

CHAPTER IV

RESULTS AND DISCUSSION

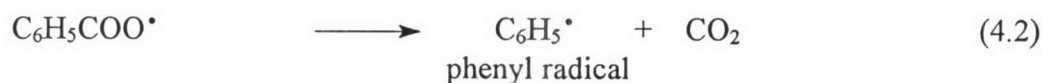
In this chapter, the grafting characteristics, the chemical structures, the molecular weights and the morphology of starch-g-PMMA copolymers, synthesized via free radicals polymerization using BPO as an initiator in aqueous medium at 80°C, were reported.

4.1 Mechanism and Products of Graft Copolymerization

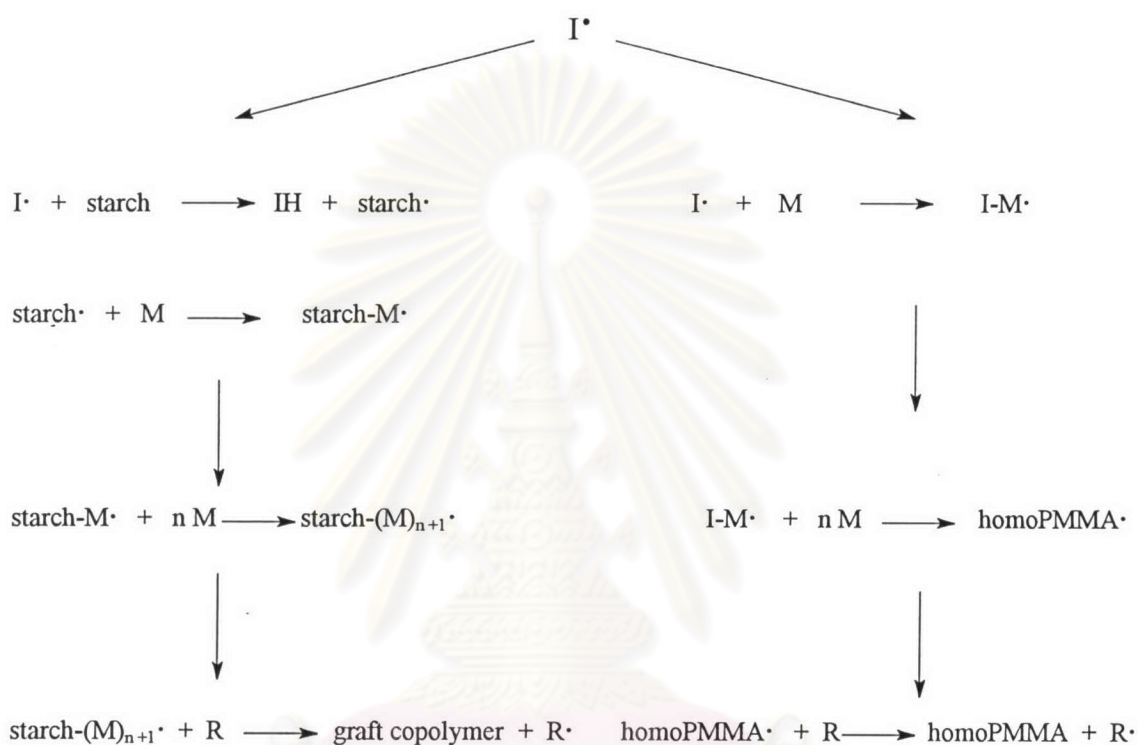
Reaction involving free radicals has been the most widely applied mechanism in the grafting process. The principal reaction responsible for the formation of graft copolymers seems to be the reaction of radical transfer to polymer. This reaction was originally thought most likely to occur by transfer from a growing polymer chain, but in some cases, grafting results chiefly from the direct attack of the polymer by an initiator radical. The following mechanism is proposed for graft copolymerization of MMA monomer onto starch backbone using BPO as an initiator. In order to produce primary radicals, BPO undergoes thermal dissociation as:



Benzoyloxy radicals ($\text{C}_6\text{H}_5\text{COO}^\bullet$) can further dissociate into phenyl radicals and carbon dioxide.



Benzoyloxy and phenyl radicals formed can either initiate grafting of MMA onto starch backbone via hydrogen abstraction or homopolymerization of MMA via free radical addition. These interactions can be occurred in two different pathways as schematically presented below.



where $\text{I}^\bullet = \text{C}_6\text{H}_5\text{COO}^\bullet$ or $\text{C}_6\text{H}_5^\bullet$

R can be starch, monomer, initiator, solvent, or homoPMMA

According to all above mechanism, the product obtained from graft copolymerization would mostly be a mixture of starch-g-PMMA and homoPMMA in the form of fine white powder as shown in Figure 4.1. After homoPMMA removal by Soxhlet extraction, the resulted product expected to be starch-g-PMMA became coarse white powder, as shown in Figure 4.2. On the other hand, as demonstrated in Figure 4.3, homoPMMA flakes were translucent and white. Figure 4.4 shows slightly yellowish residue expected to be grafted PMMA obtained from acid hydrolysis of starch-g-PMMA. By further characterizations, the existences of these products were proved as presented in the following sections.

