

Grafting of Poly(methyl methacrylate) in Aqueous Slurries of Wood Pulp

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Synopsis

Methods for initiating the free radical graft polymerization of methyl methacrylate onto wood pulp were investigated. Processes considered were all carried out in water slurries of the cellulose, for simplicity and low cost. Of the methods studied only three provided high conversions of monomer to polymer and reasonably good grafting efficiencies. These are ceric ion initiation, a redox reaction with ferrous ion and hydrogen peroxide, and initiation by potassium permanganate/nitric acid mixtures. The ferrous ion/peroxide redox system appears to be the best procedure overall, since it is inexpensive and environmentally innocuous. The best grafting frequency obtained was about one graft per 800 anhydroglucose units in the cellulose. High molecular weight poly(methyl methacrylate) polymers were made, with the grafted species larger than the corresponding homopolymers.

INTRODUCTION

There is considerable current interest in the grafting of thermoplastics onto cellulose to obtain moldable products with high concentrations of the relatively inexpensive cellulose. It is expected that the fibrous cellulose may reinforce the thermoplastic. In order for this development to be feasible, it is necessary that the grafting reaction chosen be simple and low-cost. Free radical initiated graft polymerizations in water slurries of cellulose would seem to have the best prospects of meeting these criteria.

When process conditions have been selected to this extent the major experimental variable remaining is the specific method of initiation. Many procedures have been reported.¹ It is difficult to assess their efficiencies, however, because the various experiments which have been reported are not performed with comparable reagents or reaction conditions.

We have therefore surveyed the literature and selected for further study eight promising free radical initiation methods for grafting reactions in water on wood pulp. The requirements we have been seeking are: high conversion of monomer to polymer; fast reaction times; relatively high grafting efficiency and use of inexpensive reagents.

Methyl methacrylate was chosen as the monomer for these experiments. There is considerably more information available on polystyrene grafting reactions; but methyl methacrylate is a more reactive monomer, and it was felt that conclusions from the grafting reactions of methyl methacrylate

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would be more generally applicable to vinyl monomers. The cellulose substrate used here is a wood pulp, chosen because of its ready availability in clean form, along with its low cost.

EXPERIMENTAL

All grafting reactions were carried out in a 500-mL reaction kettle equipped with a stirrer and reflux condenser. The experiments were performed under N_2 atmosphere and in a constant temperature bath.

Methyl methacrylate monomer was washed three times with 10% aqueous NaOH and three times with water, to remove inhibitors. The monomer was then distilled.

The cellulose was dissolving grade wood pulp from Canadian International Paper Co. This material is a bleached hardwood sulphite pulp containing 92.9% alpha cellulose, 96.2% rayon cellulose, 0.094% ash, 0.009% Cu, 34 ppm Fe, 1 ppm Cu and 0.22% resin. Its viscosity was reported by the supplier to be 10.5 xanthate seconds. Sheets of pulp were cut into small pieces, weighed and swollen in water. Swelling was accomplished by boiling 4 g wood pulp in 200 mL deionized water for at least 1 h. Overnight storage of swollen cellulose in water had no marked effect on subsequent grafting reactions.

Eight grafting reactions were examined. Experimental details of the different methods were as follows.

Hydrazine²

Swollen wood pulp, 3 g, was steeped in a 1% hydrazine solution made by dissolving 3 mL 85% $H_2NNH_2 \cdot H_2O$ in 250 mL of distilled water. The steeping process was allowed to continue at room temperature, with stirring, for 1 h. The cellulose slurry was filtered, and the wood pulp was stirred twice for 20 min each with distilled water and then filtered. The "treated" wood pulp was slurried into 300 mL of water containing 0.32 g $K_2S_2O_8$ and stirred under N_2 for 30 min at a given temperature. The graft polymerization reaction was attempted at 25°C, 40°C, and 60°C. Monomer, 16 mL, was added, and the reaction was allowed to proceed at the particular temperature overnight (18–24 h).

Ceric Ammonium Nitrate³

Two cellulose/monomer ratios were investigated.

(b)1. Swollen cellulose, 16.9344 g, was added to a solution containing 335 mL distilled water, 0.5690 g $Ce(NH_4)_2(NO_3)_6$, and 4.1 mL 1N HNO_3 . This mixture was stirred with N_2 sparging at 30°C for 30–45 min. Monomer, 20 mL, was then added, and the reaction was allowed to proceed for 3 h.

(b)2. Swollen cellulose, 1 g, 15 mL of a stock solution [1.3712 g $Ce(NH_4)_2(NO_3)_6$ and 25 mL 1N HNO_3 ; initiator concentration (~ 5 mM)] and 280 mL of distilled water were stirred under an N_2 atmosphere for 30–45 min at 35°C. Methyl methacrylate, 5 mL, was then added, and the reaction was continued for 10–20 h.

