Vanadium-Cyclohexanone-Initiated Graft Copolymerization of Methyl Methacrylate onto Jute Fibers

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Synopsis

Graft copolymerization of methyl methacrylate (MMA) was carried out on jute fibers using a V^{5+}-cyclohexanone redox initiator system. The effect of the concentration of acid, monomer, and V^{5+} on graft yield have been studied. In order to obtain optimum conditions of grafting, the effects of temperature, acid, reaction medium, solvent, and some inorganic salts on graft yield have been investigated. The most remarkable features of the investigation include the proposition of a mechanism and derivation of rate expression for the grafting process. More than 100% grafting could be achieved with the present system.

INTRODUCTION

Hebeish and coworkers[1-9] have made a significant contribution to the kinetic study of grafting of vinyl monomers onto cellulose and its derivatives, as well as cellulosic fibers (like cotton) and their derivatives. Much less has been reported, however, regarding graft copolymerization of jute fibers. The kinetics of grafting of acrylonitrile on defatted and bleached jute fibers was studied.[10] Although some x-ray diffraction studies have been made on MMA-grafted jute,[11] not much is known about the conditions of grafting of jute fibers with MMA. Very recently, the ceric ion-initiated graft copolymerization of MMA onto jute fibers have been studied.[12] In our previous communication,[13] we have reported the grafting of MMA onto jute fibers using a $KMnO_4$-malonic acid redox initiator system. The present investigation reports a kinetic study of the V^{5+}-cyclohexanone-initiated graft copolymerization of MMA onto jute fibers. This system has proved to be the most effective so far studied in grafting of jute fibers. This has also demonstrated how the role of substrate is important in grafting reactions initiated by metal ions.

EXPERIMENTAL

The pretreatment of the jute fibers was done as mentioned in our previous communication.[13]

Purified monomer (methyl methacrylate), vanadium solution (prepared from ammonium *meta*-vanadate), and sulfuric acid (AnalaR) were used for the grafting process.

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Before initiating graft copolymerization, the jute fibers were soaked with an appropriate quantity of monomer for about 5 min. The graft copolymerization was carried out in Pyrex tubes with $B_{24/29}$ standard joints. Appropriate quantities of reaction mixture containing jute fiber, monomer M, sulfuric acid, cyclohexanone CH, and vanadium solution were taken in the reaction vessels. The reactions were carried out for specific times at three different temperatures, 50, 60, and 70°C. After the specified time interval, the reaction was arrested by quenching the vessel in ice-cold water. The homopolymer along with the grafted jute fibers were filtered off, washed with distilled water, and dried to constant weight. Finally the fibers were extracted with acetone in a Soxhlet apparatus for 12 h to dissolve all the homopolymers. The percentage of grafting and rate of grafting were estimated as follows.

$$\% \text{ grafting (GY)} = \left(\frac{\text{dry wt of grafted jute} - \text{dry wt of original jute}}{\text{dry wt of original jute}} \right) \times 100$$

$$\text{Rate of grafting } R_G = \frac{1000 \times W}{V \times t \times M}$$

where W = weight of the monomer grafted on the fiber
V = volume of the mixture
t = time (s)
M = molecular weight of the monomer (MMA)

RESULTS AND DISCUSSION

Effect of Time on Graft Yield

Figure 1 shows the effect of time on graft yield. It was observed that graft yield increases up to 2 h, but after 2 h, it decreases to some extent. This may be attributed to the partial dissolution of grafted fiber on prolonged exposure to the temperature. Thus, an optimum grafting efficiency is obtained with 2 h.

Effect of Temperature

Although it has been found that grafting onto jute fiber becomes barely possible below 50°C, further increase of temperature up to 70°C did not have an appreciable influence on the percentage of grafting. Unlike the grafting of other natural fibers, like silk, which takes place at ordinary temperatures,[14] grafting onto jute fiber requires a higher temperature, possibly because of the rigidity of its cellulosic structure.