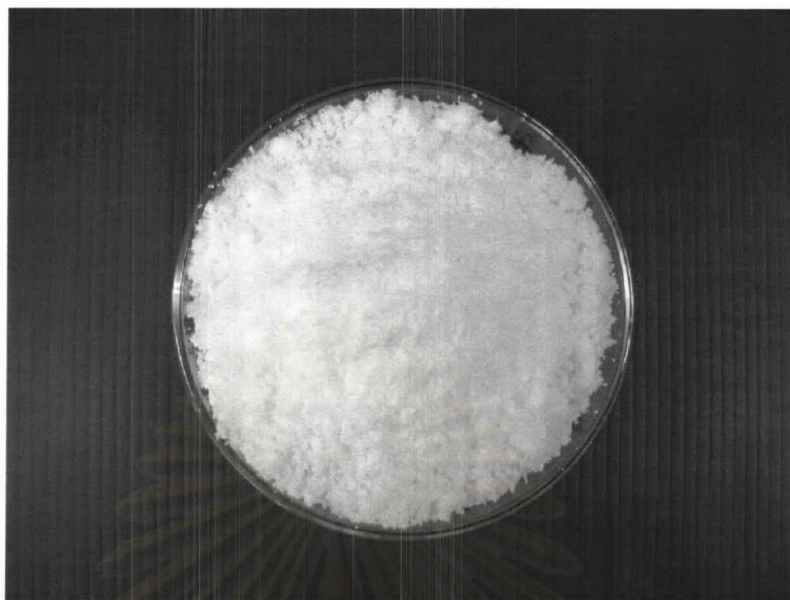


Figure 4.1 Product obtained from graft copolymerization

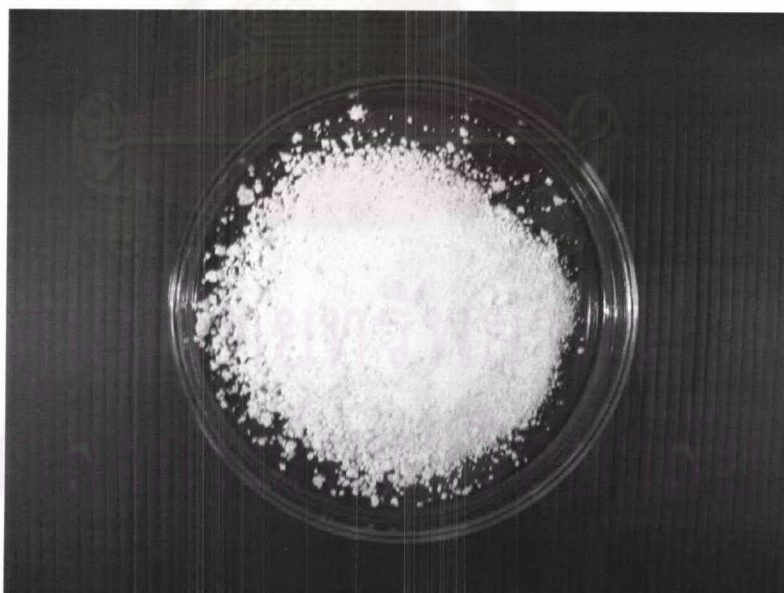


Figure 4.2 Starch-g-PMMA after Soxhlet extraction

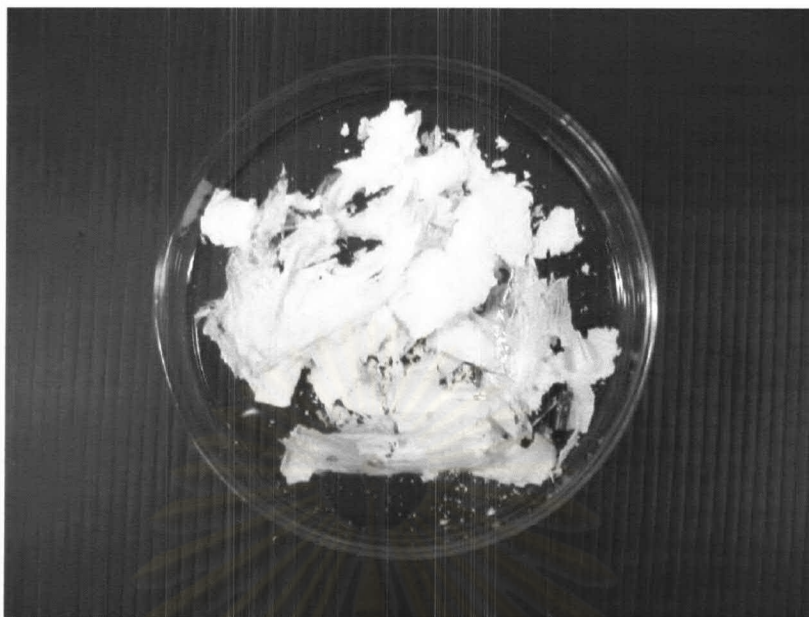


Figure 4.3 HomoPMMA removed by Soxhlet extraction

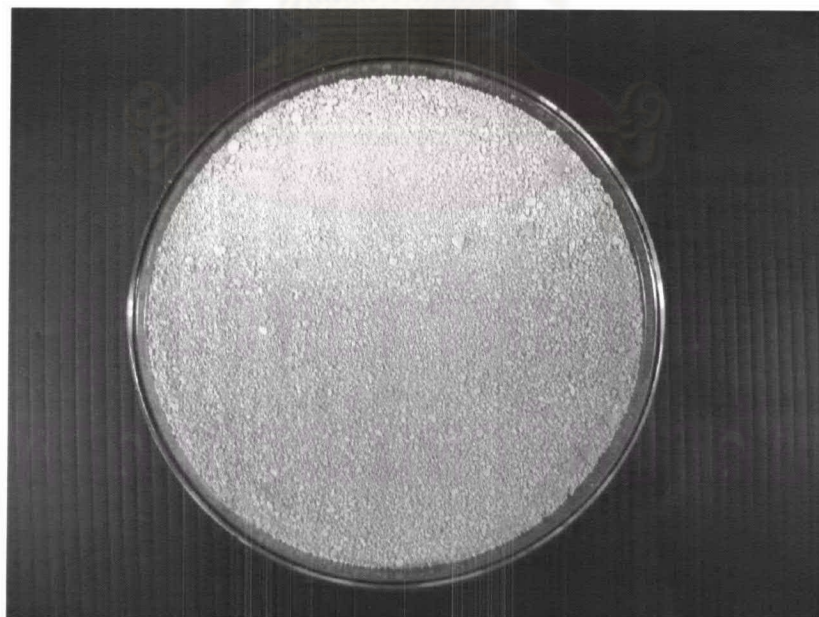


Figure 4.4 Grafted PMMA obtained from acid hydrolysis

4.2 Chemical Structural Analysis

As previously mentioned, the product obtained from graft copolymerization would be a mixture of starch-g-PMMA and homoPMMA. Therefore, Soxhlet extraction was used to separate these two components. Then acid hydrolysis was employed to hydrolyze starch segments of the graft copolymer in order to obtain grafted PMMA. The chemical structures of the products resulting from each step were analyzed by Fourier transform infrared (FT-IR) spectroscopy and the results are presented in Figure 4.5.

The FT-IR spectrum of cassava starch in Figure 4.5 (a) displays the characteristic peaks of O-H stretching at wavenumber range of 3500-3100 cm^{-1} , C-H stretching at 2932 cm^{-1} , and C-O stretching at 1025 cm^{-1} .

In Figure 4.5 (b), two characteristic strong absorption peaks of ester groups in PMMA reference are observed. While the peak at 1730 cm^{-1} corresponds to C=O stretching, the peak at 1253 and 1145 cm^{-1} are the characteristic of C-O stretching. In addition, the peaks corresponding to C-H stretching are observed at wavenumber of 2993 and 2952 cm^{-1} .

