Grafting Vinyl Monomers onto Silk Fibers: Graft Copolymerization of Methyl Methacrylate onto Silk Using Acetylacetonate Mn(III) Complex

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Synopsis

The graft copolymerization of methyl methacrylate onto Mulberry silk fibers was studied in aqueous solution using Mn(acac)$_3$ as initiator. Perchloric acid was found to catalyze the reaction. The rate of grafting was investigated by varying the concentration of the monomer and the complex, acidity of the medium, the solvent composition of the reaction medium, the surfactants, and the inhibitors. The graft yield increases with increasing concentration of Mn(acac)$_3$ up to 0.01 mol/L, decreasing thereafter. Increase of MMA concentration up to 0.56 mol/L increases graft yield, and thereafter it decreases. Among the various vinyl monomers studied, MMA was found to be most suitable for grafting. Grafting increases up to 7.5×10^{-3} mol/L of HClO$_4$ concentration, and thereafter it decreases. A suitable reaction scheme has been proposed and a rate equation has been derived. The energy of activation has been calculated from the Arrhenius plot. The chain transfer constants for various chain transfer solvents have been evaluated from the average molecular weight ($\overline{M}$) of grafted poly(methyl methacrylate).

INTRODUCTION

Acetylacetonate complexes of some metals at their higher valency states are known as excellent initiators for vinyl polymerization. Such complexes produce acetylacetonate free radicals upon heating.[1] The generation of the free radical takes place by the homolysis of an M—O bond, the metal being reduced to a lower valency state. Several authors[2-7] have effected polymerization of vinyl monomers employing chelates like Co(acac)$_3$, Mn(acac)$_3$, VO(acac)$_2$, Fe(acac)$_3$, etc. Kasting et al.[4,5] have pointed out that of the several metal acetylacetonates, those of Co(III) and Mn(III) are most active.

The successful use of such chelates for grafting vinyl monomers onto various natural and synthetic fibers have been reported by Nayak et al. and several other workers.[8-10] We have reported the graft copolymerization of methyl methacrylate (MMA) onto native and modified Indian Chokla Wool using Mn(acac)$_3$,[11,12] Fe(acac)$_3$[13] and VO(acac)$_2$[14] as initiators. Several workers[15,16] graft copolymerized vinyl monomers onto silk employing various redox systems. We have reported grafting of methyl methacrylate onto Mulberry silk using VO(acac)$_2$ and Co(acac)$_3$ as initiators.[17,18]

The present work describes the kinetics and mechanism of graft copolymerization of methyl methacrylate and other vinyl monomers onto Mul-
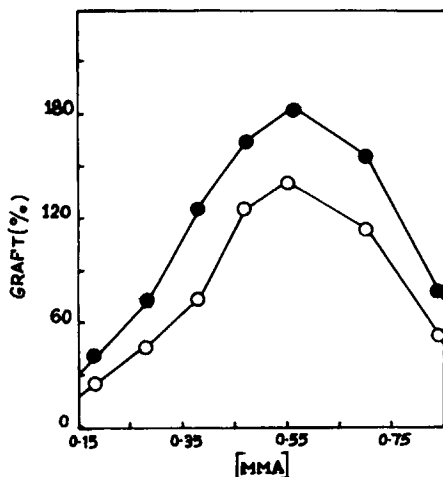
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SAMAL, SAHU, AND NAYAK

Fig. 1. Effect of [MMA] on graft yield: $[HClO_4] = 6.5 \times 10^{-3}$ mol/L, [ethyl acetate] = 0.894 mol/L, M:L = 1:100, 50°C, 4 h, $[Mn(acac)_3]$ (mol/L): (○) 0.005; (●) 0.0075.

berry silk fibers using $Mn(acac)_3$ as the initiator. The chelate forms a number of 1:1 adducts with several monodentate ligands and the suitability of such adducts as initiators has been studied also. The IR and PMR spectral analysis, SEM studies, and thermogravimetric analysis of the grafted samples will be reported in our subsequent communications.
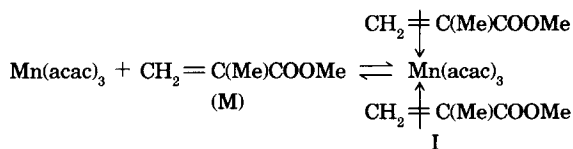
EXPERIMENTAL

Purification of silk, monomers, solvents, methods of rate measurement, and calculation of percentage of graft yield have been reported in our previous communications.[16] Adducts of $Mn(acac)_3$ with monodentate ligands like isoquinoline, p-toluidine, and γ-picoline are prepared by refluxing ethanolic solution of the complex and ligands in equimolar proportions and crystallized in CCl_4 medium *in vacuo*.

