Synthesis of Cassava Starch-*g*-Poly(methyl methacrylate) Copolymers with Benzoyl Peroxide as an Initiator

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ABSTRACT: Graft copolymers of cassava starch and methyl methacrylate (MMA) were synthesized by free-radical polymerization with benzoyl peroxide (BPO) as an initiator in an aqueous medium at 80°C. The formation of graft copolymers was confirmed by analysis of the obtained products with Fourier transform infrared spectroscopy and scanning electron microscopy. The effects of the amount of cassava starch, the amount of MMA monomer, the amount of BPO, and the reaction time on the grafting characteristics were studied. The optimum condition for grafting were obtained when 5 g of cassava starch, 5 g of MMA, 0.1 g of BPO, and a reaction time of 3 h were used. These condition provided a graft copolymer with 25.00% add-on, 81.40% monomer conversion, 54.30% homopoly(methyl methacrylate) formed, 45.70% grafting efficiency, 37.20% grafting ratio, and 95.54% yield. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4083–4089, 2006

Key words: graft copolymers; initiators; irradiation

INTRODUCTION

Because of considerable interest in the preparation of biodegradable products based on natural polymers such as starch, many techniques have been developed to modify the chemical and physical properties of those natural polymers. Many studies have been reported for chemical attachments of synthetic polymers onto starch via free-radical graft copolymerizations. The initiations of such reactions begin when free radicals generated on starch molecules react with vinyl monomers. Several methods have been used to generate these free radicals, and they can be divided into two categories: irradiation and chemical initiations.

Irradiation initiation has been very popular in recent years. It has been applied to an enormous number of graft copolymerizations.[1–7] Although it seems to have many advantages, not only the ease of grafting but also a high grafting efficiency and good properties in the resultant graft copolymers, irradiation is an expensive and dangerous technique. Consequently, the safety of controlling equipment and pilot-scale production have become serious problems.

In addition to irradiation initiation, free radicals on a starch backbone can be generated by chemical methods. The grafting of vinyl monomers onto starch has been accomplished with various types of free-radical initiators, including ceric ammonium nitrate,[8] potassium persulfate,[9] manganic pyrophosphate,[10] potassium permanganate,[11] and a ferrous ammonium sulfate–hydrogen peroxide system.[12]

In this article, an alternative method with another type of initiator for the synthesis of a starch graft copolymer based on cassava starch and methyl methacrylate (MMA) monomer is presented. Benzoyl peroxide (BPO) was chosen as the initiator for this method due to its low cost, ease of handling, and safe polymerization system. This initiator was successfully used to initiate graftings of MMA onto gelatin[13] and of styrene onto cassava starch.[14]

EXPERIMENTAL

Materials

Cassava starch was kindly provided by Thai Wah Co., Ltd. This starch had standard specification as follows: maximum moisture content = 13%, maximum ash = 0.20%, maximum pulp = 0.20%, pH = 4.00–7.00, and maximum viscosity = 550 Brabender units. The MMA monomer was kindly provided by Sumipex (Thailand) Co., Ltd. BPO was purchased from Ajax Chemicals. Acetone, methanol hydrochloric acid 37% (HCl), and tetrahydrofuran were purchased from Labscan Asia Co., Ltd. (Thailand). Sodium hydroxide (NaOH) was produced by Merck (Germany).

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Methods

Synthesis of the graft copolymers

Distilled water (90 cm^3) was poured into a 500-cm^3 four-necked, round-bottom flask placed in a heating mantle and equipped with a mechanical stirrer, a condenser, a thermometer, and a nitrogen inlet. It was stirred at room temperature under nitrogen atmosphere for 10 min. Cassava starch was then added to the flask, and the solution was stirred for 30 min. A solution of BPO in 10 cm^3 of acetone and 5 cm^3 of distilled water was added to the starch slurry. After the mixture for was stirred continuously for 10 min, MMA monomer and 5 cm^3 of distilled water were added, and the mixture was stirred for another 10 min. It was then heated to 80°C, and the reaction was carried out at this temperature for the remainder of the reaction time. After the reaction finished, the mixture was poured into excess methanol. The precipitate was filtered, washed with methanol, dried in an oven at 60°C for 24 h, and kept in a desiccator.

