Grafting Vinyl Monomers onto Cellulose. VII. Graft Copolymerization of Methyl Methacrylate onto Cellulose Using Acetylacetonato Cobalt(III) Complex

The use of chelate complexes for initiating vinyl polymerization has attracted attention in recent years.[1-7] It has been predicted that the initiation process is essentially the scission of a ligand to generate a free radical by the reduction of the metal to a lower valency state.

The ability of certain metal chelates to produce free radicals when heated was first pointed out by Arnett and Mendelsohn[3] in the course of investigation on the oxidation of these compounds. Kasting et al.[1,8] reported that the simple acetylacetonate of Mn(III) and Co(III) are most active initiators. Bamford and Lind[2] reported the polymerization of vinyl monomers using manganicacetylacetonate complexes. Otsu et al.[5,9] have studied the polymerization of some vinyl monomers using a large number of metal acetylacetonate. Recently, we reported the vinyl polymerization and graft copolymerization using acetylacetonato manganese(III) complex as the initiator.[10,11]

This communication presents the kinetics and mechanism of graft copolymerization of methyl methacrylate onto cellulose using acetylacetonato cobalt(III) complex.

EXPERIMENTAL

The cellulose samples used were of gift sample from J. K. Synthetics, Kota, India. The cellulose was scored by the usual procedure.[12] Methyl methacrylate was purified by the method mentioned in our previous communication.[12] $Co(acac)_3$ was prepared by the reaction of cobalt carbonate with acetylacetone.[13] Sulphuric acid was of AnalaR grade. The modified cellulose was prepared using standard procedures, and the reaction was carried out according to our previous communication.[12]

RESULTS AND DISCUSSION

The effect of acetylacetonato cobalt(III) complex concentration on the graft yield has been studied within the range 2.50×10^{-5}–$25 \times 10^{-5}M$, using different monomer concentration, i.e., 0.4694–0.9388M (Fig. 1). The perusal of the results indicates that, with increasing complex concentration up to $12.5 \times 10^{-5}M$, the graft yield increases and thereafter it decreases. In the initial stages, with increasing the complex concentration, the number of grafting sites on the backbone of the fiber in-

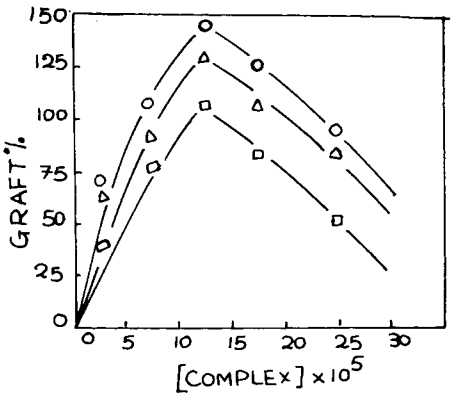

Fig. 1. Effect of $[Co(acac)_3]$ on graft yield: $[H_2SO_4] = 1.5 \times 10^{-2}M$; ether = 2.5% (v/v); temp = 70°C; time = 3 h; M:L = 1:100; (○) [MMA] = 0.4694M; (△) [MMA] = 0.7041M; (□) [MMA] = 0.9388M.

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creases by the interaction of the fiber with the complex, resulting the increase in graft yield. But beyond $12.5 \times 10^{-5}M$ of the complex concentration, the complex might interact with the monomer molecules, producing homopolymers, thereby decreasing graft yield. The plots of R_p vs. $[\text{complex}]^{1/2}$ are linear, passing through the origin (Fig. 2), which suggests that the order of the reaction with respect to complex is 0.5. Typical time conversion curves at 70°C for various acid concentration (0.75×10^{-2}–$7.5 \times 10^{-2}M$) are shown in Figure 3. It has been observed that the graft-on percentage increases with increasing acid concentration up to $1.50 \times 10^{-2}M$, and thereafter it decreases significantly. The grafting reaction has been studied using the monomer concentration within the range of 0.281–$1.032M$ at different complex concentrations (7.5×10^{-5}–$17.5 \times 10^{-5}M$) (Fig. 4). It is observed that, with increasing monomer concentration up to $0.6571M$, the graft yield increases and thereafter it decreases. The higher rates of grafting observed by increasing the monomer concentration could be ascribed due to the following reasons: (1) Complexation of cellulose with monomer which enhances the reactivity, thereby increasing the graft percentage: (2) the monomer molecule might form some type of charge transfer complex with the oxidant which favors grafting; (3) the other reasons might be gel effect. But at higher concentration of the monomer, there is a competition between combination and disproportionation of PMMA macroradical in solution. When the concentration of PMMA macroradical increased, the rate of their combination and disproportionation increased faster than the rate of their combination with cellulose molecules. On the other hand, the rate of monomer diffusion was bound to be progressively affected by the polymer deposit formed, which, of course, grew most rapidly when high concentration of monomer were used. The plots of R_p vs. monomer concentration are linear, indicating that the order of the reaction with respect to

