

Synthesis and Characterization of Starch-Poly(methyl methacrylate) Graft Copolymers

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ABSTRACT: The graft copolymerization was carried out by methyl methacrylate with starch in which azobisisobutyronitrile was used as an initiator. The grafting reactions were carried out within a 65–95°C temperature range, and the effect of the monomer, initiator concentrations, and the amount of starch on the graft yield were also investigated. The maximum graft yield was obtained at a azobisisobutyronitrile concentration of 2.0×10^{-3} mol/L. The overall rate activation energy of the reaction was found to be 89.42

kJ/mol. The grafted starches were characterized with infrared spectroscopy, scanning electron microscopy, and thermogravimetry. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 53–57, 2002

Key words: starch; grafting; methyl methacrylate; azobisisobutyronitrile

INTRODUCTION

Starch is an abundant, inexpensive, renewable, and fully biodegradable natural raw material. However, starch by itself is unsuitable for most uses as a plastic because of its poor physical properties (mechanical properties, dimensional stability).

Graft copolymerization is one of the efficient methods to modify natural^{1–3} and synthetic polymers.^{4–6} In this way, it is possible to modify many different properties in the starch such as elasticity, sorbancy, ion exchange capabilities, thermal resistance, and resistance to microbiological attack.^{7–9}

Starch has been used as a model substrate for graft investigations mainly because of the ease with which vinyl monomers undergo grafting onto it. There are many reports upon chemical^{10–12} and radiation¹³-initiated grafting studies for the modification of starch.

Starch graft copolymers are becoming increasingly important because of their potential applications in industry. It has been used as hydrogels, flocculants, ion exchangers, superabsorbents, and so on.¹⁴ Starch graft copolymers could be achieved primarily by free radical initiated.^{15–18}

This work presents a detailed study on the grafting of methyl methacrylate onto starch using azobisisobutyronitrile. The effects of various experimental conditions such as initiator and monomer concentrations,

amount of starch, polymerization time, and temperature were also investigated.

EXPERIMENTAL

Materials and methods

Starch (Merck) was dried at 60°C for 24 h before use. Methyl methacrylate (MMA) (Merck) was washed with 5% NaOH three times, dried over CaCl₂, and distilled under a vacuum at 46°C. Azobisisobutyronitrile (AIBN) (BDH) was recrystallized twice from methanol and dried over P₂O₅ in a vacuum desiccator. All other chemicals were chemically pure grade.

Preparation of graft copolymer

A known weight of starch was placed in a 100-mL polymerization tube and AIBN, at suitable concentration dissolved in 1 mL acetone, was added upon it. The total volume was made up to 30 mL with distilled water after the addition of monomer and the mixture was vigorously mixed. The mixture was then placed in a water bath (Lauda D40 S, Germany) adjusted to the polymerization temperature. At the end of polymerization, the polymerization tube was taken from the water bath and 50 mL of acetone was added and kept for a night. The crude product was recovered by filtration. It is a mixture of ungrafted starch, homopolyMMA and polyMMA-grafted starch.

The crude product was treated by boiling water by changing the washing water at least three times for 2 h to remove ungrafted starch, and then extracted with acetone in a Soxhlet for 2 h to remove the ho-

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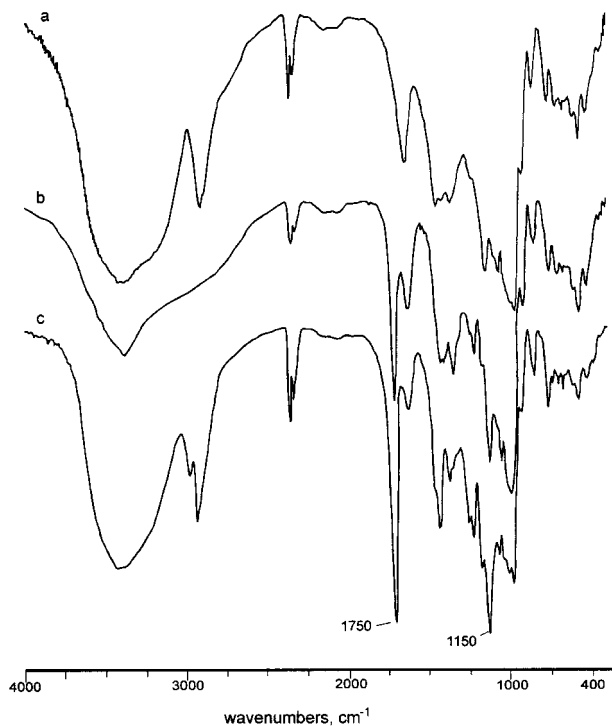