DISCUSSION

Effect of Monomer Concentration

Silk was graft copolymerized within the range 0.1878–0.8449 mol/L of MMA concentration at different concentrations of the initiator. It is observed that the graft yield increases upto 0.5634 mol/L decreasing thereafter (Fig. 1).

The initial increasing trend could be ascribed to (1) the complexation of silk with monomer, (2) the ease of formation of a charge-transfer complex (I) between the monomer (M) and the initiator, and (3) gel effect.[19]:

$$Mn(acac)_3 + \underset{(M)}{CH_2 = C(Me)COOMe} \rightleftharpoons \underset{I}{\overset{\textstyle CH_2 = C(Me)COOMe}{\underset{\textstyle CH_2 = C(Me)COOMe}{\big| \quad Mn(acac)_3 \quad \big|}}}$$

At higher concentrations of the monomer, the rate of combination and disproportionation of poly(methyl methacrylate) (PMMA) macroradical is increased faster than the rate of their combination with silk.[20] Besides, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed and this effect is more pronounced at higher concentrations of the monomer.[21]

Among the various monomers studied, MMA was found to be most active; the order of reactivity being MMA > methyl methacrylate (MA) > ethyl acrylate (EA) > acrylonitrile (AN) > acrylic acid (AA) (Fig. 2). This trend suggests the formation of a charge transfer complex I which subsequently breaks down to give the initiating free radical. The charge transfer complex I would be formed with maximum ease in case of MMA. The +I effect of the substituted —Me group increases the π-electron density of the monomer, thus making it easier to coordinate the metal chelate. In case of AN and AA the —CN and —COOH groups significantly decrease the π-electron density, leading to decreased reactivity. The decreasing order of graft yield from MA to BA is largely due to steric hindrance. The approach of the monomer to form charge transfer complex with the initiator is sterically hindered.

Effect of Initiator Concentration

The rate of grafting was investigated by varying the $Mn(acac)_3$ concentration within the range 0.003–0.025 mol/L. The data indicate that the graft yield increases with increasing concentration of $Mn(acac)_3$ up to 0.01 mol/L and thereafter it decreases (Fig. 3).

In the initial stages, a charge transfer complex is probably formed between the active groups on silk backbone and the chelate and monomer. Hence the conentration of the chelate and the monomer is increased in the
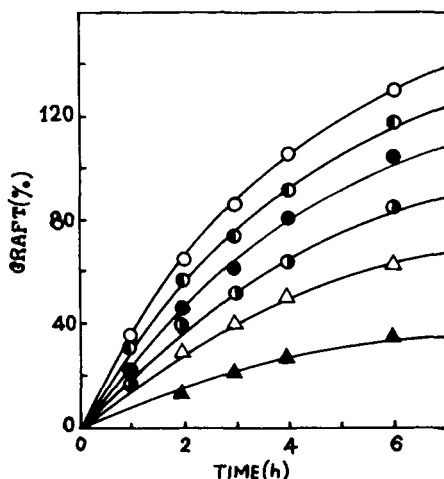

