

# Syntheses and Characterization of Starch–Poly(methacrylic acid) Graft Copolymers

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Received 18 September 1996; accepted 6 May 1997

**ABSTRACT:** Methacrylic acid (MA) was graft polymerized onto starch using  $Ce^{4+}$  initiator in aqueous medium. The dependence of grafting on the reaction variables, such as monomer and initiator concentration and time and temperature, was studied in detail. Acid hydrolysis and infrared (IR) spectroscopy were used for the confirmation of graft copolymer formation. Further, a representative graft copolymer was characterized by x-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The solubility/swellability and the gelatinization characteristics of the copolymers are also reported. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1399–1403, 1997

**Key words:** starch; methacrylic acid; grafting; cerium; infrared; x-ray diffraction; thermogravimetric analysis; differential scanning calorimetry

## INTRODUCTION

Grafting has been used as an important technique for modifying physical and chemical properties of polymers. Graft polymerization results from the formation of an active site at a point on a polymer molecule other than its end and exposure to a second monomer. Most graft copolymers are formed by radical polymerization. In many instances, the transfer reaction involves abstraction of a hydrogen atom.

Starch graft copolymers are becoming increasingly important because of their potential applications in industry.<sup>1–3</sup> The wide range of available vinyl and other monomers suggests that grafting is a powerful method for producing substantial modification in starch properties, thereby enlarging its range of utilization. Methacrylic acid (MA) has been graft polymerized onto starch using various initiator systems, such as potassium persulfate,<sup>4–5</sup> ammonium peroxydisulfate,<sup>1</sup> manganese

(IV)–acid system,<sup>6</sup> hydrogen peroxide–ferrous ammonium sulfate,<sup>7</sup> etc. However, no attempt has been made to graft-polymerize MA using tetravalent cerium as initiator. The present study, therefore, essentially reports the graft polymerization of MA onto starch using  $Ce^{4+}$  as initiator. The factors affecting the graft polymerization have also been investigated.

## EXPERIMENTAL

### Materials and Methods

Dried maize starch (Laxmi Starch Co., India) was used in the graft polymerizations. Methacrylic acid (Sisco-chem, India) was distilled under reduced pressure prior to use. Ceric ammonium nitrate (CAN) (J. T. Baker Chemical Co., USA) was oven-dried at 110°C and then kept in a desiccator for further use. All the other chemicals and solvents were of analytical grade and used without further purification.

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**Table I Effect of Methacrylic Acid Concentration on Graft Polymerization onto Starch<sup>a</sup>**

Methacrylic Acid (mol/100 mL)	Grafting Efficiency (%)	Grafting (%)
0.012	8.45	7.79
0.023	9.30	8.51
0.047	19.55	16.35
0.070	20.00	16.66

<sup>a</sup> Reaction conditions: starch, 2 g; CAN,  $1 \times 10^{-3}$  mol/100 mL; water, 100 mL; time, 3 h; temperature, 30°C.

### Graft Polymerization

Two grams of dried starch was dispersed in 100 mL of distilled water taken in a two-necked round bottom flask and kept in a constant temperature water bath maintained at the required temperature. Nitrogen purging for 10 minutes was carried out to remove the dissolved oxygen from the reaction mixture. A predetermined amount of CAN (prepared as 0.1M in 1N nitric acid) was added to the starch slurry and allowed to react for 10 minutes, followed by addition of MA with constant stirring. A nitrogen atmosphere was maintained throughout the reaction period. The experimental details are given in the footnote to Tables I–IV. After the required reaction time, the mixture was filtered through Whatman filter paper no. 54 and washed with water. The product, typically white or slightly yellowish-white powder, was dried in an oven at 110°C for more than 24 h to constant weight. It consisted only of starch–poly(methacrylic acid) graft copolymer [*s-g-p*(MA)], as the homopolymer of methacrylic acid formed, being water soluble, was removed during the filtration and washing.<sup>8</sup>

**Table II Effect of Initiator Concentration on Graft Polymerization of Methacrylic Acid onto Starch<sup>a</sup>**

CAN $\times 10^4$ (mol 100 mL)	Grafting Efficiency (%)	Grafting (%)
2	7.65	7.11
4	9.65	8.80
6	13.95	12.24
8	10.90	9.83
10	9.30	8.51

<sup>a</sup> Reaction conditions: starch, 2 g; MA, 0.023 mol/100 mL; water, 100 mL; time, 3 h; temperature, 30°C.