The FT-IR spectrum of starch-g-PMMA before extraction is shown in Figure 4.5 (c). It can be seen that the product shows the characteristic peaks of both cassava starch and PMMA. After Soxhlet extraction, all the characteristic peaks of cassava starch and PMMA still exist in the spectrum with less intensities in those peaks as shown in Figure 4.5 (d). This suggests that homoPMMA was removed while grafted PMMA still attach on starch backbone. Figure 4.5 (e) manifests the FT-IR spectrum of the removed homoPMMA. It displays all characteristic peaks as same as PMMA reference. In addition, Figure 4.5 (f) shows the FT-IR spectrum of hydrolyzed product obtained after acid hydrolysis of the graft copolymer. Its spectrum also resembles to that of PMMA reference. This suggests that this hydrolyzed product is grafted PMMA. Therefore, based on these FT-IR spectra, it can be concluded that the graft copolymer of cassava starch and MMA monomer could be synthesized via free radical polymerization using BPO as an initiator as proposed in this research.

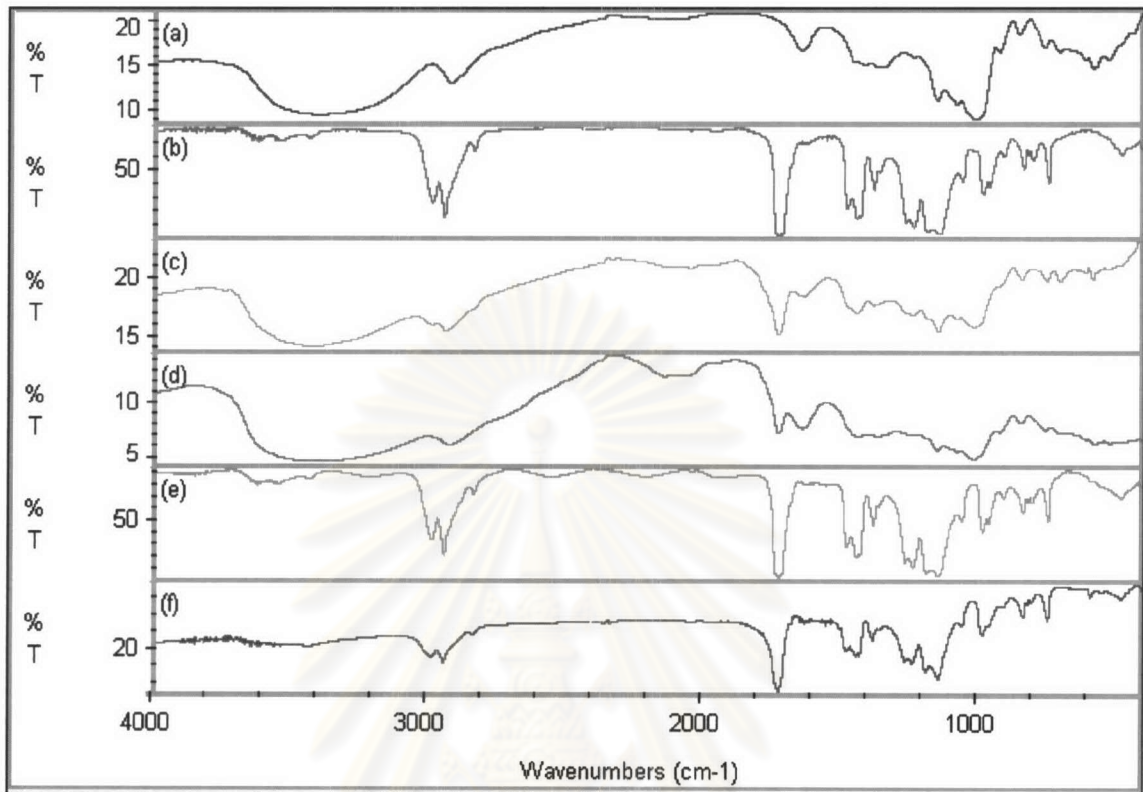


Figure 4.5 FT-IR spectra of cassava starch (a), PMMA reference (b), starch-*g*-PMMA copolymer before and after Soxhlet extraction (c and d), homoPMMA (e) and grafted PMMA (f)

4.3 Morphological Study

Surface morphology of graft copolymers and their components was studied by SEM and the results are presented as follows.

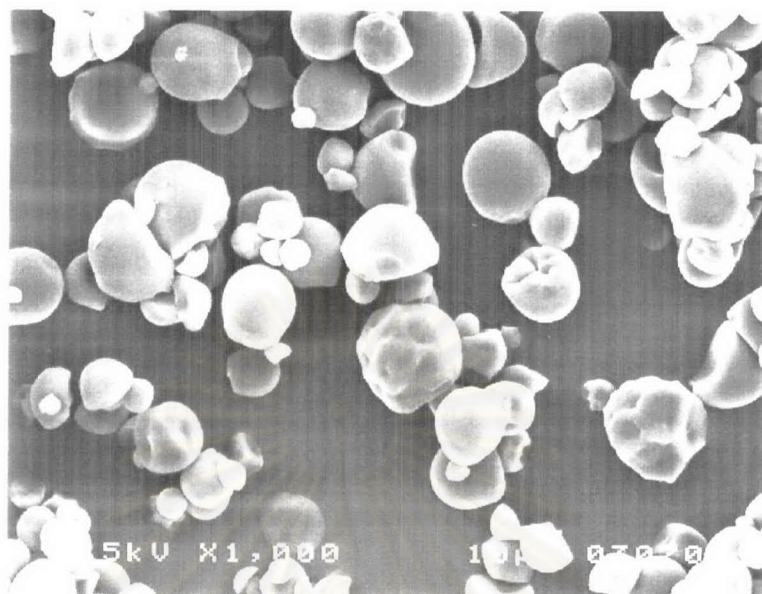
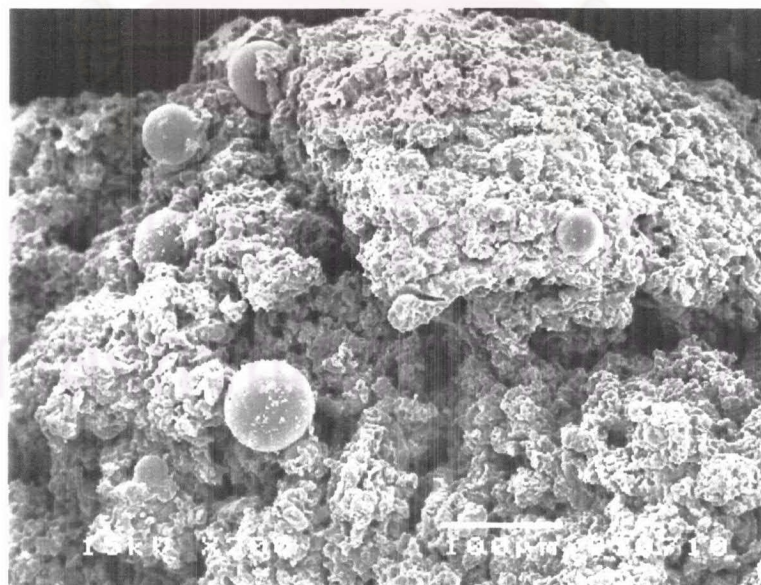