Fig. 2. Effect of vinyl monomers on graft yield: $[Mn(acac)_3]$ = 0.006 mol/L, [ethyl acetate] = 0.894 mol/L, $[HClO_4]$ = 4.5 × 10^{-3} mol/L, M:L = 1:100, 50°C, [M] = 0.4 mol/L; (○) MMA; (◑) MA; (●) EA; (◐) BA; (△) AN; (▲) AA.
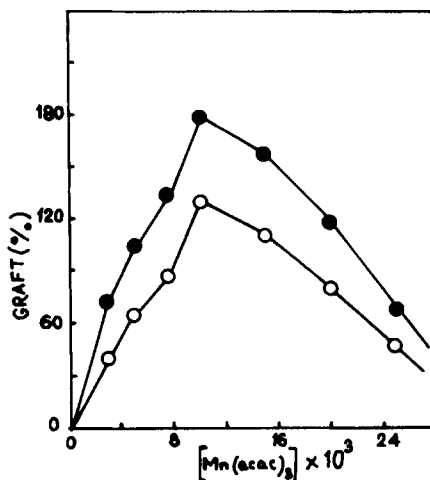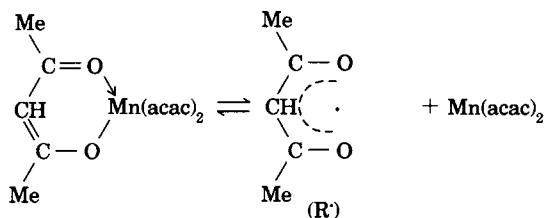
Fig. 3. Effect of initiator concentration on graft yield: [HClO$_4$] = 5 × 10^{-3} mol/L, [ethyl acetate] = 1.277 mol/L, M:L = 1:100, 3 h, 50°C, [MMA] (mol/L): (○) 0.3756; (●) 0.4694.

vicinity of the fiber matrix. This assists the homolysis of the metal–oxygen bond forming acetylacetonate free radical (R·):

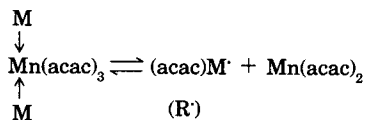Several monodentate ligands (L) like isoquinoline (IQ), γ-picoline (PL), and p-toluidine (TD) are found to form adducts (II) with Mn(acac)$_3$. The adducts are found to be better initiators for grafting. The additional ligand increases the electron density on the metal, and the homolytic cleavage of metal–oxygen bond presumably becomes easier:
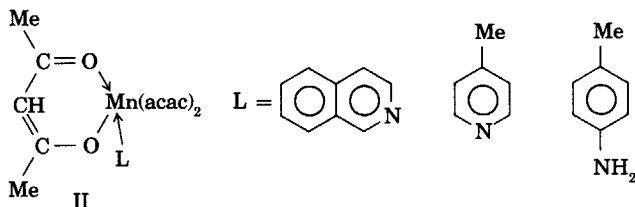
The formation of acetylacetonate free radical is assisted by the solvent and the monomer.[13] Bamford et al.[22] have suggested that the solvent molecules (S) assist the decomposition of the chelate by stabilizing the divalent chelate (III) generated in the process:
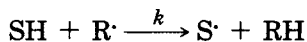
$$Mn(acac)_3 \xrightleftharpoons{+2S} acac\cdot + \overset{\displaystyle S}{\underset{\displaystyle S}{Mn(acac)_2}}$$

III
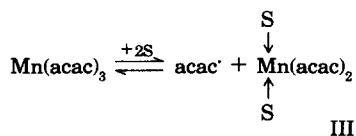
The charge transfer complex I formed by the π-electron coordination of the monomers breaks down easily to form the initiating free radical in combination with the monomer:

$$\begin{array}{c}
\text{M} \\
\downarrow \\
\text{Mn(acac)}_3 \rightleftharpoons \text{(acac)M}^{\cdot} + \text{Mn(acac)}_2 \\
\uparrow \\
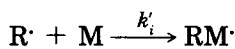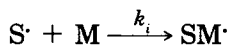\text{M} \qquad\qquad \text{(R}^{\cdot}\text{)}
\end{array}$$

The free radicals formed interact with the active sites on the silk matrix forming silk macroradical. Monomer molecules form propagating chains at such radical sites, forming grafted silk. At higher concentrations of the complex, the free radicals produced on silk might be oxidized thus terminating reactive sites. In addition, the complex might interact with growing PMMA macroradicals producing homopolymer.

