Grafting Vinyl Monomers onto Nylon 6. VI. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Using Acetylacetonate Complex of Mn(III), Co(III), and Fe(III)

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Synopsis

The graft copolymerization of methyl methacrylate onto nylon 6 using metal complexes of Mn^{3+}, Co^{3+}, and Fe^{3+} as initiators was studied. The rate of polymerization, R_p, increased with increasing complex concentrations in the initial stages; but it decreased upon further increase of complex concentrations. With increasing monomer concentrations, the rate of polymerization increased progressively. The graft yield increased with increasing temperature within the range 60–75°C. A suitable kinetic scheme is presented and rate equations are derived.

INTRODUCTION

Arnett and Mendelsohn[1] were first to report that certain metal chelates with O,O donor atoms in the ligand molecule yield free radicals during thermal decomposition. Since then, the interest of many authors has been focused on the study of the kinetics and mechanism of initiation of radical polymerization of vinyl and diene monomers by metal chelates.[2–17] Among the metal chelates, acetylacetonate complexes of certain transition elements such as Mn^{3+}, Co^{3+}, Ni^{2+}, and Fe^{3+} have attracted attention in recent years.[13]

Nayak and co-workers[18–30] have used a large number of metal and nonmetal ions for grafting vinyl monomers onto a number of natural and synthetic fibers. However, not much work has been published on the use of metal chelates as initiators for grafting vinyl monomers onto these fibers. Recently, we reported the graft copolymerization of methyl methacrylate onto cellulose using the Mn(III)–acetylacetonate complex.[27]

This report presents the results of studies of graft copolymerization of methyl methacrylate onto nylon 6 using acetylacetonate complexes of Mn^{3+}, Co^{3+}, and Fe^{3+}.

EXPERIMENTAL

Nylon 6 fibers were kindly supplied by J. K. Synthetics, Kota, Rajsthan, India. The acetylacetonate complexes of Mn^{3+}, Co^{3+}, and Fe^{3+} were prepared according to the literature.[31,32] The graft copolymerization was carried out according to our previous methods.[18–30]

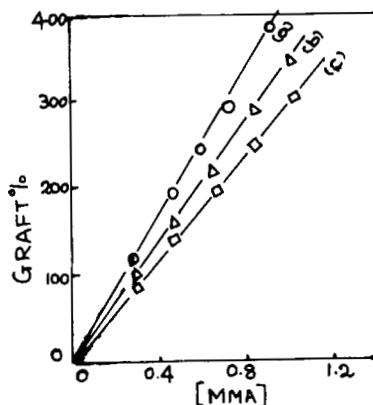Fig. 1. Effect of monomer concentration: (a) $[Mn(acac)_3] = 6.60 \times 10^{-2} M$; $[HClO_4] = 13.86 \times 10^{-2} M$; time = 6 h, temp. = 70°C; M:L = 1:100. (b) $[Co(acac)_3] = 2.50 \times 10^{-5} M$; $[H_2SO_4] = 7.5 \times 10^{-2} M$; time = 6 h; temp. = 70°C; M:L = 1:100. (c) $[Fe(acac)_3] = 7.5 \times 10^{-5} M$; $[H_2SO_4] = 7.5 \times 10^{-2} M$; time = 6 hr; temp. = 70°C; M:L = 1:100.

RESULTS AND DISCUSSION

Monomer Concentration

The effect of monomer concentration on the polymerization reaction was evaluated by changing the monomer concentrations within the range 2.81×10^{-1}–$10.32 \times 10^{-1} M$ for the three acetylacetonate chelate complexes (Fig. 1). It is observed that increasing the monomer concentration causes an outstanding enhancement in the graft yield. The enhancement of grafting at higher monomer concentrations could be interpreted in terms of the gel effect.

Initiator Concentration

The effect of the initiator concentration on graft yield was investigated by varying the initiator from very low to very high concentrations (Fig. 2). The results indicate that with increasing chelate concentration, graft yield increases.
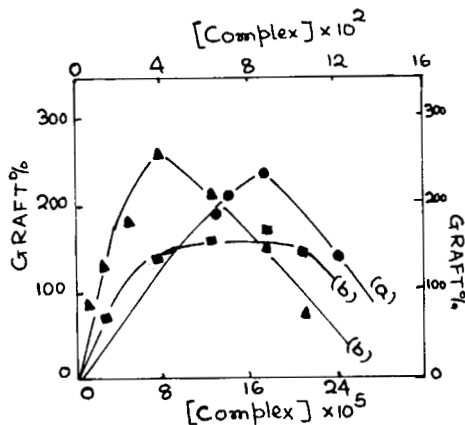

Fig. 2. Effect of complex concentration: (a) $[MMA] = 0.4694 M$; $[HClO_4] = 13.86 \times 10^{-2} M$; time = 6 h; temp. = 70°C; M:L = 1:100; (●) $[Mn(acac)_3]$. (b) $[MMA] = 0.4694 M$; $[H_2SO_4] = 7.5 \times 10^{-2} M$; time = 6 h; temp. = 70°C; M:L = 1:100; (▲) $[Co(acac)_3]$; (■) $[Fe(acac)_3]$.
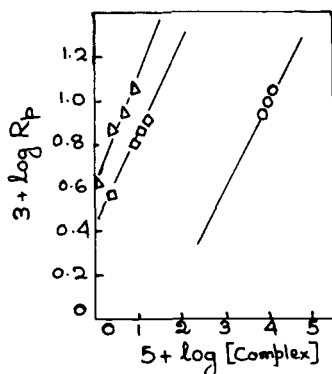
Fig. 3. Plot of log R_p vs. log [complex]:   (O) [Mn(acac)$_3$]; (△) [Co(acac)$_3$]; (□) [Fe(acac)$_3$].

