Preparation and Characterization of Poly(methyl methacrylate) Grafted Sago Starch Using Potassium Persulfate as Redox Initiator

Isam Y. M. Qudsieh,[1,2] A. Fakhru'l-Razi,[2] Suleyman A. Muyibi,[3] Mansor B. Ahmad,[1] M. Z. Ab. Rahman,[1] Wan Md Zin Wan Yunus[1]

[1]Department of Chemistry, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[2]Department of Chemical and Environmental Engineering, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[3]Department of Civil and Water Resources Engineering, Faculty of Engineering, University of Maiduguri, PMB 1069 Maiduguri Borno State, Nigeria

ABSTRACT: In this article, the graft copolymerization of methyl methacrylate (MMA) onto sago starch (AGU) was carried out in aqueous medium using potassium persulfate (PPS) under nitrogen gas atmosphere. The maximum percentage of grafting achieved was 90% under optimized conditions of reaction temperature, monomer, PPS, AGU, and reaction period corresponding to 50°C, 47 mmol, 1.82 mmol, 6.17×10^{-3} mol L^{-1}, and 1.5 h, respectively. The grafting of MMA onto sago starch was confirmed by the differences in infrared spectroscopy. The viscosity measurement and the average molecular weight determination were estimated using Huggin's and Mark Houwink's equations, respectively. This material may have application as a biodegradable plastic. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1891–1897, 2004

Key words: free radical polymerization; sago starch; viscosity; methyl methacrylate; potassium persulfate; graft copolymerization; average molecular weight

INTRODUCTION

Sago starch, produced from pith of the sago palm, is a useful resource for commercial raw materials and foodstuffs and it is an important product of South Asia. Sago (*Metroxylon sagu*) has been an economically important crop of Malaysia.[1] The export of sago starch is the fifth highest revenue earner in the agricultural sector after pepper, rubber, palm oil, and cocoa.[2] Starch in its native form exists in relatively inert granular structures, which are composed of macromolecules arranged in a polycrystalline state.[3,4] Starch is one of the cheapest and most readily available of all natural polymers. It is a high polymer composed of repeating *1,4-α-D-glucopyranosyl units* (often called anhydroglucose units or simply AGU) and, generally, a mixture of linear and branched components.[1,2] Natural polymers such as starch, cellulose, alginic acid, and guar gum are very often used as flocculants in surface water, domestic and industrial wastewater treatment.[5] Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic polymers.[6] Graft copolymers have been used as aids in enhanced oil recovery applications and also as flocculating agents.[7,8]

Chemical modification of starch via vinyl graft copolymerization constitutes a powerful means of improving starch properties, thereby enlarging the range of its utilization. Primarily, free radical-initiated processes could achieve starch graft copolymers. Emphasis is placed on high-energy ionization radiation and redox systems.[9] Grafting is generally considered to result from propagation by radical sites generated on the polymer substrate. A number of studies investigated the graft copolymerization of vinyl monomers such as methyl methacrylate (MMA) onto curdlan, *N*-vinyl pyrrolidone onto gelatin, methyl acrylate (MA) onto potato starch, MA onto sago starch, and vinyl pyrrolidone onto chitosan.[10–16] In this article we report on the grafting of MMA onto sago starch using potassium persulfate (PPS) as redox initiator. The effects of the reaction temperature, the reaction period, MMA concentration, and initiator concentration were investigated. Furthermore, viscosity measurements and average molecular weight determinations were made.

EXPERIMENTAL

Materials

Sago starch was purchased from Wee Kwong Sdn. Bhd., Malaysia, and used without any further purification. MMA was supplied by Fluka (Switzerland) and used after the stabilizer was removed by an aluminum oxide column. PPS analytical grade AR was produced from Mallinckrodt (Mexico) and used as received. Acetone was purchased from Merck (Germany). Methanol grade was obtained from J. T. Baker. Hydrochloric acid was obtained from Hamburg Chemicals (Germany).

FT-IR spectroscopy

The spectra of sago starch, grafted copolymer (sago starch-g-PMMA), and side chain polymer were recorded on a Perkin–Elmer 1725X-Fourier transform infrared (FTIR) spectrophotometer using a potassium bromide disc technique and the scanning of the FTIR spectrophotometer was carried out from 4000 to 400 cm^{-1}.

