

Graft Polymerization of Methyl Methacrylate onto Polyvinyl Alcohol Using Ce^{4+} Initiator

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ABSTRACT: Methyl methacrylate (MMA) was graft polymerized onto polyvinyl alcohol (PVA) using ceric ammonium sulfate as an initiator in aqueous medium. The grafting efficiency of MMA was studied as a function of monomer and initiator concentration, time, pH, and temperature. Grafting efficiency was found to be optimum at a particular level of ceric ammonium sulfate ($3.16 \times 10^{-3} \text{ mol L}^{-1}$), PVA (1.0 g L^{-1}), MMA (0.469 mol L^{-1}), H_2SO_4 (0.188 mol L^{-1}), temperature (45°C), and time (4 h). The probable reasons for the influence of reaction variable on the observed trend of MMA towards grafting have been discussed. Acid hydrolysis and infrared spectroscopy were used for the confirmation of graft copolymer formation. Thermogravimetric analysis of PVA and a representative graft copolymer were studied. The solubility/swellability and the gelatinization characteristics are also reported. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 523–527, 1998

Key words: polyvinyl alcohol; methyl methacrylate; ceric ammonium sulfate; grafting

INTRODUCTION

Graft polymerization is one of the techniques used by a polymer chemist for modifying the chemical and physical properties of a polymer.¹ In the last 3–4 decades, an in-depth study has been made on the synthesis, characterization, and applications of graft copolymers. Polyvinyl alcohol (PVA) is a known biomedical polymer.² Haung and colleagues³ conducted graft copolymerization of acrylic acid onto PVA. Nigam and his coworkers⁴ studied grafting of polystyrene onto PVA. These are mainly performed by methods of chemical initiation and high-energy radiation. Polymers that have inherent antimicrobial properties are generally selected for modification of biomedical polymers. Graft copolymerization of starch and other natural macromolecules can be initi-

ated by transition metal ions⁵ of which Fe^{3+} , Cu^{2+} , Co^{3+} , V^{3+} , and Cr^{6+} are the most commonly used initiators. Ce^{4+} was widely used in the graft modification of cellulose,⁶ fiber,⁷ gelatin,⁸ and starch.⁹

The present investigation deals with the detailed study on some major factors that affect graft polymerization of methyl methacrylate (MMA) onto PVA using ceric ammonium sulfate (CAS) as initiator in aqueous mediums of different pH.

EXPERIMENTAL

Materials

PVA (Burgoyne Burbidges Company, India) was used in graft polymerizations. MMA (Merck, Schuchardt) was purified before use.¹⁰ CAS (E. Merck, India) was dried before use. All other chemicals and solvents were of analytical grade and used without further purification.

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Graft Copolymerization

Graft polymerization reactions were conducted in a two-necked round-bottomed flask kept in a constant temperature water bath maintained at the required temperature. A definite amount of PVA was soaked with a requisite quantity of MMA for ~ 15 min before the start of graft polymerization. Water and sulfuric acid were then added to the reaction mixture. Nitrogen atmosphere was maintained throughout the reaction period. After the specified time interval, the reaction was arrested by quenching with hydroquinone. To remove homopolymers, samples were precipitated out with acetone. Finally, the samples were extracted with an acetone–water mixture in a Soxhlet apparatus for 4 h to dissolve all the homopolymers. The colorless product was dried under vacuum at 50°C for > 24 h to a constant weight.

Evidence of Grafting

Figure 1 shows the infrared (IR) spectra of PVA and a representative PVA-*g*-poly-MMA (PMMA). The spectrum of the grafted PVA indicates a strong absorption band at 1720 cm⁻¹, which is absent in the IR spectrum of PVA. The absorption peak at 1720 cm⁻¹ is due to the presence of the ester group.^{11–16} This provides substantial evidence of grafting onto PVA. To separate the grafted side-chain polymer from the PVA backbone, the grafted copolymer was subjected to acid hydrolysis¹⁷ in a 1 mol L⁻¹ HCl solution at 105°C for 24 h. The IR spectrum of the dried product was found to be identical with that reported for PMMA, which unambiguously indicated the PVA-*g*-PMMA formation.

The IR spectrum was recorded on Perkin–Elmer (no. 883) spectrophotometer in the range of 4000 to 400 cm⁻¹ using KBr pellets for sample preparation (10–15%, w/w).

