

# Graft Copolymerization of Methyl Acrylate onto Sago Starch Using Ceric Ammonium Nitrate as an Initiator

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**ABSTRACT:** The graft copolymerization of methyl acrylate onto sago starch was carried out by a free radical initiating process. The free radicals were produced by the chemical initiation method in which ceric ammonium nitrate was used as an initiator. It was found that the percentages of grafting, grafting efficiency, and rate of grafting were all dependent on the concentration of ceric ammonium nitrate (CAN), methyl acrylate (MA), sago starch (AGU), mineral acid ( $\text{H}_2\text{SO}_4$ ), and reaction temperature and period. The variables affecting the graft copolymerization were thoroughly examined. The optimum yield of grafting was obtained when the concentration of CAN, MA, AGU, and  $\text{H}_2\text{SO}_4$  were used at  $8.77 \times 10^{-3}$ , 0.803, 0.135, and 0.175 mol L<sup>-1</sup>, respectively. The optimum reaction temperature and period were 50°C and 60 min, respectively. The rate of graft polymerization was explored on the basis of experimental results and reaction mechanism. The evidence of grafted copolymers was investigated by using FTIR spectroscopy, TG, and DSC analysis. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 516–523, 2000

**Key words:** graft copolymerization; sago starch; free radical; monomer and poly (methyl acrylate) polymer

## INTRODUCTION

Graft copolymerization of vinyl monomers onto starch by a free radical initiating system is an excellent method for preparing composites of starch with synthetic polymers; numerous monomers with a free radical initiating system have been investigated.<sup>1,2</sup> The graft copolymer of acrylate monomers onto starch may be used as biodegradable mulch in agriculture, medicine, and food packages. Dennerberg et al.<sup>3</sup> reported that graft copolymerization of methyl acrylate (MA) onto corn starch initiated by ceric ammonium nitrate (CAN) and the starch portion of these extradiates

is susceptible to fungal attack. The formation of poly(methyl acrylate) graft onto the rigid starch matrix produces graft copolymers that yield leathery plastics on extrusion processing.<sup>4</sup> Grafting has been used as an important technique for modifying physical and chemical properties of polymers. For example, by grafting various monomers onto starch, it is possible to modify many different properties in the polymer, such as elasticity, sorbancy, ion exchange capabilities, thermal resistance, and resistance to microbiological attack.<sup>5,6</sup> A redox system generally comprises the transition metal ions that exist in various oxidation states. Such oxidized metal ions may directly oxidize sago starch to initiate the transition of free radicals for grafting. A detailed study of MA with sago starch (AGU) has been presented by CAN initiation, and it will be further extended to the preparation of ion-exchange materials.

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## EXPERIMENTAL

### Materials and Methods

AGU was purchased from Tepung Sago Industries Ltd. (Malaysia). It was dried at 60°C for 24 h before use. The MA monomer was obtained from Merck Co. (Rahway, NJ). To remove inhibitor, MA was passed through columns filled with chromatographic grade activated alumina. The monomer was stored at -10°C; CAN (BDH Chemicals, Poole, UK), methanol (Beaker), and other chemicals used were analytical reagent grades.

### Graft Copolymerization

The reactions were carried out in 250-mL three-neck flasks equipped with a stirrer and condenser and immersed into thermostat water bath. The N<sub>2</sub> gas was purged into the flask to remove the presence of oxygen during the operation. The starch slurry was prepared from 1.25 g AGU, and 50 mL distilled water was preheated at 80°C for about 30 min with stirring. After it was gelatinized, the flask contents were then cooled to the required temperature and then 1.05 mL diluted

sulfuric acid (H<sub>2</sub>SO<sub>4</sub> : H<sub>2</sub>O; 1 : 1) was added to the reaction mixture. After 5 min the required milliliters of 0.1M CAN solution was added, and the reaction mixture was mixed homogeneously. Exactly 10 min later, the required amount of monomer (MA) was added to the mixture, and the mixture was stirred for specific periods. When the reaction was complete, the product was cooled under running tap water and poured into 200 mL of methanol to induce precipitation. The grafted products were washed several times with methanol/water (4 : 1), and then the products were oven dried at 50°C to constant weight.