Preparation of graft copolymer

The grafting reaction was carried out in a round-bottom flask equipped with a reflux condenser and a nitrogen gas inlet. To control the reaction temperature, the flask was placed in a thermostated water bath equipped with a magnetic stirrer. The sago starch slurry was prepared from 1.0 g sago starch (6.17 $\times$ 10^{-3} mol L^{-1} AGU). Gelatinized sago starch was obtained by heating the slurry in the flask for 30 min at 80°C. The initiation process to produce free radicals onto sago starch chains was carried out after the gelatinized sago starch was cooled to a desired graft copolymerization temperature. The initiator used was PPS, and it was added into the gelatinized sago starch 15 min before the addition of the monomer. All reactions (gelatinization, initiation, and propagation) were carried out under nitrogen gas atmosphere and the reaction mixture was continuously stirred during these reactions. At the end of the propagation reaction, the product was precipitated in methanol, filtered using a sintered glass filter of porosity 2, and then dried at 60°C in an oven to a constant weight.

Poly(methyl methacrylate) (PMMA), which was also formed during the graft copolymerization reaction, was separated from the grafted polymer by Soxhlet extraction. Acetone was used as the solvent and each extraction was carried out for 8 h. The purified copolymer was dried in an oven at 60°C to a constant weight. To ensure the complete removal of the homopolymer, the above extraction was carried out three times for each sample. The data used in Figures 2–6 were the average of the results of the triplicate experiments and the percentage of error was less than 5%. The graft copolymerization reaction was characterized by %G, %GE, %H, and %TC, which were calculated according to Fakhru'l-Razi, A. et al.[17] as follows

$$\% \text{ Grafting (\%G)} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

$$\% \text{ Homopolymer (\%H)} = \frac{W_4 - W_2}{W_3} \times 100 \qquad (2)$$

$$\% \text{ Total conversion (\%TC)} = \frac{W_4 - W_1}{W_3} \times 100 \qquad (3)$$

$$\% \text{ Grafting efficiency (\%GE)} = \frac{W_2 - W_1}{W_3} \times 100, \qquad (4)$$

where
W_1 is the weight of sago starch, W_2 is the weight of PMMA grafted sago starch, W_3 is the weight of the monomer, and W_4 is the weight of PMMA grafted sago starch and homopolymer.

Acid hydrolysis of sago starch-g-PMMA by hydrochloric acid solution

Destruction of the sago starch component in sago starch-g-PMMA was carried out by acid hydrolysis. This was carried out by heating under reflux of 1.0 g copolymer in 100 mL of 0.5 M hydrochloric acid for 6 h at 70°C. The residue was then filtered, washed using distilled water, and dried in an oven at 60°C.[18]

Viscosity measurement and the average molecular weight determination

PMMA solutions were prepared by dissolving the required amount of PMMA obtained from the acid hydrolysis in acetone at 30°C. An Ubbelohde viscometer was used to measure the reduced viscosity. Huggin's and Mark Houwink's equations were used to estimate the viscosity of the PMMA solution and its average molecular weight, respectively.