Thermogravimetric Analysis (TGA)

TGA was conducted using a Stanton Redcraft Thermal Analysis (STA780) in air at a rate of 10°C per minute within the temperature range of 25–600°C.

RESULTS AND DISCUSSION

Grafting Parameter

Percentage grafting (PG), grafting efficiency (GE), and rate of grafting (R_g)¹⁷ were used to evaluate the graft copolymerization.

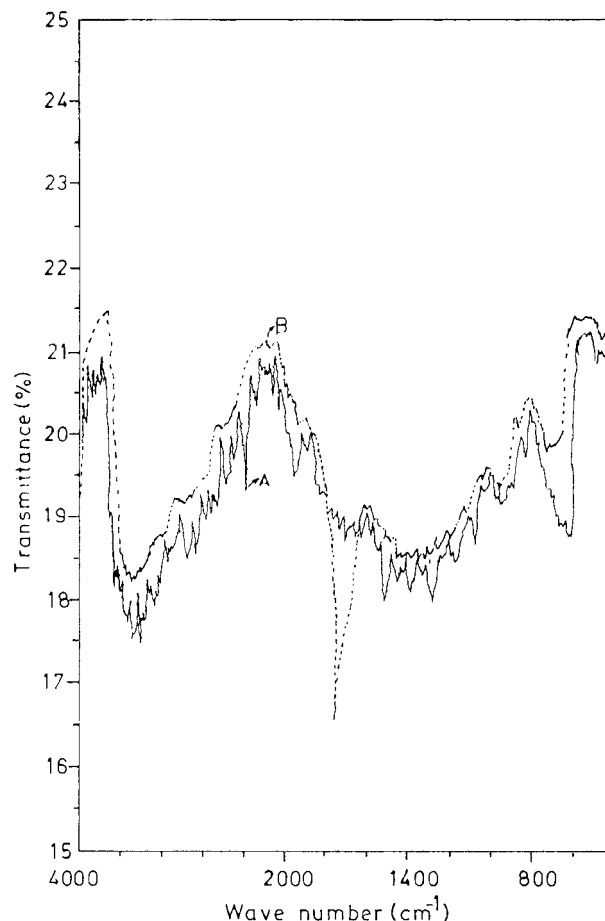


Figure 1 IR spectra of (A) root-PVA and (B) PVA-*g*-PMMA.

$$GE (\%) = \frac{\text{Weight of PMMA grafted}}{\text{Weight of MMA charged}} \times 100$$

$$PG (\%) = \frac{\text{Weight of PMMA grafted}}{\text{Weight of graft copolymer}} \times 100$$

$$R_g = \frac{\text{Weight of PMMA grafted}}{\text{Mol. wt. of MMA} \times \text{reaction time(s)} \times \text{reaction volume (m}^3\text{)}}$$

In the following text, the explanation put forward for the observed trend in (%) GE holds true for (%) grafting also.

Effect of Initiator Concentration

The results obtained by changing the initiator concentration for the graft polymerization are presented in Figure 2. It is observed that the GE increases with an increase in CAS concentration

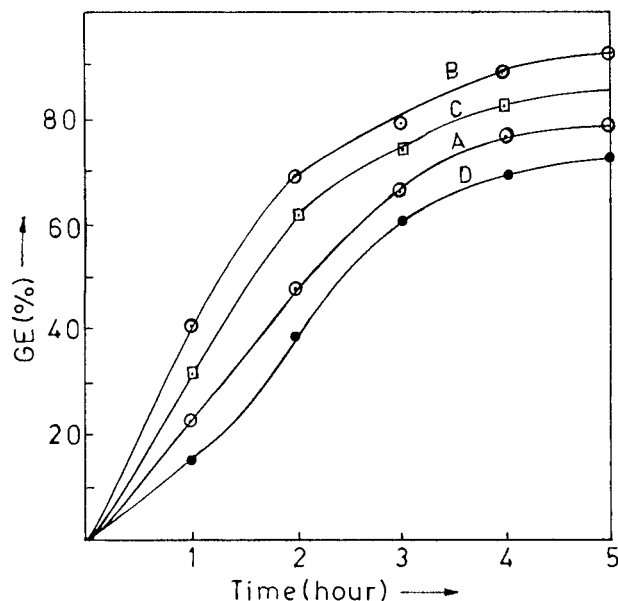


Figure 2 Effect of time and initiator concentration on grafting. $[PVA] = 1.0 \text{ g L}^{-1}$, $[MMA] = 0.469 \text{ mol L}^{-1}$, $[H_2SO_4] = 0.188 \text{ mol L}^{-1}$, temperature = 45°C , (A) $[CAS] = 1.58 \times 10^{-3} \text{ mol L}^{-1}$, (B) $[CAS] = 3.16 \times 10^{-3} \text{ mol L}^{-1}$, (C) $[CAS] = 4.74 \times 10^{-3} \text{ mol L}^{-1}$, and (D) $[CAS] = 6.32 \times 10^{-3} \text{ mol L}^{-1}$.

