\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{OCH_3}{|}}{C=O}}{|}}{C}{-}C{-}R \rightarrow R{-}\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{NHR'}{|}}{C=O}}{|}}{C}{-}C{-}R}$$

Nucleophilic displacement of suitable groups by the amine groups of PEI can also be used as the basis of grafting reactions. Reaction of 10% poly(vinyl chloride) (PVC) with 2·5% PEI in DMF led to a gel in 8 h at 80°C, indicating the occurrence of a nucleophilic displacement reaction of chloride (in secondary positions) by amine groups.

In similar work, Tashiro (1986) reacted excess PEI with RCH_2Cl groups of polystyrene-divinylbenzene beads swelled in dioxane at 100°C for 113 h, but achieved only about 15–20% reaction of $—CH_2Cl$ groups. Since the present reaction conditions were significantly milder, and the nucleophilic reaction involved a secondary carbon atom instead of a primary one, having the compounds in solution increases the reactivity compared to having merely swollen, cross-linked polymers.

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