Huggin's equation is

$$\eta_{sp} = [\eta] + K'[\eta]^2 C \qquad (5)$$

$$\eta_{sp} = \eta_{red} C, \qquad (6)$$

where η_{sp} is the specific viscosity, η_{red} is the reduced viscosity, C is the concentration of the polymer, and K' is Huggin's constant. The values of $[\eta]$ were determined from the intercepts of the straight line of (η_{sp}/C)-C plot.
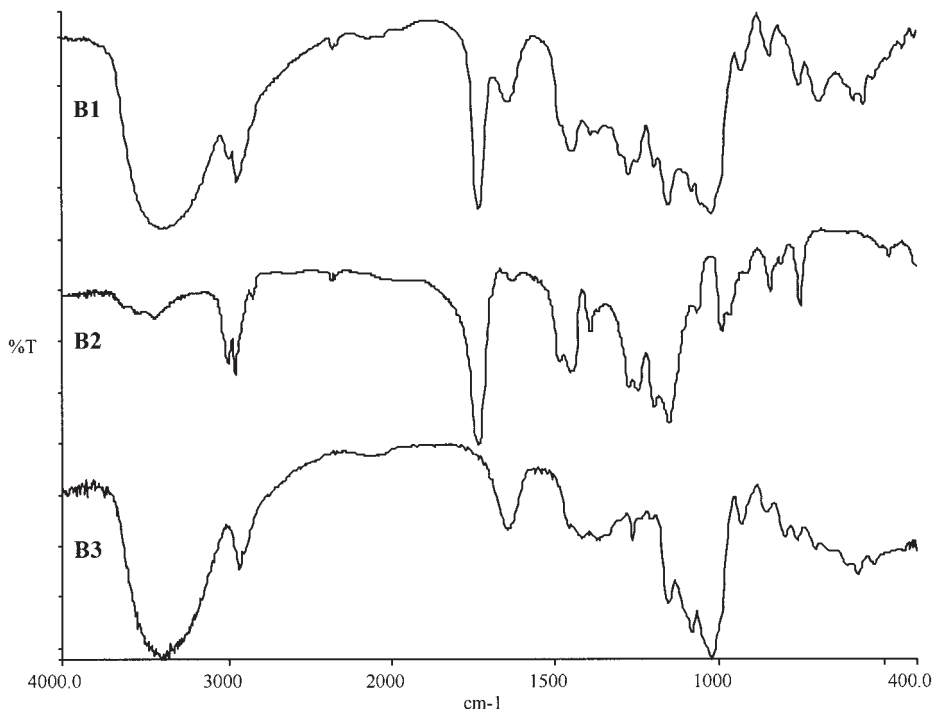
Figure 1 FTIR spectra of PMMA grafted sago starch (spectrum B1), PMMA (spectrum B2), and sago starch (spectrum B3).

Mark Houwink's equation is

$$[\eta] = K\bar{M}_v^a, \tag{7}$$

where $K = 7.7 \times 10^{-3}$ g.ml^{-1} and $a = 0.70$ for PMMA in acetone. $\bar{M}_v$ is the average molecular weight. The average molecular weights were calculated using Eq. 7.[19,20]
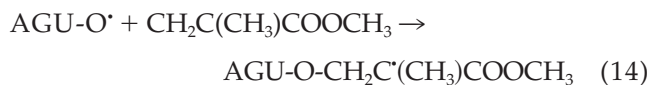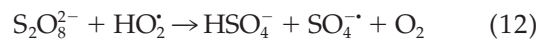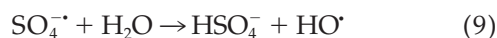
RESULTS AND DISCUSSION

Evidence of grafting and FTIR spectrum analysis

FTIR spectra of sago starch-g-PMMA, PMMA, and sago starch are shown in Figure 1 (spectrum B1 to spectrum B3). FTIR spectrum of the sago starch-g-PMMA (Fig. 1, spectrum B1) indicates the appearance of a broad region (1200–1000 cm^{-1}), which was not observed in the spectrum of sago starch (Fig. 1, spectrum B3), and at the same time the presence of a C=O group (1733 cm^{-1}) for the grafted product which was observed at 1732 cm^{-1} in the spectrum of PMMA (Fig. 1, spectrum B2). However, there was a broad peak at approximately 3407 cm^{-1}, which could be due to the stretching frequency of the other hydroxyl group. The new peaks at 845 and 755 cm^{-1} are due to the stretching of the CH$_2$CH$_2$ group. The other two small peaks at 2994 and 2949 cm^{-1} were assigned to the -OCH$_3$ group and CH-aliphatic group, respectively. The appearance of the new peaks in the spectrum of sago starch-g-PMMA gave supporting evidence for the grafted product and suggested that MMA had been successfully grafted onto sago starch.[21,22] Generally,

potassium persulfate is used as initiator for graft polymerizations. When an aqueous solution of persulfate is heated, it composes to yield sulfate radical along with the other free radical species. Potassium persulfate reacts directly with sago starch to produce radicals on the polymer backbone.[1,17,23]

The mechanism of the graft copolymerization of MMA onto sago starch can be seen in Eqs. (8–15).[24]

