

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

(a) Acetone, analytical reagent grade produced by E. Meark, was used without further purification.

(b) Benzene, analytical reagent grade produced by J. T. Baker Inc., was used without further purification.

(c) Benzoyl peroxide (BPO) was produced by AJAX Chemicals. In this experiment, unpurified and purified forms were used.

Purification of BPO: 20 g of BPO and 100 cm³ of chloroform were mixed in a 500 cm³ beaker and stirred until the mixture was homogeneous. Then 100 cm³ of methanol was added to the mixture and it was stirred for 5 min. After that, the beaker was placed in an ice bath until BPO completely recrystallized. The BPO crystals were collected and dried in a hood. The above process was repeated once again and finally, the purified BPO (white, transparent, and needle crystal form) was obtained. It was kept in a refrigerator at 4°C until use.

(d) Cassava starch, obtained from Thai Wah Co., Ltd., was produced from *tapioca* cultivated in summer. This starch has minimum standard basis as follows: 13% moisture content (min.), 0.20% ash (max.), 0.20% pulp (ml max.), pH value of 4.00-7.00 and viscosity of 550 B.U.. It was dried in an oven at 60°C for 24 hours and kept in a desiccator.

Preparation of Starch Gel: 100 cm³ of distilled water was poured into a 500 cm³ four-necked round bottom flask placed in a heating mantle (Whatman, Rota mantle F) and stirred under nitrogen atmosphere using a magnetic bar for 10 min. After that, 5 g of starch was added to the water. The mixture was heated up to 80°C and stirred at this temperature for 2 hours. Then the starch gel was poured into an excess methanol, dried in an oven (Fisher Scientific, Isotemp) at 60°C for 24 hours, and kept in a desiccator. The obtained sample was used as a reference for further characterization.

(e) Chloroform, analytical reagent grade produced by E. Meark, was used without further purification.

(f) Dimethyl sulfoxide (DMSO), analytical reagent grade produced by Riedel-de Haën GmbH, was used without further purification.

(g) Hydrochloric acid, analytical reagent grade produced by Fluka Chemic GmbH., was used without further purification.

(h) Methanol, analytical reagent grade produced by E. Meark, was used for purification of BPO whereas general purpose grade, obtained from P.P.M. Chemical Ltd., was used as received.

(i) Sodium hydroxide, produced by Fluka Chemic GmbH., was used as received.

(j) Sodium sulfate anhydrous, produced by Freax, was used as received.

(k) Styrene monomer was obtained from Dow Chemical Co., Ltd. It was purified by washing initially three times with 10% aqueous sodium hydroxide solution and followed by distilled water until pH of monomer became 7. Then sodium sulfate anhydrous was added to the monomer. The mixture was kept in a refrigerator at 4°C overnight and then sodium sulfate anhydrous was removed by filtration. The purified

monomer was stored in a refrigerator until use. Prior to use, this purified monomer was removed from the refrigerator and placed in a hood until its temperature reached the room temperature.

Preparation of Polystyrene reference: 100 cm³ of distilled water was poured into a 500 cm³ four-necked round bottom flask and stirred under nitrogen atmosphere using a magnetic bar for about 20 min. Styrene monomer (5 g) was added into the water. The mixture was stirred for 10 min and then 0.5 g of purified benzoyl peroxide was added into the mixture. The mixture was stirred for another 10 min and then it was heated up to 80°C and stirred at this temperature for 2 hours. After that, it was poured into the methanol, filtered, washed with excess methanol, dried in an oven, and kept in a desiccator. The obtained polystyrene was used as a reference for further characterization.

(l) Tetrahydrofuran (THF), analytical reagent grade produced by Fluka Chemic GmbH., was used without further purification.

(m) Toluene, analytical reagent grade produced by Mallinckrodt Specialty Chemicals Co., was used without further purification.

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3.2 Experimental Procedure

Preparation process of starch-*g*-polystyrene copolymer can be divided into 3 sections as shown in Figure 3.1. Section A is a graft copolymerization procedure for grafting styrene monomer onto starch. Section B is an extraction method for removing homopolystyrene from the copolymer. The pure starch-*g*-polystyrene copolymer is obtained from this process. Section C is an acid hydrolysis of graft copolymer. The purpose of this step is to hydrolyze starch backbone in order to obtain grafted polystyrene.

