Notes

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

Recently, attention has been paid to find new initiating systems of radical reactions based particularly on chelate complexes of transition metals.[1-4] The initiating species are believed to be the ligand radicals formed, i.e., under homolytic scission of the metal–oxygen bond of metal acetylacetonates. At the same time, the formal valence of the metal is reduced by one which is confirmed by spectral and ESR measurements.[5] The efficiency of initiation of metal chelates could be enhanced by addition of various compounds, mainly halogen containing compounds[2] and compounds of electron donating substances[6] such as dioxane, dimethyl sulfoxide, etc. In the majority of the cases reported so far, the polymerization proceeds via a typical free radical process. Kasting et al.[2] reported the polymerization of MMA by $Mn(acac)_3$ halogen compounds.

Nayak et al.[7] reported grafting onto cellulose using V^{5+} as the initiator. In the present investigation, the authors report the graft copolymerization of methyl methacrylate onto cellulose using an acetylacetonato manganese(III) complex as the initiator.

EXPERIMENTAL

The cellulose was purified in the usual manner.[7] MMA was washed by the method mentioned in our previous communication.[8] $Mn(acac)_3$ was prepared by the reaction of manganese chloride with acetyl acetone.[9] Perchloric acid was of Analar grade. The modified cellulose was prepared using standard procedures, and reaction was carried out according to our previous communication.[8]

RESULTS AND DISCUSSION

The graft copolymerization of methyl methacrylate onto cellulose was studied in aqueous medium. The rate of grafting was calculated by varying monomer, acid, initiator concentration, and temperature. With an increase in monomer concentration within the range of 0.2816–1.0326 mole/l., (Fig. 1) at various complex concentrations, the rate of grafting increases. The probable explanation for this finding might be due to (1) the complexation of cellulose with monomer, which is favored by an increase in monomer concentration, and (2) gel effect, i.e., increase in viscosity of the medium owing to the solubility of poly(methyl methacrylate) in its own monomer. This solubility could be more pronounced with an increase in monomer concentration, causing hindrance in termination,
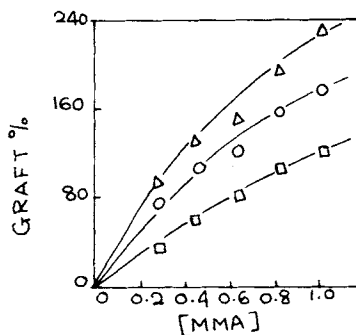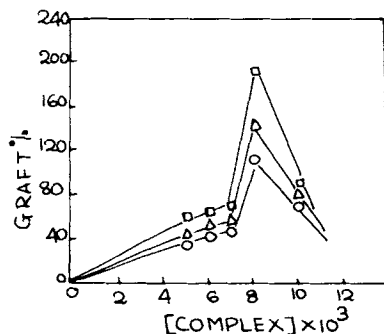

Fig. 1. Effect of [MMA] on graft yield. $[HClO_4] = 2.33 \times 10^{-3}$ mole/l.; dioxan = 7.5% v/v; M:L = 1:100; time = 6 hr; temp. = 70°C; (O) [complex] = 6.5×10^{-3} mole/l.; (□) [complex] = 5.0×10^{-3} mole/l.; (△) [complex] = 8.0×10^{-3} mole/l.

Fig. 2. Effect of [complex] on graft yield. $[HClO_4]$ = 2.33 × 10^{-3} mole; dioxan = 7.5% (v/v); M:L = 1:100; time = 6 hr; temp. = 70°C; (O) [MMA] = 0.4694 mole/l.; (△) [MMA] = 0.7041 mole/l.; (□) [MMA] = 0.9388 mole/l.

particularly by coupling of growing polymer chains. The gel effect also causes swelling of cellulose, thus facilitating the diffusion of monomer to growing chains and active sites on the backbone and thereby enhancing grafting. The effect of perchloric acid concentration was studied by varying the concentration of perchloric acid from 2.33 × 10^{-3} to 46.60 × 10^{-3} mole/l. The graft yield increases up to 4.66 × 10^{-3} mole/l. and decreases thereafter.

The temperature was varied from 60 to 75°C. The rate of grafting was increased by increasing the temperature. From the Arrhenius plot of log R_p vs. $1/T$, the overall activation energy was computed to be 5.8 kcal/mole. The rate of grafting was studied in the presence of acetone and methanol. The interesting observation was that in both cases increase in solvent percentage resulted in the decrease of the rate of grafting. This might be due to the fact that at higher solvent concentration the solvent acts as chain terminator. The grafting reaction was carried out with differently modified cellulose, and the graft yield followed the order cotton treated with 6N NaOH > untreated cellulose > oxidized cellulose > crosslinked cellulose. The same finding was observed by Nayak et al.[7] while grafting methyl methacrylate onto cellulose using V^{5+} as the initiator.