up to $3.16 \times 10^{-3} \text{ mol L}^{-1}$ and then decreases with a further increase in Ce^{4+} concentration. This can be reasonably explained as follows: as the initiator level increases, the number of free radicals on the PVA backbone increases. This accounts for the substantial increment in GE up to a certain CAS content, beyond which the decrease in GE may be ascribed to (1) the abundance of the free radical species causing faster rate of termination of the chain radicals via bimolecular collision¹; (2) the excess Ce^{4+} may act as a terminator¹⁸; and (3) hindrances to the diffusion of monomer molecules to the active sites on PVA due to the excess of Ce^{4+} ions present in the reaction mixture resulting in preferential homopolymerization.¹ These observations are in close agreement with the report by Patnaik and colleagues.¹⁹

Effect of PVA Concentration

The changes in GE with the variation of PVA concentration are shown in Figure 3. It is evident from the figure that the GE increases with increase in PVA concentration up to 1.0 g L^{-1} and then decreases with a further increment of PVA level. The increase in GE is attributed to the formation of a higher number of radical sites on the PVA back-

bone. A subsequent decrease can be explained on the basis of increase in viscosity of the medium.²⁰

Effect of Monomer Concentration

Figure 4 shows the GE of MMA onto PVA as a function of monomer concentration. It indicates that the GE increases with increasing concentration of MMA initially and then decreases with an increase of MMA beyond 0.469 mol L^{-1} . The initial increase in GE could be associated with the greater availability of monomer molecules in the proximity of PVA. As a result, the chance of molecular collision of the reactants will be greater. Once this is the case, grafting of MMA onto PVA would be favored because of the immobility of PVA macroradicals (sites for grafting). The decrease in GE after a certain level (0.469 mol L^{-1}) of MMA is probably due to the chain transfer from the PVA macroradical onto the monomer.¹⁷

Effect of Acid Concentration

Figure 5 shows the effect of sulfuric acid concentration on GE of MMA onto PVA in the presence of Ce^{4+} initiator. It is observed that the optimum acid concentration is 0.188 mol L^{-1} . The system having no acid content gives rise to poor GE prob-

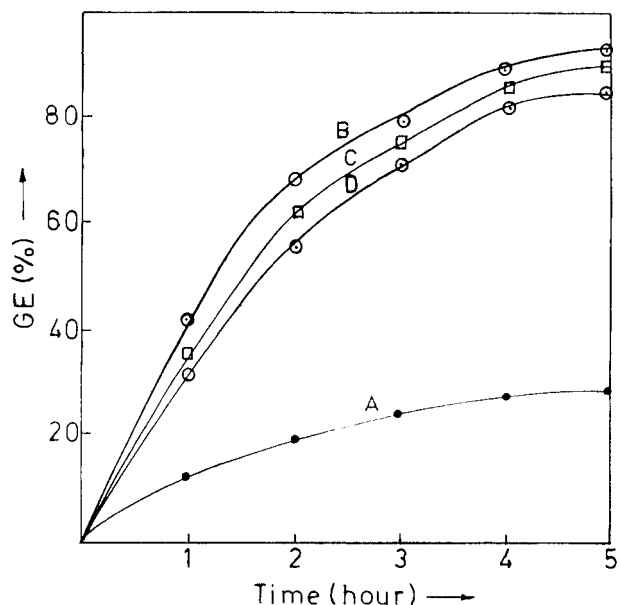


Figure 3 Effect of time and PVA concentration on grafting. $[MMA] = 0.469 \text{ mol L}^{-1}$, $[CAS] = 3.16 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2SO_4] = 0.188 \text{ mol L}^{-1}$, temperature = 45°C , (A) $[PVA] = 0.5 \text{ g L}^{-1}$ (B) $[PVA] = 1.0 \text{ g L}^{-1}$ (C) $[PVA] = 1.5 \text{ g L}^{-1}$ (D) $[PVA] = 2.0 \text{ g L}^{-1}$.

