

Graft Copolymerization of Methyl Methacrylate onto Wool by Use of Ferrous Ion–Peroxdiphosphate

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Synopsis

Polymethyl methacrylate has been graft copolymerized onto wool using a ferrous ion–peroxodiphosphate initiator system in an aqueous methanol medium. Graft copolymerization was carried out at 20°C, 30°C, 40°C, and 50°C. The rate of grafting was found to be dependent on the concentrations of monomer (MMA), ferrous ion (Fe^{2+}), peroxodiphosphate (PP), wool (w), and reaction temperature. [Acid], solvent composition and ionic strength were also varied to study their effect on grafting. Based on the experimental results, a suitable kinetic scheme was proposed. Rate and thermodynamic parameters were also varied to study their effect on grafting. Based on the experimental results, a suitable kinetic scheme was proposed. Rate and thermodynamic parameters were also evaluated.

INTRODUCTION

Conventional radical initiators like persulphate,¹ benzoyl peroxide,² azobisisobutyronitrile,³ and Fenton's reagent⁴ were used for the graft copolymerization of vinyl monomers onto wool. In the present paper, we report the kinetics of graft copolymerization of methyl methacrylate onto wool in presence of ferrous ion–peroxodiphosphate in aqueous methanol medium (25% v/v).

EXPERIMENTAL

Wool (Binny Ltd., Bangalore) and peroxodiphosphate (FMC, U.S.A.) were used as such. Methanol (Lab reagent, Madras) dehydrated with quick lime was used (bp 65°C). All other chemicals used were of AnalaR grade. Kinetic runs were carried out in conical flasks (250 mL) fitted with a nitrogen inlet and outlet. Wool (0.2 g) was suspended in the reaction medium, and required amounts of ferrous sulphate solution and monomer were added to this. The reaction mixture was thermostated at $50 \pm 0.1^\circ\text{C}$ and flushed with oxygen free nitrogen for 20 min. At the end of deaeration, the required amount of peroxodiphosphate solution was added to the reaction mixture. The reaction vessel was sealed with rubber gaskets to ensure inert atmosphere. The reaction was arrested after a definite time interval by immediately cooling the reaction vessel in ice cold water. The grafted wool was filtered from the reaction mixture using an IG 3 sintered glass filter. It was washed several times with distilled water, dried at 60°C, conditioned at 65% RH, and weighed to constant weight. The rate of grafting (R_g) was calculated from the weight of graft obtained.⁵ A kinetic scheme was proposed with the experimentally obtained data. Alkaline solubility was determined by the method of Harris and Smith.⁶ Dye uptake was determined from visible

spectral data obtained using the UV vis-spectrophotometer. The tensile strength of the fibers was determined using an Instron tensile tester at a crosshead speed of 0.5 cm/min and chart speed of 10 cm/min. Chain length measurements were done⁷ by the viscometric method, using benzene solvent at 25°C for the isolated grafts which were obtained by the acid digestion method.

RESULTS AND DISCUSSION

The rate of grafting (R_g) was found to be directly proportional to the first power of [MMA], half-power of [PP], and 0.32 power of $[Fe^{2+}]$ [Fig. 1(A)–1(C)]. The chain length was directly dependent on $[MMA]^{1.0}$ and inversely dependent on $[PP]^{0.5}$ and $[Fe^{2+}]^{0.32}$ [Fig. 2(A)–2(c)]. Due to the unavailability of enough grafted wool sample, the proportionality of chain length with respect to wool could not be determined. From the observed experimental data a probable reaction mechanism was proposed and rate expressions for R_g and n were derived.

(i) Production of wool radical ($W\cdot$)⁸:

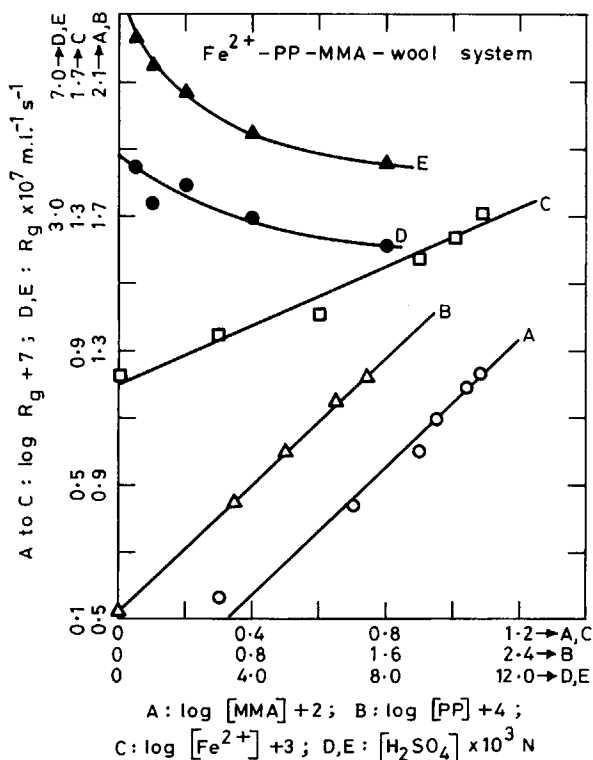
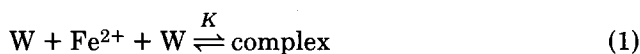
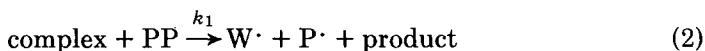


Fig. 1. Dependence of rate of grafting (R_g) on (A) [monomer], (B) [peroxodiphosphate], (C) [ferrous ion], (D,E) [sulphuric acid] at 50°C. (A) $[PP] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[Fe^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g; pH = 2.6. (B) $[Fe^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[MMA] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g; pH = 2.5–2.9. (C) $[PP] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[MMA] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g; pH = 2.4–1.5. (D) $[Fe^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[PP] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g; $[MMA] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; μ not maintained constant. (E) $[Fe^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[PP] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g; $[MMA] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; $\mu = 0.095M$.



(ii) Initiation with monomer (M):



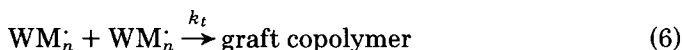
(iii) Propagation:



⋮ ⋮ ⋮ ⋮



(iv) Mutual termination of graft polymer radical:



(v) Radical recombination:



Hence,

$$R_g = k_g [\text{PP}]^{1/2} [\text{Fe}^{2+}]^{1/2} [\text{W}] [\text{M}] \quad (8)$$

where $k_g = k_p k_i^{1/2} K^{1/2} / k_t^{1/2}$ and chain length

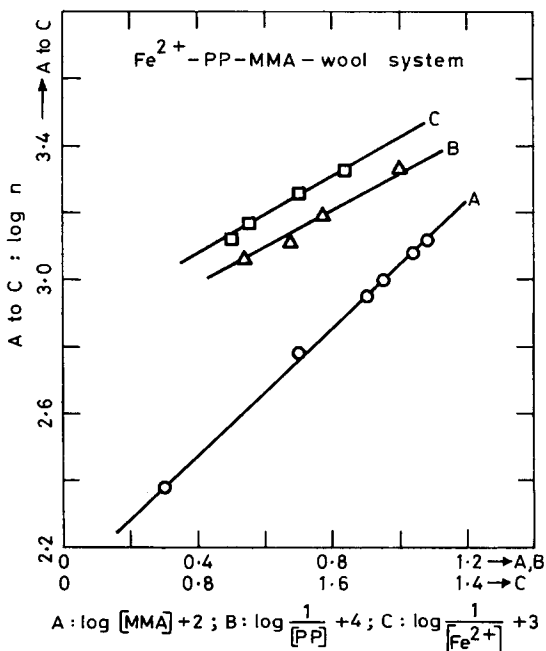


Fig. 2. Chain length dependence on (A) [monomer]; (B) [peroxodiphosphate]; (C) [ferrous ion] at 50°C. (A) $[\text{PP}] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[\text{Fe}^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g. (B) $[\text{Fe}^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[\text{MMA}] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g. (C) $[\text{PP}] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[\text{MMA}] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g.

$$n = k_p [M] / k_t^{1/2} k_i^{1/2} K^{1/2} [PP]^{1/2} [Fe^{2+}]^{1/2} [W]$$

The expected order of one for wool with respect to R_g was not observed. Below 0.17 g of wool, it was independent of wool, and above this weight a steep increase and decrease in R_g values were obtained [Fig. 3(A)]. This may be due to the catalytic effect of wool on the rate of grafting in this system.