Effect of Jute Fiber Amount on Graft Copolymerization

Figure 2 shows the effect of the amount of jute fiber on the graft yield. It is seen that, within the range studied, the graft yield increases by increasing the amount of jute fibers in the polymerization system. This suggests that the integrated surface area of fiber greatly affects the diffusion

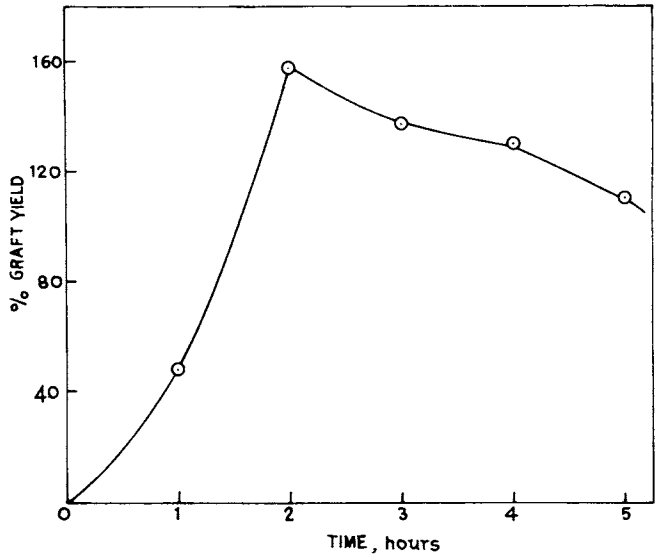

Fig. 1. Effect of time on graft copolymerization: jute = 0.1 g, $[V^{5+}]$ = 0.005 *M*, [MMA] = 0.467 *M*, [CH] = 0.241 M, $[H_2SO_4]$ = 0.05 M, temperature = 50°C.

of monomer and free radical species. It is rather possible that the reducing properties of jute contribute to the activation of the V^{5+}-cyclohexanone redox system, thereby giving rise to higher grafting.

Effect of Cyclohexanone on Graft Copolymerization

Figure 3 represents the effect of cyclohexanone on graft yield at two different temperatures (50 and 70°C). At all temperatures, the percentage of grafting increase steadily from 0.048 mol/L to 0.193 mol/L of cyclohexanone up to a maximum and thereafter decreases. This decrease is probably

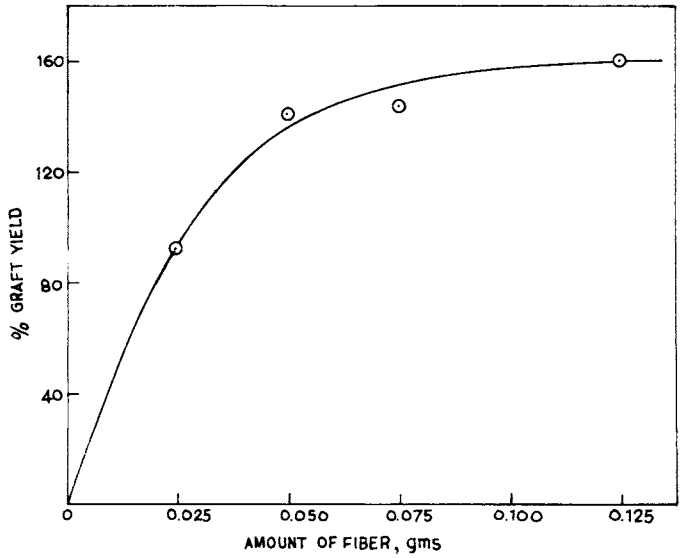

Fig. 2. Effect of jute fiber on graft copolymerization: [MMA] = 0.467 M, [CH] = 0.241 M, $[V^{5+}]$ = 0.005 M, $[H_2SO_4]$ = 0.075 M; (○) 50°C.