Figure 4.6 SEM photomicrograph of cassava starch granules



**Figure 4.7 SEM photomicrograph of starch-g-PMMA copolymer
before Soxhlet extraction**

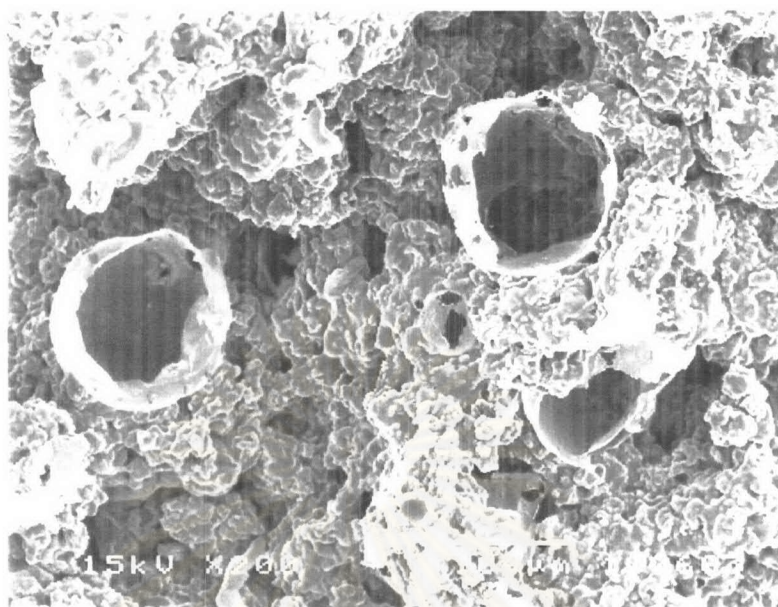


Figure 4.8 SEM photomicrograph of starch-g-PMMA copolymer after Soxhlet extraction

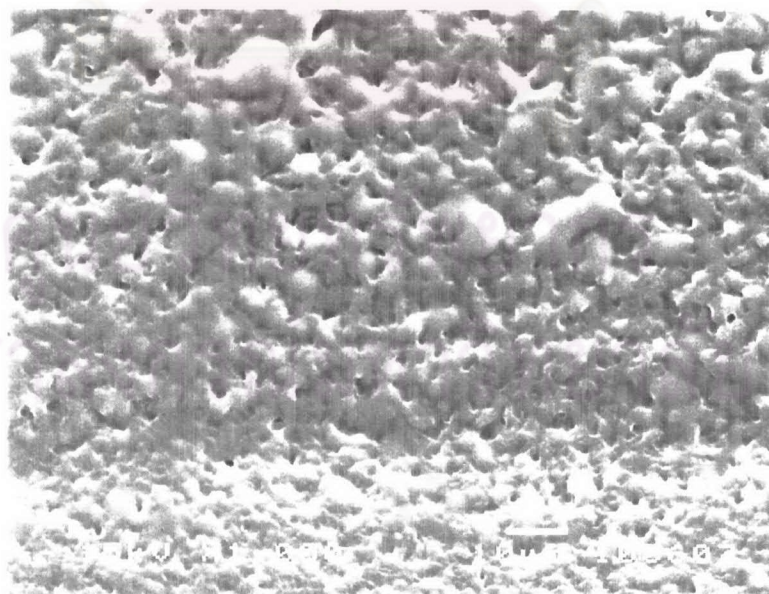


Figure 4.9 SEM photomicrograph of homoPMMA



Figure 4.10 SEM photomicrograph of grafted PMMA

Figure 4.6 shows SEM photomicrograph of cassava starch granules. These granules vary in shape and size; however, mostly are in spherical shapes which are truncated at one end. Their diameters may range from 5 to 35 μm but usually 20 μm .

SEM photomicrograph of starch-*g*-PMMA copolymer before Soxhlet extraction in Figure 4.7. It is obviously seen that the obtained graft copolymers have rough surface embedding with various sizes of spherical beads of homoPMMA. After Soxhlet extraction such beads disappeared, as seen in SEM photomicrograph of starch-*g*-PMMA copolymer after Soxhlet extraction in Figure 4.8. These spherical beads were achieved since the process used for grafting could produce the conditions for suspension polymerization of homoPMMA. Due to stirring and hydrophobic characteristic of MMA monomer, the monomer droplets were formed and since BPO was soluble in these droplets; therefore, the polymerization of homoPMMA occurred in these droplets. Consequently, the spherical beads of homoPMMA were obtained. This similar phenomenon can be observed in the synthesis of cassava starch-*g*-polystyrene via free radical polymerization using BPO as an initiator as previously reported by Kiratitanavit [37].

HomoPMMA and grafted PMMA were also analyzed by SEM, and their photomicrographs are exhibited in Figure 4.9 and 4.10, respectively.

4.4 Effects of Reaction Parameters on Grafting Characteristics

Graft copolymerization of MMA monomer onto cassava starch was carried out at 80°C using various amounts of both reactants and BPO, and different reaction times. Effects of these reaction parameters on grafting characteristics including percent yield, percent monomer conversion, percent homopolymer formation, percent grafting efficiency, percent grafting ratio, and percent add-on were studied and reported.

For all discussion, the abbreviation: formula A, B, C is used. A represents the amount of cassava starch, B represents the amount of MMA monomer and C represents the amount of BPO.

4.4.1 Effects of Reaction Parameters on Percent Yield

After graft copolymerization, the obtained product was weighed and percent yield was calculated. The effects of all reaction parameters on percent yield are exhibited in Figure 4.11. The details of all experimental data and calculations are shown in Appendix A.

The results shown in Figure 4.11 indicate that the reaction time has slightly effect on the percent yield. However, it is obviously seen that the amounts of both reactants and BPO show significant effects on such values. As the amount of BPO increases, the tendency for initiation increases; hence, the opportunity of MMA monomer to form MMA oligomers and PMMA increases. Since these products cannot dissolve in both water and methanol used respectively as a solvent for grafting process and a nonsolvent in precipitating and washing steps, they can be collected. On the other hand, small molecules such as unreacted MMA monomers can dissolve in methanol; therefore, they will be removed in washing step. Consequently, lower yields are obtained as MMA content increases. Furthermore, it can be seen from Figure 4.11 that the lowest percent yield (41.06%) was obtained when 2.5 g of starch, 7.5 g of MMA monomer, 0.01 g of BPO, and the reaction time of 1 hour were used.

