Graft Copolymerization of Methylmethacrylate onto Caesarweed Fibers by the Potassium Permanganate–Toluene Redox System

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SYNOPSIS

Preliminary investigations have been conducted on the graft copolymerization of methylmethacrylate onto Caesarweed fiber, initiated by potassium permanganate and the toluene redox system. The percentage graft yield increased with permanganate up to 132% in the concentration range, 1.0×10^{-2} to 5.0×10^{-2} M at 40°C. The effects of varying concentrations of toluene, acids, and monomer on graft yield were also investigated. Graft yield increased initially and then decreased on varying the concentrations of toluene from 2×10^{-2} to 20×10^{-2} M. The graft yield increased with temperature between 20 and 50°C. At 60°C, the graft yield decreased considerably by up to 60% of the value at 50°C. The calculated activation energies for the overall reaction, and for the initiation process, are 9.15 and 9.30 Kcal mol^{-1}, respectively. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Grafting of synthetic polymers onto cellulosic and protein fibers has received considerable attention[1-12] because, in some cases, grafting yields copolymers with improved physicochemical properties with industrial and commercial value. Specifically, grafting of acrylonitrile onto jute fibers[13] resulted in the fibers' improved extensibility and light fastness. Similarly, grafting of methylmethacrylate onto jute fibers[14] yielded a copolymer with an enhanced thermal property. However, for cellulosic fibers, different morphological features of the polymer matrices are known to account for varying grafting characteristics.[15,16]

Caesarweed, *Urena lobata* I, is of the mallow family, Malvacea, which is one of the most important of all fiber plant families. The plant is cultivated in warm regions of several countries, including West Africa, and it often grows wild in abundance. The bast fibers are cellulosic materials, closely resembling jute, but somewhat shorter and coarser. The fibers are used as substitutes for jute and find local application in the production of twines and sacks. Information about the chemical composition and morphological properties of the fibers is sparse; neither is there any report on the grafting of synthetic polymer onto the fibers.

This article presents the results of a preliminary study of the graft copolymerization of methylmethacrylate (MMA) onto Caesarweed fibers, initiated by acidified potassium permanganate and the toluene redox system.

EXPERIMENTAL

Toluene (BDH) was treated with sulfuric acid and was washed copiously with distilled water to neutral pH. It was dried over anhydrous calcium chloride and was fractionally distilled before use.

Methylmethacrylate (Aldrich Corp.) was washed with 5% aqueous sodium hydroxide and sodium chloride solutions, was dried over anhydrous calcium chloride, and was then fractionally distilled. The middle fraction of the monomer was collected and was stored under refrigerated conditions.

All other reagents, that is, potassium permanganate, glacial acetic acid, and sulfuric acid (~18

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M), were BDH analytical reagent grades and were used as supplied.

The Caesarweed plant was collected from the University's botanical garden in Yola. The fiber was refluxed in methanol for three hours and was air dried. Holocellulose was obtained from the fibers by the method described by Okieimen and Ebhoaye.[17] The holocellulose was bleached by steeping in sodium hypochlorite solution for 50 min at 30°C. It was rinsed in a large volume of distilled water and was air-dried to a constant weight.

The graft copolymerization reaction was carried out in a 250 mL pyrex conical flask fitted with a standard joint stopper. The required amounts of the reagents, that is, glacial acetic acid, sulfuric acid, and toluene, were introduced into the flask and distilled water was added up to 50 mL. 0.5 g of the fiber was dispersed in the mixture and was allowed to soak for 10 min while the flask was kept in a thermostated water bath, regulated to within ±0.05°C.

The required amount of potassium permanganate was introduced into the flask, which was swirled gently and was allowed to stand for 10 min before the monomer was added to it.

The polymerization was stopped by the addition of 5 mL of 1% hydroquinone solution. The grafted fiber was filtered, washed with distilled water, and soxhlet-extracted with methyl ethyl ketone for three hours to remove ungrafted polymethylmethacrylate. The fiber was washed again with distilled water and was dried in an oven at 40°C to constant weight.

The percentage graft and percentage efficiency were calculated from the relation:

$$\% \text{ Grafting} = [(W_2 - W_1)/W_1] \times 100$$

$$\% \text{ Efficiency} = [(W_2 - W_1)/W_3] \times 100$$

where W_1, W_2, and W_3 are the weights of fiber, the grafted fiber, and the monomer, respectively.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

Figure 1 represents the effect of methylmethacrylate (MMA) concentration on the graft yield at 40°C. The percentage graft increases initially over the monomer concentration range of 0.1 to 0.4 M and then decreases. The percentage graft at the optimum monomer concentration of 0.4 M is 48.8%, corresponding to the percentage efficiency in the grafted monomer, which was 12.1%.