Ferrous Ammonium Sulfate²

Swollen cellulose, 3 g, was steeped for 30 min in a 1% solution of $\text{Fe}(\text{NH}_4)\text{SO}_4$, which had been made up with freshly deaerated water. The wood pulp was filtered off and washed with copious amounts of deaerated distilled water. It was then transferred to a flask equipped with a stirrer and condenser. Deaerated distilled water, 285 mL, 15 mL methyl methacrylate, and 3 mL of a 3% H_2O_2 solution were added. The mixture was refluxed under an N_2 atmosphere for 2.5 h.

Ammonium Metavanadate⁴

Swollen cellulose, 4.5 g., and 10 mL of a stock solution (6.3 mL concd H_2SO_4 , 0.8774 g ammonium metavanadate (NH_4VO_3) in 380 mL distilled water) were stirred under N_2 for 30 min at 70°C. Monomer, 15 mL, was added, and the reaction was allowed to proceed for 5 h. Other experiments, in which the reaction time was as long as 20 h, did not produce significantly higher conversions than those observed in 5 h experiments.

Thiourea/Ferric Chloride⁵

Swollen cellulose, 3–4 g, was steeped in 1M solution of FeCl_3 for 1 h, filtered and washed with large amounts of deionized water. The pulp was then added to a solution of 0.9880 g thiourea in 280 mL deionized water. After 15 min stirring under N_2 15 mL concd HNO_3 was added, followed 5 min later by 17 mL methyl methacrylate. The polymerization reaction was allowed to proceed for 16 h at 60°C.

Persulfate/Thiourea/Silver Nitrate⁶

Swollen cellulose, 3–4 g, was added to a solution of 0.3458 g thiourea, 1.6274 g $\text{K}_2\text{S}_2\text{O}_8$, and 270 mL deionized water. The mixture was stirred under N_2 for 90 min, and 15 mL methyl methacrylate was added, followed by 5 mL of a 0.06M AgNO_3 solution. The reaction was allowed to proceed for 16 h at 50°C.

$\text{KMnO}_4/\text{HNO}_3$

Two methods were employed.

(g)1⁷. Swollen cellulose, 5 g, was added to a solution containing 0.477 g KMnO_4 and 250 mL deionized water. The mixture was stirred under nitrogen for 30–40 min and 50 mL concd HNO_3 was added, followed by 15 mL of methyl methacrylate monomer. The polymerization reaction was allowed to proceed at 50°C for 3.5 h.

(g)2⁸. Swollen cellulose, 5 g, was added to a solution of 0.48 g KMnO_4 in 280 mL deionized water. The mixture was kept stirring under nitrogen for 30–40 min, and then 20 mL methyl methacrylate monomer and 1.2 mL concd H_2SO_4 were added to the mixture. The polymerization reaction was allowed to proceed for 5 h at 50°C.

The reaction products were filtered off, dried and characterized as follows:

$$\% \text{ conversion} = \frac{\text{wt crude product} - \text{initial wt cellulose}}{\text{wt monomer charged}} \times 100$$

The products were Soxhlet-extracted with chloroform for periods ranging from 5 to 7 days. This separates grafted copolymer from the homopolymer, which is soluble in CCl_3 . The extent of grafting was then determined according to the following definitions:

$$\begin{aligned} \% \text{ grafting} &= \text{ratio of wt increase to wt of initial cellulose} \\ &= \frac{\text{wt Soxhlet-extracted product} - \text{initial wt cellulose}}{\text{initial wt cellulose}} \times 100 \end{aligned}$$

Grafting efficiency is the ratio of the amount of grafted monomer to the total weight of monomer that was polymerized:

$$= \frac{\text{wt Soxhlet-extracted product} - \text{initial wt cellulose}}{\text{wt crude product} - \text{initial wt cellulose}} \times 100$$

Percent add-on is the amount of pure copolymer (extracted product) which is noncellulosic:

$$= \frac{\text{wt Soxhlet-extracted product} - \text{initial wt cellulose}}{\text{wt Soxhlet-extracted product}} \times 100$$

The products from the most promising reactions were characterized further by first hydrolyzing the cellulose. This was accomplished by refluxing the graft copolymer in 25*N* HCl overnight, with stirring. The cooled product was then filtered through a cellulose thimble, and the residual insoluble material was Soxhlet-extracted with chloroform for 4–7 days. Only 40–60% of the grafted poly(methyl methacrylate) could be recovered in this extraction. This is probably because the cellulose component was not completely broken down. The procedure did, however, provide samples for molecular weight measurements of the methacrylate graft polymer.