3.2.1 Preparation of Starch-*g*-polystyrene Copolymer

3.2.1.1 Graft Copolymerization Process

A suitable mixing method for graft copolymerization was chosen from the following methods (as described in sections (a)-(c)). The determination was carried out in terms of percent add-on, percent conversion, percent homopolystyrene formation, percent grafting efficiency, percent grafting ratio, and percent yield.

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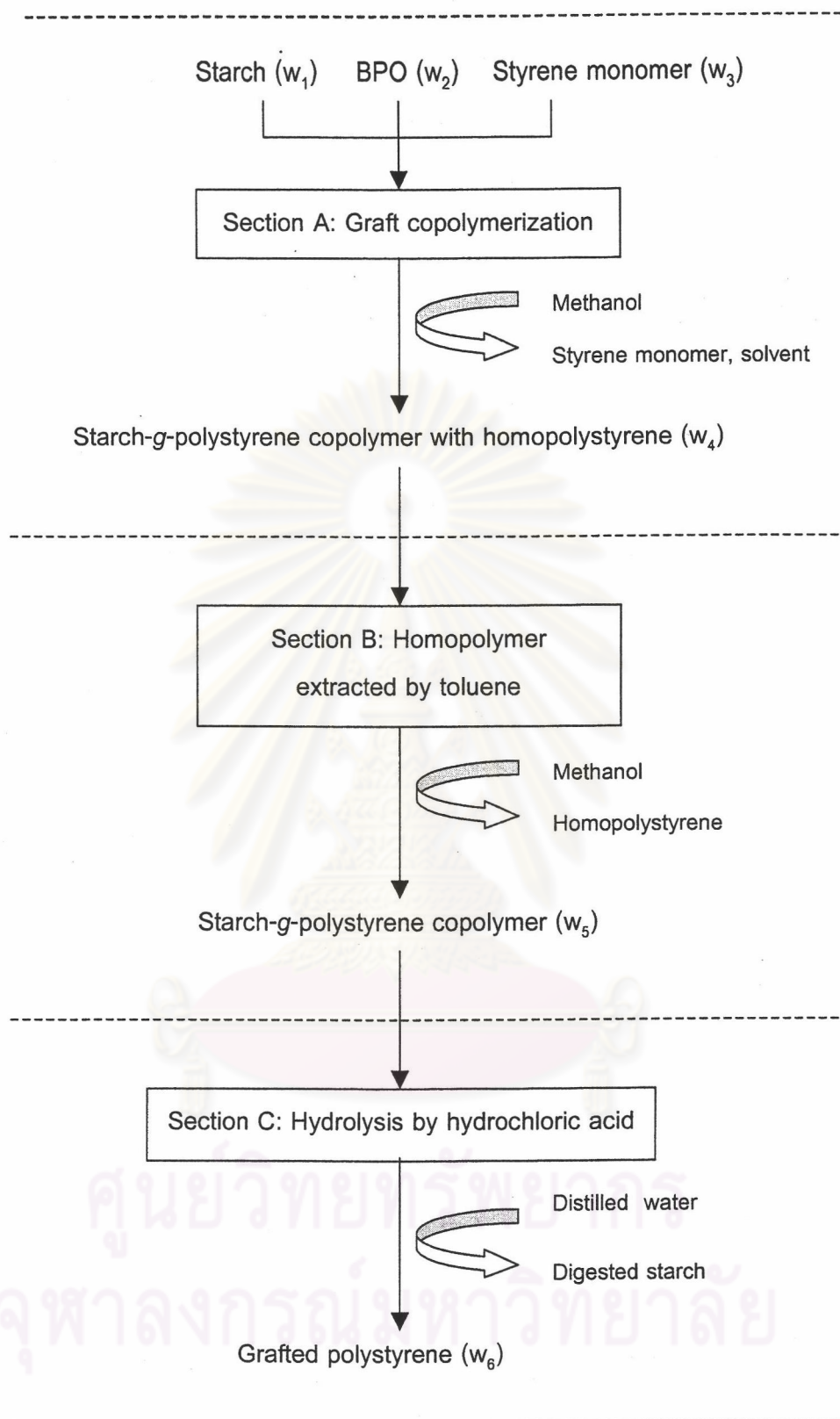


Figure 3.1 Preparation process of starch-g-polystyrene copolymer.