To determine the optimum conditions for this graft copolymerization system, the reaction parameters, including the amounts of BPO, cassava starch, and MMA monomer and the reaction time, were varied. The amounts of BPO used were 0.01, 0.1, and 1.0 g, whereas the reaction times included 1, 2, 3, 4, and 5 h. The effects of the amounts of the reactants on the grafting characteristics of the graft copolymers were investigated in three cases as follows:

1. The amounts of the two reactants were equal. In this case, 5 g of cassava starch and 5 g of MMA monomer were used.
2. The amount of MMA monomer was higher than that of cassava starch. In this case, 2.5 g of cassava starch and 7.5 g of MMA monomer were used.
3. The amount of cassava starch was higher than that of MMA monomer. In this case, 7.5 g of cassava starch and 2.5 g of MMA monomer were used.

After all of the graft copolymers were synthesized, each dried product was subjected to Soxhlet extraction to remove homopoly(methyl methacrylate) (homoPMMA). The extraction was done at 70°C for 10 h with acetone as the solvent. The weight of homoPMMA was calculated as shown in the following equation:

$$\text{Weight of homoPMMA} = \text{Weight after extraction} - \text{Weight before extraction} \quad (1)$$

For further characterization, the separation of poly(methyl methacrylate) (PMMA) grafted on starch (grafted PMMA) from the starch backbone was done by acid hydrolysis. In a 250-cm^3 Erlenmeyer flask equipped with a condenser, the starch-*g*-PMMA copolymer was weighed and stirred in 200 cm^3 of 3 *N* HCl. The mixture was refluxed for 2 h. The water-insoluble polymer was filtered and washed with distilled water until its pH was approximately 7. Then, it was dried in an oven at 60°C for 24 h. The product was allowed to cool to room temperature before it was weighed.

Characterization of the graft copolymers

Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet Impact 400D spectrophotometer to characterize chemical structures of the samples. The dried powder samples were mixed with KBr and pressed into disc form by hydraulic compression. The samples were scanned at a frequency range of 4000–400 cm^{-1} with 32 consecutive scans and a 4-cm^{-1} resolution.

A Jeol JSM-5410 LV scanning electron microscope was used to observe sample morphology. Before testing, the sample was dried in an oven at 60°C for 24 h and kept in a desiccator. Then, the sample was mounted on the stub with double sticky tape. The sample was then coated with a thin evaporated layer of gold to improve conductivity and to prevent electron charging on the surface. The scanning electron microscope was operated at 15 kV.

Determination of the grafting characteristics[14,15]

Six grafting characteristics of the synthesized graft copolymers were determined from the following equations:

$$\text{Yield (\%)} = \frac{\text{Weight of starch-}g\text{-PMMA copolymer with homoPMMA}}{\text{Weight of starch} + \text{Weight of BPO} + \text{Weight of MMA monomer}} \times 100 \quad (2)$$

$$\text{Conversion (\%)} = \frac{\text{Weight of homoPMMA} + \text{Weight of grafted PMMA}}{\text{Weight of MMA monomer}} \times 100 \quad (3)$$

$$\text{HomoPMMA formation (\%)} = \frac{\text{Weight of homoPMMA}}{\text{Weight of grafted PMMA} + \text{Weight of homoPMMA}} \times 100 \quad (4)$$

Grafting efficiency (%)

$$= \frac{\text{Weight of grafted PMMA}}{\text{Weight of grafted PMMA} + \text{Weight of homoPMMA}} \times 100 \quad (5)$$

% Grafting ratio

$$= \frac{\text{Weight of grafted PMMA}}{\text{Weight of starch}} \times 100 \quad (6)$$

% Add-on

$$= \frac{\text{Weight of grafted PMMA}}{\text{Weight of starch-}g\text{-PMMA copolymer}} \times 100 \quad (7)$$

RESULTS AND DISCUSSION

The following mechanisms are proposed for the graft copolymerization of MMA monomer onto the starch backbone with BPO as an initiator. To produce primary radicals, BPO underwent thermal dissociation to benzoyloxy and phenyl radicals.[16] These radicals could either initiate the grafting of MMA onto the starch backbone via hydrogen abstraction or the homopolymerization of MMA via free-radical addition.

