

# Grafting of partially hydrolysed poly(methyl methacrylate) onto mesylated cellulose acetate

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(Received 19 March 1987; accepted 8 June 1987)

A new synthetic route to cellulose graft polymers by nucleophilic displacement of mesylate groups from mesyl cellulose acetate (MCA) by the polystyrylcarboxylate anion has been recently reported by us. This approach to cellulosic graft polymers overcomes the drawbacks of the radical polymerization methods and allows for precise control of parameters such as the molecular weight and molecular weight distribution of the grafted side chains, higher degree of substitution on the cellulose backbone, the number and nature of grafted side chains and overall better control and reproducibility of the grafting process. In this report, partially hydrolysed poly(methyl methacrylate) was successfully grafted on to mesylated cellulose acetate in excellent yields by nucleophilic displacement of mesylate groups in less than 60 min at 75°C.

(Keywords: mesylated cellulose acetate; grafting; poly(methyl methacrylate); nucleophilic displacement)

## INTRODUCTION

Grafting of synthetic polymers onto cellulose and cellulose derivatives allows the preparation of new materials whose properties may be tailored by controlling parameters such as the molecular weight of the grafted side chains, the number of side chains, the type of the grafted side chains, the nature of the backbone-graft linkage, and the amount of crosslinking. In the past this has been difficult to achieve with graft copolymers of cellulose and cellulose derivatives since such graft copolymers were usually produced by free radical polymerization techniques. Stannett has reviewed the problems associated with free radical polymerization techniques in detail<sup>1</sup>.

In previous work<sup>2,3</sup> we have shown that carboxy-terminated polymers can be grafted onto mesylated cellulose acetate and mesylated *o*-methyl cellulose by nucleophilic displacement of the mesylate groups. Thus, the polystyrylcarboxylate anion produced by anionic polymerization techniques, was grafted onto the mesylated cellulose derivatives with complete control over the grafting reaction<sup>2</sup>. Similarly, polyamide carboxylate was grafted onto mesylated cellulose acetate<sup>3</sup>.

In this study, we partially hydrolysed poly(methyl methacrylate) to generate a few carboxylate anion functionalities, using potassium hydroxide in refluxing ethanol (Figure 1)<sup>4</sup>. The partially hydrolysed poly(methyl methacrylate) was then successfully grafted onto mesylated cellulose acetate and mesylated *o*-methyl cellulose in excellent yields, via nucleophilic displacement of the mesylate groups by the carboxylate anions (Figure 2).

## EXPERIMENTAL

### Materials

Poly(methyl methacrylate) (catalogue no. 20,033-6) was obtained from Aldrich Chemical Co. (Milwaukee, 0032-3861/87/132176-03\$03.00  
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WI, USA). The average molecular weight was given as 12 000. Cellulose acetate with a degree of substitution (DS) of 2.5 was mesylated to give one product with mesyl DS of 0.46 and a second product of DS 0.21 as described previously<sup>2</sup>. *O*-methyl cellulose (DS 1.7) was also permethylated.

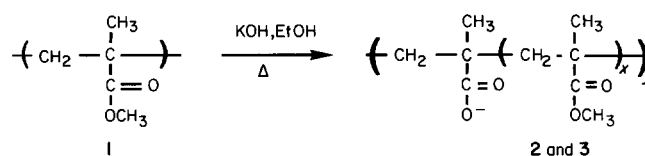


Figure 1 Partial hydrolysis of poly(methyl methacrylate) in refluxing ethanolic potassium hydroxide. Product 2 corresponds to hydrolysis with 0.2 M KOH and product 3 with 0.5 M KOH