Figure 1 The FTIR spectra of (a) pure starch, (b) pure polyMMA, (c) 54.5% polyMMA-grafted starch.

mopolyMMA. The resulting polyMMA-grafted starch was dried and weighted.

The percent graft yield ($G\%$) based upon the initial amount of starch was calculated from the weight of initial starch (w_i) and polyMMA-grafted starch (w_s) as follow:

$$G\% = (w_s/w_i) \times 100$$

Rate measurement

The rate of grafting (Rg) was calculated as follows:

Rate of grafting (Rg)

$$= (G\% \cdot W_i \cdot 1000)/(100 \cdot V \cdot t \cdot M)$$

where $G\%$ is the percent graft yield, W_i is the weight of initial starch, V is the total volume of the reaction mixture, t is the reaction time, and M is the molecular weight of the MMA.

IR spectra

The infrared spectra of the samples were taken with MATTSON 1000 Model FTIR spectrophotometer using KBr pellets.

Thermogravimetric analysis

The thermogravimetric analysis were carried out in nitrogen atmosphere with a flow rate of 200 mL/min using a Rheometric Scientific 1000+ Model thermal analyzer. The samples were heated up to 600°C at a rate of 10°C/min starting from the room temperature.

Scanning electron microscopy

Micrographs were taken with JEOL-JEM 100 CX II Model scanning electron microscope.

RESULTS AND DISCUSSION

Evidence of grafting by FTIR spectra

Figure 1(a)–(c) gives the FTIR spectra of pure starch, homopoly MMA, and 54.5% polyMMA-grafted starch, respectively. The spectrum of the grafted starch showed both the characteristic absorption of starch at 3000–3800 cm^{-1} due to OH stretching band and characteristic absorption of MMA homopolymer at 1750 and 1150 cm^{-1} coming from the carbonyl groups.

Influence of reaction parameters

Effect of time and temperature on grafting

The effect of polymerization time and temperature upon the graft yield is presented in Figure 2. It is seen that increasing the temperature from 65 to 95°C causes a significant increase in the grafting rate and graft yield. There was no induction period for any of the four temperatures employed. The maximum graft yield (38.0%) was observed at 95°C.

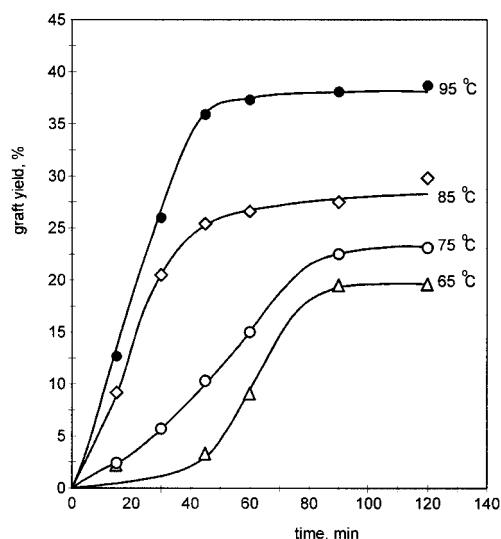


Figure 2 Change of the graft yield with temperature and the polymerization time: AIBN concentration = 2.0×10^{-3} mol/L, MMA concentration = 0.313 mol/L, time = 120 min.

TABLE I
Values of the Rate of Grafting (R_g)
at Various Temperatures^a

Temperature (°C)	$1/T \times 10^3$	$R_g \times 10^5$ (mol/L s)	$\log R_g + 5$
75	2.872	1.333	0.1249
85	2.792	5.111	0.7085
95	2.716	7.072	0.8496

^a[AIBN] = 2.0×10^{-3} mol/L; [MMA] = 0.313 mol/L; time = 15 min.