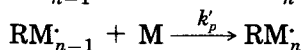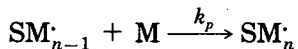### Reaction Mechanism and Rate Equation
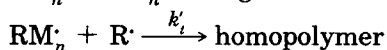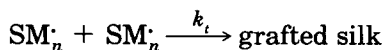
Production of free radical on silk backbone:

$$\text{SH} + \text{R}^{\cdot} \xrightarrow{k} \text{S}^{\cdot} + \text{RH}$$

Initiation:

$$\text{S}^{\cdot} + \text{M} \xrightarrow{k_i} \text{SM}^{\cdot}$$
$$\text{R}^{\cdot} + \text{M} \xrightarrow{k_i'} \text{RM}^{\cdot}$$

Propogation:

$$\text{SM}^{\cdot}_{n-1} + \text{M} \xrightarrow{k_p} \text{SM}^{\cdot}_{n}$$
$$\text{RM}^{\cdot}_{n-1} + \text{M} \xrightarrow{k_p'} \text{RM}^{\cdot}_{n}$$

Termination:

$$\text{SM}^{\cdot}_{n} + \text{SM}^{\cdot}_{n} \xrightarrow{k_t} \text{grafted silk}$$
$$\text{RM}^{\cdot}_{n} + \text{R}^{\cdot} \xrightarrow{k_t'} \text{homopolymer}$$

Oxidation:

$$\text{S}^{\cdot} + \text{Mn(acac)}_3 \longrightarrow \text{oxidation products of silk} + \text{Mn(acac)}_2$$
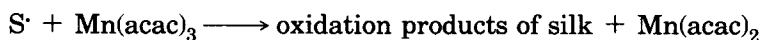
where SH is silk fiber and S· is the corresponding radical. Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows:

$$-\frac{d[\text{S}\cdot]}{dt} = k[\text{SH}]\,[\text{complex}] - k_i[\text{S}\cdot]\,[\text{M}] = 0,\ [\text{S}\cdot] = \frac{k[\text{SH}]\,[\text{complex}]}{k_i[\text{M}]}$$

$$-\frac{d[\text{SM}\cdot_n]}{dt} = k_i[\text{S}\cdot]\,[\text{M}] - k_t[\text{SM}\cdot_n]^2 = 0,\ [\text{SM}\cdot_n] = \left(\frac{k_i[\text{S}\cdot]\,[\text{M}]}{k_t}\right)^{\!1/2}$$
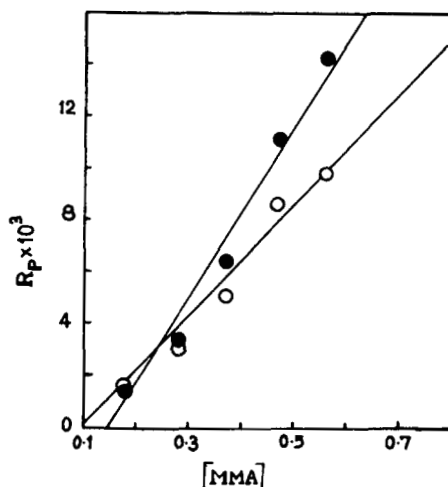
Fig. 4. Plot of R_p vs. [M]: (●) 2 h, (○) 4 h.

Then, putting the value of [S·] in the above equation,

$$[SM\cdot_n] = \left(\frac{k[SH]\,[\text{complex}]}{k_t}\right)^{1/2}$$

Then,

$$R_p = k_p(k/k_t)^{1/2}[SH]^{1/2}[\text{complex}]^{1/2}[M]$$

Plots of R_p vs. [M] (Fig. 4) and R_p vs. [complex]$^{1/2}$ (Fig. 5) are linear confirming the validity of the above reaction scheme.

Effect of Temperature

The graft copolymerization was studied at 40°C, 45°C, 50°C, and 55°C. Results indicate that, with increasing temperature, the graft yield increases. This can be ascribed to (1) greater ease of acetylacetonate free radical formation, (2) increased solubility, and (3) enhanced diffusion rate of the monomer.
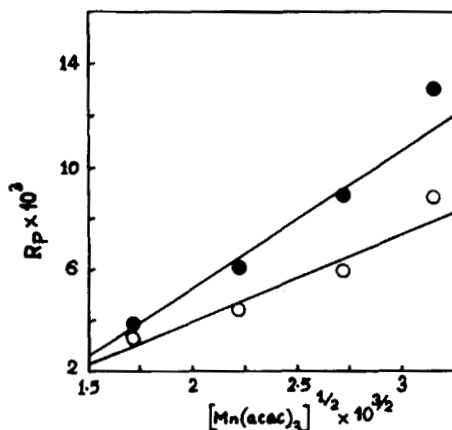

