Grafting Vinyl Monomers onto Silk Fibers. XIV. Graft Copolymerization of Methyl Methacrylate onto Silk Using Peroxydiphosphate–Ascorbic Acid Redox System

INTRODUCTION

Literature surveys reveal that peroxydisulfate has been used extensively for both vinyl polymerization and grafting onto several natural and synthetic fibers.[1-9] Though peroxydiphosphate is isoelectronic with peroxydisulfate, relatively little attention has been paid to the use of peroxydiphosphate as an initiator for vinyl polymerization.

Nayak, Lenka, and Mishra[10-13] have reported grafting onto silk, wood, and cellulose using peroxydiphosphate as the initiator. This note presents the results of graft copolymerization of methyl methacrylate onto silk using peroxydiphosphate–ascorbic acid as the initiator.
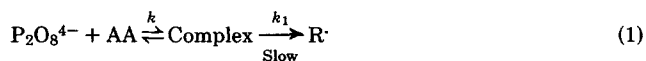
EXPERIMENTAL

The raw silk fibers were collected from Government Silk Factory, Jabalpur, India, and were purified in the usual manner.[14] MMA was washed by the method mentioned in our previous note.[14] Potassium peroxydiphosphate (a gift sample from F.M.C. Corp. USA), ascorbic acid (AR,BDH), H_2SO_4 ($\simeq 18M$ AR,BDH) were used. The grafting reaction was carried out according to our previous note.[14]

RESULTS AND DISCUSSION

The graft copolymerization of methyl methacrylate onto silk was studied in aqueous medium. The rate of grafting was calculated by varying monomer, acid, initiator, ascorbic acid concentration, and temperature. The rate of grafting has been found to increase with the increase in monomer concentration within the range of $(27.56–103.26) \times 10^{-2}M$ (Fig. 1). The reasons might be (1) the complexation of silk with monomer, which is required for enhancing monomer reactivity, would be favored at higher monomer concentration, (2) gel effect, i.e., the solubility of poly(methyl methacrylate) in its own monomer thereby increasing the viscosity of the medium and hindering the mutual termination of the growing chains.

The effect of ascorbic acid concentration was studied by varying the concentration of ascorbic acid from 0.5 to $5.0 \times 10^{-3}M$. The graft yield increases up to $3.5 \times 10^{-3}M$ and thereafter decreases. Edwards[15,16] and Sigla[17] reported that oxyanion reactions are acid dependent. Hence, as the concentration of acid is increased, more active species like $H_3P_2O_8^-$ and $H_2P_2O_8^{-2}$ are formed, which are responsible for creating a large number of free radicals on the silk backbone, and hence, facilitate the occurrence of grafting. The temperature was varied from 40 to 60°C. The rate of grafting was increased by increasing the temperature.

The effect of some solvents were studied; HCOOH proved to be the most effective for grafting. On the other hand, swelling solvents such as dimethyl formamide and ethanol proved to be ineffective. The initiator concentration was varied from 3.5 to $10.0 \times 10^{-3}M$. The graft yield increases to $5.0 \times 10^{-3}M$, and thereafter decreases (Fig. 2). In the presence of acid, peroxydiphosphate dissociates to give rise to $H_2PO_4^-$, OH^-, and HPO_4^{--} (R·) radicals which interact with the groups present on the silk backbone producing silk macroradicals. Secondly, $P_2O_8^{4-}$ might form a complex with ascorbic acid which breaks down giving rise to the ascorbic acid free radical (R·), which is the active species for initiation:

$$P_2O_8^{4-} + AA \overset{k}{\rightleftharpoons} \text{Complex} \underset{\text{Slow}}{\overset{k_1}{\longrightarrow}} R\cdot \tag{1}$$

$$\text{\textbackslash\textbackslash\textbackslash SH} + R\cdot \overset{k_2}{\longrightarrow} \text{\textbackslash\textbackslash\textbackslash S}\cdot + RH \tag{2}$$

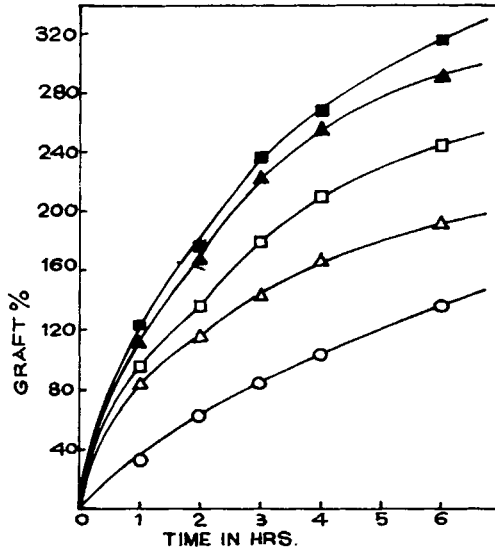where ⋙SH → active groups present on silk backbone. ⋙S· → silk macroradical.

Fig. 1. Effect of [MMA] on graft yield: $[PP] = 5.0 \times 10^{-3}M$; $[H^+] = 1.5 \times 10^{-2}M$; $[AA] = 3.5 \times 10^{-3}M$; Temp. $= 50°C$; $M:L = 1:100$; (O) $[MMA] = 27.56 \times 10^{-2}M$; ($\triangle$) $[MMA] = 46.94 \times 10^{-2}M$; ($\square$) $[MMA] = 65.71 \times 10^{-2}M$; ($\blacktriangle$) $[MMA] = 84.59 \times 10^{-2}M$; ($\blacksquare$) $[MMA] = 103.26 \times 10^{-2}M$.