But at very high chelate concentrations, a trend for the graft yield to decrease is noticed.

The metal chelates of Mn^{+3}, Co^{+3}, and Fe^{+3} decompose to yield acetylacetone radical or radical in combination with monomer, as represented below:

I

$$Me(acac)_x + M \rightleftharpoons [M \longrightarrow Me(acac)_x] \longrightarrow (acac) - M^. + Me(acac)_{x-1}$$
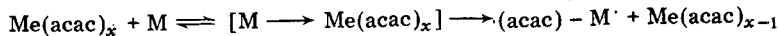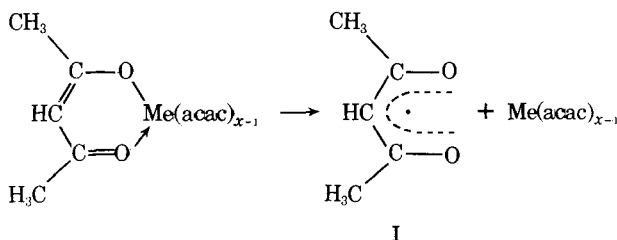
II

The free radicals I and II may participate in (a) direct abstraction of hydrogen atom from the polyamide backbone to yield a polyamide macroradical capable of initiating grafting; (b) termination process with growing polymer chain; (c)
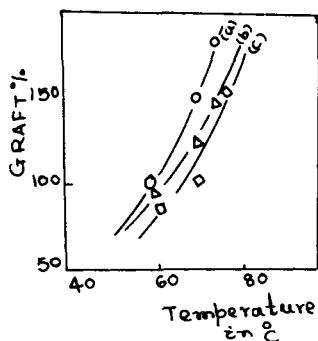

Fig. 4. Effect of temperature: (a) [Mn(acac)$_3$] = 7.70 × 10^{-2} M; [HClO$_4$] = 13.86 × 10^{-2} M; [MMA] = 0.4694 M; time = 3 h; M:L = 1:100.   (b) [Co(acac)$_3$] = 7.5 × 10^{-5} M; [H$_2$SO$_4$] = 7.5 × 10^{-2} M; [MMA] = 0.4694 M; time = 3 h; M:L = 1:100.   (c) [Fe(acac)$_3$] = 17.50 × 10^{-5} M; [H$_2$SO$_4$] = 7.5 × 10^{-2} M; [MMA] = 0.4694 M; time = 3 h; M:L = 1:100.
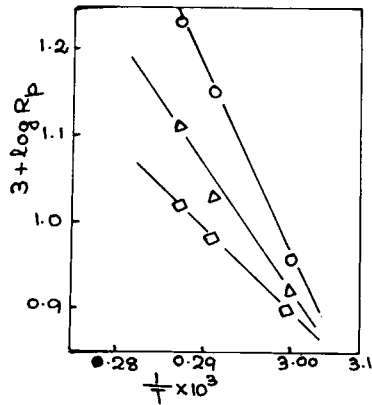
Fig. 5. Arrhenius plot of log R_p vs. $1/T$: (O) [Mn(acac)$_3$]; ($\triangle$) [Co(acac)$_3$]; ($\square$) [Fe(acac)$_3$].

combination of the free radical species, in particular the secondary free radical species; (d) termination process with the polyamide macroradicals. At lower chelate concentrations, the effect of (a) seems to prevail over the combined effects of (b), (c), and (d), thereby increasing the graft yield. The opposite holds true at higher initiator concentrations.
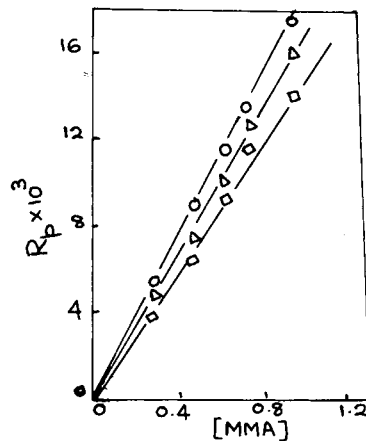

Fig. 6. Plot of log R_p vs. [MMA]: (O) [Mn(acac)$_3$]; ($\triangle$) [Co(acac)$_3$]; ($\square$) [Fe(acac)$_3$].
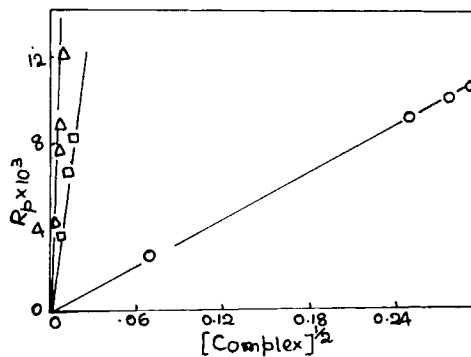
Fig. 7. Plot of log R_p vs. [complex]$^{1/2}$: (O) [Mn(acac)$_3$]; ($\triangle$) [Co(acac)$_3$]; ($\square$) [Fe(acac)$_3$].