(a) Using the Starch Pre-gel and Adding the Initiator at Room Temperature (Method A)

90 cm³ of distilled water was poured into a 500 cm³ four-necked round bottom flask placed in a heating mantle and equipped with a condenser and other glassware (see Figure 3.2). The distilled water was stirred by magnetic bar at room temperature under nitrogen atmosphere for 10 min. Cassava starch (5 g) was added to the water and stirred for 10 min. The slurry was then heated up to 80°C and stirred for 60-70 min. The speed of the magnetic bar was increased as the starch became gel in this stage.

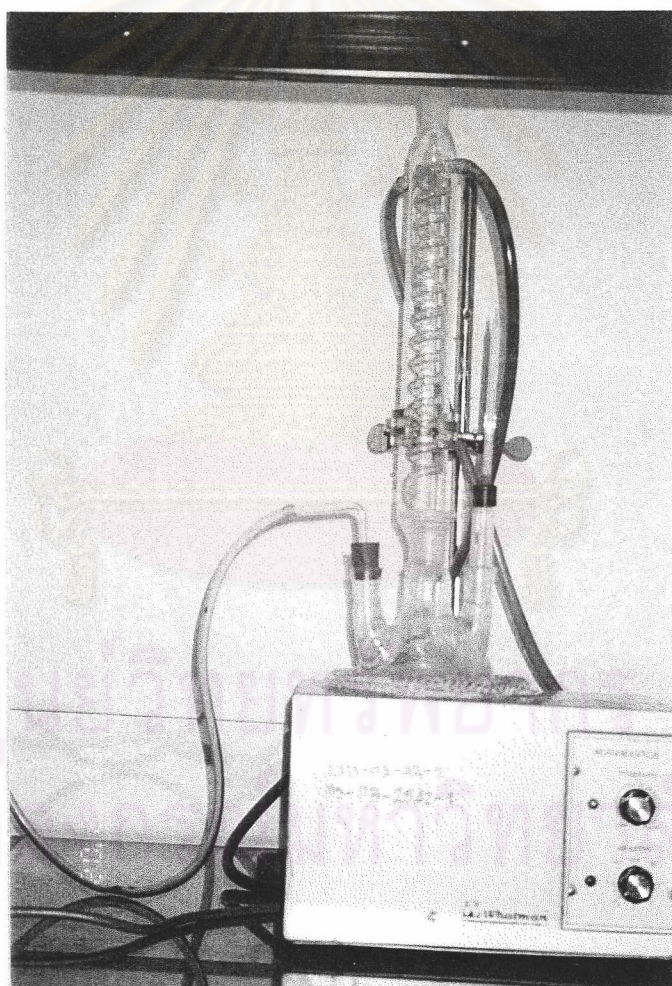


Figure 3.2 Synthesis equipment for Section A.

The starch gel was cooled to room temperature (RT) and stirred for about 15-20 min. With 10 min constant stirring, a solution of 1.0 g of BPO in 10 cm³ of acetone was added to the starch gel followed by an addition of 10 cm³ of distilled water. Then 5 g of styrene monomer and 5 ml of water were added respectively. The mixture was heated up to 80°C under nitrogen atmosphere and this temperature was maintained throughout the reaction period.

After two hours, the reaction mixture was poured into the beaker containing methanol and kept overnight. Then the reaction mixture was filtered through Whatman filter paper No. 41. The white opaque product was washed with methanol twice and dried in an oven at 60°C for a minimum of 24 hours to constant the weight. After that, the product was kept in a desiccator until it cooled down to room temperature and then weighed. The detail of this section is shown in Figure 3.3.