**Table III Effect of Time on Graft Polymerization of Methacrylic Acid onto Starch<sup>a</sup>**

Time (min)	Grafting Efficiency (%)	Grafting (%)
30	7.00	6.54
60	7.60	7.06
90	8.00	7.41
120	11.05	9.95
150	13.65	12.01
180	13.95	12.24

<sup>a</sup> Reaction conditions: starch, 2 g; MA, 0.023 mol/100 mL; CAN,  $6 \times 10^{-4}$  mol/100 mL; water, 100 mL; temperature, 30°C.

### Confirmation for Graft Copolymer Formation

#### 1) Infrared Spectroscopy

Infrared (IR) spectra of the graft copolymers were recorded on Shimadzu FTIR-4200 dual beam spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$  using KBr pellets for sample preparation (10–15% *w/w*).

#### Acid Hydrolysis

In order to separate the grafted polymer from starch backbone, the *s-g-p*(MA) copolymer was subjected to acid hydrolysis.<sup>8</sup> A clear solution was obtained on refluxing the graft copolymer in 1N hydrochloric acid for 1 h. To isolate the grafted poly(MA), the solution was cooled in an ice bath and treated with an excess of ethyl acetate. The precipitate formed was collected and washed with dimethyl formamide in order to ensure complete removal of starch hydrolysis products. It was further purified by repeated precipitation into ethyl acetate from its solution in hot water and finally

**Table IV Effect of Temperature on Graft Polymerization of Methacrylic Acid onto Starch<sup>a</sup>**

Temperature (°C)	Grafting Efficiency (%)	Grafting (%)
30	13.95	12.24
35	14.15	12.40
40	14.75	12.85
45	16.10	13.87
50	17.75	15.07

<sup>a</sup> Reaction conditions: starch, 2 g; MA, 0.023 mol/100 mL; CAN,  $6 \times 10^{-4}$  mol/100 mL; water, 100 mL; time, 3 h.

dried. The IR spectrum of the dried product was found to be identical with that reported for poly(MA), which unambiguously indicated the *s-g-p*(MA) formation.

### X-ray Diffraction

Nickel-filtered  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15404$  nm) operated on an x-ray diffractometer (model Rigaku D/Max-IIIB) was used as a source under the operational conditions of 30 kV and 20 mA. X-ray diffraction of representative graft copolymer was scanned from 5 to 70° at a scan speed of 2°/min.

### Thermal Analysis

Thermogravimetric analyses (TGA) of starch and *s-g-p*(MA) copolymer (starch: MA 1 : 1 *w/w* feed ratio) were recorded on Mettler TA 4000 thermal analyzer from ambient to 500°C at a heating rate of 10°C/min in air.

The glass transition temperature of starch and *s-g-p*(MA) (starch: MA 1 : 1 *w/w* feed ratio) was determined by differential scanning calorimetry (DSC) on a DuPont 9900 thermal analyzer at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### IR Spectroscopy

IR spectra of the graft copolymers showed absorption bands at 3800–3000  $\text{cm}^{-1}$  (very broad, —OH stretching), characteristic of starch, and at 1724  $\text{cm}^{-1}$  (strong, C=O stretching), which is the characteristic of MA. This testified the existence of grafting.

### Grafting Parameters

The graft polymerization parameters<sup>9</sup> used in the present study are as follows.

Grafting efficiency (%)

$$= \frac{\text{weight of polymer grafted}}{\text{weight of monomer charged}} \times 100$$

$$\text{Grafting (\%)} = \frac{\text{weight of polymer grafted}}{\text{weight of graft copolymer}} \times 100$$

For the above calculations, the solubility of starch in water (mainly due to its linear amylose component) has to be taken into account. In the present

study, the loss in weight of starch due to the solubility of its amylose component was checked, and the average of such three trials was found to be 0.13 g per 2.00 g of starch, which was added to the final weight of the reaction product.