The effect of inhibitor such as picryl chloride was also studied while carrying out the grafting reaction. The rate of grafting decreased with increasing inhibitor concentration. With increase in the percentage of grafting, the percentage of moisture regain decreased. The complex concentration was varied from 5 × 10^{-3} to 10 × 10^{-3} mole/l. at various monomer concentrations (Fig. 2). The graft yield increased up to 8 × 10^{-3} mole/l. and decreased thereafter. In the initial stages, the complex will form free radicals on the backbone of cellulose, which increases the rate of grafting; but beyond a certain concentration of complex, there will be abundance of free radicals which might terminate the growing chain, suggesting a linear type of termination.
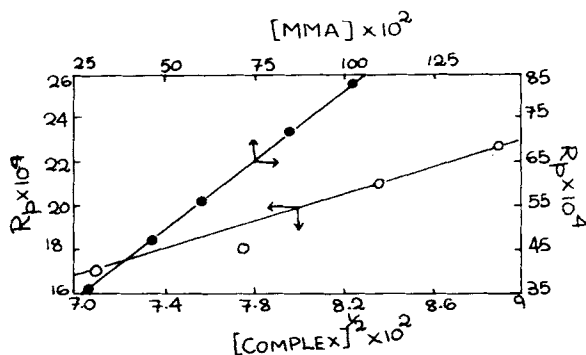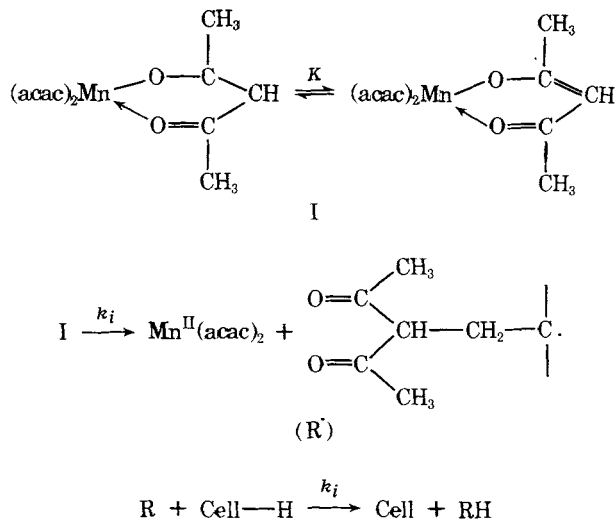

Fig. 3. (a) Plot of R_p vs. [complex]$^{1/2}$.   (b) Plot of R_p vs. [M].

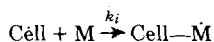## Mechanism

The first step is the formation of activated species (I) in equilibrium with $Mn(acac)_3$. Species I then breaks in the presence of dioxan to give $Mn^{II}(acac)_2$ and the free radical (R̊). The free radical (R̊) then initiates grafting. The reaction scheme is as follows:

I

(R̊)

$$R + Cell\!-\!\!-\!\!H \xrightarrow{k_i} Cell + RH$$
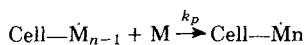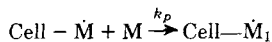
(where Cėll is cellulose macroradical).

Initiation:

$$Cėll + M \xrightarrow{k_i} Cell\!-\!\dot{M}$$

Propagation:

$$Cell - \dot{M} + M \xrightarrow{k_p} Cell\!-\!\dot{M}_1$$

$$Cell\!-\!\dot{M}_{n-1} + M \xrightarrow{k_p} Cell\!-\!\dot{M}n$$

Termination:

$$Cell\!-\!\dot{M}n + Cell\!-\!\dot{M}n \xrightarrow{k_t} polymer$$

$$Cell\!-\!\dot{M}n + complex \xrightarrow{k_t} polymer$$
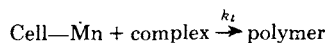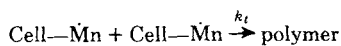
Considering a steady-state principle for [R̊], [Cell], [Cell—Ṁ] etc., the rate of polymerization was derived to be

$$R_p = k_p \left[\left(\frac{Kk_1 k_i}{k_t} \right) ([Cell][complex])^{1/2} \right] [M]$$

The plots of R_p vs. [M] and R_p vs. $[complex]^{1/2}$ (Fig. 3) were linear, confirming the validity of the above reaction scheme.

References

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