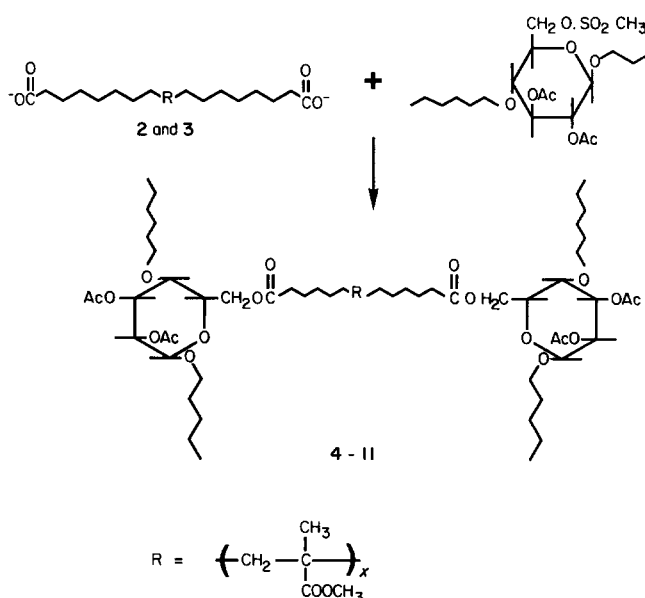


Figure 2 Grafting of partially hydrolysed poly(methyl methacrylate) onto mesylated cellulose acetate

**Table 1** Results of grafting reactions

Product number	Substrate	PMMA <sup>a</sup> product	Gelation time (min)	Yields (%)	
				Crude	Graft
4	MCA <sup>b</sup> (DS 0.46)	3	20	100	100
5	MCA (DS 0.46)	3	23	101	99
6	MCA (DS 0.21)	3	36	88	98
7	MCA (DS 0.21)	3	35	90	99
8	MCA (DS 0.46)	2	42	100	98
9	MCA (DS 0.46)	2	44	98	98
10	MCA (DS 0.21)	2	—	88	86
11	MCA (DS 0.21)	2	—	85	84
12	MMC <sup>c</sup>	3	29	95	99
13	MMC	3	36	99	99

<sup>a</sup> 1 is unhydrolysed PMMA homopolymer; 2 is 0.2 M KOH hydrolysed PMMA homopolymer; and 3 is 0.5 M KOH hydrolysed PMMA homopolymer

<sup>b</sup> MCA denotes mesylated cellulose acetate

<sup>c</sup> MMC denotes mesylated *o*-methyl cellulose

### Hydrolysis of poly(methyl methacrylate)

Poly(methyl methacrylate) (20 g) was added to 0.5 M or 0.2 M KOH in ethanol (125 ml). The polymer dissolved upon warming to refluxing temperature and refluxing was continued for 24 h. Under these conditions the 0.5 M KOH solution gives about 8% hydrolysis of the methyl ester, while the 0.2 M KOH gives about 3% hydrolysis<sup>4</sup>, corresponding to 9.6 and 3.6 carboxylate groups per chain, on the average, respectively. The hydrolysed polymer was isolated by decanting the KOH/ethanol solution at room temperature. The polymer was then recrystallized in ethanol (200 ml) with about 80% recovery being achieved in both cases.

### Grafting reaction

Each grafting reaction was carried out using mesylated cellulose acetate or *o*-methyl cellulose (1.00 g) and hydrolysed poly(methyl methacrylate) (1.00 g) dissolved in *N,N*-dimethyl formamide (DMF) (20 ml). The solutions were heated at 75°C for 20 h. The time required for gelation (since crosslinking takes place) to occur was noted (Table 1).

The graft polymers were precipitated in methanol, washed, dried and weighed. The products were then extracted with refluxing ethanol to remove ungrafted poly(methyl methacrylate) homopolymer.

Grafting yields were calculated as the wt% of the poly(methyl methacrylate) (PMMA) which attaches to the cellulose backbone and is given as:

$$\frac{(\text{Mass PMMA used} - \text{Mass PMMA recovered in toluene})}{\text{Mass PMMA used}} \times 100\%$$

No grafting was observed if the unhydrolysed poly(methyl methacrylate) was used.