### Effect of Monomer Concentration

It is clear from Table I that the magnitude of grafting is directly related to the MA concentration within the range studied. The enhancement in grafting efficiency (GE) on increasing MA concentration could be associated with the greater availability of MA molecules in the proximity of starch macroradicals (sites for grafting).

### Effect of Initiator Concentration

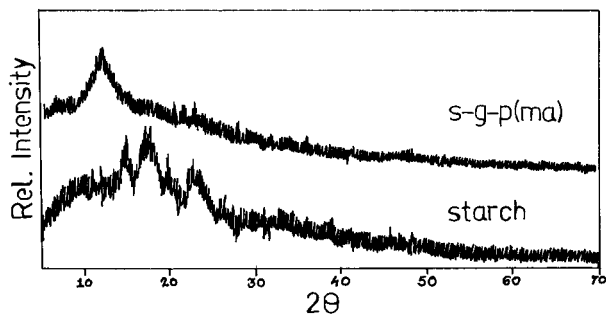
The grafting efficiency exhibits progressive improvement with CAN concentration (Table II), reaches a maximum at  $6 \times 10^{-4}$  mol/100 mL and then gradually decreases. This can be explained as follows: as the CAN concentration increases, the number of free radicals on the starch backbone increases, which accounts for the substantial increment in GE up to a certain CAN concentration. Thereafter, the decrease in GE may be attributed to primary radical termination, i.e., the reaction of free radicals on the starch backbone with excess of ceric ion to yield oxidized products, which are incapable of initiating polymerization.

### Effect of Time

It is evident from Table III that the GE increases with time up to 150 min and then levels off. The leveling of GE after a certain time can be attributed to the depletion of initiator and monomer concentration with the progress of the reaction. It is also likely that during the course of grafting, starch undergoes modification, as some of the hydroxyl group sites are now occupied by the graft chains, and the modified starch derived from there is not amenable for grafting as the unmodified starch.

### Effect of Temperature

It was observed that higher the temperature, the higher the GE (Table IV). This favorable effect of temperature on grafting could be ascribed to (1) enhanced diffusion of MA into the starch structure, (2) swelling of starch, (3) increase in the mobility of monomer molecules and their collision



**Figure 1** XRD patterns of starch and *s-g-p(ma)* copolymer.

with starch macroradicals, and (4) increased propagation of starch grafts.

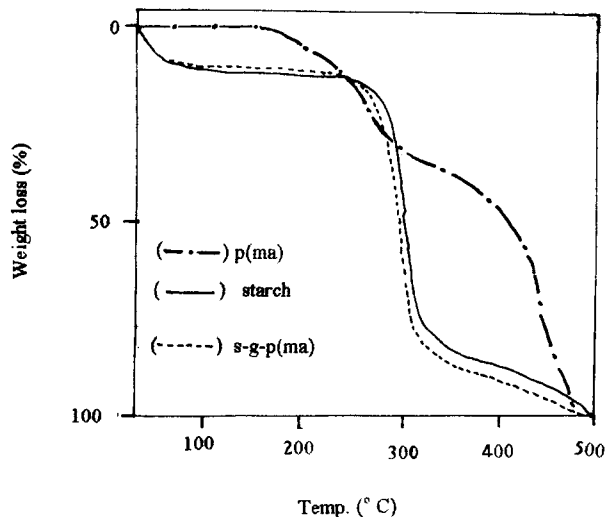
From the above discussion, it is clear that in spite of the profound effect of reaction variables on the percentage of grafting, the overall level of grafting is very low. Here, it should be noted that primarily a vinyl monomer has its own radical polymerizability, including rate constants for initiation, propagation, and termination, which decides the level of grafting on a particular substrate. In other words, the intrinsic ability of MA to graft polymerize onto starch is very low. Moreover,  $Ce^{4+}$  is also not an ideal initiator for grafting MA onto starch as it has a tendency to homopolymerize MA along with the grafting reaction.<sup>10</sup>

#### X-ray Diffraction

Figure 1 exhibits the XRD pattern of starch and the *s-g-p(MA)* copolymer. It can be seen that the XRD of starch shows four peaks, indicating low crystallinity. Further, on grafting MA, the four peaks get merged into one, suggesting that the crystal phase was also involved, along with the amorphous phase during the grafting reaction.

