Grafting of Polystyrene onto Cellulose Acetate by Nucleophilic Displacement of Mesylate Groups Using the Polystyrylcarboxylate Anion

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ABSTRACT: With few exceptions, grafting of polystyrene onto cellulose and cellulose derivatives is carried out by mechanisms involving free radical addition. These methods give large amounts of ungrafted homopolymer, little control over the molecular weight of the grafted polystyrene, and numerous other problems. By introducing methanesulfonyl (mesyl) groups on cellulose acetate, we have found that the polystyrylcarboxylate anion prepared by anionic polymerization techniques will displace the mesylate group and form an ester linkage with the cellulose backbone in a homogeneous-phase reaction. The reaction is essentially complete at 75 °C after 20 h. Grafting yields appear to be limited by the efficiency of carboxylation of the polystyrene.

Introduction

Grafting of synthetic vinyl polymers onto cellulose and cellulose derivatives offers the potential of preparing a new class of engineering materials. Properties of the derived graft polymers may be tailored to meet certain specifications by controlling parameters such as the molecular weight of the grafted side chains, the number of grafted side chains, and the type of grafted side chains.

With few exceptions, preparation of cellulosic graft polymers involves radical polymerization methods.[1-3] Radical polymerization, however, has several disadvantages. The molecular weight is very high, and the molecular weight distribution is polydisperse. Reproducibility of this method is poor, and there is little control over the grafting process. The net result is that grafting involves only a few high molecular weight molecules with a low level of graft substitution. These problems have been reviewed in detail.[4]

Preparation of a polymer with a suitably reactive end group, which then reacts with another backbone polymer, allows much greater control over the properties of the polymer. The preparation of polystyrene by an anionic mechanism allows precise control over the molecular weight with a monodisperse distribution. The polystyryl carbanion is strongly basic and its direct use requires protection of the cellulose hydroxyl groups, otherwise simple abstraction of a proton will yield the homopolymer as a side product. In addition, other side reactions can also occur. However, by modifying the chain-end carbanion to a more controllable, less reactive group, one can obtain better control of the grafting process with negligible side reactions.[5]

In this study we have modified the highly reactive polystyryl carbanion by capping with carbon dioxide to generate the polystyrylcarboxylate anion. This anion is not sufficiently reactive to displace acetate groups from cellulose acetate. It is, however, sufficiently nucleophilic to displace better leaving groups like the mesylate group from a mesylated cellulose acetate backbone, with the concomitant formation of an ester linkage. A further advantage of the direct use of polystyrylcarboxylate anion over the polystyryl carbanion is that water does not interfere with the grafting reaction. Figures 1 and 2 show the synthetic scheme for the polystyrylcarboxylate anions, and Figures 3 and 4 show the reaction scheme for the grafting process.

Experimental Section

General Methods. Tetrahydrofuran (THF) for the preparation of polystyryl carbanion was freshly distilled from sodium benzophenone complex and transferred by syringe techniques under dry nitrogen. All other solvents were reagent grade and used as supplied, without further purification or drying. Gel permeation chromatography (GPC) was carried out on two 10^3-Å ultrastyragel columns (Waters) with THF (HPLC grade) as eluent at 1.6 mL/min. Elemental analysis was carried out at the Microanalysis Laboratory of Purdue University.

Preparation of Polystyrylmono- and -Dicarboxylate Anions. Products 1 and 2 (Figures 1 and 2). The polystyryl mono- and dicarbanions were prepared in THF by using *n*-butyllithium and sodium naphthalene as the initiators, respectively, at −78 °C. The carbanions were reacted with dry carbon dioxide. The products were precipitated in methanol, filtered, washed with water and methanol, and dried. GPC analysis established values for the molecular weights as 6200 for the polystyrylmonocarboxylate and 10 900 for the polystyryldicarboxylate products.