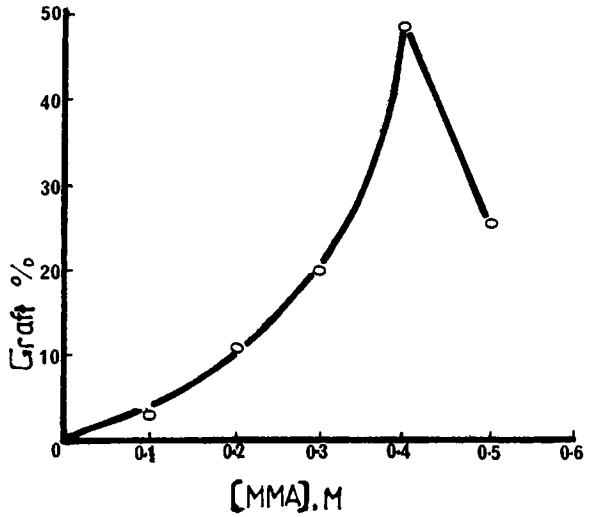

Figure 1 Effect of [MMA] on graft yield: [$KMnO_4$] = 2.5×10^{-2} M, [TL] = 2×10^{-2} M, [AcOH] = 5.2 M, [H^+] = 0.18 M, Time = 6 h, Temperature = 40°C.

The apparent acceleration in the graft yield may be attributed to the gel effect, resulting from an enhanced solubility of polymethylmethacrylate in its monomer. This would consequently increase the viscosity of the reaction medium and a reduced rate of termination by the coupling of growing polymer chains. The decrease in the graft yield at a monomer concentration higher than 0.4 M may be due to an enhanced homopolymer formation by chain transfer to monomer.

Effect of Initiator Concentration

The percentage graft increases with the concentration of permanganate in the range 1×10^{-2} to 5×10^{-2} M, as shown in Figure 2. At the concentration of 1×10^{-2} M of permanganate, the percentage graft is zero. For the graft copolymerization of methylmethacrylate, initiated by a redox couple consisting of permanganate and toluene, the following mechanism is proposed:

Initiation

$$Mn^{4+} + TL \overset{K}{\rightleftharpoons} \text{Complex} \overset{k_1}{\rightarrow} TL^{\bullet} + Mn^{3+} + H^+$$

$$\text{Cell} + TL^{\bullet} \overset{k_2}{\rightarrow} \text{Cell}^{\bullet} + TLH$$

$$\text{Cell}^{\bullet} + M \overset{k_i}{\rightarrow} \text{Cell} - M^{\bullet}$$

Propagation

$$\text{Cell} - M^{\bullet} + M \overset{k_p}{\rightarrow} \text{Cell} - M\dot{n}$$

$$\text{Cell} - M\dot{n} + M \overset{k_p}{\rightarrow} \text{Cell} - M\dot{n} + 1$$

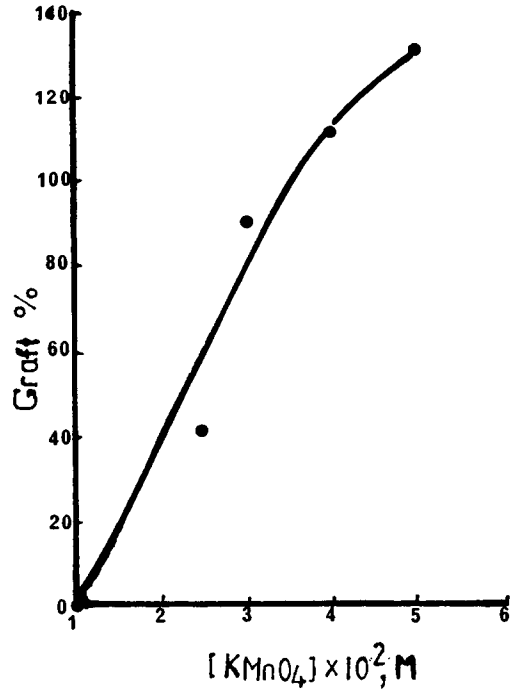

Figure 2 Effect of [$KMnO_4$] on graft yield: [MMA] = 0.4 M, [TL] = 10×10^{-2} M, [AcOH] = 5.2 M, [H^+] = 0.18 M, Time = 6 h, Temperature = 40°C.