Rate and Thermodynamic Parameters

The constant k_g was evaluated from the plots of (i) R_g vs. $[PP]^{0.5}$, (ii) R_g vs. $[MMA]^{1.0}$, and (iii) R_g vs. $[Fe^{2+}]^{0.5}$, and the average was taken (2.55×10^{-3}). The overall activation energy was evaluated to be $10.4 \text{ kcal}\cdot\text{mol}^{-1}$. ΔS^\ddagger , ΔH^\ddagger , and ΔG^\ddagger were found to be $-82.44 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mol}^{-1}$, $9.76 \text{ kcal}\cdot\text{mol}^{-1}$, and $36.38 \text{ kcal}\cdot\text{mol}^{-1}$, respectively.

Effect of [Sulphuric Acid] on R_g

Increasing the concentration of sulphuric acid (both when μ was maintained constant and not maintained constant) decreased the rate of grafting [Figs. 1(E) and 1(D)]. The initial pH of the reaction medium was 2.8, where the predominant species present was $H_2P_2O_8^-$ (nearly 100%). As the pH decreased, the percentage of this species also decreased, and formation of higher protonated species took place.⁹ The latter species may not be as effective as $H_2P_2O_8^-$ hence accounting for the decrease in R_g .

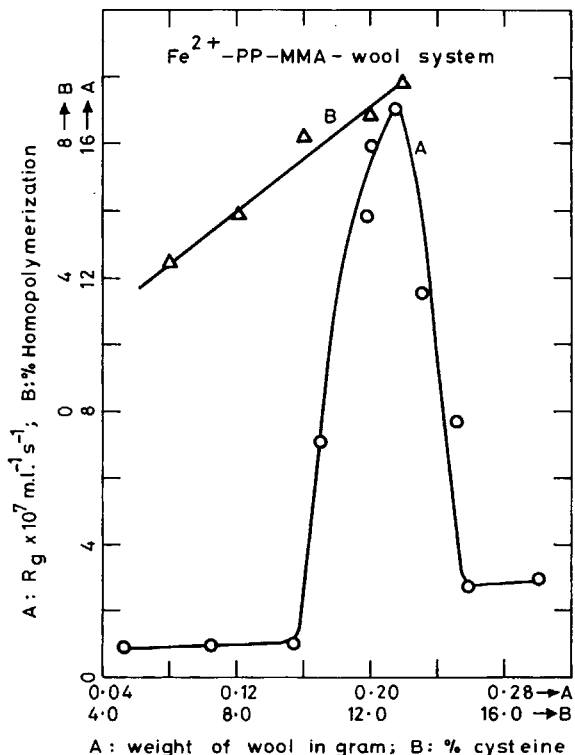


Fig. 3. (A) Effect of wool on rate of grafting; (B) homopolymerization with cysteine at 50°C. (A,B) $[Fe^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[PP] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[MMA] = 0.1058 \text{ m}\cdot\text{L}^{-1}$.

Effect of Ionic Strength

Ionic strength was varied from 0.1 to 0.5 $\text{m}\cdot\text{L}^{-1}$ using sodium perchlorate. The rate of grafting was found to decrease with increasing amounts of sodium perchlorate [Fig. 4(A)].

Effect of Methanol

When methanol composition in the reaction medium was varied from 0% to 100% (v/v), the maximum value of R_g was noticed at 25% of methanol [Fig. 4(B)]. By increasing the composition of methanol, the viscosity of the methanol-water mixture increased, and the dielectric constant of the above binary mixture decreased. The increase in viscosity increased the rate of grafting by facilitating the diffusion of reactants in the reaction medium but a decrease in dielectric constant decreased the rate of grafting probably by forming ion pairs, thus decreasing the available concentration of the ionic reactants needed for the activation step. Due to the combination of these effects, the change in the amount of methanol in the reaction medium gave maximum grafting at 25% methanol.