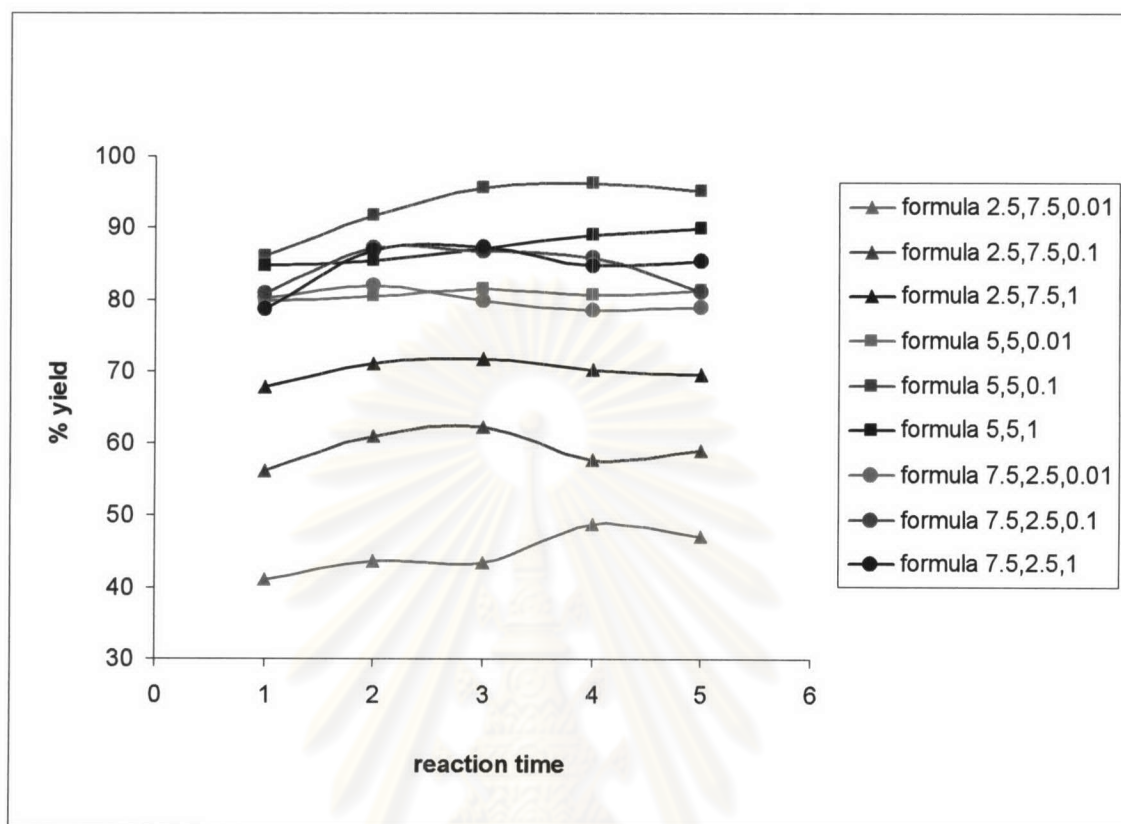


Figure 4.11 Effects of reaction parameters on percent yield

4.4.2 Effects of Reaction Parameters on Percent Monomer Conversion

The effects of the amount of reactants, the amount of BPO, and the reaction time on percent monomer conversion are shown in Figure 4.12. The details of all experimental data and calculations are shown in Appendix A.

From Figure 4.12, the results indicate that the amount of BPO is the main parameter affecting the percent monomer conversion. It is clearly seen that as the amount of BPO increases, the percent monomer conversion tends to increase. This is because higher amount of BPO results in higher probability for initiations of both graft copolymerization and homopolymerization of MMA monomers.

The amount of reactants also shows significant effect on percent monomer conversion. When comparing among the same experimental series, the highest percent monomer conversion is achieved when the amount of starch and MMA monomer is equal. Since the viscosities of the systems increase with increasing the amount of the starch, it is more difficult for every molecular species to diffuse to each other. Consequently, the initiation and the propagation of the systems decrease. On the other hand, at low amount of starch, the viscosities of the systems decrease. As a result, the termination can easily occur since it is a diffusion controlled reaction and this results in less reactive sites for both grafting and homopolymerization.