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet} \tag{8}$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + HO^\bullet \tag{9}$$

$$2HO^\bullet \rightarrow HOOH \tag{10}$$

$$HO^\bullet + HOOH \rightarrow H_2O + HO_2^\bullet \tag{11}$$

$$S_2O_8^{2-} + HO_2^\bullet \rightarrow HSO_4^- + SO_4^{-\bullet} + O_2 \tag{12}$$

$$AGU\text{-}OH + R^\bullet \rightarrow AGU\text{-}O^\bullet + RH \tag{13}$$

$$AGU\text{-}O^\bullet + CH_2C(CH_3)COOCH_3 \rightarrow$$
$$AGU\text{-}O\text{-}CH_2C^\bullet(CH_3)COOCH_3 \tag{14}$$

$$\xrightarrow{CH_2C(CH_3)COOCH_3} \text{Graft Copolymer} \tag{15}$$

where AGU-OH is sago starch and $R^\bullet$ is free-radical species.
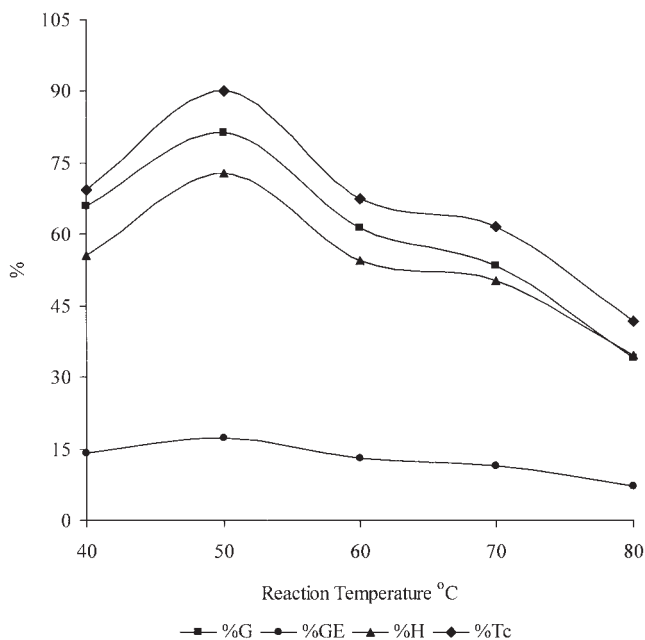
Figure 2 Effects of the reaction temperature on the grafting of PMMA onto sago starch prepared using PPS as an initiator. (Other reaction conditions: AGU, 6.71×10^{-3} mol L^{-1}; MMA, 47 mmol; reaction period, 1 h).

In general, due to the lack of solubility of the graft copolymers in most of the common organic solvents, nuclear magnetic resonance (NMR) techniques cannot be used. However, the conformation of the graft copolymer can be obtained indirectly by the acid hydrolysis technique, in conjunction with infrared spectroscopy.[24,25]

Effects of the reaction temperature

To study the effect of the reaction temperature, the graft copolymerization of MMA onto sago starch using PPS as an initiator was carried out at five temperatures ranging from 40 to 80°C and the results are presented in Figure 2. The optimum temperature for the %G was observed at 50°C. Further increase of the reaction temperature led to decrease of the %G, which probably attributed to the formation of the unstable complex formed by the initiator with the starch or probably due to the dominance of the termination reaction.[26] The %GE slightly increased with the increase of temperature up to 50°C. The %H and the %TC followed the same trend as %G. The results are in agreement with the studies of Lagos and Rayes[21] and Trimnell et al.[27] who used Fe^{+2}/H_2O_2 (Fenton's Reagent) and a ceric initiating system to graft MMA onto chitosan and MA onto granular cornstarch, respectively. Similar results were also obtained when Rahman et al. grafted MA onto sago starch.[16]
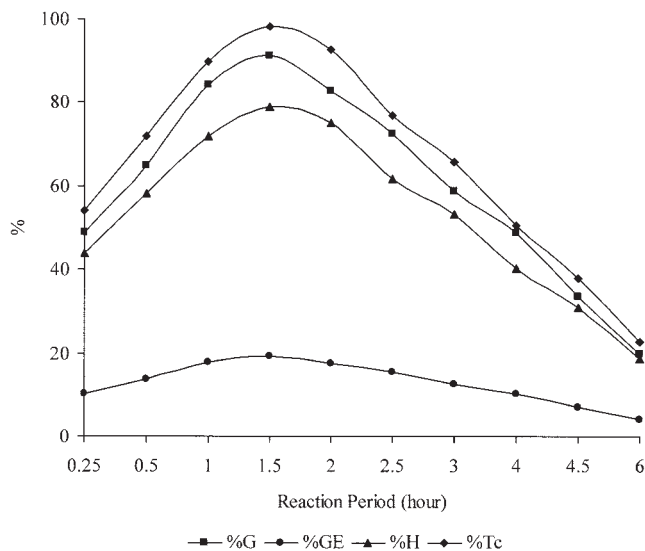

Figure 3 Effects of the reaction period on the grafting of PMMA onto sago starch prepared using PPS as an initiator. (Other reaction conditions: AGU, 6.71×10^{-3} mol L^{-1}; PPS, 3.699 mmol; MMA, 47 mmol; reaction temperature, 50°C).