## RESULTS AND DISCUSSION

### Grafting reaction

Partially hydrolysed poly(methyl methacrylate) carboxylate anion 2 and 3 (Figures 1 and 2) having on average 3.6 and 9.6 carboxylate groups, respectively, was grafted onto mesylated cellulose acetate and *o*-methyl cellulose in DMF at 75°C by second order nucleophilic

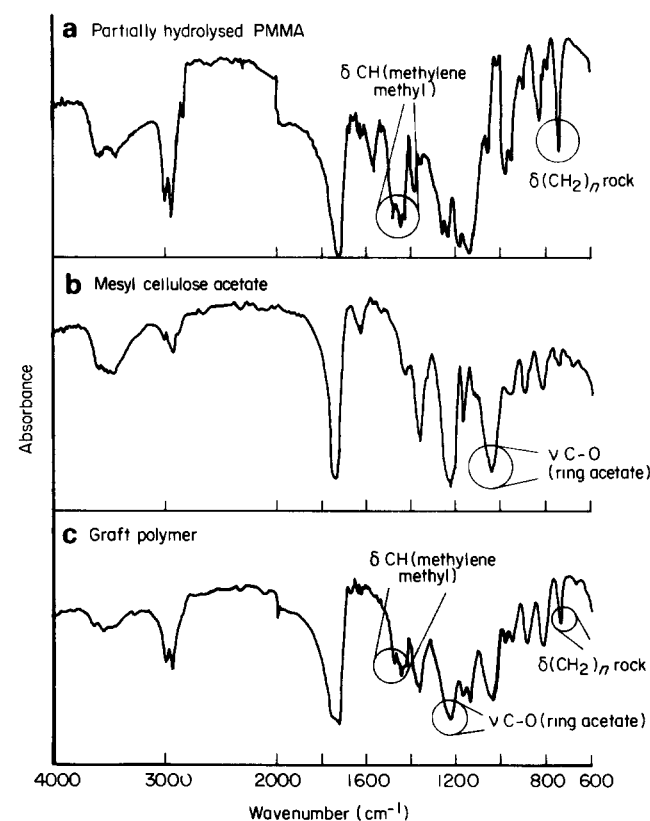
displacement (S<sub>N</sub>2) reaction. Grafting yields were calculated as the wt% of poly(methyl methacrylate) that is covalently linked to the cellulose backbone, determined after ethanol (refluxing) extraction. Ethanol extraction removes poly(methyl methacrylate) homopolymer present in the reaction product. Quantitative yields of the graft polymer were obtained at 75°C in a very short reaction period (35–45 min). The results of the grafting reactions are shown in Table 1.

Because there are several active sites on the poly(methyl methacrylate) polymer, as well as on the mesylated cellulose acetate, the products form gels. The carboxylate groups of poly(methyl methacrylate) are on tertiary carbon atoms, making them 'hindered' acids, however, the nucleophilic displacement, occurred relatively quickly as monitored by the gelation times. Others have also shown that 'hindered' carboxylate nucleophiles react about as quickly as 'unhindered' carboxylate nucleophiles<sup>5–7</sup>.

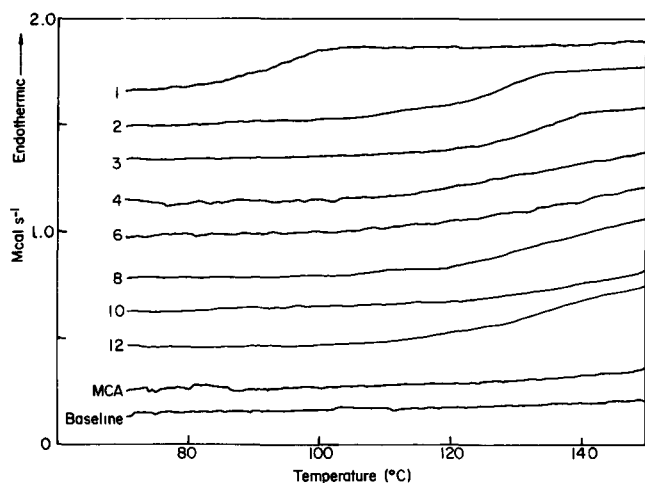
The gelation times for poly(methyl methacrylate) graft polymers of the mesylated cellulose derivatives is much shorter (by several hours) than the sodium salt of dicarboxy-terminated polystyrene<sup>2</sup>. This may be due to the presence of more active sites per chain, and also due to the use of large cations such as potassium as the counterion of the carboxylate anion. Carboxylate anions with potassium counterion undergo faster nucleophilic displacement reactions compared with smaller cations such as sodium and lithium<sup>5–7</sup>.