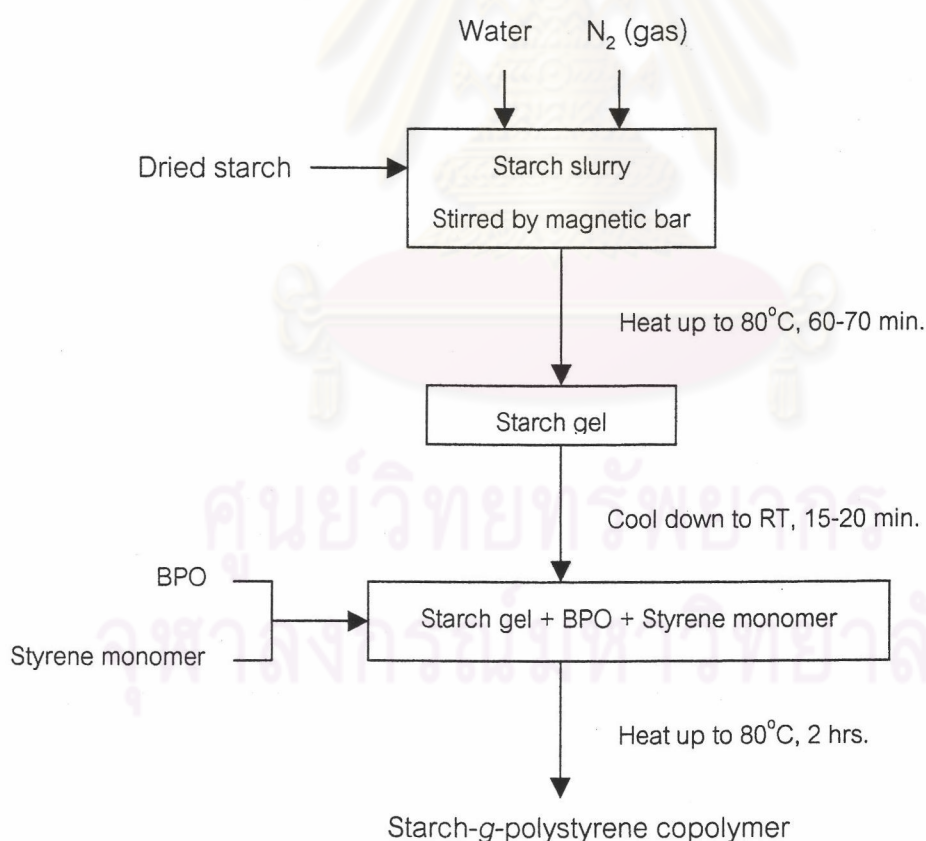


Figure 3.3 Graft copolymerization process using Method A.

(b) Using the Starch Pre-gel and Adding the Initiator at the Pre-gel Temperature (Method B)

The similar method as described in the first paragraph section 3.2.1.1 (a) was employed but after pre-gel at 80°C for 60-70 min, a solution of BPO dissolved in acetone was added to the starch gel at 80°C and stirred for about 10-15 min. After that, 5 g of styrene monomer and 5 ml of water were added respectively and stirred for 2 hours under nitrogen atmosphere. The next step was employed as described in the third paragraph of section 3.2.1.1 (a). The detail of this process is shown in Figure 3.4.

