

Graft Copolymerization onto Rubber. VI. Graft Copolymerization of Methyl Methacrylate onto Rubber Using Acetylacetonate Complex of Manganese(III)

INTRODUCTION

In recent years, attempts have been made to find new initiating systems of radical reactions particularly based on chelate complexes of transition metals.¹⁻⁴ It has been predicted that the initiation process is essentially the scission of a ligand to generate a free radical and 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 Mendelsons¹ in the course of investigations on the oxidation of these compounds. Kastning et al.² reported that the acetylacetonate complex of Mn(III) and Co(III) are active initiators. Bamford and Lind³ reported the copolymerization of vinyl monomers using the manganese acetylacetonate complex. Recently Lenka et al. reported vinyl⁵ and graft copolymerizations⁶⁻⁸ using acetylacetonate complexes of Mn(III), Co(III), and Fe(III). This communication presents the kinetics and mechanism of graft copolymerization of methyl methacrylate onto rubber using acetylacetonate complex of Mn(III).

EXPERIMENTAL

Crepper natural rubber with ash content 0.6% and acetone extract = 2.2% was obtained as a gift sample from Dr. S. K. De of IIT, Kharagpur. The purification of monomers, preparation of stock solution of acetylacetonate complex of Mn(III), and the method of rate measurements were discussed in our previous communication.⁵⁻⁸ The grafted product was extracted with benzene to remove homopolymer completely. The percentage of grafting was calculated according to our previous procedure.

RESULTS AND DISCUSSION

The effect of the acetylacetonate complex of manganese(III) concentration on the graft yield has been studied within the range of 3–18 $\times 10^{-3}$ m/L. The plot of R_p vs. $[\text{Mn}(\text{acac})_3]$ (Fig. 1) shows that with the increase of complex concentration up to 12 $\times 10^{-3}$ m/L the rate

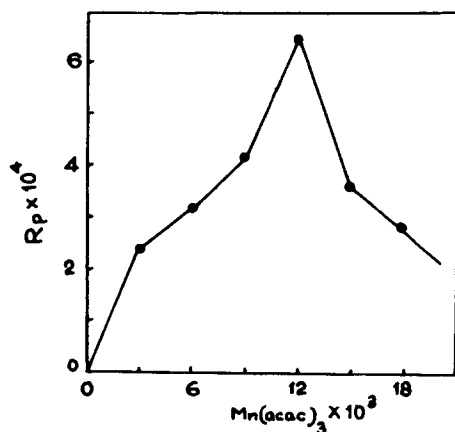


Fig. 1. Plot of R_p vs. $[\text{Mn}(\text{acac})_3]$: $[\text{MMA}] = 0.9388$ m/L; $[\text{H}_2\text{SO}_4] = 0.3$ m/L; temp = 50°C; time = 5 h.

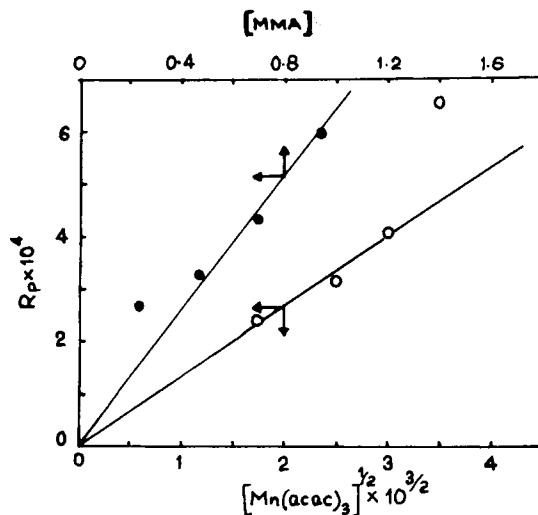


Fig. 2. Plot of R_p vs. $[\text{Mn}(\text{acac})_3]^{1/2}$ (○); plot of R_p vs. $[\text{monomer}]$ (●); $[\text{Mn}(\text{acac})_3] = 0.006 \text{ m/L}$; $[\text{H}_2\text{SO}_4] = 0.3 \text{ m/L}$; temp = 50°C ; time = 5 h.