Grafting

Initiation:

$$\mathrm{I_2} \rightarrow 2\mathrm{I}^{\cdot} \quad (8)$$

$$\mathrm{I}^{\cdot} + \text{Starch} \rightarrow \text{Starch}^{\cdot} + \mathrm{IH}$$

$$\text{Starch}^{\cdot} + \mathrm{M} \rightarrow \text{Starch-M}^{\cdot}$$

Propagation:

$$\text{Starch-M}^{\cdot} \xrightarrow{\mathrm{nM}} \text{Starch-(M)}^{\cdot}_{\mathrm{n+1}} \quad (9)$$

Termination:

$$\text{Starch-(M)}^{\cdot}_{n+1} + I\text{-}(M)^{\cdot}_{n+1} \rightarrow \underset{\text{Copolymer}}{\text{Starch-(M)}_{n+1}} + \underset{\text{HomoPMMA}}{\text{I-(M)}_{n+1}} \quad (10)$$

Chain-transfer reaction

$$\text{Starch-(M)}^{\cdot}_{n+1} + \text{Starch} \rightarrow \underset{\text{Copolymer}}{\text{Starch-(M)}_{n+1}\text{-H}} + \text{Starch}^{\cdot} \quad (11)$$

Homopolymerization

Initiation:

$$\mathrm{I_2} \rightarrow 2\mathrm{I}^{\cdot} \quad (12)$$

$$I^{\cdot} + M \rightarrow IM^{\cdot}$$

Propagation:

$$\mathrm{IM}^{\cdot} \xrightarrow{\mathrm{nM}} \text{I-(M)}^{\cdot}_{n+1} \quad (13)$$

Termination:

$$2\text{I-(M)}^{\cdot}_{n+1} \rightarrow \underset{\text{homoPMMA}}{2\text{I-(M)}_{n+1}} \quad (14)$$

Chain-transfer reaction

$$\text{I-(M)}^{\cdot}_{n+1} + \text{Starch} \rightarrow \underset{\text{homoPMMA}}{\text{I-(M)}_{n+1}\text{-H}} + \text{Starch}^{\cdot} \quad (15)$$

According to the previous mechanisms, the product obtained from graft copolymerization would have mostly been a mixture of starch-*g*-PMMA and homoPMMA, which was confirmed by further characterization.

As shown in Figure 1(a), the FTIR spectrum of cassava starch displayed the characteristic peaks of O—H stretching at wave number range of 3500–3100 cm^{-1}, C—H stretching at 2932 cm^{-1}, and C—O stretching at 1025 cm^{-1}. In Figure 1(b), two characteristic strong absorption peaks of ester groups in the PMMA reference were observed. Although the peak at 1730 cm^{-1} corresponded to C=O stretching, the peaks at 1253 and 1145 cm^{-1} were the characteristic of C—O stretching. In addition, peaks corresponding to C—H stretching were observed at wave numbers of 2993 and 2952 cm^{-1}.

The FTIR spectrum of starch-*g*-PMMA before extraction is shown in Figure 1(c). As shown, the product showed characteristic peaks of both cassava starch and PMMA. After Soxhlet extraction, all of the characteristic peaks of cassava starch and PMMA still existed in the spectrum with smaller intensities in those peaks, as shown in Figure 1(d). This suggests that homoPMMA was removed, whereas grafted PMMA was still attached on the starch backbone. Figure 1(e) shows the FTIR spectrum of the removed homoPMMA. It displays all of the characteristic peaks of the PMMA reference. In addition, Figure 1(f) shows the FTIR spectrum of hydrolyzed product obtained after acid hydrolysis of the graft copolymer. Its spectrum also resembles that of PMMA reference. This suggests that this hydrolyzed product was grafted PMMA. Therefore, on the basis of these FTIR spectra, we concluded that the graft copolymer of cassava