Mesylation of Cellulose Acetate. Mesylation of 10 g of cellulose acetate (Eastman Kodak, 40% acetyl, degree of substitution (DS), 2.5) was carried out by the procedure of Wolfrom et al.[6] with 6 mL of methanesulfonyl (mesyl) chloride in 200 mL of pyridine for 4 days at room temperature. Elemental analysis gave 45.61% C, 5.52% H, and 4.90% S corresponding to mesyl substitution of 0.46 mesyl groups per anhydroglucose unit. Cellulose acetate with a lower mesyl content was prepared by reacting 50 g of cellulose acetate in 500 mL of pyridine and 3.50 mL of mesyl chloride for 1 day at room temperature. Elemental analysis gave 46.70% C, 5.68% H, and 2.42% S, corresponding to a DS of 0.21 for the mesyl groups.

Grafting Reaction (Figures 3 and 4). The grafting reaction was carried out by adding 0.50 g of mesylated cellulose acetate and 1.00 g of polystyrylcarboxylate to a 25-mL Erlenmeyer flask with 20 mL of solvent (4:1 dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO):THF, or, in a few reactions, other solvents). When Me_2SO was used as the solvent, some THF was added in order to dissolve the polystyrene. The reaction was carried out at 75 °C for 20 h, or under other conditions as noted.

The graft polymers 3 and 4 were precipitated with 200 mL of 4:1 methanol:water, filtered, washed with water and methanol, and dried. The product was then extracted with 100 mL of toluene with gentle shaking for 24 h to remove any unreacted polystyrene and polystyrylcarboxylate salt. The product was then filtered, washed with toluene, dried, and weighed. The toluene extract and washings were combined. The amount of unreacted homopolymer present in each of the toluene extracts was determined after evaporation of the toluene. The grafting yield was calculated as the weight percent of the polystyrene (PS) that attaches to the cellulose backbone and is given as

$$\frac{\text{(wt PS used)} - \text{(wt PS recovered in toluene)}}{\text{(wt PS used)}} \times 100\% \quad (1)$$

UV Analysis of Graft Polymer. UV measurements in CH_2Cl_2 at 260 nm of the THF-soluble graft polymers (product 3) were used to determine the polystyrene contents of the graft polymers.[7,8] Polystyrene homopolymer and mesylated cellulose acetate dis-

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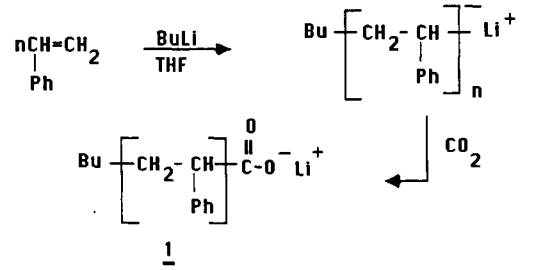

Figure 1. Reaction scheme for the formation of polystyrylmonocarboxylate anion.

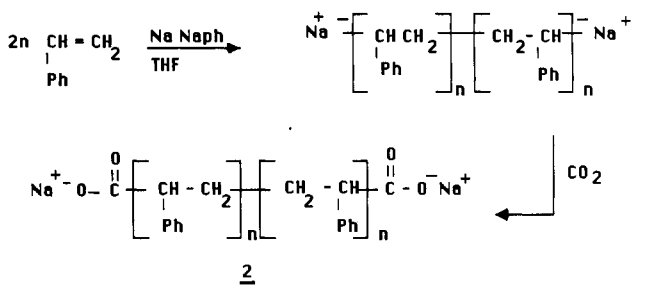

Figure 2. Reaction scheme for the formation of polystyryldicarboxylate anion.