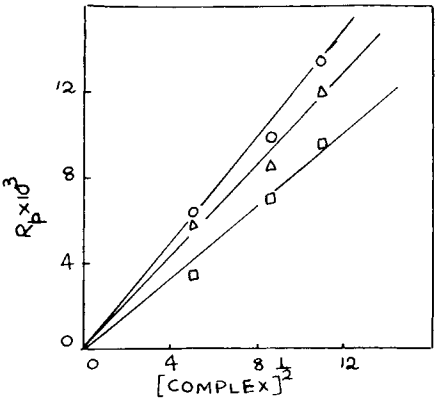


Fig. 2. Plot of R_p vs. $[\text{Co(acac)}_3]^{1/2}$: $[H_2SO_4] = 1.5 \times 10^{-2}M$; ether = 2.5% (v/v); temp = 70°C; time = 3 h; M:L = 1:100; (○) [MMA] = $0.4694M$; (△) [MMA] = $0.7041M$; (□) [MMA] = $0.9388M$.

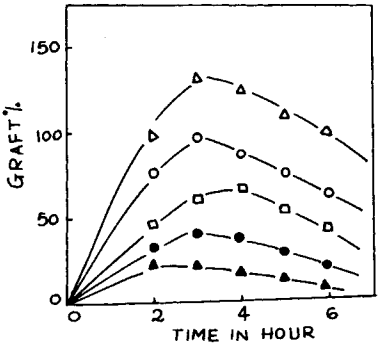


Fig. 3. Effect of $[H_2SO_4]$ on graft yield: $[\text{Co(acac)}_3] = 12.50 \times 10^{-5}M$; [MMA] = $0.4694M$; ether = 2.50% (v/v); temp = 70°C; M:L = 1:100; (○) $[H_2SO_4] = 0.75 \times 10^{-2}M$; (△) $[H_2SO_4] = 1.50 \times 10^{-2}M$; (□) $[H_2SO_4] = 3.00 \times 10^{-2}M$; (●) $[H_2SO_4] = 4.5 \times 10^{-2}M$; (▲) $[H_2SO_4] = 7.5 \times 10^{-2}M$.

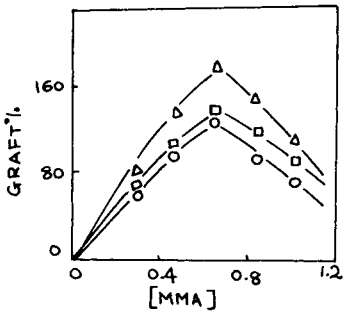


Fig. 4. Effect of [MMA] on graft yield: $[H_2SO_4] = 1.5 \times 10^{-2}M$; ether = 2.5% (v/v); temp = 70°C; time = 3 hr; M:L = 1:100; (○) $[Co(acac)_3] = 7.5 \times 10^{-5}M$; (△) $[Co(acac)_3] = 12.5 \times 10^{-5}M$; (□) $[Co(acac)_3] = 17.5 \times 10^{-5}M$.

monomer is unity (Fig. 5). The grafting reaction was carried out at different temperatuares ranging from 50°C to 75°C, keeping the concentration of all other reagents constant (Fig. 6). The graft yield increases with increasing temperature up to 70°C, and thereafter it decreases. From the Arrhenius plot of log R_p vs. $1/T$ (Fig. 7), the overall activation energy was computed to be 5.10 kcal/mol. In

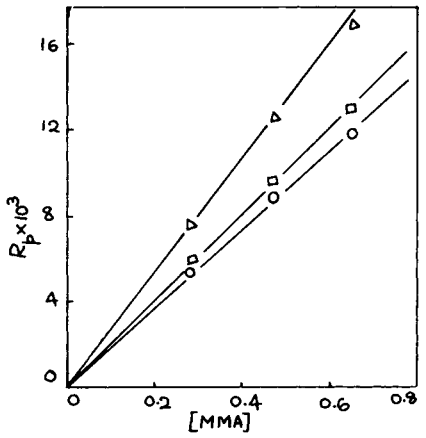


Fig. 5. Plot of R_p vs. [MMA]: $[H_2SO_4] = 1.5 \times 10^{-2}M$; ether = 2.5% (v/v); temp = 70°C; time = 3 h; M:L = 1:100 (○) $[Co(acac)_3] = 7.5 \times 10^{-2}M$; (△) $[Co(acac)_3] = 12.5 \times 10^{-5}M$; (▲) $[Co(acac)_3] = 17.5 \times 10^{-5}M$.