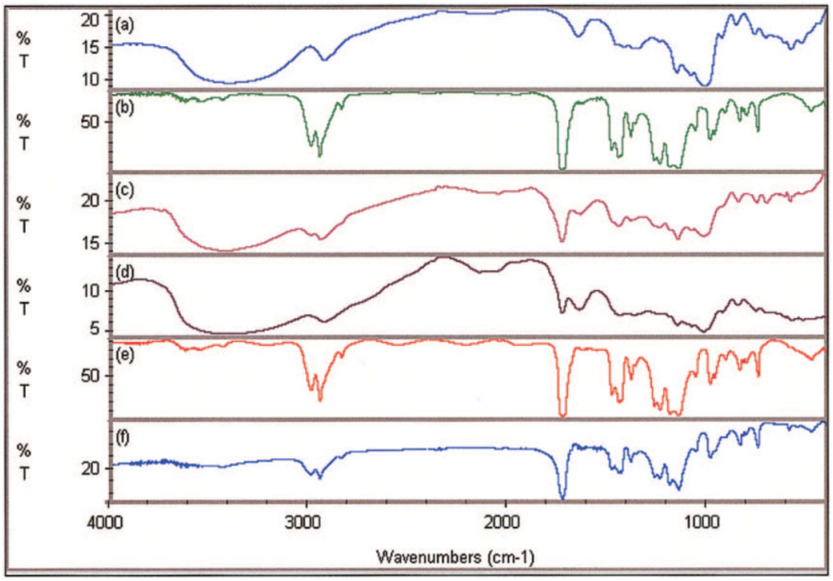
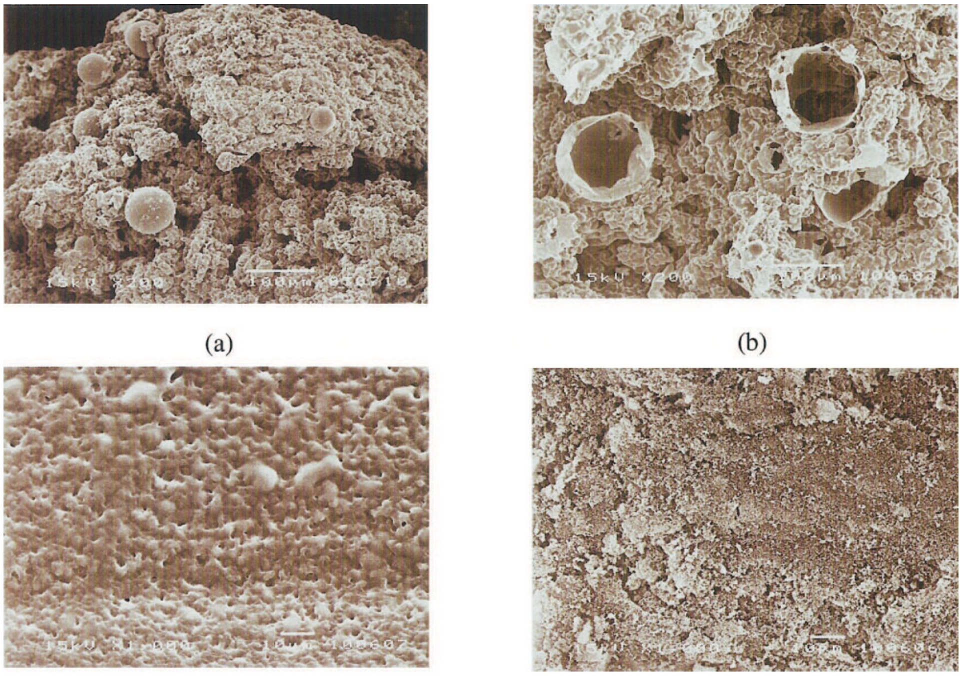


Figure 1 FTIR spectra of (a) cassava starch, (b) the PMMA reference, the starch-*g*-PMMA copolymer (c) before and (d) after Soxhlet extraction, (e) homoPMMA, and (f) grafted PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

starch and MMA monomer was synthesized via free-radical polymerization with BPO as the initiator, as proposed in this research.

The scanning electron microscopy (SEM) photographs shown in Figure 2 also confirmed the existence of the starch-*g*-PMMA copolymer and its accompanying byproduct, homoPMMA. From the SEM photograph of the starch-*g*-PMMA copolymer before Soxhlet extraction [Fig. 2(a)], it is obvious that the obtained graft copolymers had rough surface embedding with various sizes of spherical beads of homoPMMA. After Soxhlet extraction such beads disap-


(a)

(b)

(c)

(d)

Figure 2 SEM photographs of the starch-*g*-PMMA copolymer (a) before and (b) after Soxhlet extraction, (c) homoPMMA, and (d) grafted PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

peared, as shown in the SEM photograph of the starch-*g*-PMMA copolymer after Soxhlet extraction [Fig. 2(b)]. These spherical beads were achieved because the process used for grafting could produce the conditions for the suspension polymerization of homoPMMA. Because of stirring and the hydrophobic characteristics of the MMA monomer, monomer droplets were formed, and because BPO was soluble in these droplets, the polymerization of homoPMMA occurred in these droplets. Consequently, spherical beads of homoPMMA were obtained. HomoPMMA and grafted PMMA were also analyzed by SEM, and their photomicrographs are shown in Figure 2(c) and 2(d), respectively.