### Extraction of Homopolymer and Determination of Graft Level

Exactly 2000 g of the above crude products was taken and extracted with the acetone in a soxhlets extractor for 24 h to remove poly(methyl acrylate) homopolymer, and pure copolymers were then dried at 50°C to constant weight.<sup>4</sup>

The percentage of grafting ( $P_g$ ) and grafting efficiency ( $G_e$ ); rate of graft polymerization ( $R_g$ ) were determined by the following formula<sup>7</sup>:

$$\text{Percentage of grafting } (P_g) = \frac{\text{weight of grafted polymer}}{\text{weight of backbone}} \times 100$$

$$\text{Grafting efficiency } (G_e) = \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer} + \text{weight of homopolymer}} \times 100$$

$$\text{Rate of graft polymerization } (R_g) = \frac{\text{weight of grafted polymer}}{(\text{MW of monomer}) \times [\text{reaction time (s)}] \times [\text{volume (mL)}]} \times 1000 \text{ (mol L}^{-1} \text{ s}^{-1}\text{)}$$

### Side-Chain Separation

Grafted side chains were removed from the starch backbone using the procedure recommended by Dennerberg et al.<sup>3</sup> Approximately 0.50 g of poly(methyl acrylate) grafted AGU sample was placed in a 100-mL flask with 50 mL glacial acetic acid. The flask was fitted with a condenser, and the mixture was refluxed for 1 h. After swelling the grafted side chains, 5 mL of perchloric acid (60%) was added dropwise, and within a few minutes, the mixture turned into a clear solution. The product was immediately poured into ice water to precipitate the poly(methyl acrylate) side chains. The precipi-

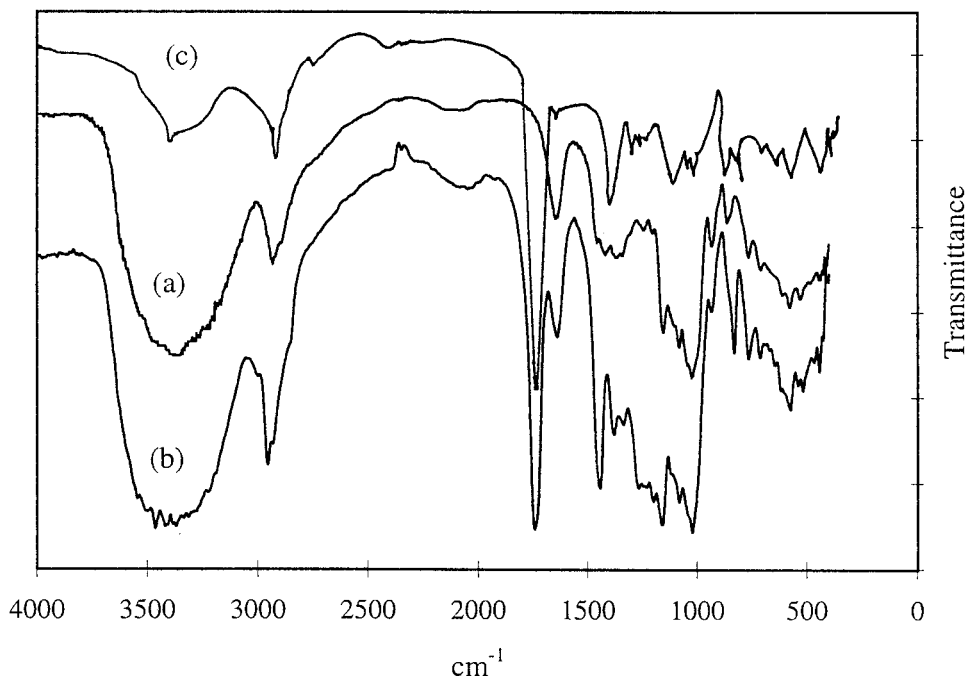
tate was thoroughly washed to neutral state and dried at 50°C to a constant weight.