The favorable effect of temperature (up to 95°C) on grafting could be ascribed to: (a) enhanced diffusion of MMA into the starch structure, (b) the swellability of starch, (c) increase in the mobility of MMA molecules and their collision with starch macroradicals, and (d) increased propagation of starch grafts.¹⁸

The leveling of graft yield after a certain time (saturation graft yield) can be attributed to a decrease in the initiator and monomer concentration with the progress of the reaction.⁷

The rates of grafting (R_g) calculated for the experimental temperatures are given in Table I. The slope of the $\log R_g$ vs. $1/T$ graph shows that the overall activation energy for grafting is 89.42 kJ/mol within the 75–95°C temperature range (Fig. 3).

Effect of initiator concentration

The effect of the variation of initiator concentration on the graft yield was evaluated by changing the concentration of AIBN in the 0.125×10^{-3} – 6.0×10^{-3} mol/L range and keeping the concentrations of all other conditions constant (Fig. 4). From this figure the graft yield rapidly increases up to an AIBN concentration of 2.0×10^{-3} mol/L, and reaches a maximum graft yield value of 29.8%. A gradual decrease in graft yield was observed at higher initiator concentrations. This de-

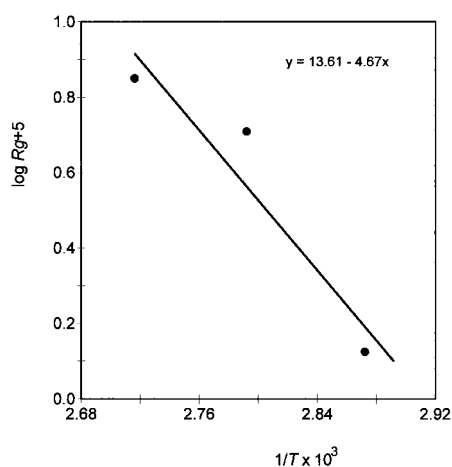


Figure 3 $1/T$ vs. $\log R_g$ plot for grafting of MMA upon starch using AIBN.

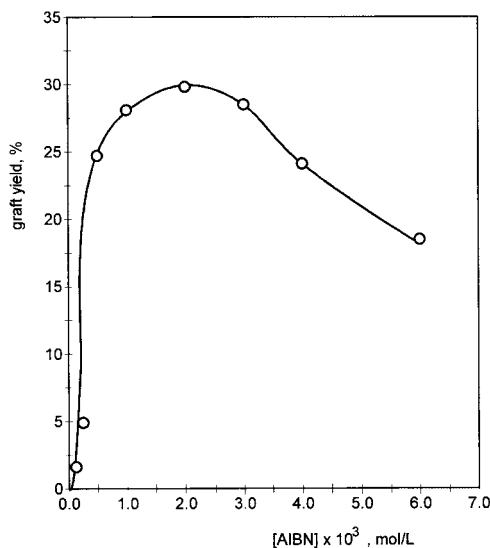


Figure 4 Change of the graft yield with initiator concentration: MMA concentration = 0.313 mol/L, temperature = 85°C, time = 120 min.

pendence of graft yield upon the initiator concentration is a typical behavior, and is frequently observed in free radical grafting of various monomers onto starch.^{10,14}

The increase in AIBN concentration increases the radical concentration in the medium that cleaves a hydrogen from the starch main chain and creates active sites on the starch macromolecules.⁷ In addition, the increase in initiator concentration increases the number of active homopolyMMA chains in the medium.

Another factor that creates suitable sites for grafting reactions to take place are the chain transfer reactions between the active MMA homopolymer chains and the starch macromolecules.

However, the increase of AIBN concentration above 2.0×10^{-3} mol/L makes the radical concentration excessive in the medium causing the rate of termination reactions to increase and graft yield to decrease.