Effects of reaction period

Investigation on the effects of the reaction periods on the %G was also carried out and the results are shown in Figure 3. The %G increased with the increase in the reaction period up to 1.5 h. The %G was observed to decrease when the reaction period was increased be-
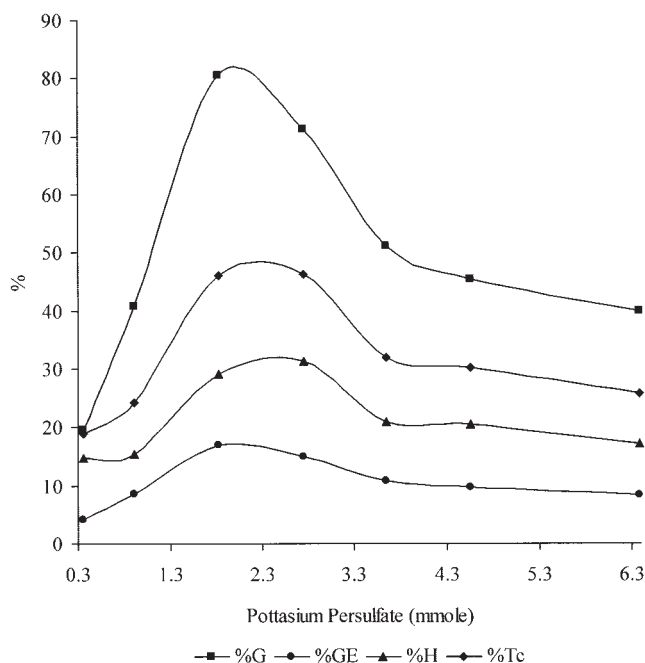

Figure 4 Effects of the PPS initiator concentration on the grafting of PMMA onto sago starch. (Other reaction conditions: AGU, 6.71×10^{-3} mol L^{-1}; MMA, 47 mmol; reaction period, 1 h; reaction temperature, 50°C).

yond 1.5 h. The decrease of the %G after the maximum could be due to the reduction of the reactive sites exposed to the MMA as a result of the increase in viscosity of the solution. This may have made it very difficult for MMA to react with these sites. The %H and the %TC followed the same trend as the %G. It was reported that the %G decreased after the optimum period when homogeneous conditions were used.[28] But the %GE was not affected by the reaction period.[26] Similar results had been obtained when Kojima et al.[29] grafted MMA onto chitin by using tributylborane as an initiator and also when Rahman et al. used ceric ion in the grafting of MA onto sago starch.[16]

Effects of the amount of initiator

The effects of the amount of PPS initiator on the %G, %H, %TC, and %GE are given in Figure 4. The maximum %G was observed when the amount of the initiator was 1.82 mmol. Upon further increase in the amount of the initiator, the %G was decreased. The decrease of the %G when the amount of initiator was increased may be due to an increase in the number of starch radicals terminated prior to monomer addition. Another factor that may be contributed to the decrease in grafting levels at higher initiator concentration is an increase in the homopolymer formation, which competes with the grafting reaction for available monomer.[14,16] The %H, %TC, and %GE followed a similar trend but with different magnitudes. Likewise, the same result was obtained by Hebeish et al.[30] who used a potassium persulfate/sodium thiosulfate redox initiation system at a certain ratio to graft MA onto maize starch. Similar results were also obtained when MA was grafted onto sago starch.[16]

Effects of the amount of the monomer

Effects of the amount of the monomer on the %G, %H, %TC, and %GE are presented in Figure 5. The maximum %G was observed when the amount of MMA was 47 mmol. However, further increase of the amount of MMA reduced the %G. The decrease of %G with the increase of MMA amount could be due to the formation of free radicals in the MMA that led to the formation of the homopolymer. On the other hand, the %H and %TC followed the same trend as the %G but the %GE was slightly decreased after the optimum point. These observations were also recorded when Fenton's reagent and ceric ion were used as initiators.[16,17]