Evidently, the amounts of both the reactants and BPO and the reaction times affected the grafting characteristics of the synthesized graft copolymers, as shown in Figure 3, where the numbers in the formulas represent the amounts of cassava starch, MMA monomer, and BPO, respectively.

The results presented in Figure 3(a) indicate that the reaction time had a slight effect on the percentage yield. However, it was obvious that the amounts of both the reactants and BPO showed significant effects on such values. As the amount of BPO increased, the tendency for initiation increased; hence, the opportunity for the MMA monomer to form MMA oligomers and PMMA increased. Because these products could not dissolve in both water as a solvent for grafting process and methanol as a nonsolvent in precipitating and washing steps, they could be collected. On the other hand, small molecules, such as unreacted MMA monomers, could dissolve in methanol; therefore, they were removed in the washing step. Consequently, lower yields were obtained as MMA content increased.

As shown in Figure 3(b), the results indicate that the amount of BPO was the main parameter affecting the percentage monomer conversion. It was clear that as the amount of BPO increased, the percentage monomer conversion tended to increase. This was because a higher amount of BPO resulted in a higher probability for initiations of both the graft copolymerization and the homopolymerization of the MMA monomers. The amount of reactants also showed significant effects on the percentage monomer conversion. When data among the same experimental series were compared, the highest percentage monomer conversion was achieved when the amount of starch and MMA monomer was equal. Because the viscosities of the systems increased with increasing amounts of the starch, it was more difficult for every molecular species to diffuse to each other. Consequently, the initiation and the propagation of the systems decreased. On the other hand, at low amounts of starch, the viscosities of the systems decreased. As a result, termination could easily occur because it was a diffusion-controlled reaction, and this resulted in fewer reactive sites for both grafting and homopolymerization. Furthermore, the reaction time also affected the percentage monomer conversion for each experimental formula. This suggests that there was a suitable reaction time for each formula to complete the reaction. If the reaction time was too short, the reaction was not completed. On the other hand, if the reaction time was too long, the possibility of chain degradation arose.

As evident from Figure 3(c,d), the amount of BPO was the main parameter affecting the percentage homopolymer formation and the percentage grafting efficiency. Because a higher amount of BPO resulted in a larger number of free radicals generated, the initiations of both the graft copolymerization and homopolymerization of MMA monomers increased. However, at a high BPO content, too many free radicals were formed from BPO dissociation. As a result, an addition to MMA monomers was more thermodynamically favorable than hydrogen abstraction, which resulted in graft initiation. Therefore, the probability of graft initiation decreased, whereas that of homopolymerization increased. Similar observations were reported by Misra et al.[17] However, due to an increase in the viscosities of the systems as the amount of starch increased, the systems with high amounts of starch showed lower percentages of homopolymer formation than those with equal amounts of starch and MMA monomer.

The results in Figure 3(e) suggest that the amount of reactants was the main parameter affecting percentage grafting ratio. It was clear that a high percentage grafting ratio could be obtained only when the amount of MMA monomer was higher than the amount of starch. This was because when MMA molecules increased, the probability for grafting also increased. However, the amount of BPO and the reaction time also effected this characteristic by means previously described. These results follow same trend as the percentage add-on in Figure 3(f) because these two characteristics only differed from each other in terms of weights of starch and starch-*g*-PMMA copolymer.

CONCLUSIONS

On the basis of the overall results, we concluded that cassava starch-*g*-PMMA copolymer was synthesized by the grafting technique chosen in this research. The formation of the graft copolymer was confirmed initially by FTIR spectra. The absorption band of C=O stretching appeared at 1730 cm^{-1}. This band was the characteristic band of the carbonyl group existing in PMMA. Therefore, this indicated that PMMA was grafted onto the cassava starch backbone. The formation of cassava starch-*g*-PMMA was also supported by SEM analysis. The grafting characteristics of the obtained cassava starch-*g*-PMMA were affected by sev-