### FTIR Analysis

Infrared (IR) spectra of polymer samples were obtained from Fourier transform-IR (FTIR) spectrometer (Perkin-Elmer 1725, Norwalk, CT). The KBr pellets of AGU, poly(methyl acrylate)-grafted AGU, and side-chain poly(methyl acrylate) were prepared for the IR spectra recordings.

### Thermogravimetry Analysis

Thermogravimetry (TG) experiments were carried out using a DuPont Thermal Analyzer



**Figure 1** FTIR spectra of (a) sago starch, (b) poly(methyl acrylate) grafted sago starch, and (c) side-chain poly(methyl acrylate).

(Model 990, Wilmington, DE). The analysis was carried out in  $N_2$  atmosphere from room temperature to  $1000^\circ C$  at a heating rate of  $10^\circ C \text{ min}^{-1}$  with an  $N_2$  flow rate of  $50 \text{ mL min}^{-1}$ . Thermograms were obtained by plotting percent residual weight against temperature.

#### Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) experiments were performed using Polymer Laboratories differential scanning calorimeter with an  $N_2$  flow rate of  $50 \text{ mL min}^{-1}$ . The DSC thermograms were obtained from samples of AGU and poly(methyl acrylate)-grafted AGU packed into ordinary Al pans and heated at the rate of  $10^\circ C \text{ min}^{-1}$ .

## RESULTS AND DISCUSSION

#### Evidence of Grafting by FTIR Spectra

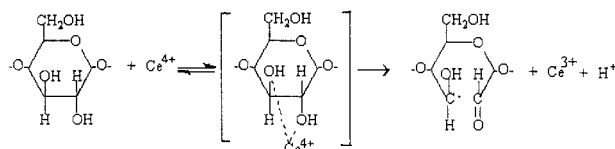
Infrared spectrum of AGU is shown in Figure 1(a); it indicates the characteristic absorption bands of starch at  $3402$  and  $1646 \text{ cm}^{-1}$ , due to O—H stretching and bending modes, respectively. Additional characteristic absorption bands of AGU appear at  $2930$  and  $1024 \text{ cm}^{-1}$ , due to

C—H stretching and bending, respectively [Fig. 1(a)]. IR spectrum of purified poly(methyl acrylate)-grafted AGU shows a new characteristic absorption band of poly(methyl acrylate) at  $1741 \text{ cm}^{-1}$  of C=O stretching mode in addition to the same absorption bands of starch shown in Figure 1(b). In Figure 1(b), the poly(methyl acrylate) can be identified in copolymers on the basis of the band at  $828 \text{ cm}^{-1}$ . The spectrum of side-chain polymer was identical to the spectrum of standard poly(methyl acrylate) shown in Figure 1(c). These results proved that the polymeric product was poly(methyl acrylate)-grafted AGU.

#### Reaction Mechanism

Although several reports have been published on the graft copolymerization mechanisms of the vinyl monomer onto starch macromolecules,<sup>3,4,8</sup> the proposed mechanism used in this study was based on the same principle as that by Ceresa.<sup>8</sup> The first step of the mechanism is that the cerium ion attacks the starch molecules and forms a starch-ceric complex. The  $Ce^{4+}$  ion in the complex is then reduced to a  $Ce^{3+}$  ion, and a hydrogen atom is oxidized. Consequently, a free radical is formed onto starch, while the bond is broken into carbon atoms 2

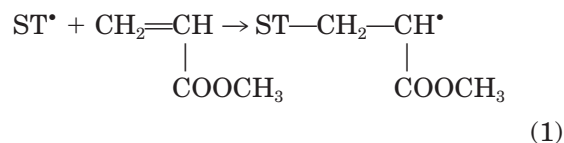
and 3 of the glucopyranose unit. The polymeric starch free radical so formed may react with monomer to initiate graft copolymerization. In the presence of vinyl monomer, the starch free radical was added to the double bond of vinyl monomer, resulting in a covalent bond between



monomer and starch to create the chain reaction for propagation. Termination of the graft