Viscosity measurement and determination of the average molecular weight

The usual method employed to measure the solution and solvent viscosities was either an Ostwald viscom-
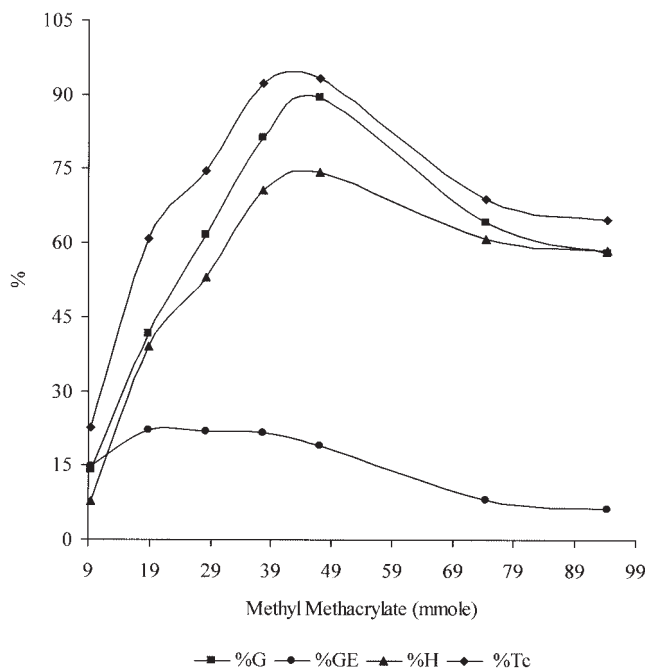

Figure 5 Effects of the monomer concentration on the grafting of PMMA onto sago starch prepared using PPS as an initiator. (Other reaction conditions: AGU, 6.71×10^{-3} mol L^{-1}; PPS, 3.699 mmol; reaction period, 1 h; reaction temperature, 50°C).

eter or a modified version due to Ubbelohde. In this study, an Ubbelohde viscometer was used. The measurement was carried out at 30°C. Huggin's and Mark Houwink's equations were used to determine the $\bar{M}_v$ of the samples.

The intrinsic viscosity $[\eta]$ was calculated from the intercept of the straight lines. Values of $[\eta]$ were obtained (see Fig. 6) for graft copolymers of 19.63, 48.80, 65.84, 83, and 90%G prepared using PPS as an initiator were 18.74, 47.79, 55.42, 64.28, and 69.68 mL.g^{-1}, respectively. The $\bar{M}_v$'s, which were calculated for the copolymers, were 0.69×10^5, 2.6×10^5, 3.2×10^5, 4.0×10^5, and 4.5×10^5, respectively. Increases of $[\eta]$ with the increase of the %G, and the $\bar{M}_v$ with the increase of %G are shown in Figure 6. Enhancement of $[\eta]$ and $\bar{M}_v$ values with the increase of %G could be due to the increase of the side chain length of the copolymer (Fig. 7).[31]