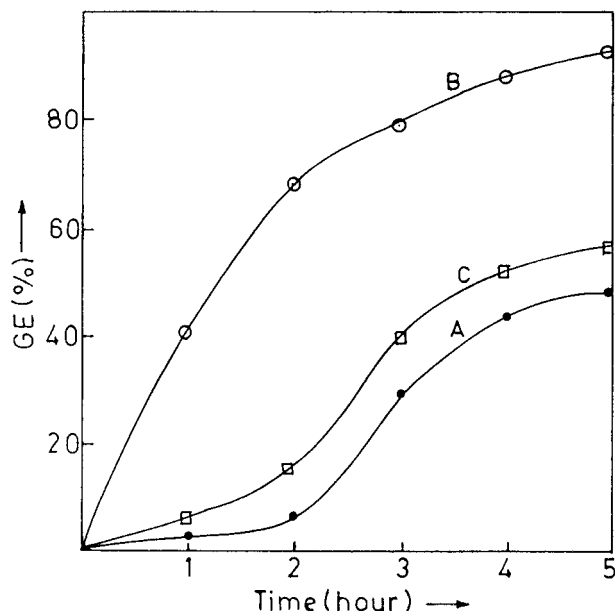


Figure 4 Effect of time and monomer concentration on grafting. $[PVA] = 1.0 \text{ g L}^{-1}$, $[CAS] = 3.16 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2SO_4] = 0.188 \text{ mol L}^{-1}$, temperature = 45°C , (A) $[MMA] = 0.2345 \text{ mol L}^{-1}$, (B) $[MMA] = 0.4690 \text{ mol L}^{-1}$, and (C) $[MMA] = 0.7040 \text{ mol L}^{-1}$.

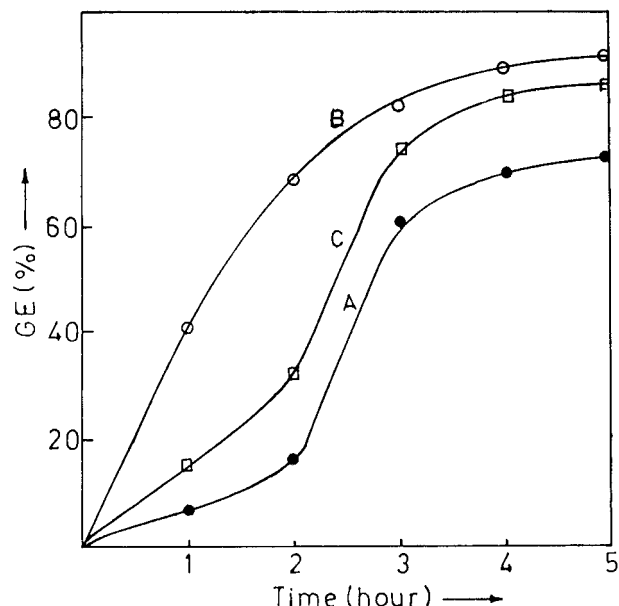


Figure 5 Effect of time and acid concentration on grafting. $[PVA] = 1.0 \text{ g L}^{-1}$, $[MMA] = 0.469 \text{ mol L}^{-1}$, $[CAS] = 3.16 \times 10^{-3} \text{ mol L}^{-1}$, temperature = 45°C , (A) $[H_2SO_4] = 0.0 \text{ mol L}^{-1}$, (B) $[H_2SO_4] = 0.188 \text{ mol L}^{-1}$, and (C) $[H_2SO_4] = 0.376 \text{ mol L}^{-1}$.

ably due to the hydrolysis of CAS in the absence of acid. The decrease in GE with the increase in sulfuric acid content beyond 0.188 mol L^{-1} may be ascribed due to the dehydration of PVA molecules in the presence of sulfuric acid.