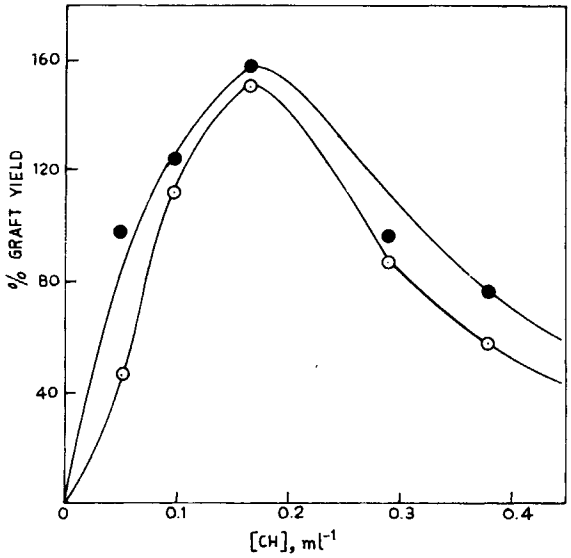

Fig. 3. Effect of cyclohexanone on graft copolymerization: jute = 0.1 g, [MMA] = 0.467 M, $[V^{5+}]$ = 0.005 M, $[H_2SO_4]$ = 0.075 M; (○) 50°C, (●) 70°C.

due to the formation of a radical scavenger at the higher cyclohexanone concentration.

Effect of Monomer on Grafting

The effect of monomer on graft yield has been studied within the concentration range 0.093–0.748 mol/L at three different temperatures, 50, 60, and 70°C, keeping the concentration of all other reagents fixed. The percentage of graft yield increases with an increase in monomer concentration up to 0.561 mol/L and thereafter decreases. Figure 4 illustrates this

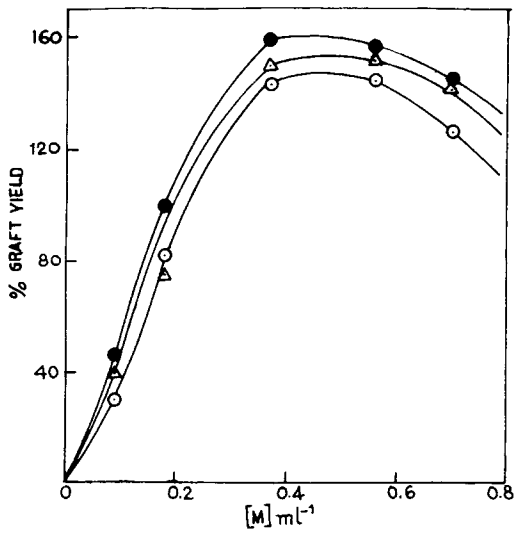

Fig. 4. Effect of monomer on grafting: jute = 0.1 g, [CH] = 0.241 M, $[H_2SO_4]$ = 0.075 M, $[V^{5+}]$ = 0.005 M; (○) 50°C; (△) 60°C; (●) 70°C.

behavior. This is possibly due to the competition between homopolymerization and grafting, where the former prevails over the latter at higher MMA concentration.

Effect of Metal Ion on Graft Copolymerization

The effect of concentration of V^{5+} on the percentage of graft yield has been shown in Fig. 5. The experimental data reveal a consistent decrease in the percentage of grafting with an increase in metal ion concentration beyond 0.005 mol/L. Our derived rate expression fully supports this kind of observation.

Effect of Reaction Medium

The reaction medium plays an important role in graft copolymerization reactions. By lowering the concentration of acid, the percentage of grafting is remarkably enhanced. On the other hand, the increase in concentration of acid is not only unfavorable to grafting, but it also destroys some of the useful properties of fibers. Proof for this will be reported in our subsequent communications. The graft yield follows the following order, with the solvents added in equal proportions (5% v/v): control > DMF > MeOH > acetone > dioxane. Similarly, the effect of neutral salt when added in equivalent molar concentrations follows the order control > NaCl > $MnSO_4$ > $CuSO_4$ > K_2SO_4. Table I reveals the above results.