CONCLUSION

The synthesis of poly(methyl methacrylate) grafted sago starch was carried out from methyl methacrylate and sago starch using potassium persulfate as an initiator. It was found that the gelatinized sago starch could be grafted with MMA using PPS as a redox initiator. The optimum conditions that gave the maximum %G (90%) using 6.17×10^{-3} mol L^{-1} of AGU were as follows: reaction temperature, 50°C; reaction
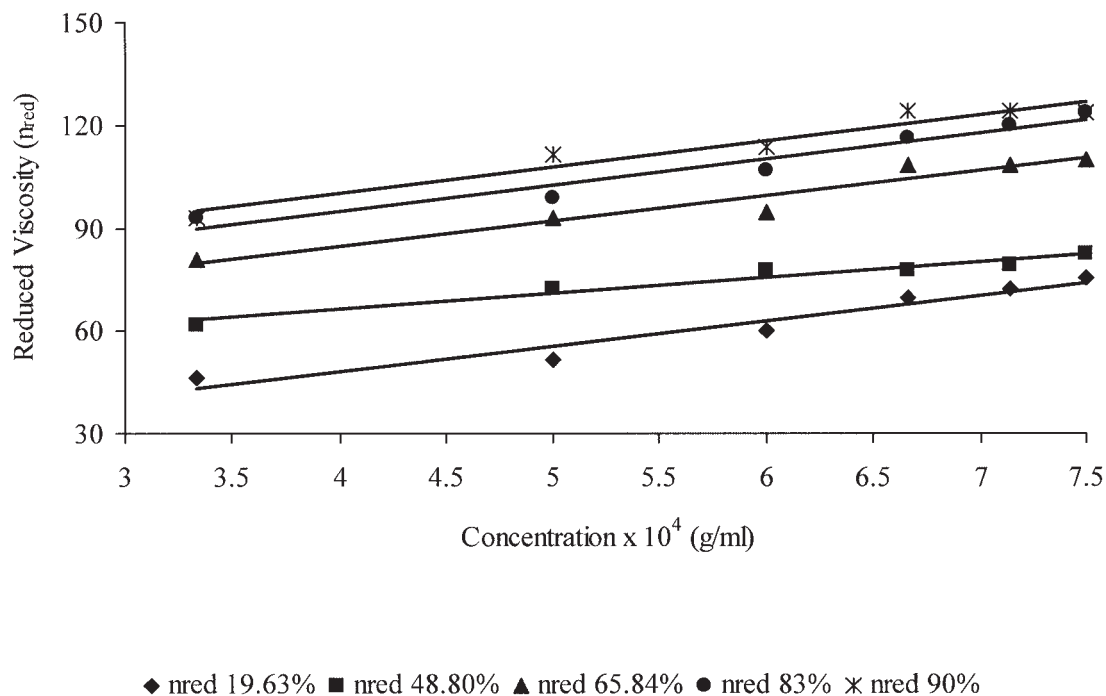
Figure 6 Reduced viscosities of PMMA obtained from 19.63, 48.80, 65.84, 83, and 90% grafting of sago starch-g-PMMA prepared using PPS as an initiator.

period, 1.5 h; the amount of PPS initiator, 1.82 mmol; and the amount of MMA, 47 mmol. Destruction of the sago starch component in sago starch-g-PMMA can be achieved by using 100 mL of 0.5 M hydrochloric acid for 6 h at 70°C under reflux of 1.0 g copolymer. The appearance of 1733 and 3407 cm^{-1} bands in the FTIR spectrum of the grafted sago starch indicated that

MMA had been successfully grafted onto sago starch. FTIR spectra of the hydrolyzed sago starch-g-PMMA copolymers were identical to the spectrum of pure MMA, which also suggested that the product of the copolymerization was sago starch-g-PMMA. The $\bar{M}_v$ of the copolymers that were obtained from the viscosity study were observed to increase with the increase
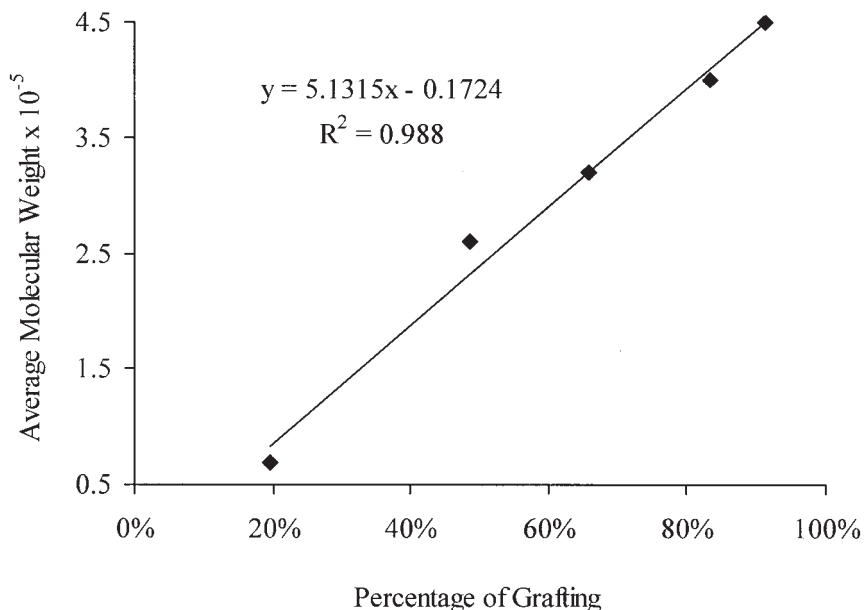

Figure 7 Average molecular weight with different percentages of grafting of PMMA onto sago starch prepared using PPS as an initiator.

of the %G. The $\bar{M}_v$ of the branched chain of the sago starch-g-PMMA (90%G) prepared by the PPS initiator at the optimum conditions was 4.5×10^5.