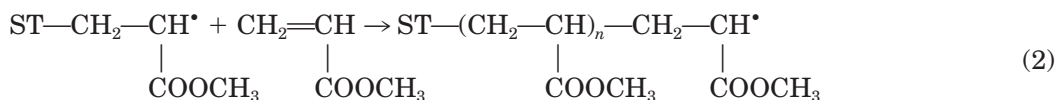
copolymerization is through a combination of two radicals. The reaction scheme of MA with AGU initiated by CAN is as follows:

and

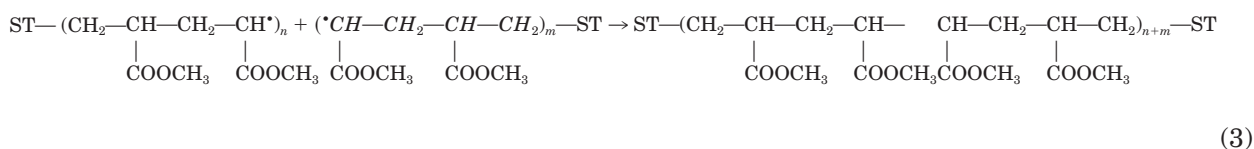


where  $\text{ST}^{\bullet}$  is free radical of sago starch molecule.

Propagation:



Termination:



### Effect of Reaction Temperature

Temperature constitutes one of the vital factors in determining the extent of grafting. In general, grafting yield increases with the increase of temperature until a limit is attained.<sup>6</sup> Increase of temperature, in fact, may lead to several effects on grafting, such as (i) starch may be swelled to larger extent; (ii) solubility of the monomer may be increased; (iii) diffusion of monomer to the grafting sites may be increased; (iv) initiating redox system may be easily decomposed; (v) rate of initiation and propagation may be enhanced; and (vi) rate of termination may increase. If one considers all these factors, it is immediately evident that the operation of factors (i–v) will lead to an increase in grafting, whereas the factor (vi) will have the reverse effect on grafting. The limitation in grafting

yield, as mentioned above, may be explained as due to the operation of factor (vi) in the presence of other factors.

In this study the effect of temperature on the yield of grafting was investigated at four different temperatures: 30, 40, 50, and 60°C. The percentage of grafting increased with the increase of temperature from 30 to 50°C. The maximum 54.40% of grafting was observed at 50°C, which was presumably the optimum condition of grafting. Beyond the temperature, the percentage of grafting was decreased as shown in Table I. This was attributed to the fact that with an increase in temperature, more and more radicals are formed, which enhance the grafting. However, the increase in temperature beyond a specific limit causes increased extent of radical termination, thus reducing the graft level.

**Table I** Effect of Reaction Conditions on the Yield of Graft Copolymers

Effect of Temperature		Effect of Acid Concentration		Effect of Reaction Period	
Temperature (°C) <sup>a</sup>	% of Grafting	[H <sub>2</sub> SO <sub>4</sub> ] (/mol L <sup>-1</sup> ) <sup>b</sup>	% of Grafting	Reaction Period (min) <sup>c</sup>	% of Grafting
30	45.90	0.087	52.01	30	26.80
40	51.00	0.175	54.40	60	54.40
50	54.40	0.350	47.90	120	20.10
60	51.20	0.526	45.79	180	19.96

Concentrations of [AGU], [MA], and [CAN] were 0.135, 0.385, and  $8.77 \times 10^{-3}$  mol L<sup>-1</sup>, respectively.

<sup>a</sup> Other conditions: reaction period, 60 min and [H<sub>2</sub>SO<sub>4</sub>], 0.175 mol L<sup>-1</sup>.

<sup>b</sup> Other conditions: temperature, 50°C and reaction period, 60 min.