### Infra-red spectra of the products

Figure 3 shows representative infra-red (i.r.) spectra of (1) partially hydrolysed PMMA; (2) mesylated cellulose



**Figure 3** Infra-red spectra of (a) partially hydrolysed poly(methyl methacrylate) (2), (b) mesylated cellulose acetate, and (c) graft polymer product



**Figure 4** Differential scanning calorimetry (10°C/min scan rate) of products. Curve numbers correspond to product numbers of Table 1. Samples were previously heated and cooled at 10°C per second. Poly(methyl methacrylate) homopolymers (15 mg) and graft copolymers (30 mg) were used

acetate; and (3) the graft polymer product. The partial hydrolysis of poly(methyl methacrylate) did not appreciably change its i.r. spectrum compared with the unhydrolysed polymer. However, the appearance of a new peak at  $1550\text{ cm}^{-1}$  in the spectrum of the partially hydrolysed PMMA can be readily attributed to the C–O antisymmetric and symmetric stretching of the carboxylate ion.

Mesyl cellulose acetate and poly(methyl methacrylate) have unique characteristic bands which can be used to prove the existence of both components in the graft polymer product. Partially hydrolysed PMMA (Figure 3) has a diagnostic  $720\text{ cm}^{-1}$  band due to methylene rocking vibrations, which invariably always appears in compounds with at least four contiguous  $-\text{CH}_2$  groups<sup>8</sup>. The characteristic  $1470\text{--}1440\text{ cm}^{-1}$  methylene and methyl bending vibrations are also readily apparent in the spectrum. Mesyl cellulose acetate (Figure 3) does not have any strong bands in these regions, but has its own  $1030\text{ cm}^{-1}$  band, which is absent in the PMMA spectrum. This band is attributed to  $\nu\text{C}=\text{O}$  stretch of a ring acetate band<sup>9</sup>. Both compounds exhibited strong carbonyl stretching vibrations which appear at  $1720\text{ cm}^{-1}$  for PMMA and  $1730\text{--}1750\text{ cm}^{-1}$  for MCA.

The i.r. spectrum of the graft polymer product (Figure 3) showed all of the unique peaks attributable to the PMMA and MCA. In addition, strong carbonyl stretching vibrations in the  $1720\text{--}1750\text{ cm}^{-1}$  region and an enhanced  $-\text{CH}$  stretching vibration just below  $3000\text{ cm}^{-1}$  was evident. Thus, this study established that the ethanol-extracted (to remove any unreacted PMMA) reaction product had PMMA grafted onto the cellulose backbone as shown in Figure 2.

#### Differential scanning calorimetry of the products

Figure 4 shows the results of differential scanning calorimetry of the different products. Hydrolysis of poly(methyl methacrylate) increases the glass transition temperature from approximately  $100^\circ\text{C}$  (product 1) to  $130^\circ\text{C}$  (product 2 with 3% hydrolysis of ester groups) and to  $140^\circ\text{C}$  (product 3–8% hydrolysis of ester groups). This effect has been observed in other polymers previously<sup>10</sup>. The crosslinked graft copolymers, on the other hand, do not show a well defined glass transition temperature, but show a gradual increase in specific heat in the range of the poly(methyl methacrylate) homopolymer's glass transition temperatures.

#### ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. CBT-8502498.

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