Termination $\text{Cell} - \dot{\text{M}}\text{n} + \text{Cell} - \dot{\text{M}}\text{n} \xrightarrow{k_{tr}}$ Copolymer

$\text{Cell} - \dot{\text{M}}\text{n} + \text{Mn}^{3+} \xrightarrow{k_{tr'}} \text{Cell} - \text{Mn} + \text{Mn}^{2+}$

Chain Transfer $\text{Cell} - \dot{\text{M}}\text{n} + \text{M} \xrightarrow{k_{tr}} \text{Cell} - \text{Mn} + \text{M}^{\cdot}$

where TL, TL$^{\cdot}$, M, and Cell represent toluene, toluene radical, monomer, and Caesarweed fiber, respectively. As is shown in Figure 2, the increase in percentage graft yield is not linear, that is, the relative increase in percentage graft yield decreases with an increase in the permanganate concentration. This suggests an increase in termination processes, which may involve Mn^{3+} at a high concentration of the permanganate, as represented in the reaction scheme above.

Effect of Toluene Concentration

In a previous report by Das et al.,[14] toluene has been shown to enhance and to retard the graft copolymerization of methylmethacrylate onto jute fiber. In combination with permanganate as a redox couple, toluene exhibits similar features, as shown in Figure 3. That is, toluene increases the percentage graft over the concentration range 2×10^{-2} to 4.0×10^{-2} M and then decreases the yield at higher concentrations. The decrease in graft yield is accompanied by a decrease in the formation of homopolymer. Hence, the retardation effect of toluene may arise from an enhanced termination of radicals on the fibers and on the grafted copolymer by toluene radicals.

Effect of Acid Concentration

Table I is a collection of results representing the effect of acid [sulfuric (H^+) and glacial acetic acids (AcOH)] on the percentage graft yield. In the concentration range 1.75–7.0 M, glacial acetic acid increased the percentage graft fourfold, which then decreased upon further increase in concentration.

Similarly, over the concentration range 3.7×10^{-2} to 22.1×10^{-2} M, sulfuric acid increased the percentage graft fourfold and then decreased it thereafter. The increase in graft yield is consistent with the ability of the acids to enhance the oxidizing

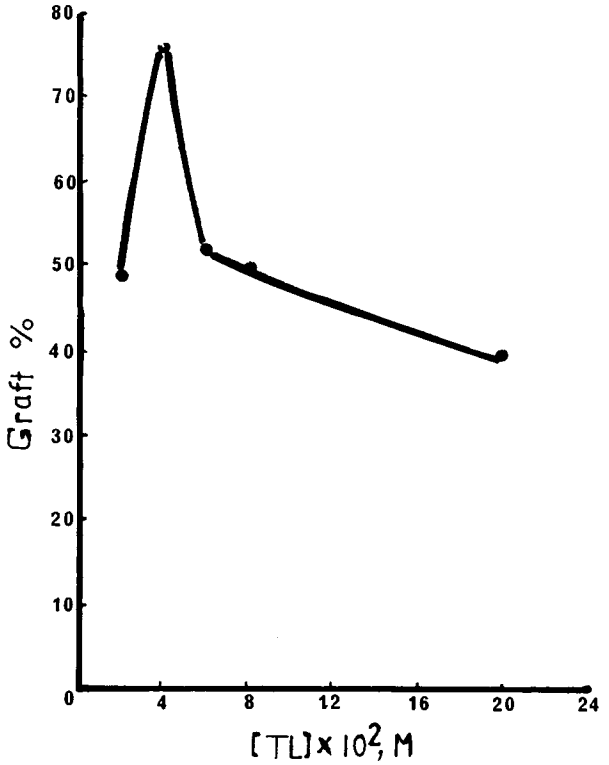

Figure 3 Effect of [TL] on graft yield: [MMA] = 0.4 M, [$KMnO_4$] = 2.5×10^{-2} M, [AcOH] = 5.2 M, [H^+] = 0.18 M, Time = 6 h, Temperature = 40°C.

Table I Effect of (H^+) and (AcOH) on Graft Yield[a]

[AcOH] (M)	10^2 [H^+] (M)	Graft (%)	Efficiency (%)
1.75	18	2.42	1.2
3.50	18	12.32	6.2
5.2	18	10.95	5.5
7.0	18	23.40	11.7
8.7	18	4.54	2.3
5.2	3.7	20.38	10.2
5.2	7.4	42.80	21.4
5.2	14.7	48.56	24.3
5.2	22.1	78.22	39.11
5.2	29.4	30.40	15.2

[a] [MMA] = 0.2 M, [$KMnO_4$] = 2.5×10^{-2} M, [TL] = 2×10^{-2} M, Time = 6 h, Temperature = 40°C.

power of permanganate. However, high concentrations of the acid may reduce the graft yield by:

1. Making more complex the manganate cation with the anion of the acid, thereby rendering it less potent as an oxidizing agent.
2. Facilitating the dissolution by hydrolysis of grafted polymer chains.