<sup>c</sup> Other conditions: temperature, 50°C and [H<sub>2</sub>SO<sub>4</sub>], 0.175 mol L<sup>-1</sup>.

### Effect of Acid Concentration

The process of graft copolymerization, whether initiated chemically or otherwise, has been strongly dependent on the pH of the medium from which the grafting is carried out. The effect of sulfuric acid concentration on percentage of grafting is presented in Table I. The optimum percentage of grafting (54.40%) was achieved at 0.175 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; beyond this acid concentration, the grafting percentage decreased. The use of mineral acids in the grafting process assists in the enhancement of graft level both by causing inter- and intracrystalline swelling of the substrate.<sup>9</sup> Acids also acted as a catalyst in the hydrolysis of starch, leading to uncoiling of the chains and improving the monomer's accessibility. A higher concentration of acid, however, can cause degradation of the backbone as well as of the graft chains. Initial increase in the extent of grafting may be associated with the fact that the acid catalyses the grafting reaction and enhances the oxidizing capacity of the initiator. The subsequent decrease in grafting may be related to the abundance of H<sup>+</sup>, which may act as a free radical terminator.

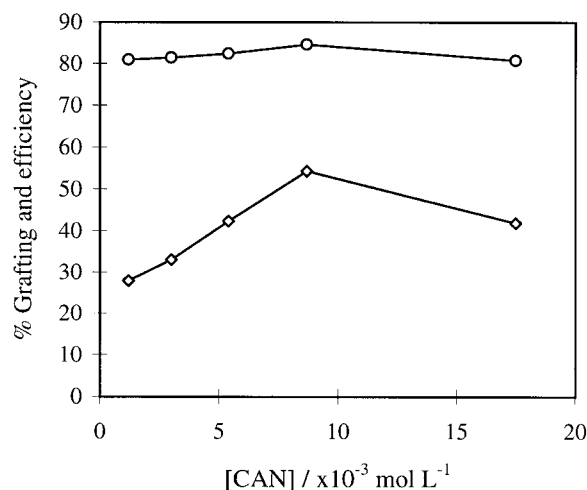
### Effect of Reaction Period

The effect of the reaction period on the percentage of grafting is also shown in Table I. The maximum percentage of grafting (54.40%) was observed at 60 min, and thereafter gradually decreased until it leveled off. The decrease in grafting rates and eventual leveling off of the grafting values have been attributed to decreases in monomer and catalyst concentrations as well as to the retardation of diffusion because of the formation of polymer at the starch surface.<sup>10</sup> Another possible explana-

tion for the leveling off of grafting values with time is the reduction in the number of sites available for grafting.

### Effect of Initiator Concentration

In the case of grafting initiated by a chemical initiator, the extent of grafting increases with the increase of initiator concentration up to a certain limit, beyond which grafting no longer increases. This has been ascribed to the decay of the macroradicals themselves by their reaction with the initiator.<sup>6</sup> The effect of Ce<sup>4+</sup> initiator on the yield of grafting increased with the increase of CAN concentration from 1.20 to  $8.77 \times 10^{-3}$  mol L<sup>-1</sup>, as shown in Figure 2. The highest percentages of



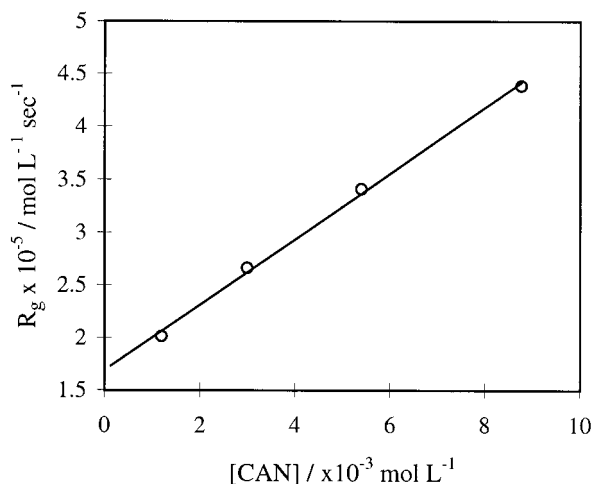
**Figure 2** Effect of initiator [CAN] concentration on the percentage of grafting. Temperature, 50°C; [MA], 0.385 mol L<sup>-1</sup>; [AGU], 0.135 mol L<sup>-1</sup>; reaction period, 60 min; [H<sub>2</sub>SO<sub>4</sub>], 0.175 mol L<sup>-1</sup>. —◇—, grafting (%); —○—, efficiency (%).