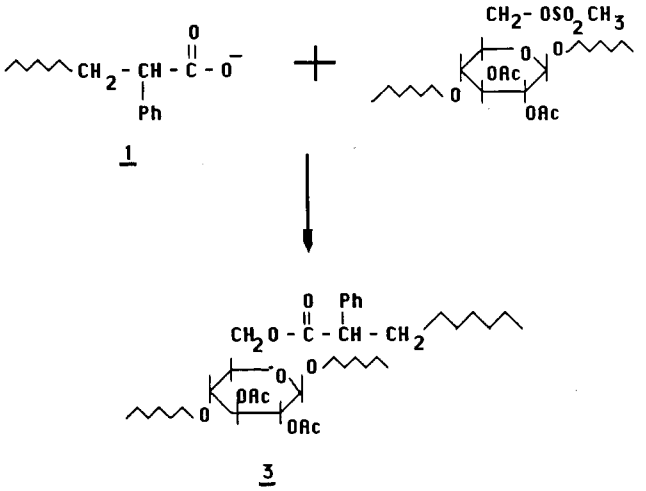

Figure 3. Reaction mechanism for the grafting of polystyrylcarboxylate anion onto mesylated cellulose acetate.

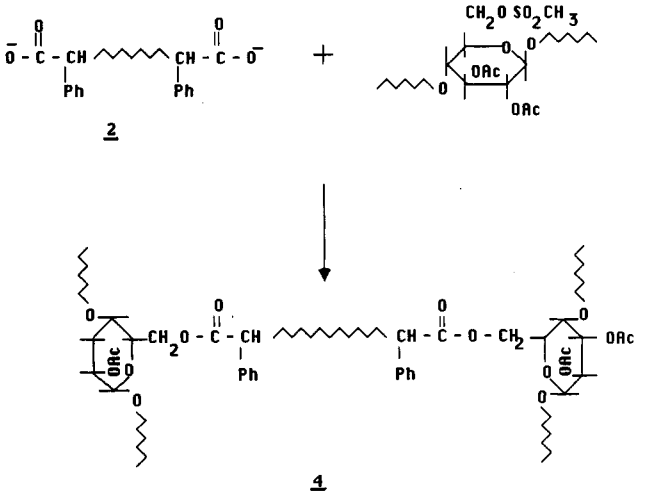

Figure 4. Formation of a cross-linked graft polymer by reaction with polystyryldicarboxylate anion.

solved in CH_2Cl_2 were used to make a standard curve.

Alkaline Hydrolysis of Graft Polymer. Some of the products were subjected to mild alkaline hydrolysis. Pulverized product (200 mg) was added to 50 mL of 15% aqueous ammonia at room temperature for 3 days with mixing. The residue was extracted with THF to remove released polystyrene, mesylate, and acetate.

Table I
Results of Grafting Experiments at 75 °C and 20 h

prod.	solvent	grafting[a] yield, %	PS content,[b,c] wt %	PS content by UV, wt %	AGU[d] per PS chain
3a	DMF	68	57.6	58.2	17.0
3b	Me_2SO/THF	60	54.5	59.9	19.3
4a	DMF	90.5	64.4		22.5
4b	Me_2SO/THF	88.5	63.9		23.0

[a] Percent by weight of the PS grafted. [b] Determined from the weight increase. [c] The molecular weight of the polystyrylmonocarboxylate is 6200 (product 3); the molecular weight of the polystyryldicarboxylate anion is 10900 (product 4). [d] Number of anhydroglucose units per polystyrene side chain.

Results and Discussion

Monodisperse polystyrylcarboxylate anions **1** and **2** (Figures 1 and 2), prepared by end capping the anionically polymerized polystyryl carbanion with carbon dioxide, were grafted onto mesylated cellulose acetate in various solvents by a second-order nucleophilic displacement (S_N2) type reaction. Several reaction temperatures and times were investigated until conditions suitable for high grafting yields were found. Grafting yields were calculated as the weight percent of polystyrene that is covalently linked to the cellulose backbone, determined after toluene extraction. Toluene extraction removes polystyrene and lithium polystyrylcarboxylate homopolymers present in the reaction product.

Initial grafting reactions with the mesylated cellulose acetate and lithium polystyrylcarboxylate were carried out at room temperature for 3 days in acetone and methylene chloride. Analysis of these samples showed that about 5–15% grafting yields were realized. Modifying the reaction conditions to 50 °C in Me_2SO/THF for 3 days gave grafting yields of 45%. Optimum conditions with a temperature of 75 °C for a reaction time of 20 h were then used in the remaining grafting reactions.