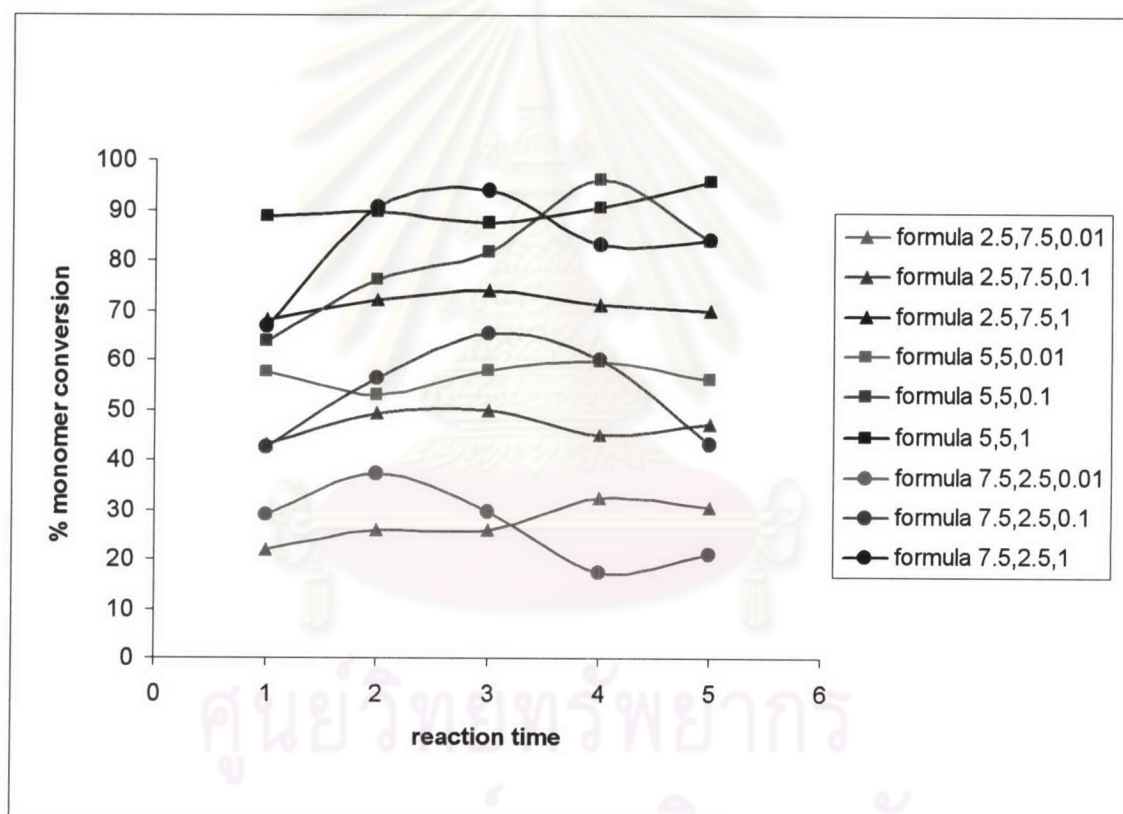


Figure 4.12 Effects of reaction parameters on percent monomer conversion

From Figure 4.12, it can also be seen that the reaction time also affect the percent monomer conversion for each experimental formula. This suggests that there is a suitable reaction time for each formula in order to complete the reaction. If the reaction time is too short, the reaction time does not complete. On the other hand, if the reaction time is too long, a possibility of chain degradation can occur.

4.4.3 Effects of Reaction Parameters on Percent Homopolymer Formation

Theoretically, graft copolymerization of vinyl monomers onto starch backbone is always accompanied by a homopolymer formation. Hence, MMA monomers in the reaction mixture not only grafted on starch backbone, but also formed homoPMMA. The effects of the amount of reactants, the amount of BPO, and the reaction time on percent homopolymer formation are shown in Figure 4.13. The details of all experimental data and calculations are shown in Appendix A.

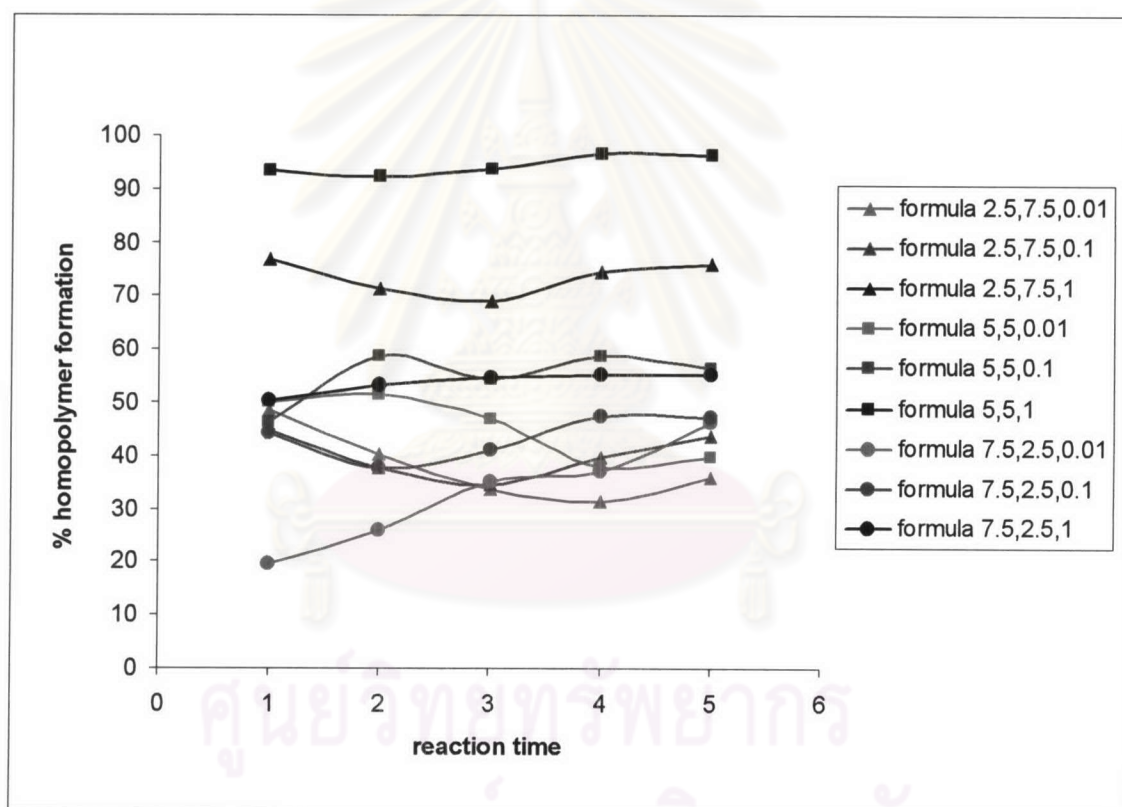


Figure 4.13 Effects of reaction parameters on percent homopolymer formation

It can be evidently seen from Figure 4.13 that the amount of BPO is the main parameter affecting the percent homopolymer formation. Since higher the amount of BPO is used, higher the free radicals are generated, the initiations of both graft copolymerization and homopolymerization of MMA monomers increase. However, at high BPO content, too many free radicals are formed from BPO dissociation. As a

result, an addition to MMA monomers is more thermodynamically favorable than hydrogen abstraction which results in graft initiation. Therefore, the probability of graft initiation decreases while that of homopolymerization increases. Similar observations were reported by Kiratitanavit [37] and Misra [43]. However, due to an increase in the viscosities of the systems as the amount of starch increases; therefore, the systems with high amounts of starch show lower percent homopolymer formation than those with equal amount of starch and MMA monomers.