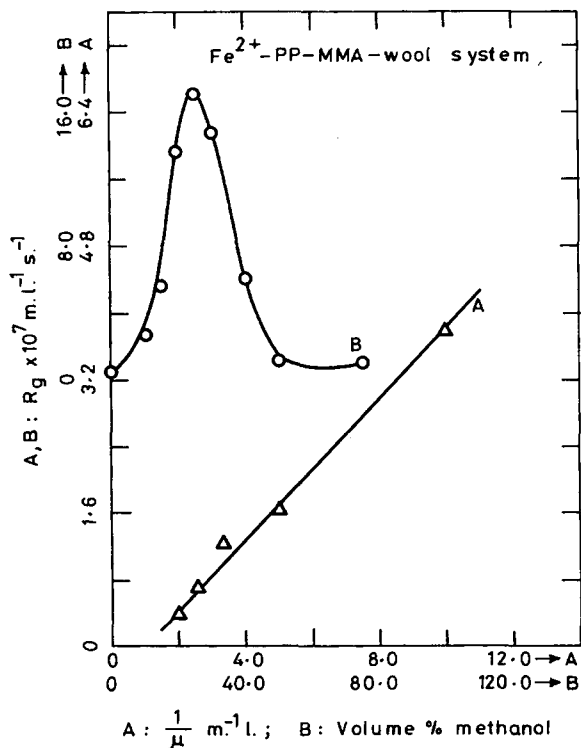


Fig. 4. Dependence of rate of grafting on (A) ionic strength and (B) methanol composition at 50°C. (A,B) $[\text{PP}] = 3 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[\text{Fe}^{2+}] = 10 \times 10^{-3} \text{ m}\cdot\text{L}^{-1}$; $[\text{MMA}] = 0.1058 \text{ m}\cdot\text{L}^{-1}$; wool = 0.2 g.

Effect of Temperature

Increase of temperature from 20°C to 50°C produced an increase in the rate of grafting at different monomer concentrations (Table I). The increase in the rate of grafting may be due to the creation of more free radicals in the reaction medium, the swellability of wool, the solubility of monomer in the reaction medium and its diffusion into fibers, and initiation and propagation of the graft.

Proof of Grafting

The side chains were isolated by a two-step acid digestion method.¹⁰ The infrared spectra was taken using a Perkin-Elmer Model 337 grating infrared spectrophotometer for the isolated residue. The presence of amide and ester absorption bands^{11,12} was seen in the spectra taken. NMR spectra also confirmed the above result.

Site of Grafting

When wool was replaced by amino acids like glycine, alanine, phenyl alanine, cysteine, glutamic acid, aspartic acid, etc., and the polymerization conducted under similar conditions only cysteine produced homopolymer showing that —SH groups of cysteine participated in the initiation reaction [Fig. 3(B)]. The probable reactive site on the wool backbone may be the —SH group of cysteine present in it.

Properties of Grafted Wool Fibers

Dye uptake for the grafted wool fibers was greater than that of the original wool fiber (Table II), though with increase in % grafting a decrease in dye uptake was noticed. At lower % grafting, the diffusion of dye into the reactive sites in wool was easy. At higher % grafting, the deposited polymethyl methacrylate probably made the diffusion of dye into the fiber difficult. Hence, with increasing percent grafting, % dye uptake by the grafted wool was lowered. Alkali

TABLE I
PP-Fe²⁺-MMA-Wool^a in Aqueous Methanol Medium. Temperature Variation

[MMA] (m·L ⁻¹)	$R_g \times 10^7 \text{ m}\cdot\text{L}^{-1}\cdot\text{S}^{-1}$			
	20°C	30°C	40°C	50°C
0.0235	—	1.18	—	3.64
0.0470	0.54	2.32	4.69	6.94
0.0750	0.83	4.02	7.14	10.78
0.0940	—	4.64	—	15.64
0.1058	—	5.18	—	15.40
0.1175	—	6.00	—	17.18
0.1300	1.54	6.67	12.34	—
0.1410	1.72	7.24	13.00	—
0.1500	1.80	7.66	14.10	—
0.1600	2.15	8.35	15.24	—
0.1800	2.34	8.86	16.35	—

^a [Fe²⁺] = 10 × 10⁻³ m·L⁻¹; solvent = 25% methanol (v/v); [PP] = 3 × 10⁻³ m·L⁻¹; wool = 0.2 g; pH = 2.8; time = 240 min.

TABLE II
Properties of Grafted and Original Wool Fibers

% grafting	% dye uptake	Alkaline solubility	Tensile strength (kg/mm ²)
0	14.40	16.86	17.79
10.28	—	10.80	—
19.95	—	9.80	—
29.66	—	8.20	13.48
33.70	28.13	—	—
43.51	25.00	7.16	13.28
92.90	21.87	—	—
119.10	18.75	—	—

breaks the disulphide linkage present in wool thereby the wool dissolves. This linkage is probably protected by grafting, thus accounting for the decreased alkaline solubility with increasing % grafting. The tensile strength for the grafted wool fiber was less than that of the original wool sample (Table II).

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