Allowing the reaction to proceed for 72 h in DMF at 75 °C did not significantly change the yield. This evidence indicates that the grafting reaction is essentially complete after 20 h at 75 °C and that the grafting yield is limited only by the efficiency of the carboxylation reaction of polystyrene. In fact, the graft yields obtained in the reactions of the polystyrylmonocarboxylate anions under the optimum conditions are close to the expected efficiency of carboxylation of 78–90%.[7] During the carboxylation of the polystyryl carbanion, side products dipolystyryl ketone and tripolystyrylmethanol can be formed;[7] however, these would not be grafted onto the cellulose chain. The technique of using carboxylate-terminated polymers to displace mesylate groups from suitable backbone polymers should have application to graft polymerization reactions in general.

The reaction of the mesylated cellulose acetate (MCA) with the polystyrylmonocarboxylate anion resulted in graft polymer product **3** (Figure 3), soluble in THF; however, reaction with the polystyryldicarboxylate anion resulted in the formation of a solid gel (product 4), indicative of cross-linking. Cross-linking is to be expected since both ends of the polystyrene chain could potentially react with the mesylate groups on the cellulose backbone as shown in Figure 4. The results are shown in Table I. In the case of THF-soluble products **3a** and **3b** the PS contents determined from the weight increase were in good agreement

Table II
Results of Grafting Experiments at 75 °C and 20 h

prod.	elem anal. C	H	S	N	O
MCA[a]	45.61	5.52	4.90		43.97
3a	70.07	6.90	2.83	0.37	19.83
3b	68.62	6.90	2.32		22.16
4a	73.37	6.84	2.52	0.16	17.11
4b	71.64	8.85	1.68		17.83
3a (hydrolyzed)	65.98	6.76	2.11		25.15
4a (hydrolyzed)	71.10	6.71	1.57		20.62

[a] Mesylated cellulose acetate (mesyl DS 0.46).

with those obtained by UV analysis.

Proof of Grafting. The increase in weight of the toluene-extracted products obtained, compared to the original weight of mesylated cellulose acetate, showed that grafting had occurred. Furthermore, the fact that the toluene-extracted polystyrene decreases dramatically with increasing reaction temperature indicates that a grafting reaction is occurring. Analysis of the products obtained from the reaction of the mesylated cellulose acetate with the polystyrylmonocarboxylate anion by GPC gave peaks corresponding to a molecular weight higher than the mesylated cellulose acetate, with no peaks in the range of the molecular weight of the homopolymer.

Elemental analysis of the reaction products and the starting material, namely mesylated cellulose acetate (mesyl DS 0.46), is shown in Table II. There is a marked increase in the carbon and hydrogen percentages with a corresponding decrease in the oxygen and sulfur percentages of the reaction product as compared to the starting mesylated cellulose acetate. Thus, elemental analysis data is also in conformity with the grafting of polystyrene onto the cellulose backbone by displacement of the mesylate groups. In the case of the reactions performed in DMF, little nitrogen was incorporated. Figure 5 shows IR spectra of a 50–50 blend of polystyrene–cellulose acetate, MCA-PS graft polymer product **3**, and product **3** after hydrolysis with ammonia. The IR spectra are virtually identical. Characteristic peaks of polystyrene such as the aromatic C–H vibration above 3000 cm^{-1} and the aromatic ring vibrations at 1500–1600 cm^{-1} as well as the strong carbonyl band at 1740 cm^{-1} of the cellulose acetate are present. However, toluene extraction removes over 98% of polystyrene homopolymer from the cellulose acetate–polystyrene blends which have been precipitated from solution just as the graft polymers are precipitated during their isolation. Thus, the presence of the polystyrene bands in the IR spectra of the toluene-extracted graft polymers confirms the formation of a covalent link between polystyrene and the cellulose backbone.