4.4.4 Effects of Reaction Parameters on Percent Grafting Efficiency

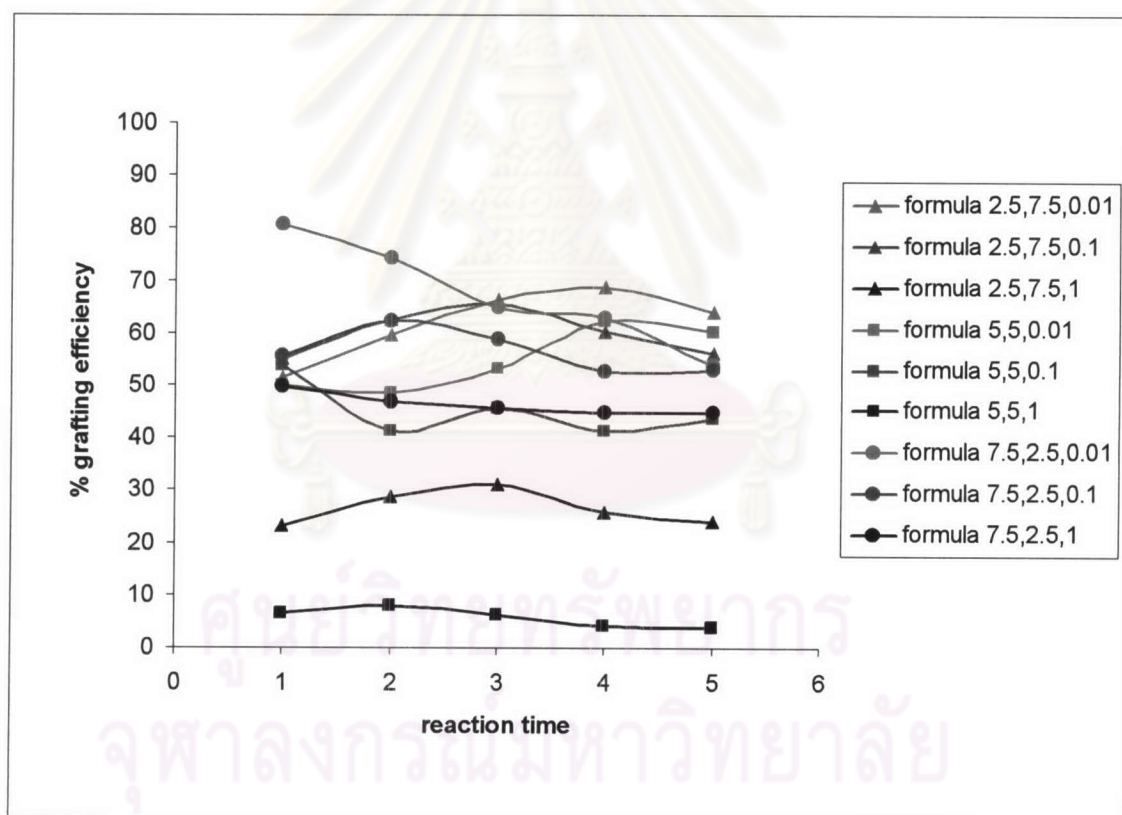


Figure 4.14 Effects of reaction parameters on percent grafting efficiency

Figure 4.14 demonstrates the effects of the amounts of reactants, the amount of BPO, and the reaction time on the percent grafting efficiency. The details of all experimental data and calculations are also shown in Appendix A.

In principals, there is the correlation between percent grafting efficiency and percent homopolymer formation. As previously described, graft copolymerization is always accompanied by a homopolymer formation. If the homopolymer formation is high, the percent grafting efficiency will be low.

4.4.5 Effects of Reaction Parameters on Percent Grafting Ratio

The effects of the amounts of reactants, the amount of BPO, and the reaction time on the grafting ratio are exhibited by all curves in Figure 4.15. The details of all experimental data and calculations are already shown in Appendix A.

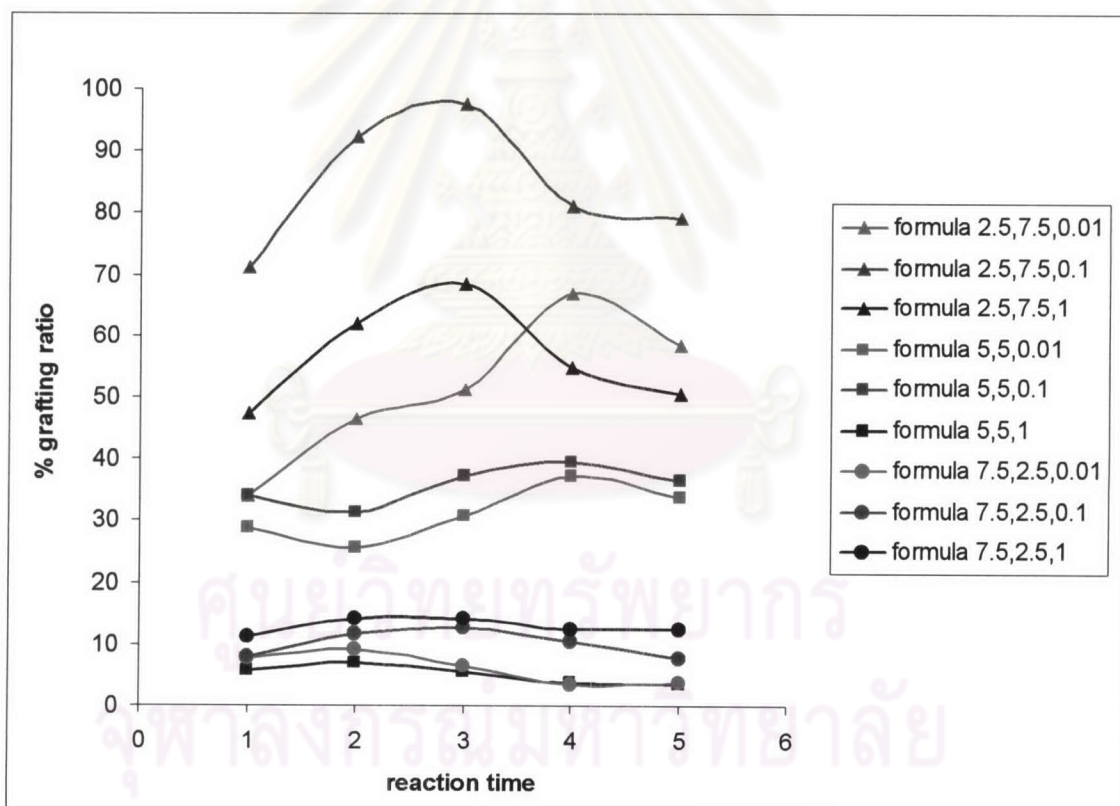


Figure 4.15 Effects of reaction parameters on percent grafting ratio

The results shown in Figure 4.15 indicate that the amount of reactants is the main parameter affecting percent grafting ratio. It is clearly seen that high percentage grafting ratio can be obtained only when the amount of MMA monomer is higher than

the amount of starch. This is because when MMA molecules increase, the probability for grafting also increases. However, the amount of BPO and the reaction time also have effects on this characteristic by means as previously described in aforementioned sections.