The molecular weights of the corresponding grafted and homopolymer poly(methyl methacrylate)s were determined by gel permeation chromatography in tetrahydrofuran. The apparatus used was a Waters ALC 100 Liquid Chromatograph with four polystyrene gel columns with nominal pore sizes of 10^3 , 10^4 , 10^5 , and 10^6 Å. Molecular weights were measured by calibration with anionic polystyrene standard materials. A hydrodynamic volume calibration method was used.⁹⁻¹¹ The Mark-Houwink constants used in this procedure are $K_0 = 85 \times 10^{-3} \text{ cm}^3 \cdot \text{g}^{-1}$, $K = 14.1 \text{ cm}^3 \cdot \text{g}^{-1}$, and $a = 0.70$ (polystyrene)¹² and $K_0 = 69.0 \times 10^{-3} \text{ cm}^3 \cdot \text{g}^{-1}$, $K = 12.8 \times 10^{-3} \text{ cm}^3 \cdot \text{g}^{-1}$, and $a = 0.69$ poly(methyl methacrylate).¹³

Once the number average molecular weight of the grafted poly(methyl methacrylate) was measured the grafting frequency could be calculated from

$$\text{grafting frequency} = \frac{\text{anhydroglucose units (mol)}}{\text{grafted PMMA (mol)}}$$

TABLE I
Results of Grafting Reactions

Method	Conversion (%)	Grafting (%)	Grafting efficiency (%)	Add-on (%)	Remarks
Hydrazine	37.2	11.2	7.8	16.8	40°C
	85.6	33.1	7.7	24.9	60°C
Ceric ion	97.2	78.2	66.2	43.9	Method (b)1 30°C
	58.7	157.1	59.5	64.6	Method (b)2 35°C
Ferrous ammonium sulfate	93.5	189.0	42.0	65.4	Reflux
Ammonium metavanadate	36.5	88.6	70.7	47.0	70°C
Thiourea/ferric chloride	55.8	23.3	8.5	18.9	60°C
Persulfate/thiourea/AgNO ₃	23.7	8.7	12.1	8.0	50°C
Potassium permanganate/HNO ₃	81.4	79.0	35.4	44.1	Method (g)1 50°C
Potassium permanganate/H ₂ SO ₄	88.0	81.6	19.2	45.0	Method (g)2 50°C

RESULTS AND DISCUSSION

Table I lists the results of the various grafting experiments. Three procedures appear to be preferable, taking into account overall conversion and grafting. These are ceric ammonium nitrate [method (b)1³], ferrous ammonium sulphate [method (c)²], and potassium permanganate/nitric acid [method g(1)⁷].

Molecular weights of the poly(methyl methacrylate) polymers produced in these experiments are summarized in Table II. In all cases the grafted polymers have higher molecular weights than the homopolymers formed in the same reaction.

Molecular weight distributions are all broad; the standard deviation of the number or weight distribution is \geq the respective mean of that distribution (\bar{M}_n or \bar{M}_w). The distributions are skewed to high molecular weights. The grafted polystyrenes all have higher molecular weights and broader molecular weight distributions than the ungrafted homopolymer made in the same polymerization reactions. This indicates the occurrence of autoacceleration effects which can probably be ascribed to restrictions of the mobility of macroradical ends by the cellulose matrix¹⁵.

It is not surprising that the molar masses of the grafted polymers depend on the method of initiating free radical sites on the cellulose substrate.¹⁶ The bottom row in Table II lists grafting frequency values. It can be seen that ceric ion initiation produced fewer grafted sites than either of the other two methods.

TABLE II
Molecular Weights of Poly(methyl Methacrylate)

Molecular weight parameters ^{1,4}	Ceric Ammonium nitrate		Ferrous ammonium sulfate		Permanganate/HNO ₃	
	Homopolymer	Graft	Homopolymer	Graft	Homopolymer	Graft
\bar{M}_n	270,000	355,000	87,000	226,000	14,500	110,000
\bar{M}_w	823,000	1,069,000	565,000	919,000	287,000	469,000
\bar{M}_z	1,452,000	2,300,000	1,195,000	1,830,000	963,000	1,047,000
Standard dev. (no. dist.)	386,000	503,000	204,000	396,000	63,000	199,000
Standard dev. (wt. dist.)	720,000	1,150,000	597,000	915,000	440,000	520,000
Skewness (no. dist.)	3.2	4.4	5.6	4.2	15.4	5.1
Skewness (wt. dist.)	1.7	4.8	1.9	1.8	3.3	2.4
Grafting frequency (no. moles anhydro-glucose/no. moles grafted PMMA)	—	2800	—	740	—	860

The ferrous ammonium sulfate and $\text{KMnO}_4/\text{HNO}_3$ methods produced more even grafting in the sense that about four times as many anhydroglucose units were anchored to poly(methyl methacrylate) than in the case of ceric ion grafting. This difference may, however, simply reflect the use of higher temperatures in the former two reactions.

Grafting frequency is not as high in any of these procedures as would be desired for optimal reinforcement of the synthetic polymer by cellulose fibres.

On balance, the ferrous sulphate procedure² is probably the most effective grafting method of those studied. Conversion of monomer to polymer can be made practically quantitative; the ingredients are relatively inexpensive and environmentally innocuous, and the grafting efficiency is fairly good.

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