Reaction Mechanism

In a system containing ammonium *meta*-vanadate, MMA, cyclohexanone, and jute fibers, V^{5+} may interact with cyclohexanone (R) to form a complex that dissociates, giving rise to a free radical. This radical, along with V^{5+}, abstracts hydrogen from the jute molecule, yielding a macroradical ($J^{\cdot}$). The following is an outline of the reaction mechanism.

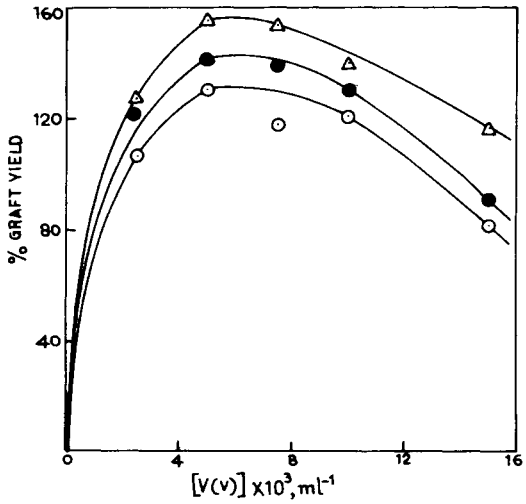

Fig. 5. Effect of metal ion V^{5+} on graft copolymerization: jute = 0.1 g, [MMA] = 0.467 M, [CH] = 0.241 M, [H_2SO_4] = 0.075 M, (○) 50°C; (△) 60°C; (●) 70°C.

TABLE I[a]

Effect of salt and solvent, temperature = 60°C				Effect of sulfuric acid, Temp. = 70°C	
Solvent 5% (v/v)	% Grafting	[Salt] = 0.1 M	% Grafting	$[H_2SO_4]$ (*M*)	% Grafting
Control	155.8	NaCl	132.4	0.025	171.2
Dioxane	87.6	$CuSO_4$	105.2	0.050	160.07
DMF	132.0	$MnSO_4$	111.7	0.075	150.38
Acetone	115.6	K_2SO_4	99.4	0.10	140.6
Methanol	118.2	Control	155.6	0.125	128.52

[a] Jute = 0.1 g, [MMA] = 0.0467 M, [CH] = 0.241 M, $[V^{5+}]$ = 0.005 M, $[H_2SO_4]$ = 0.075 M, time = 2 h.

Initiation:

$$V^{5+} + \text{cyclohexanone} \underset{}{\overset{K}{\rightleftharpoons}} \text{Complex}$$

$$\xrightarrow{k_1} R\cdot + V^{4+} + H^+$$

$$JH + R\cdot \xrightarrow{k_2} J\cdot + RH$$

$$J\cdot + M \xrightarrow{k_i} JM\cdot$$

Propagation:

$$JM\cdot + M \xrightarrow{k_p} JM_2^{\cdot}$$

$$\vdots \qquad\qquad \vdots$$

$$JM_{n-1}^{\cdot} + M \xrightarrow{k_p} JM_n^{\cdot}$$

Termination:

$$JM_n^{\cdot} + V^{5+} \xrightarrow{k_t} JM_n + V^{4+} + H^+$$

Oxidation:

$$R\cdot + V^{5+} \xrightarrow{k_o} \text{oxidation product}$$

Making use of the steady-state principle, the expression for the rate of grafting may be put forth as

$$\frac{1}{R_G} = \frac{k_t}{k_p k_1 K[M][R]}\left[1 + \frac{k_0\,[V^{5+}]}{k_2\,[JH]}\right]$$

Dependence of R_G on [*M*], $1/[V^{5+}]$, [JH], and [R], all of which were experimentally realized, favors our reaction scheme. The involvement of J· in the oxidation step was disregarded, since the expression of R_G involved proportionalities that were not experimentally realized.

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