Effect of monomer concentration

Figure 5 shows the effect of MMA concentration on the graft yield. The saturation graft yield increases from 12.5% at a monomer concentration of 0.078 mol/L to 55% at a monomer concentration of 0.469 mol/L. An increase in the monomer concentration also increases the grafting rate. There was no induction period for any of the four MMA concentrations employed.

An increase in monomer concentration increases the number of MMA molecules diffused into starch molecules. This increases the probability of starch macroradicals and growing grafted side chains to find

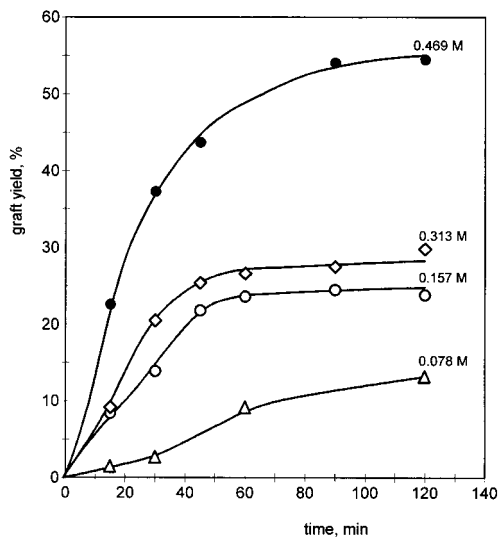


Figure 5 Change of the graft yield with monomer concentration: AIBN concentration = 2.0×10^{-3} mol/L, temperature = 85°C , time = 120 min.

monomer units to add and, therefore increases the graft yield.¹⁹

Effect of amount of starch

The change of the graft yield with variance of amount of starch was investigated. Figure 6 shows the results obtained by changing the amount of starch between 0–2.5 g.

The highest graft yield (29.8%) was obtained at an 1.5 g starch. The grafting yield, which showed a rapid increase up to this optimum amount of starch, then decreased, owing to the lowering ratio of monomer to starch.¹⁰

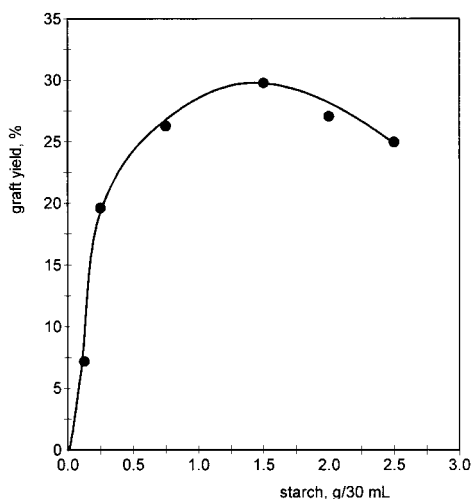


Figure 6 Change of the graft yield with amount of starch: AIBN concentration = 2.0×10^{-3} mol/L, MMA concentration = 0.313 mol/L, temperature = 85°C , time = 120 min.

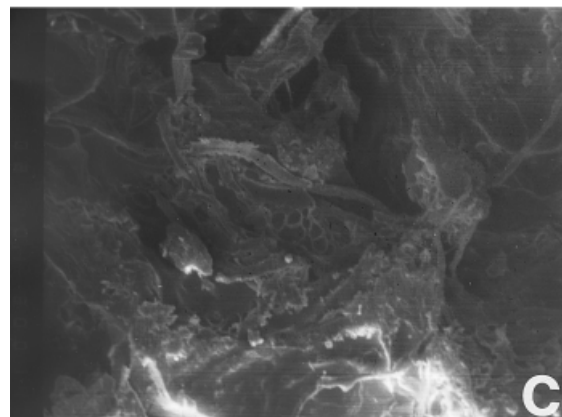
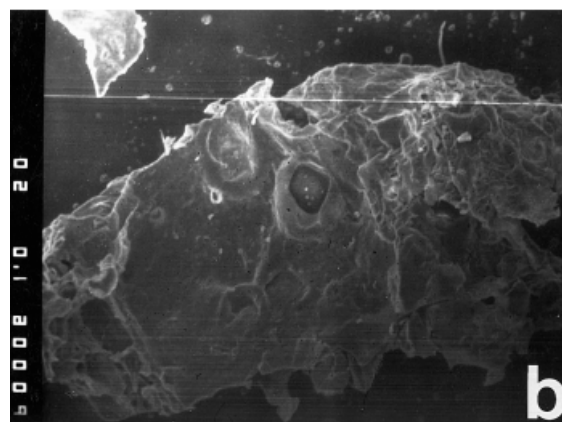
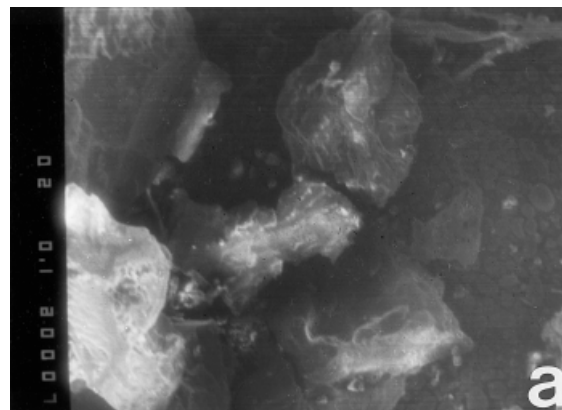