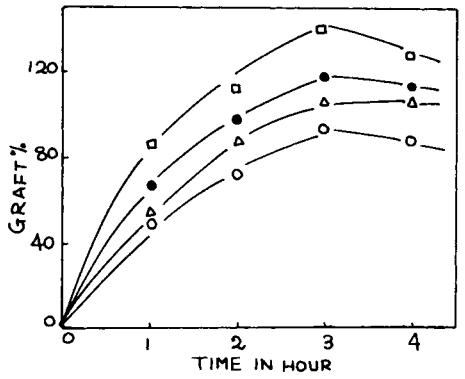


Fig. 6. Effect of temperature on graft yield: $[H_2SO_4] = 1.5 \times 10^{-2}M$; $[Co(acac)_3] = 12.50 \times 10^{-5}M$; [MMA] = $0.4694M$; ether = 2.5% (v/v); M:L = 1:100; temp (°C); (○) 50; (△) 60; (□) 70; (●) 75.

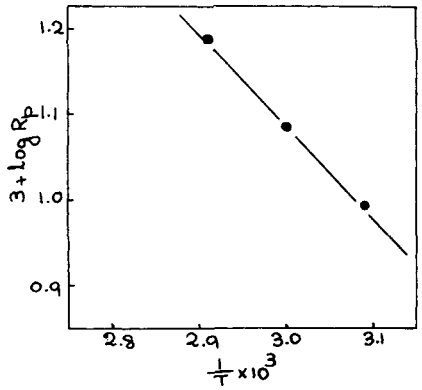
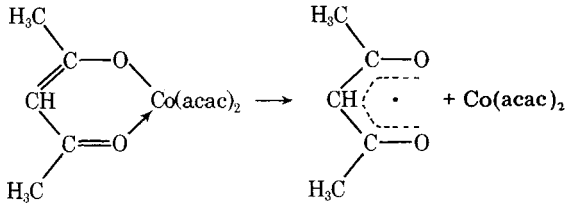


Fig. 7. Plot of log R_p vs. $1/T$.

case of modified cellulose the percentage graft follows the sequence: NaOH treated cell > untreated cell > $K_2Cr_2O_7$—H_2SO_4-oxidized cell > cyanoethylated cell > crosslinked cell > $ZnCl_2$-treated cell (Fig. 8). Further the effect of inhibitors like hydroquinone and picryl chloride has been studied within the range 5×10^{-4}–$2.5 \times 10^{-4}M$. With increasing the inhibitor concentration, the graft yield decrease rapidly.

MECHANISM

The acetylacetonate complex of Co^{3+} decomposes to yield acetylacetone radical or the radical in combination with the monomer (M) as represented below:



I

$$Co(acac)_3 + M \rightleftharpoons [M \longrightarrow Co(acac)_3] \longrightarrow (acac)\text{—}M^{\cdot} + Co(acac)_2$$

II

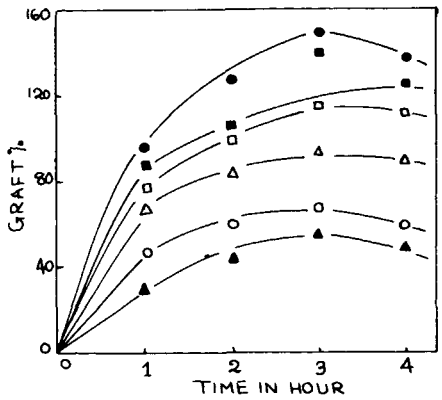


Fig. 8. Effect of nature of substrate on graft yield: $[H_2SO_4] = 1.5 \times 10^{-2}M$; $[Co(acac)_3] = 12.50 \times 10^{-5}M$; [MMA] = $0.4694M$; ether = 2.5% (v/v); temp = 70°C; M:L = 1:100; (■) untreated cell; (□) oxidized cell; (△) cyanoethylated cell; (○) crosslinked cell; (▲) zinc chloride cell; (●) NaOH treated cell.

The free radicals I or II might interact with the cellulose molecule, producing cellulose macroradicals which initiate grafting. The detail mechanism is furnished below:

$$R\cdot + \text{cell—H} \xrightarrow{k_i} \text{cell}\cdot + RH$$

Initiation:

$$\text{cell}\cdot + M \xrightarrow{k_i} \text{cell—M}\cdot$$

Propagation:

$$\text{cell—M}\cdot + M \xrightarrow{k_p} \text{cell—M}_1^{\cdot}$$

$$\text{cell—M}_{n-1}^{\cdot} + M \xrightarrow{k_p} \text{cell—M}_n^{\cdot}$$

Termination:

$$\text{cell—M}_n^{\cdot} + \text{cell—M}_m^{\cdot} \xrightarrow{k_t} \text{graft copolymer}$$

Where cell—H is cellulose, cell· is cellulose macroradical, M is monomer, K is equilibrium constant, and k_i, k_p, and k_t are rate constants. Considering steady state principle, the rate of polymerization was found to be

$$R_p = k_p \left(\frac{Kk_ik_1}{k_t}\right)^{1/2} [\text{complex}]^{1/2}[\text{cell—H}]^{1/2}[M]$$

The plot of R_p vs. $[\text{complex}]^{1/2}$ and R_p vs. [M] were linear, supporting the above reaction scheme.

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