grafting and grafting efficiencies were obtained using the CAN concentration at  $8.77 \times 10^{-3} \text{ mol L}^{-1}$ . The percentages of grafting and efficiency attained a maximum of 54.35% and 84.60%, respectively, when CAN concentration used was  $8.77 \times 10^{-3} \text{ mol L}^{-1}$ . Thereafter, the graft level decreased with a further increase in CAN concentration. The decrease of graft level at higher concentrations of CAN may be due to the efficiency of  $\text{Ce}^{4+}$  to take part in the termination of growing grafted chains and homopolymerization.<sup>11</sup>

The initial increase in percent graft with increased catalyst concentration may either be due to catalyst exhaustion or an increase in rate of grafting at low concentration.<sup>12</sup> The decrease in percent grafting at higher initiator concentration could be due to a decrease in the rate of polymerization. At higher ceric ion concentration, an increase was expected in the reaction steps involving ceric ions, leading to an increase in the number of starch radicals terminated prior to monomer addition. Another factor contributing to a decrease in grafting levels at higher initiator concentration is an increase in the homopolymer formation, which competes with the grafting reaction for available monomer.

The relation between rate of grafting and ceric ion concentration is shown in Figure 3. The rate of grafting increased linearly with ceric ion concentration from 1.20 to  $8.77 \times 10^{-3} \text{ mol L}^{-1}$  CAN, and thereafter, the rate of grafting decreased beyond  $8.77 \times 10^{-3} \text{ mol L}^{-1}$  (the deviation is omitted in Fig. 3). As pointed out earlier, a significant increase in the initiator concentration beyond



**Figure 3** Effect of initiator [CAN] concentration on the rate of grafting. Other conditions as in Figure 2.

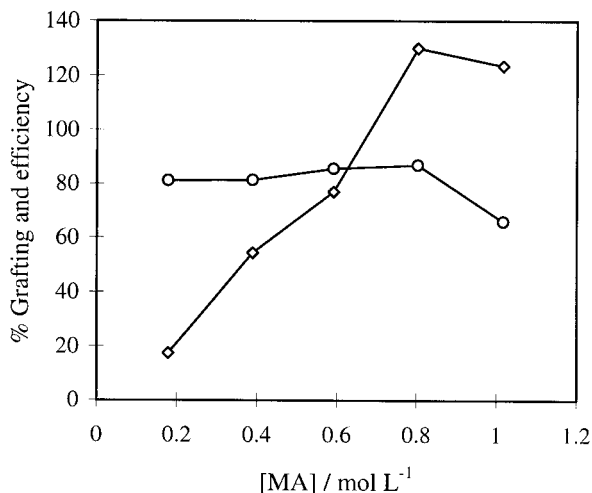
$8.77 \times 10^{-3} \text{ mol L}^{-1}$  not only facilitates the more active centers on the backbone, but also facilitates the homopolymerization.