Initiation:

$$\text{\textasciitilde\textasciitilde S}^{\cdot} + M \xrightarrow{k_i} \text{\textasciitilde\textasciitilde SM}_1^{\cdot} \tag{3}$$

Propagation:

$$\text{\textasciitilde\textasciitilde SM}_1^{\cdot} + M \xrightarrow{k_p} \text{\textasciitilde\textasciitilde SM}_2^{\cdot}$$
$$\vdots$$
$$\text{\textasciitilde\textasciitilde SM}_{n-1}^{\cdot} + M \xrightarrow{k_p} \text{\textasciitilde\textasciitilde SM}_n^{\cdot} \tag{4}$$
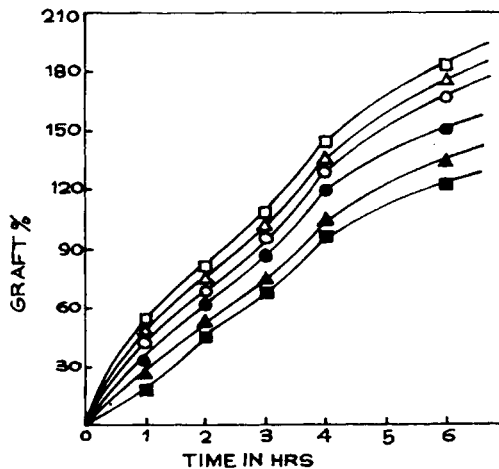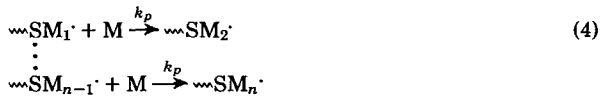

Fig. 2. Effect of [PP] on graft yield: $[MMA] = 46.94 \times 10^{-2}M$; $[H^+] = 1.5 \times 10^{-2}M$; $[AA] = 1.0 \times 10^{-3}M$; Temp. $= 50°C$; $M:L = 1:100$. (O) $[PP] = 3.5 \times 10^{-3}M$; ($\triangle$) $[PP] = 4.25 \times 10^{-3}M$; ($\square$) $[PP] = 5.0 \times 10^{-3}M$; ($\bullet$) $[PP] = 6.75 \times 10^{-3}M$; ($\blacktriangle$) $[PP] = 8.25 \times 10^{-3}M$; ($\blacksquare$) $[PP] = 10.00 \times 10^{-3}M$.
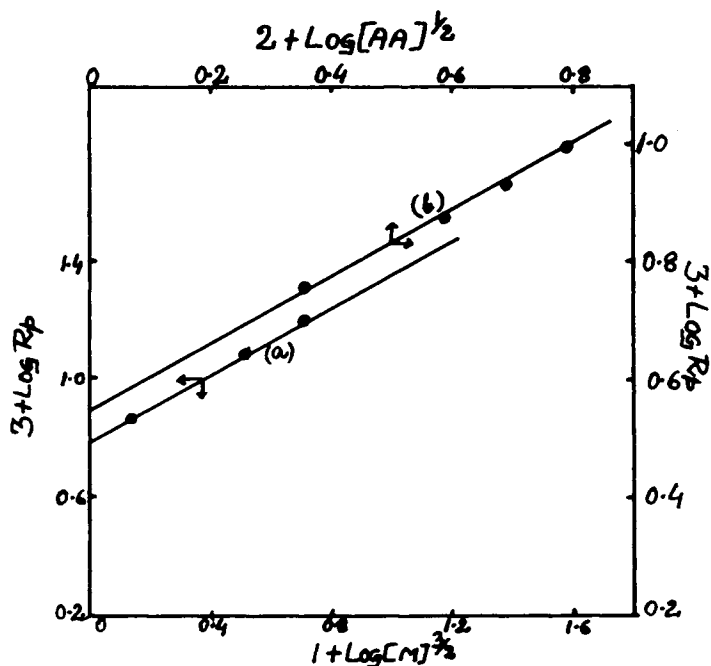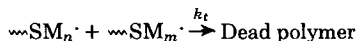
Fig. 3. (a) Plot of log [M]$^{3/2}$ vs. log R_p; (b) Plot of log [AA]$^{1/2}$ vs. log R_p for grafting MMA onto silk using peroxydiphosphate–ascorbic acid redox system.

Termination:

$$\text{wwSM}_n{}^{\cdot} + \text{wwSM}_m{}^{\cdot} \xrightarrow{k_t} \text{Dead polymer}$$

Oxidation:

$$\text{wwS}^{\cdot} + P_2O_8{}^{4-} \xrightarrow{k_o} \text{Oxidation products}$$

Considering steady-rate principle for [R$^{\cdot}$]·[S$^{\cdot}$] and [SM$^{\cdot}$] etc., the rate of polymerization was derived to be

$$R_p = k_p \left[\frac{k_i K k_1 [\text{AA}][P_2O_8{}^{4-}]}{k_t\{k_i[M] + k_o[P_2O_8{}^{4-}]\}} \right]^{1/2} [M]^{3/2}$$

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

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