4.4.6 Effects of Reaction Parameters on Percent Add-on

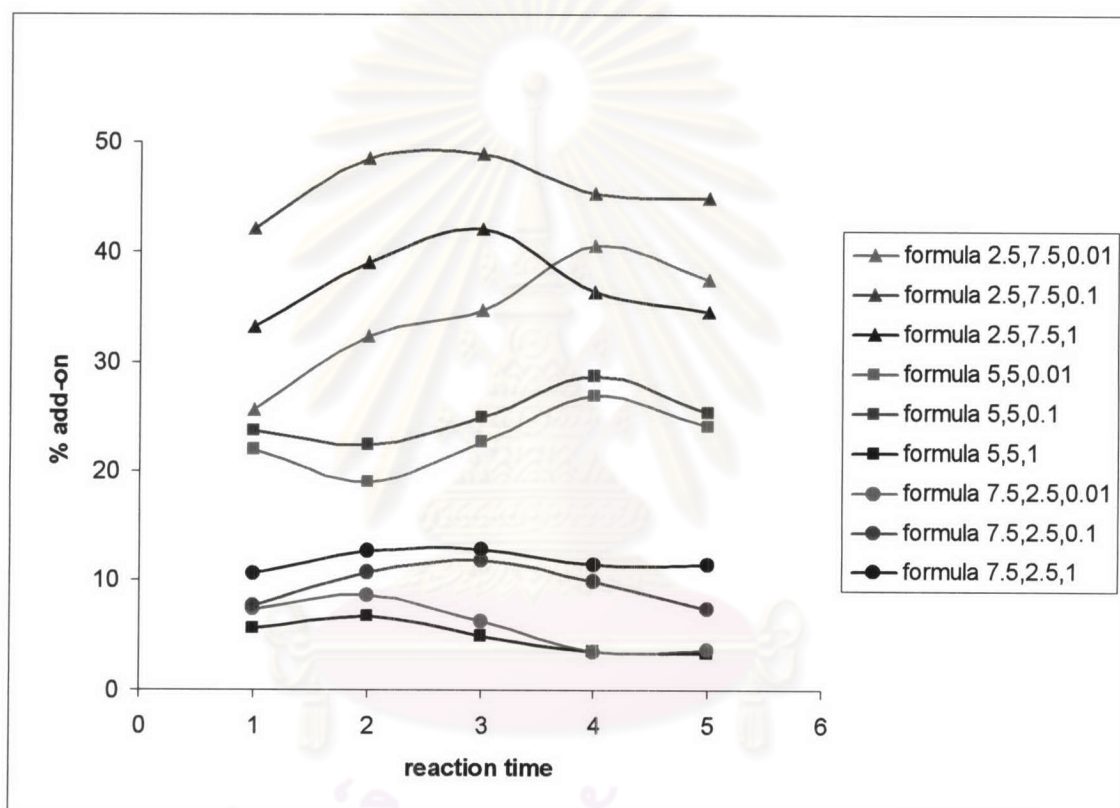


Figure 4.16 Effects of reaction parameters on percent add-on

It can be seen that the results appear in the same trend as percent grafting ratio in Figure 4.15 since these two characteristics only differ from each other by means of weights of starch and starch-g-PMMA copolymer.

Therefore, based on overall results in this section, it can be concluded that the optimum amounts of reactants are 5 g of cassava starch and 5 g of MMA monomer, the optimum amount of BPO is 0.1 g and the reaction time of 3 hours is proper for this graft copolymerization system.

4.5 Molecular Weight Determination

Molecular weights and molecular weight distributions of PMMA reference, homoPMMA, and grafted PMMA were determined by gel permeation chromatography (GPC), using tetrahydrofuran (THF) as an eluent. The weight average molecular weight, number average molecular weight, and polydispersity index of samples were analyzed by comparing with the standard calibration curves of polystyrene standard having a molecular weight range of 5,460-1,290,000.

The weight average molecular weight, \bar{M}_w , is related to the weight of the individual molecular as represented by Equation 4.18.

$$\bar{M}_w = \frac{\sum (M_i W_i)}{\sum W_i} \quad (4.3)$$

Where M_i = Molecular weight of polymer of fraction i
 W_i = Weight of the polymer in fraction i
 i = Fraction number (from 1 to x)

The number average molecular weight, \bar{M}_n , is depended on the number of molecules as represented by Equation 4.19.

$$\bar{M}_n = \frac{\sum W_i}{\sum N_i} \quad (4.4)$$

Where N_i = Number of molecules in fraction i

The \bar{M}_w and \bar{M}_n values provide a polydispersity index as the equation follows.

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} \quad (4.5)$$

Where PDI = Polydispersity index

Table 4.1 shows \bar{M}_w , \bar{M}_n and PDI of PMMA reference, homoPMMA, and grafted PMMA. The synthesis of PMMA reference has been described earlier in Section 3.2. HomoPMMA and grafted PMMA were chosen from the formulae having remarkable grafting characteristics. For all discussion, the abbreviation: formula A, B, C, D is used. A, B, C and D represents the amount of cassava starch, the amount of MMA monomer, the amount of BPO and the reaction time, respectively.

Table 4.1 \bar{M}_w , \bar{M}_n and PDI of GPC samples

Formula	Species	\bar{M}_w	\bar{M}_n	PDI
PMMA reference		5.62×10^4	1.75×10^4	3.21
2.5,7.5,0.1,3	Grafted PMMA	1.14×10^6	2.16×10^5	5.28
	HomoPMMA	8.69×10^5	1.44×10^5	6.02
5,5,0.1,3	Grafted PMMA	1.20×10^6	3.50×10^5	3.42
	HomoPMMA	1.19×10^6	3.60×10^5	3.30
5,5,1,3	Grafted PMMA	1.75×10^5	5.74×10^4	3.05
	HomoPMMA	1.45×10^5	3.41×10^4	4.25
7.5,2.5,0.1,3	Grafted PMMA	4.96×10^5	1.71×10^5	2.91
	HomoPMMA	3.25×10^5	5.60×10^4	5.80

The results suggest that homoPMMA are mostly in the form of slightly shorter chains than grafted PMMA except for that synthesized by using optimum condition. This suggests that once initiations occur, both propagation rates of graft copolymerization and homopolymerization are comparable.

4.6 Determination of Grafting Frequency

Grafting frequency is defined as the number of anhydroglucopyranose units between two PMMA chains which grafted onto cassava starch backbone. Grafting frequency could be calculated from Equation 3.8 as described in Section 3.6.2, and the results are given in Table 4.2. For all discussion, the abbreviation: formula A, B, C, D is used. A, B, C and D represents the amount of cassava starch, the amount of MMA monomer, the amount of BPO and the reaction time, respectively.

Table 4.2 Grafting frequencies of grafted PMMA

Formula	Grafting frequency
2.5,7.5,0.1,3	1,393
5,5,0.1,3	6,481
5,5,1,3	6,818
7.5,2.5,0.1,3	7,830

From Table 4.2, the grafting frequency of formulae 2.5,7.5,0.1,3 5,5,0.1,3 5,5,1,3 and 7.5,2.5,0.1,3 are 1,393 6,481 6,818 and 7,830, respectively. This means that at approximately every 1,393 6,481 6,818 and 7,830 anhydroglucopyranose units the grafted PMMA chain can be observed, respectively. It can be seen that as the amount of MMA increases, the graft copolymer contain higher numbers of grafted chains. In addition, the amount of BPO does not have any significant effect on grafting frequencies of grafted PMMA.