#### Thermal Analysis

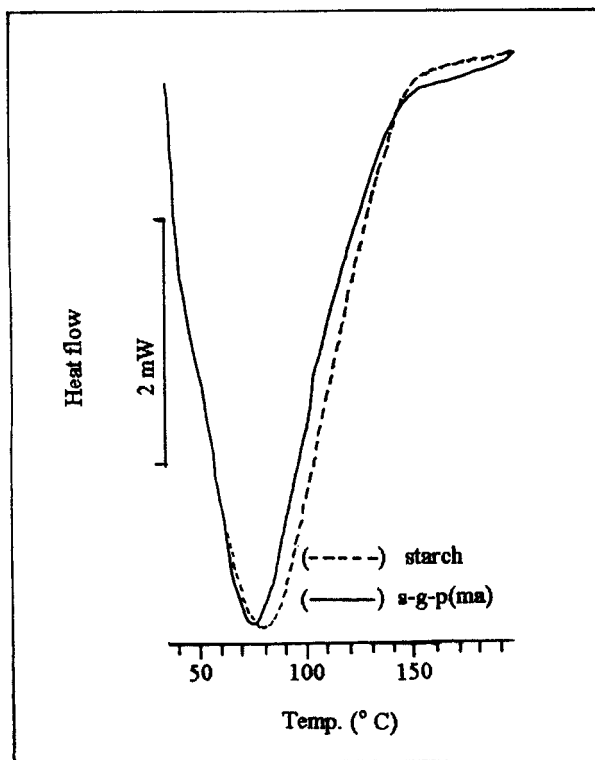
Figure 2 shows the TGA plots of starch, *s-g-p(MA)* and poly(MA). The curves showed that the thermal stability of *s-g-p(MA)* was similar to that of starch and that the graft copolymer was stable up to 250°C. The initial weight loss observed in the cases of starch and *s-g-p(MA)* is due to the loss of moisture. Poly(MA) shows an initial decomposition temperature around 200°C, as against 250°C shown by starch and *s-g-p(MA)*. However, the final decomposition temperature in all the cases was invariably found to be near 500°C.



**Figure 2** TGA of poly(ma), starch, and *s-g-p(ma)* copolymer.

The glass transition temperature ( $T_g$ ), determined by DSC (Fig. 3), of starch was found to be 80.7°C, and that of *s-g-p(MA)* was 74.8°C. The glass transition temperature of poly(methacrylic acid) is 230°C.<sup>11</sup>

The negligible difference in the thermal stabil-



**Figure 3** DSC of starch and *s-g-p(ma)* copolymer.

ity and glass transition temperature of starch and s-g-p(MA) copolymer can be easily traced to the low grafting percentage on starch ( $G = 12.24\%$ ) (Table II).

### Solubility/Swellability and Gelatinization

The solubility (qualitative study) of the graft copolymers in various polar and nonpolar solvents is as negligible as that of the substrate material, namely, starch. Dimethyl sulphoxide (DMSO) is, however, a good solvent for starch; interestingly, the graft copolymers do not dissolve in DMSO; even on heating, they just swell, indicating that crosslinking has occurred during graft polymerization. The crosslinking is probably due to chain combination of the growing graft poly(MA) microradicals.

Corn starch gelatinizes in water at around 70°C. However, the graft copolymers do not gelatinize, even after heating at 100°C, which further confirms the crosslinking of starch-poly(MA) copolymers.

### CONCLUSIONS

Methacrylic acid can be easily graft polymerized onto starch using  $Ce^{4+}$  initiator in aqueous medium. The reaction variables played an important role in the graft polymerization of MA onto starch.

However, the grafting efficiency of MA is less overall. During grafting, the starch crystalline phase was also involved along with the amorphous phase. The thermal properties of starch were less affected due to grafting. The grafting of MA onto starch negatively affects the solubility and gelatinization properties of starch.

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