### Effect of Monomer Concentration

It has been discussed that the initiation of graft copolymerization by means of a redox couple involves primarily the formation of a complex between the initiator, starch, and the monomer. Efficiency of this evidently depends on the concentration of the monomer present in the system, that is, the larger the concentration of monomer, the more favored will be the formation of such a complex that triggers the grafting process. Another parameter that is important in assessing the effect of monomer concentration on grafting is gel effect, which arises from the solubility of homopolymer in the monomer itself. A consequence of this gel effect is a higher monomer concentration. As a result of this effect, the termination rate decreases. Besides this, the gel effect helps in swelling the starch, which ultimately facilitates the diffusion of monomer to the active sites on the starch backbone, thereby enhancing the grafting. Though in general, grafting increases with the increasing concentration of monomer, there is always a limitation beyond which grafting is not favored. One of the reasons might be that swelling of the base polymer at a higher monomer concentration is not favorable for grafting.<sup>6</sup>

In this study the effect of monomer concentration on the percentage of grafting is presented in Figure 4. The percentage of grafting and grafting efficiency increased with the increase of monomer concentration from 0.178 to 0.803  $\text{mol L}^{-1}$  MA. The percentages of grafting and efficiency reached a maximum of 130.01% and 82.20%, respectively, at a monomer concentration of 0.803  $\text{mol L}^{-1}$ . The contribution of this effect would be more pronounced at higher monomer concentrations. As a result of this effect, the termination rate was decreased. However, at higher concentration of monomer beyond 0.803  $\text{mol L}^{-1}$ , the percentages of grafting and efficiency decreased because the highest percentage of homopolymer was formed in the starch-graft-poly(methyl acrylate). It is expected that swelling of the base polymer at higher monomer concentrations was not favorable for grafting.

The relation of rate of grafting and monomer concentration is shown in Figure 5. It was found that when monomer concentration increased from 0.178 to 0.803  $\text{mol L}^{-1}$ , the rate of grafting in-

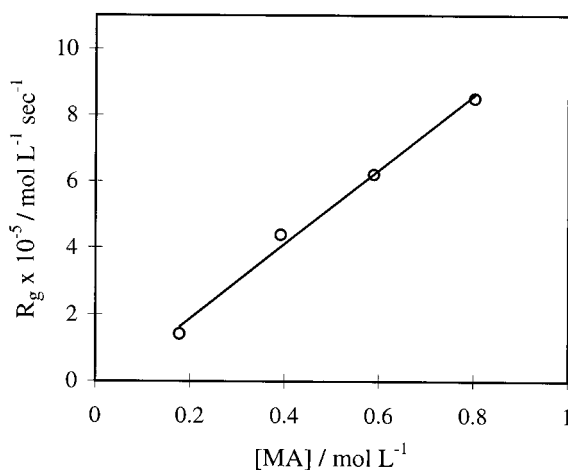


**Figure 4** Effect of monomer [MA] concentration on the percentage of grafting. Temperature, 50°C; [AGU], 0.135 mol L<sup>-1</sup>; [H<sub>2</sub>SO<sub>4</sub>], 0.175 mol L<sup>-1</sup>; reaction period, 60 min; [CAN], 8.77 × 10<sup>-3</sup> mol L<sup>-1</sup>. —◇—, grafting (%); —○—, efficiency (%).

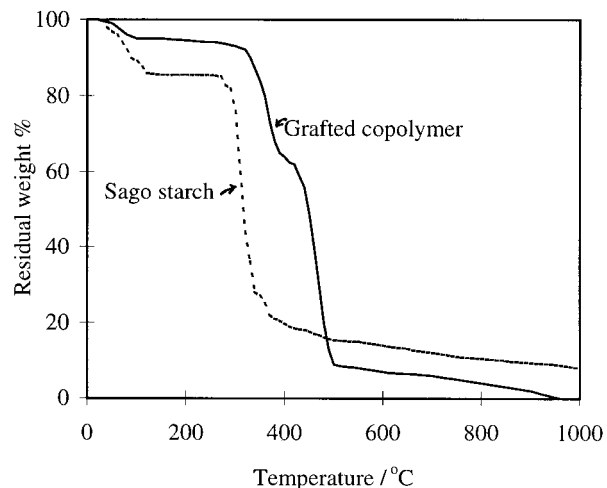
creased linearly and decreased beyond 0.803 mol L<sup>-1</sup>. At higher monomer concentrations, the rate of grafting decreased beyond 0.803 mol L<sup>-1</sup>, presumably due to the formation of more homopolymer in the growing grafted chain.