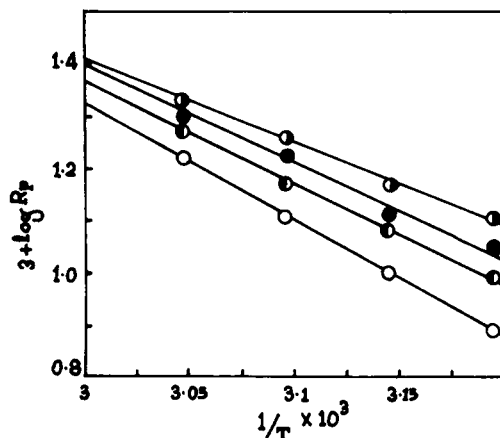Fig. 5. Plot of R_p vs. [Mn(acac)$_3$]$^{1/2}$: (●) 2 h, (○) 4 h.

Fig. 6.   Arrhenius plot of log R_p vs. $1/T$: (○) Mn(acac)$_3$; (◑) Mn(acac)$_3$(IQ); (●) Mn(acac)$_3$(TD); (◐) Mn(acac)$_3$(PL).

From the slopes of the Arrhenius plot of log R_p vs. $1/T$ (Fig. 6), the overall energy of activation (E_a) was calculated. E_a accounts for (1) energy of activation for the decomposition of the initiator (E_d), (2) energy of activation for the growing radical to chain transfer with the backbone to form silk macroradical (E_{tr}), (3) activation energy for propagation (E_p), and (4) energy of activation for termination $(E_t$. These terms are related to E_a by the expression:

$$E_a = \frac{1}{2} E_d + \frac{1}{2} E_{tr} + E_p - \frac{1}{2} E_t$$

Using the value of $E_p - \frac{1}{2} E_t = 18.9$ kJ/mol given by Tobolsky,[23] the sum $\frac{1}{2} (E_d + E_{tr})$ for the various initiators is evaluated (Table I).

The chain transfer step involves the abstraction of H· from the active centers on silk backbone by acetylacetonate free radical generated from the initiator. Evidently, the energy of activation in the chain transfer process (E_{tr}) must be identical for all the initiators. The data, therefore, indicate the following order of reactivity:

$$Mn(acac)_3 \rangle Co(acac)_3 \rangle VO(acac)_2$$
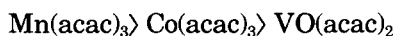
Similarly, the adducts are also more active initiators when compared to Mn(acac)$_3$. These observations are in accordance with the experimental findings.

TABLE I
Activation Energy for Various Initiators (kJ/mol)

Initiator	E_a	$\frac{1}{2}(E_d + E_{tr})$	Initiator	E_a	$\frac{1}{2}(E_d + E_{tr})$
Mn(acac)$_3$	41.0	22.1	Mn(acac)$_3$(IQ)	34.2	15.3
Co(acac)$_3$	45.8	26.9	Mn(acac)$_3$(TD)	37.0	18.1
VO(acac)$_2$	57.9	39.0	Mn(acac)$_3$(PL)	31.8	12.9
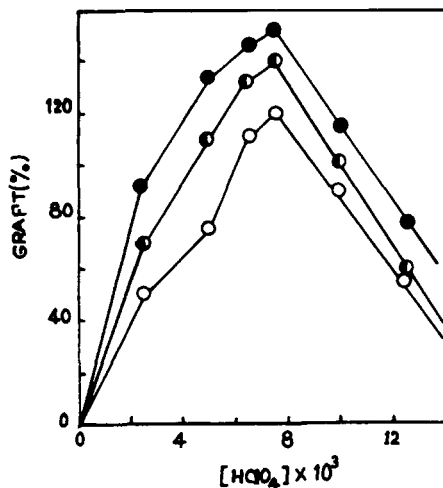
Fig. 7.   Effect of [HClO$_4$] on graft yield: [MMA] = 0.4694 mol/L, [ethyl acetate] = 1.022 mol/L, M:L = 1:100, 50°C, 3 h; [Mn(acac)$_3$] (mol/L): (○) 0.004; (◐) 0.007; (●) 0.0085.