Figure 7 SEM micrographs of MMA grafted starches at a magnification of $\times 100$: (a) pure starch, (b) 9.2%, and (c) 29.8% polyMMA-grafted starch.

Scanning electron microscopy (SEM)

The effect of MMA grafting upon the surface morphology of starch was investigated by SEM. The SEM photos of pure starch, 9.2 and 29.8% polyMMA-grafted starch at a magnification of $\times 100$ were shown in Figure 7. The photos explained that the granular structure of starch was not maintained after graft copolymerization and the grafted branch chains attached to the starch surface.^{10,12}

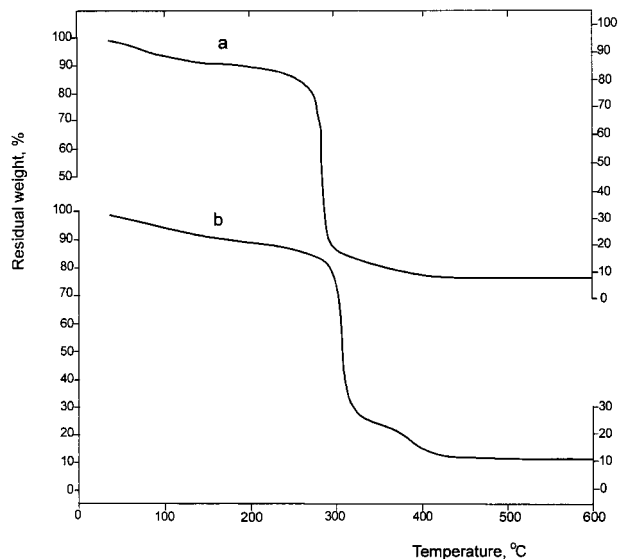


Figure 8 TGA curves of (a) pure starch, and (b) 54.5% polyMMA-grafted starch, obtained in nitrogen atmosphere at heating rate of 10°C/min.

Thermogravimetry analysis

The thermal behavior of starch and polyMMA-grafted starch was examined by the TGA analyses under N₂ atmosphere at heating rate 10°C min.⁻¹ The TGA curves for the thermal degradation of starch and 54.5% polyMMA-grafted starch are presented in Figure 8. The initial weight loss observed in the cases of starch and polyMMA-grafted starch is due to the loss of moisture. The weight loss of the pure starch started at 290°C and reached to a value of 91.39% at 600°C. The weight loss of 54.5% polyMMA-grafted starch reached a value of 89.2% at 600°C.

CONCLUSIONS

In this study it was shown that MMA can be grafted upon starch using AIBN as an organic initiator in

aqueous medium. The optimum initiator concentration is 2.0×10^{-3} mol/L respectively to obtain a higher graft yield. No optimum value for the monomer concentration and temperature was found. The graft yield was observed to increase with the monomer concentration and temperature. Finally, the thermal stability of starch was found to increase after being grafted with polyMMA.

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