Effect of Temperature on Grafting

The graft copolymerization was conducted at four different temperatures, ranging from 20 to 60°C, at constant concentrations of all reagents. The time conversion curves for the graft copolymerization are represented in Figure 4. The curves are characterized by an initial high grafting rate, which gradually decreased at longer reaction time. It may appear that partial hydrolysis and dissolution of the grafted polymer chains is responsible for this phenomenon. However, this explanation is inadequate since the conversion curve at 20°C follows the same pattern. Thus, a more probable explanation is that the termination process increases with conversion. In addition, Mn^{2+}, with increasing concentration as conversion progresses, may autocatalyze the initiation of the competitive homopolymerization reaction. The percentage graft increases overall, with temperature in the range of 20 to 50°C. This is consistent with an expected increase in swellability of the fiber and an enhanced rate of diffusion of monomer into the fiber matrix.

At 60°C, however, there is a considerable decrease in the percentage graft yield of about 60% of the value at 50°C after three hours. This may be attributed to increased chain transfer reactions, normally favored at high temperatures. Similar results have been reported[18] for graft copolymerization of acrylamide onto polyethylene terephthalate with potassium permanganate.

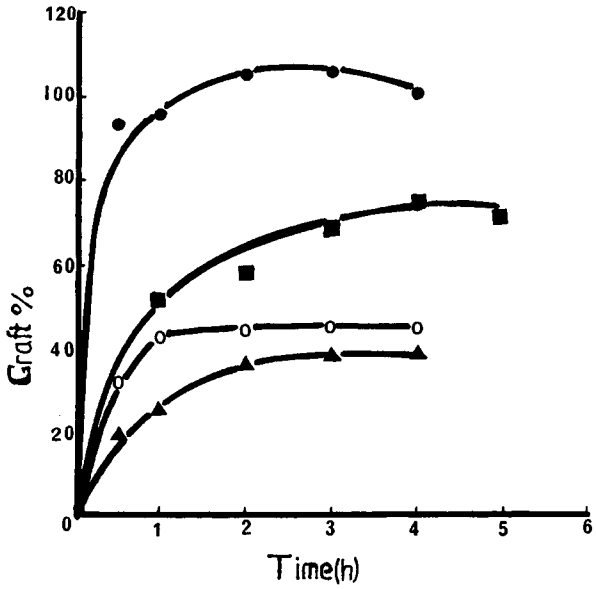

Figure 4 Effect of temperature on graft yield: [MMA] = 0.4 M, [$KMnO_4$] = 2.5×10^{-2} M, [AcOH] = 5.2 M, [TL] = 2×10^{-2} M, Temperature (°C), (▲) 20, (■) 40, (●) 50, (○) 60.

Figure 5 is an Arrhenius plot of the initial rate of graft vs. the reciprocal of temperature over the temperature range of 20 to 50°C. From the slope of the plot, the overall activation energy for the poly-

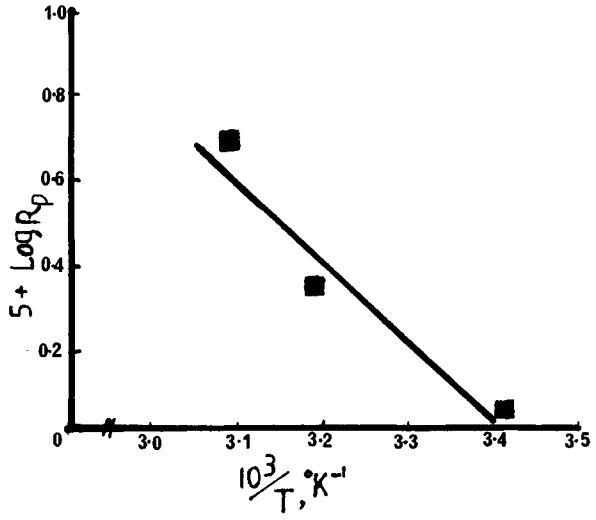

Figure 5 Arrhenius plot of the initial rate of graft vs. the reciprocal of temperature.

merization is 9.15 Kcal mol^{-1}. Using the Tobolsky's[19] relation of $E_p - \frac{1}{2} E_t = 4.5$ Kcal mol^{-1}, where E_p and E_t are the activation energies for propagation and termination; the activation energy for initiation E_d is derived from the equation,[20] $E_d = 2E_a - (2E_p - E_t)$ as 9.30 Kcal mol^{-1}.

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