Effect of Temperature

Data given in Figure 6 show the effect of temperature on graft polymerization of MMA onto PVA. It is evident from the figure that, with the increase in temperature, the GE increases, reaches a maximum at 45°C , and then decreases. The favorable effect of temperature on grafting^{1,17} could be ascribed to (1) enhanced diffusion of the MMA and CAS molecules onto the PVA structure; (2) improving the swelling capability of PVA; (3) increase in mobility of monomer molecules and their collision with macroradicals; and (4) increased propagation of grafted PVA. The decrease in GE after a certain temperature (45°C) can be attributed to higher rate of termination of the growing chain.¹

Effect of Time

Figures 2–6 show the GE of MMA onto PVA at different reaction periods. The GE increases with

the increase in reaction period. However, it should be noted that, after 4 h, the increase in GE is marginal. The effect of time on grafting can be

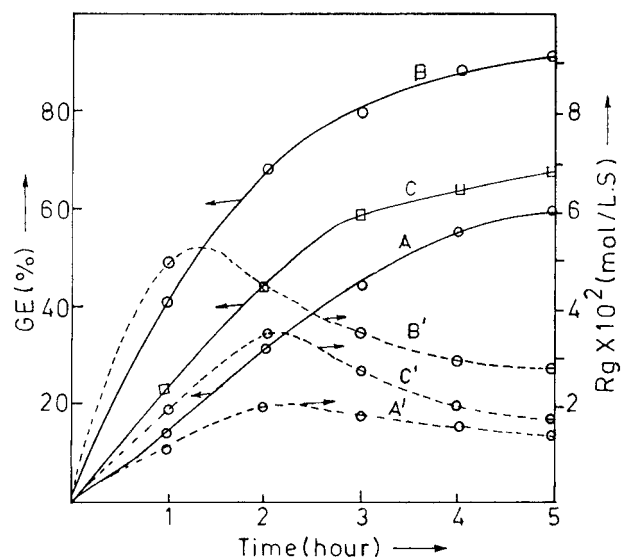


Figure 6 Effect of time and temperature on grafting efficiency and grafting rate. $[PVA] = 1.0 \text{ g L}^{-1}$, $[MMA] = 0.469 \text{ mol L}^{-1}$, $[CAS] = 3.16 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2SO_4] = 0.188 \text{ mol L}^{-1}$, (A, A') 35°C , (B, B') 45°C , and (C, C') 55°C .

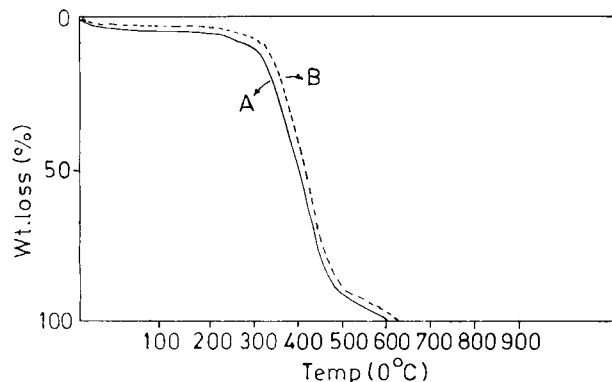


Figure 7 TGA of (A) PVA and (B) PVA-g-PMMA.

as follows: it is obvious that higher the contact time of monomer molecules with the PVA macroradical sites, the higher will be grafting; but, the leveling of GE after a certain time can only be attributed to the depletion of initiator and monomer concentration with the progress of reaction.

Grafting Rate

The variation of grafting rate (R_g) with time and temperature has been studied (Fig. 6) for the system containing PVA, MMA, CAS and H_2SO_4 at their optimum level. At a particular temperature, the R_g increases steeply with the increasing reaction time, reaches a maximum ~ 1.5 h, and then decreases gradually. This may be explained on the basis of effect of time on grafting. The grafting rate increases with the temperature up to $45^\circ C$ at each reaction interval. However, the behavior of R_g beyond $45^\circ C$ is anti-Arrhenious in nature. This may be described as the consequence of temperature effect on grafting.

TGA

Figure 7 shows the TGA plots of PVA and PVA-g-PMMA copolymer. It is evident from the figure that the thermal stability of the graft copolymer is similar to that of PVA.

Solubility and Gelatinization

The solubility (qualitative study) of the graft copolymer in various polar and nonpolar solvents is negligible with respect to the solubility shown by PVA. The reaction mixture tends to gelatinize whereas the MMA/PVA ratio is high enough.

CONCLUSIONS

MMA can be easily graft polymerized onto PVA using Ce^{4+} as an initiator in aqueous medium. The reaction variables—such as monomer, initiator, backbone polymer, pH, time, and temperature—considerably affect the efficiency of MMA toward grafting.

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