References

1. Ceresa, R. J. Block and graft copolymerization; Wiley: New York, 1973; Chap. 1.
2. Takeda, Y.; Takeda, C.; Suzuki, A.; Hizukuri, S, J. Food Sci 1989, 54, 177.
3. Azudin, M. N.; Kelvin, L. E.-T. In Proceedings of the Fourth International Sago Symposium, Koonlin, T., Ed.; The Sago Palm Research Fund: Kuching, Sarawak, Malaysia, 1991; p. 149.
4. Wang, W. J.; Powell, A.D.; Oates, C. G., Bioresource Technol 1996, 55, 55.
5. Rath, S. K.; Singh, R. P. Colloids Surf A Physicochem Eng Aspects 1998, 139, 129.
6. Deshmukh, S. R.; Sudhakar, K.; Singh, R. P. J Appl Polym Sci 1991, 43, 1091.
7. Rath, S, K.; Singh, R. P. J Appl Polym Sci 1997, 66, 1721.
8. Tripathy, T.; Pandey, S. R.; Karmakar, N. C.; Bhagat, R. P.; Singh, R. P. Eur Polym Mater 1999, 35, 2057.
9. Mostafa, K. M. J Appl Polym Sci 1995, 56, 263.
10. Gao, J. P.; Chuan, R.; Yu, J. G.; Duan, M. L. J Appl Polym Sci 1994, 53, 1091.
11. Khalil, M. I.; Faraj, S.; Abd El Fattach, S. J Appl Polym Sci 1995, 57, 335.
12. Yoshida, T.; Hattori, K.; Sawada, Y.; Choi, Y.; Uryu, T. J Polym Sci Polym Chem 1996, 34, 3060.
13. Gao, J. P.; Li, Z.; Wang, W.; Huang, M. J Appl Polym Sci 1998, 68, 1485.
14. Mingzku, L.; Rongshi, C.; Jingjia, W.; Cheng, M. J Polym Sci Polym Chem 1993, 31, 3181.
15. Yazdani-Pedram, M.; Retuert, J. J Appl Polym Sci 1997, 63, 1321.
16. Rahman, L.; Silong, S.; Zin, W. M.; Zaki Ab Rahman; M., Ahmad, M.; Haron, J. J Appl Polym Sci 2000, 76, 512.
17. Fakhru'l-Razi, A.; Qudsieh, I. Y. M.; Wan Md Z. W., Y.; Zaki Ab. Rahman, M. Z. J Appl Polym Sci 2001, 82 1375–1381.
18. Gurruchaga, M.; Goni, I.; Valero, M.; Guzman, G. M. J Appl Polym Sci 1993, 47, 1003.
19. Rebek, J. F. Experimental Methods in Polymers Chemistry; Wiley: New York, 1980; pp. 123–135.
20. Brandrup, J.; Immergut, E. H., Polymer Handbook, Eds, 2nd ed., pp. IV-12.
21. Lagos, A.; Reyes, J. J Polym Sci Polym Chem1988, 26, 985.
22. Retuert, J.; Yazdani-Pedram, M. Polym Bull 1993, 31, 559.
23. Yoshida, T.; Hattori, K.; Sawada, Y.; Choi, Y.; Uryu, T. J Polym Sci Polym Chem 1996, 34, 3060.
24. Hebeiesh, A.; Bayazeed, A.; El-Alfy, E.; Khalil, M. I. Starch/Staerke 1988, 40, 223.
25. Athawale, V. D.; Rathi, S. C. JMS Rev Macromol Chem Phys 1999, C39, 445.
26. Yazdani-Pedram, M.; Lagos, A. J Macromol Sci Chem 1995, A32, 1037.
27. Trimnell, G.; Fanta, F.; Salch, J. H. J Appl Polym Sci 1996, 60, 285.
28. Kang, B. G.; Yoon, S. H.; Lee, S. H.; Yie, J. E.; Yoon, B. S.; Suh, M. H. J Appl Polym Sci 1996, 60, 1977–1984.
29. Kojima, K.; Yoshikuni, M.; Suzuki, T. J Appl Polym Sci 1979, 24, 1587.
30. Hebeish, A.; Beliakova, M. K.; Bayazeed, A. J Appl Polym Sci 1998, 68, 1709–1715.
31. Fernandez, M. J.; Casinos, I.; Guzman, G. M. J Appl Polym Sci 1990, 41, 2221.