The off-resonance proton-decoupled ^{13}C NMR spectrum at 50 °C in dimethylformamide of the toluene-extracted graft polymer (product **3a**) is shown in Figure 6. The spectrum clearly showed signals corresponding to both cellulose and polystyrene components. Since this graft polymer product was extensively extracted with toluene to remove any polystyrene homopolymer, the presence of well-resolved intense polystyrene peaks in the NMR spectrum supported the covalent attachment of polystyrene to the cellulose backbone. Readily discernible polystyrene peaks are at (1) 146 ppm with a multiple splitting pattern due to quaternary aromatic ring carbon, (2) 125 ppm corresponding to the other aromatic ring carbons, (3) the typical methylene (CH_2) resonance splittings centered around 48 ppm, and (4) single methine (CH) resonance at 41 ppm. The chemical shifts and the splitting patterns observed are in complete agreement with

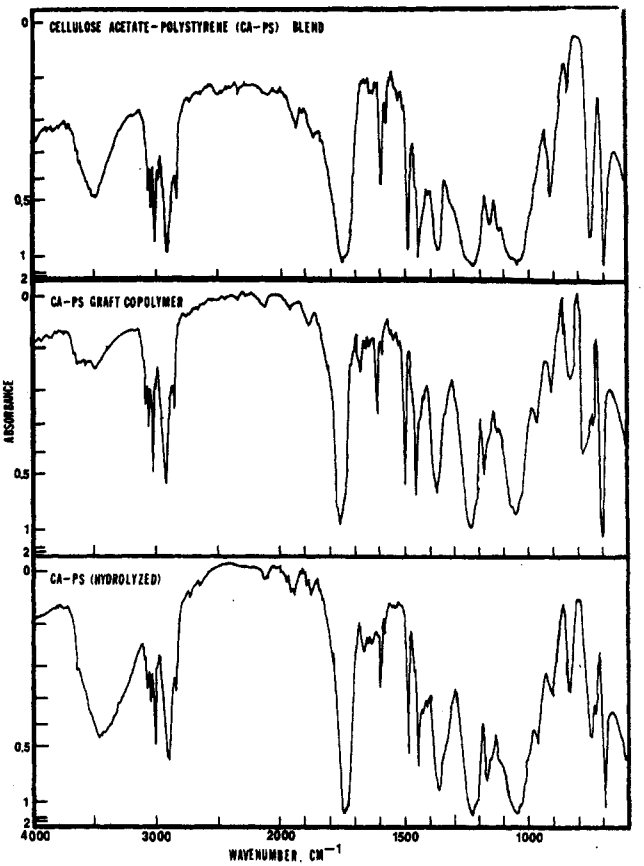

Figure 5. Infrared spectra of polystyrene–cellulose acetate graft polymers.

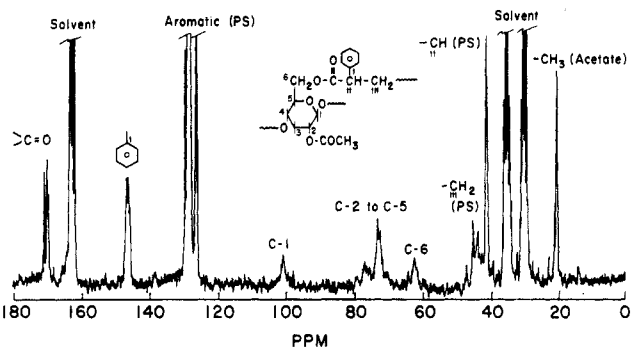

Figure 6. Off-resonance proton-decoupled ^{13}C NMR spectrum of graft polymer **3a**.

those reported for polystyrene.[9] The signals due to the cellulose are (1) the 107 ppm peak corresponding to the C-1 carbon of the anhydroglucose unit, (2) a group of signals between 70 and 80 ppm due to the C-2, C-3, C-4, and C-5 carbons, (3) the C-6 carbon signal at 63 ppm, and (4) the carbonyl carbon signal of the acetate groups on the cellulose at 170 ppm with the methyl of the acetate group appearing at 20 ppm. Each of the polystyrene peaks is much more intense than the ring C-1 to C-6 carbons of the anhydroglucose units because for every one anhydroglucose carbon there are 3.5 styrenic carbons.