It was observed that of the three complexes, $Mn(acac)_3$ was the most effective initiator; the order of reactivities of initiators was
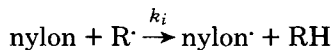
$$Mn^{3+} > Co^{3+} > Fe^{3+}$$

This order of reactivity is in agreement with the results reported by Kastning and Izawa.[33]   The high initiating ability of $Mn(acac)_3$ might be based on its structural strain, as is reported by Morosin and Brathorde.[34]   The plot of log R_p vs. log [initiator] (Fig. 3) is a straight line with slopes equal to 0.50 and 0.45, 0.55 indicating 0.5 order with respect to the initiator concentrations.
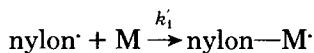
Effect of Temperature

The effect of raising the temperature up to 60–75°C is to bring about significant acceleration in the rate of grafting (Fig. 4).   The favorable effect of temperature on grafting is probably associated with (a) a faster rate of decomposition of chelates, giving rise to more free radicals; (b) enhancement in the swellability of fibers; (c) increased mobility of the monomer molecules; (d) higher rate of monomer diffusion from the reaction medium to the nylon medium; (e) enhancement in the rate of initiation and propagation of grafts.   The net effect of all these factors could be expected to yield higher grafting.

From the Arrhenius plot (Fig. 5) of log R_p vs $1/T$, the overall activation energies were found to be 9.2, 6.60, and 4.6 kcal/mol for Mn^{3+}, Co^{3+}, and Fe^{3+}, respectively.
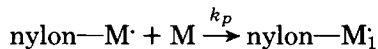
As has been pointed out by Arnett and Mendelsohn[1] and Bamford and Lind,[3] the initiation mechanism by $Me(acac)_x$ is considered to occur through the homolysis of their metal–oxygen bonds forming acetyl acetone radical or radical in combination with the monomer [R·] which initiates grafting:

$$nylon + R· \xrightarrow{k_i} nylon· + RH$$

Initiation:

$$nylon· + M \xrightarrow{k_i'} nylon\text{—}M·$$

Propagation:

$$nylon\text{—}M· + M \xrightarrow{k_p} nylon\text{—}M_1^·$$

$$\cdot$$
$$\cdot$$
$$\cdot$$
$$\cdot$$

$$nylon\text{—}M_{n-1}^· + M \xrightarrow{k_p} nylon\text{—}M_n^·$$

Termination:

$$nylon\text{—}M_n^· + nylon\text{—}M_n^· \xrightarrow{k_t} graft\ copolymer$$
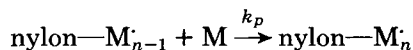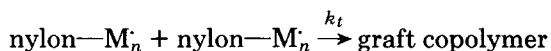
Applying steady-state assumptions to the growing radicals, we have

$$\frac{-d[\mathrm{R^{\cdot}}]}{dt} = k[\mathrm{Me(acac)_3}] - k_i[\mathrm{R^{\cdot}}][\mathrm{nylon}] = 0$$

or

$$[\mathrm{R^{\cdot}}] = \frac{k[\mathrm{Me(acac)_3}]}{k_i[\mathrm{nylon}]}$$

$$\frac{-d[\mathrm{R}M_n^{\cdot}]}{dt} = k_i'[\mathrm{nylon^{\cdot}}][\mathrm{M}] - k_t[\mathrm{nylon{-}M_n^{\cdot}}]^2 = 0$$

or

$$[\mathrm{nylon{-}M_n^{\cdot}}]^2 = \frac{k_i'}{k_t}[\mathrm{nylon^{\cdot}}][\mathrm{M}]$$

Putting the value of [nylon·] in the above expression,

$$[\mathrm{nylon{-}M_n^{\cdot}}] = \left(\frac{k}{k_t}\right)^{1/2}[\mathrm{Me(acac)_3}]^{1/2}[\mathrm{M}]$$

Further,

$$R_p = k_p[\mathrm{nylon{-}M^{\cdot}}][\mathrm{M}]$$

Hence,

$$R_p = k_p\left(\frac{k}{k_t}\right)^{1/2}[\mathrm{Me(acac)_3}]^{1/2}[\mathrm{M}]$$

Thus, the plots of R_p vs. [M] (Fig. 6) and R_p vs [complex]$^{1/2}$ (Fig. 7) were linear, indicating the validity of the reaction scheme.

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