Effect of Acid Concentration

The graft copolymerization was studied within the ranges 2.5–15.0 × 10^{-3} mol/L of HClO$_4$ concentration. With increase in acid concentration, grafting increases up to 7.5 × 10^{-3} mol/L, decreasing significantly thereafter (Fig. 7). At lower concentrations of HClO$_4$, the decomposition of the initiator is presumably facilitated, leading to the formation of a larger number of initiating free radicals. At higher concentrations of the acid, the free radical generation steps are presumably reversed:

$$Mn(acac)_3 \rightleftharpoons acac^. + Mn(acac)_2$$

$$Mn(acac)_3 + M \rightleftharpoons (acac)M^. + Mn(acac)_2$$
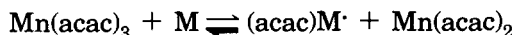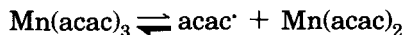
Effect of Polymerization Medium

Organic solvents greatly affect the graft yield. The effect of different types of solvents (alcoholic solvents, chain transfer solvents, organic acids, and solvents acting as solubilizers for the monomer) has been investigated. With alcoholic solvents the graft yield follows the order: MeOH ⟩ EtOH ⟩ n-Pr–OH ⟩ n-butyl–OH ⟩ amyl alcohol. With chain transfer solvents the order is CHCl$_3$ ⟩ CCl$_4$ ⟩ EtSH (yield ∼ 1%). With other solvents the order is formic acid ⟩ acetic acid ⟩ acetone ⟩ DMF ⟩ dioxane.

The dependence of grafting upon the nature of the solvent suggest that the solvents examined differed considerably in their (1) capability of swelling silk, (2) miscibility with monomer, (3) formation of solvent radical from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of silk, (5) increased concentration of the initiating free radical by assisting the degradation of the chelate, and (6) termination of the graft radical and silk macroradical via chain transfer. While the first five factors favor grafting by simplifying access and diffusion of the monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.
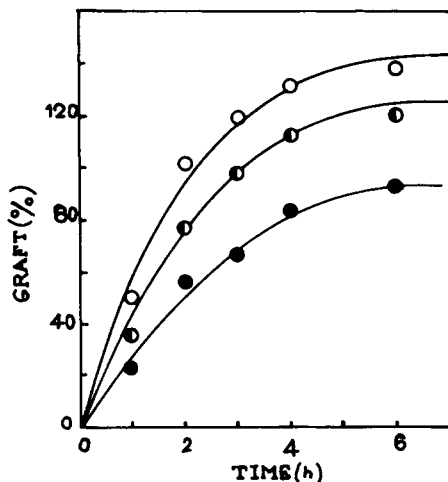
Fig. 8.   Effect of surfactants on graft yield: [Mn(acac)₃] = 0.007 mol/L, [ethyl acetate] = 0.894 mol/L, [HClO₄] = 5 × 10⁻³ mol/L, [MMA] = 0.3756 mol/L, M:L = 1:100, 50°C, surfactant at CMC: (○) NaLS; (●) CTABr; (◑) control.

In case of alcohols the order of graft yield suggests that, with increasing molecular weight of the alcohol, graft yield decreases. The lowering of graft yield could be ascribed to the adverse effect of water on the swelling of silk. The hydrophobic character of the solvent increases from methanol to amyl alcohol, thereby hindering monomer access to reactive sites on the silk.