Of great interest is the fact that hydrolysis with aqueous ammonia did not hydrolyze significant amounts of polystyrene, mesyl groups, or acetyl groups from the cellulose backbone. Some hydrolysis has occurred as indicated by the appearance of the hydroxyl peak at 3500 cm^{-1} in the IR spectrum (Figure 5) and the decrease in the carbon and sulfur percentages. However, the IR spectra of the hydrolyzed graft polymers still retain the strong carbonyl peak of the acetate groups and the aromatic C–H

stretching of polystyrene. Under these conditions of hydrolysis, the acetate groups of cellulose acetate are removed almost quantitatively. However, in the graft polymer the polystyrene seems to have a protecting effect on the acetate groups under these heterogeneous conditions of mild alkaline hydrolysis.

Grafting Degree of Substitution and Point of Attachment. The number of anhydroglucose units per grafted polystyrene chain (Table I) was calculated based on the molecular weight of the polystyrene and the polystyrene content of the graft. A high degree of substitution corresponding to one polystyryl chain per 17–23 anhydroglucose units was obtained. One polystyrene chain per 17 anhydroglucose units in product **3a** corresponds to about 16 polystyrene chains per cellulose acetate molecule based on a molecular weight of 75 000 for the cellulose acetate. Because the reaction is slow and proceeds by second-order nucleophilic displacement, the grafting of polystyrene chains is limited to the primary carbon atoms, that is, the C-6 position of the anhydroglucose units of cellulose. This is supported by preliminary experiments on grafting of polystyrene onto mesylated derivatives of cellulose acetate and methyl cellulose. There are more free primary hydroxyl groups in cellulose acetate[10] than in methyl cellulose[11] (DS = 1.7). Consequently, on mesylation, there were more mesyl groups on primary carbon atoms in cellulose acetate than the methylcellulose. Thus, reaction of the polystyrylcarboxylate ion with mesylmethylcellulose proceeded much slower and gave lower graft yields (20%) than reaction with mesylcellulose acetate. It has also been documented in literature that nucleophilic displacement of the tosylate group in a tosylated cellulose acetate occurs at the primary C-6 carbons.[12]

The presence of some water in the reaction medium does not have any deleterious effects on the coupling reaction; in fact, the only possible reaction of the polystyrylcarboxylate anion, in suitable solvents, is to displace the mesylate group. Consequently, time and reaction temperature are the only limiting conditions of graft yield in the reaction with polystyrylcarboxylate anion. In fact, the solvents were used for the grafting reaction as supplied without any further drying or purification. Another important consideration is that complete mesylation is not required. Two runs with mesylcellulose acetate of lower mesyl content (mesyl DS 0.21) in DMF at 75 °C gave a grafting yield of 40% after 20 h and 65% after 96 h.

Mansson and Westfelt[8] grafted polystyrene onto cellulose acetate with a grafting yield of up to 83% using the acid chloride of carboxylic acid terminated polystyrene. The method involved acylation of the free hydroxyl groups on the cellulose acetate by the polystyrene acid chloride and has considerable disadvantages. In order to achieve high grafting efficiencies, strictly anhydrous conditions must be used along with fairly large amounts of acylation catalysts such as 4-(dimethylamino)pyridine with long reaction periods (up to 3 days).

Conclusion

Polystyrene can be grafted onto mesylated cellulose acetate by reaction with polystyrylcarboxylate. The polystyrylcarboxylate anion displaces the mesylate groups via a SN_2 nucleophilic reaction which occurs almost quantitatively at 75 °C after 20 h under homogeneous conditions. Preparation of polystyrylcarboxylate anions by anionic polymerization techniques allows monodisperse polystyrene of any molecular weight to be grafted onto the cellulose backbone in a consistent manner.

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