of grafting increases, but with further increase of complex concentration the rate of grafting decreases. The plot of R_p vs. $[\text{complex}]^{1/2}$ is linear passing through the origin (Fig. 2) which suggests that the order of the reaction with respect to complex is 0.5. A typical conversion curve at 50°C for various acid concentrations (0.3–1.5 m/L) is shown in Figure 3. It has been observed that the graft-on percentage increases with increasing acid concentration up to 0.6 m/L, and thereafter it decreases significantly. The grafting reaction has been studied using the monomer concentration within the range of 0.2347–1.4082 m/L. It is observed that, with increasing monomer concentration up to 0.9388 m/L, the graft yield increases and thereafter it decreases. The plot of R_p vs. monomer concentration is linear, indicating that the order of the reaction with respect to monomer is unity (Fig. 2). The grafting reaction was carried out at different temperatures ranging from 40 to 60°C , keeping the concentration of all other reagents constant. The graft yield increases with increasing temperature up to 50°C and thereafter it decreases. From the Arrhenius plot of $\log R_p$ vs. $1/T$ (Fig. 4), the overall activation energy was computed to be 13.1 kcal/mol.

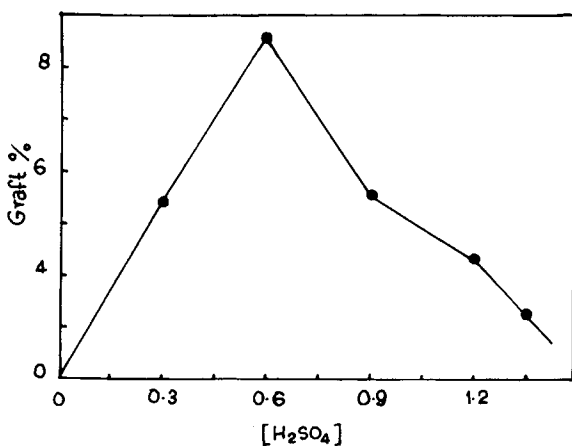


Fig. 3. Effect of $[\text{H}_2\text{SO}_4]$ on graft yield: $[\text{MMA}] = 0.9388 \text{ m/L}$; $[\text{Mn}(\text{acac})_3] = 0.012 \text{ m/L}$; temp = 50°C ; time = 5 h.

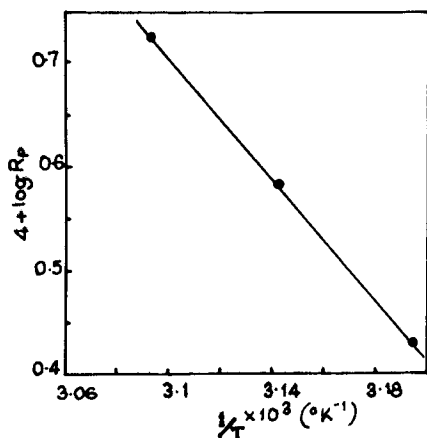
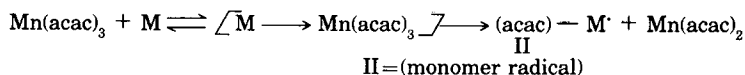
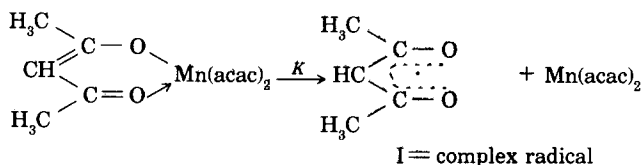


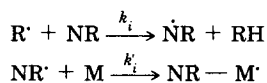
Fig. 4. Arrhenius plot of $1/T$ vs. $\log R_p$; [MMA] = 0.9338 m/L; [H₂SO₄] = 0.6 m/L [Mn(acac)₃] = 0.012 m/L; time = 5 h.; temp = 50°C.

Mechanism The acetylacetonate complex of Mn(III) decomposes to yield acetylacetonate radical or the radical in combination with the monomer (M) as represented below:

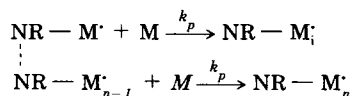


The free radicals I or II (R[•]) might interact with the rubber molecule producing rubber macroradicals which initiates grafting. The details of the mechanism are given below.

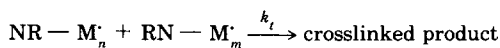
Initiation



Propagation



Termination



Considering steady state principle, for the radical the rate of polymerization, R_p , has been derived to be

$$R_p = k_p \left(\frac{Kk_i}{k_t} \right)^{1/2} [\text{Mn}(\text{acac})_3]^{1/2} [\text{M}]$$

Thus the plots of R_p vs. $[\text{M}]$ and R_p vs. $[\text{complex}]^{1/2}$ (Fig. 2) are linear, indicating the validity of the reaction scheme.

References

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