Effect of Surfactants and Inhibitors

Graft copolymerization was studied in the presence of anionic surfactant, sodium lauryl sulfate (NaLS) and cationic micelles of cetyl trimethyl ammonium bromide (CTABr) at critical micellar concentrations (CMC) (Fig. 8). It is observed that addition of NaLS increases the graft yield whereas
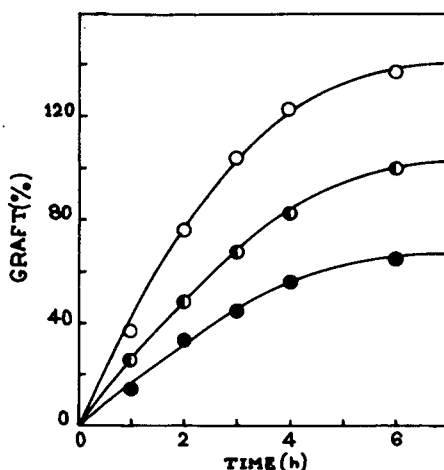

Fig. 9.   Effect of inhibitor concentration on graft yield: [Mn(acac)₃] = 0.0075 mol/L, [ethyl acetate] = 1.277 mol/L, [HClO₄] = 6 × 10⁻³ mol/L, [MMA] = 0.4694 mol/L, M:L = 1:100, 50°C. (●) Picryl chloride: (◑) hydroquinone; (○) control.

CTABr decreases it. At CMC, the micelles formed are roughly spherical in size. In case of micelles of NaLS, the sulfate ions form the Gouy–Chapman double layer.[24] The entanglement of these micelles with the silk fibers facilitates the formation of charge transfer complex with the initiator.[25] The concentration of the initiator is increased in the vicinity of the fiber which enhances the free radical formation on silk backbone, resulting in an increased graft yield. In case of CTABr, the positively charged NH_4^+ ions form the Gouy–Chapman double layer. The entanglement of the micelles with silk fiber presumably results in decreased tendency of the initiator to form charge transfer complex with the fiber.

Effect of inhibitors like picryl chloride and hydroquinone on graft yield has been studied (Fig. 9). The graft yield is greatly suppressed in presence of either inhibitor, picryl chloride being a more efficient inhibitor than hydroquinone. The extent of inhibition increases with increasing inhibitor concentration. At higher concentrations, it traps more and more free radicals, reducing the molecular size of the graft and hence decreasing the graft yield.

Determination of Chain Transfer Constants (C_M)

The grafted PMMA is regenerated by HCl-digestion technique.[12] The average molecular weight ($\overline{M}$) of such samples was determined viscometrically employing the relationship[26]:

$$[\eta] = 9.6 \times 10^{-5} (\overline{M})^{0.69}$$

The chain transfer constant for various chain transfer solvents was determined using the relationship

$$\frac{1}{\overline{P}_n} = \left(\frac{1}{\overline{P}_n}\right)_0 + C_M \frac{[S]}{[M]}$$

where $\overline{P}_n$ = degree of polymerization which is evaluated from $\overline{M}$ data and [S] = concentration of the chain transfer solvent = 1.0 mol/L.
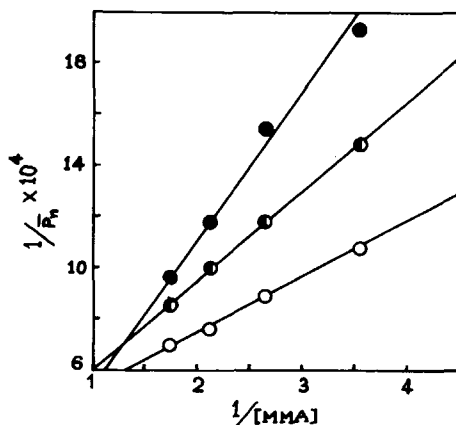

Fig. 10. Plot of $1/\overline{P}_n$ vs. $1/[M]$: (○) dioxane; (◑) $CHCl_3$; (●) CCl_4.

Keeping the concentrations of the chain transfer solvent constant, the monomer (MMA) concentration is varied in the range 0.1878–0.5634 mol/L. The average molecular weight of grafted PMMA was found to increase with increasing concentration of the monomer. The plot of $1/\overline{P}_n$ vs. $1/[M]$ (Fig. 10) was found to be linear. This is expected of the observed kinetic behavior of the system where the termination step is mutual. From the slope of the plots the chain transfer constants were found to be 2.14×10^{-4}, 3.78×10^{-4}, and 5.36×10^{-4} for dioxane, $CHCl_3$, and CCl_4, respectively.

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