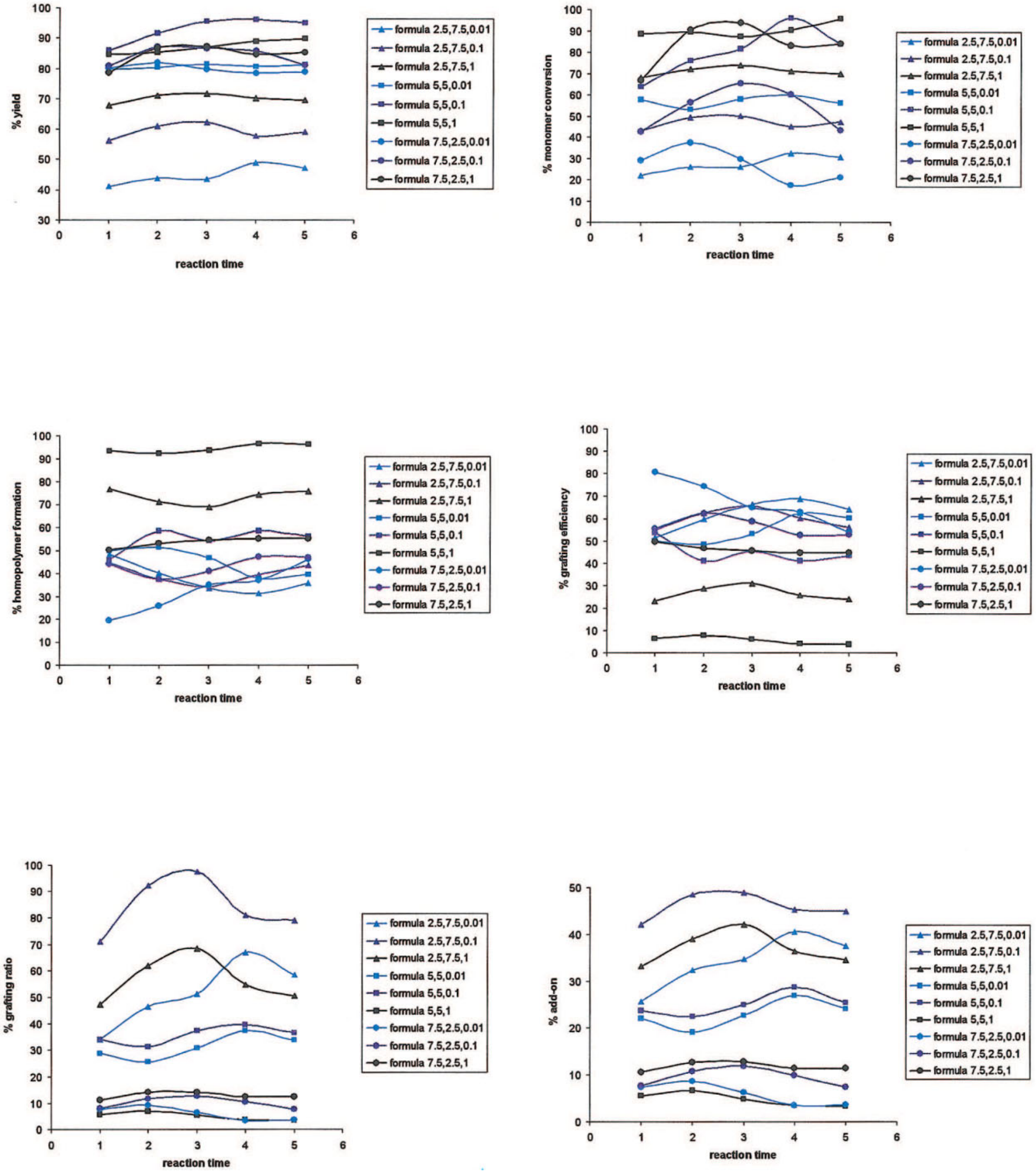


Figure 3 Grafting characteristics of starch-*g*-PMMA copolymers. (the three numbers in the formulas represent the amounts of cassava starch, MMA monomer, and BPO in that order). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

eral parameters, including the amounts of BPO and the reactants and the reaction time. When the grafting characteristics were considered, especially the percentage grafting efficiency in association with the amounts of reactants and initiator and also the time consumed in the process, the results suggest that the optimum amounts of reactants were 5 g of cassava starch and 5 g of MMA monomer; the optimum amount of BPO was 0.1 g, and a reaction time of 3 h was proper for this graft copolymerization system.

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