### Thermogravimetry Analysis

The thermal behavior of AGU and poly(methyl acrylate)-grafted AGU was examined by the TG analyses under N<sub>2</sub> atmosphere at heating rate 10°C min<sup>-1</sup>. The TG curves for the thermal degradation of AGU and poly(methyl acrylate)-

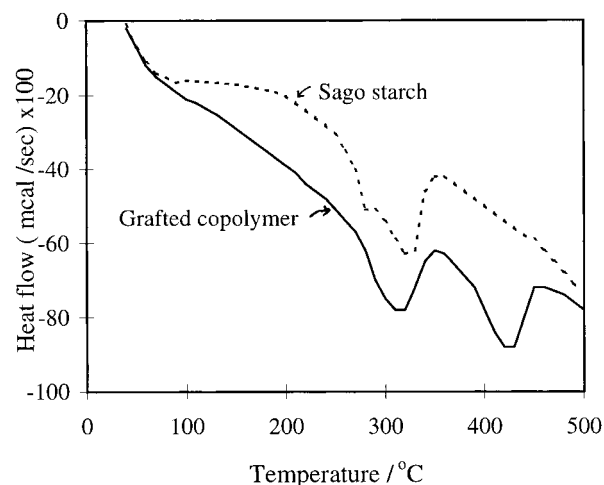


**Figure 5** Effect of monomer [MA] concentration on the rate of grafting. Other conditions as in Figure 4.



**Figure 6** Thermograms of poly(methyl acrylate)-grafted sago starch and sago starch. Plot of residual weight loss percentage versus temperature.

grafted AGU are presented in Figure 6. The weight loss occurred between 290 and 380°C for AGU, whereas the weight loss occurred between 325 to 500°C for poly(methyl acrylate)-grafted AGU. The poly(methyl acrylate)-grafted AGU was thermally stable as compared to AG up to 490°C, although there was a little moisture dehydration in both the samples up to 100°C. The sharp decomposition, about 64% weight loss, temperature was found for AGU at 330°C. In case of poly(methyl acrylate)-grafted AGU, the same weight loss, 64%, occurred at 460°C. After 490°C, the poly(methyl acrylate)-grafted AGU loses



**Figure 7** DSC thermograms of poly(methyl acrylate)-grafted polymer and sago starch. Plot of heat flow (mcal s<sup>-1</sup>) versus temperature.

weight more rapidly than AGU; in fact, the decomposition was high in this region from 490 to 1000°C. The poly(methyl acrylate)-grafted AGU decomposed completely; therefore, the residual weight of poly(methyl acrylate)-grafted AGU was lower than that of AGU.

### DSC Analysis

DSC has been very useful to explain the formation of graft copolymers. The DSC curves of AGU and poly(methyl acrylate)-grafted copolymer are presented in Figure 7. AGU showed an endothermic transition at 321°C, with a little moisture dehydration, and poly(methyl acrylate)-grafted copolymer exhibited an endothermic transition at 314 and 417°C. There was a new endothermic transition at 417°C for poly(methyl acrylate)-grafted copolymer, probably due to enhanced interaction between the carbonyl groups of grafted copolymer and the hydroxyl groups in the AGU. These results gave confirmation of the occurrence of grafting of poly(methyl acrylate) onto AGU.

### CONCLUSIONS

The synthesis of poly(methyl acrylate)-grafted AGU has been carried out with methyl acrylate and AGU using ceric ammonium nitrate as an initiator. It was found that the yield of percent grafting, grafting efficiency, and rate of graft polymerization were all dependent on the concentrations of ceric ammonium nitrate (CAN), methyl acrylate (MA), sago starch (AGU), and

mineral acid and the reaction temperature and period. The grafted copolymers were characterized by using FTIR spectroscopy, TG, and DSC analysis.

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