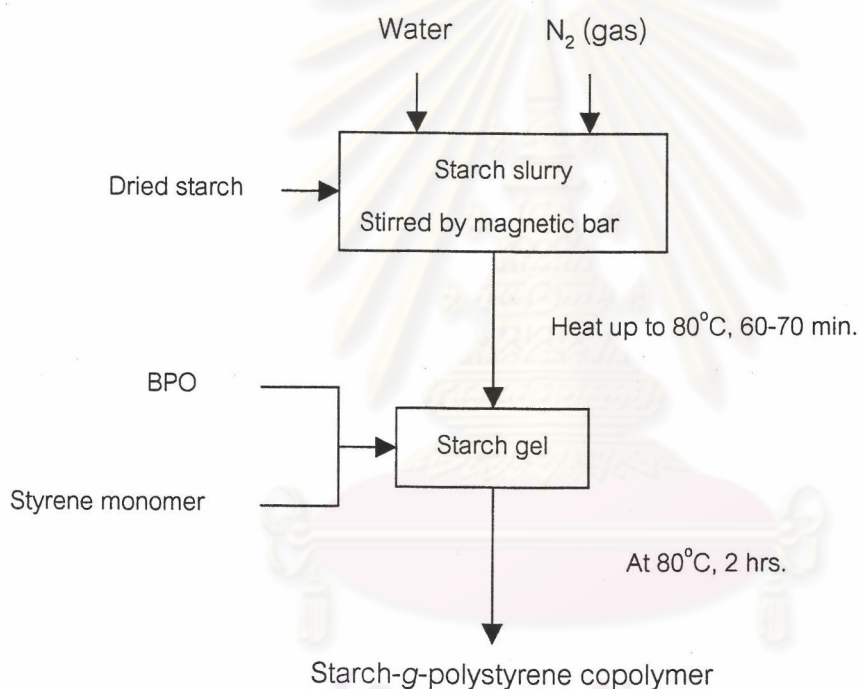


Figure 3.4 Graft copolymerization process using Method B.

(c) Mixing All Raw Materials at the Same Time (Method C)

90 cm³ of distilled water was poured into a 500 cm³ four-necked round bottom flask placed in a heating mantle and equipped with a condenser and other glassware. The distilled water was stirred by magnetic bar at room temperature under nitrogen atmosphere for 10 min. Cassava starch (5 g) was added to the water and

stirred for 30 min. A solution of 1.0 g of BPO dissolved in 10 cm³ of acetone and 10 ml of distilled water were added respectively to the starch slurry with constant stirring for 10 min. Then 5 g of monomer and 5 ml of water were added respectively. The mixture was stirred for about 10 min, then heated up to 80°C and maintained at this temperature for 2 hours. The viscous mixture was poured into methanol and kept overnight. The similar procedure as described in the section 3.2.1.1 (a) was then applied. Figure 3.5 shows the details of this process.

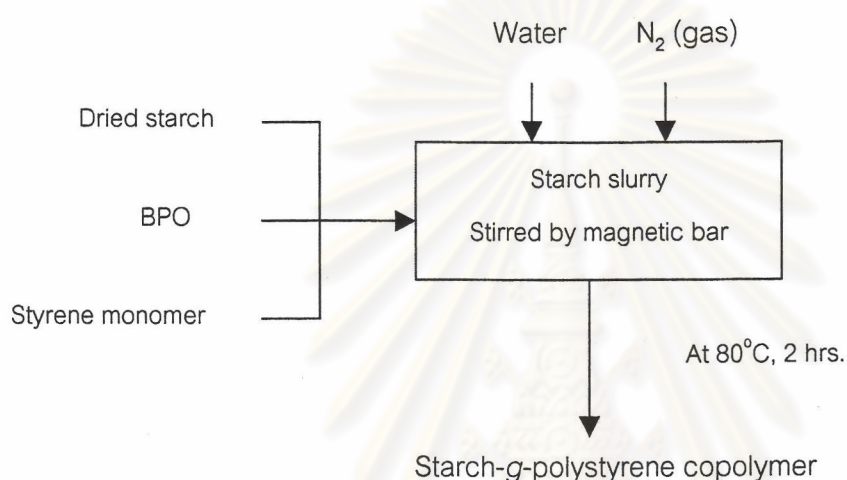


Figure 3.5 Graft copolymerization process using Method C.

It should be mentioned that two types of BPO, unpurified and purified, were used for this particular method.

3.2.1.2 Extraction of Homopolystyrene

The total of dried product was ground, weighed, and then added into the thimble inserted in the Soxhlet extractor (see Figure 3.6). Toluene, used as the solvent for extracting homopolystyrene from the product, was poured into a 500 cm³ round bottom flask equipped with the Soxhlet extractor and heated up until toluene became volatile in the Soxhlet extractor for 24 hours. Then the product was removed, filtered, washed with methanol, dried in oven at 60°C for 24 hours and then kept in a desiccator. The product was weighed to calculate an amount of homopolystyrene.

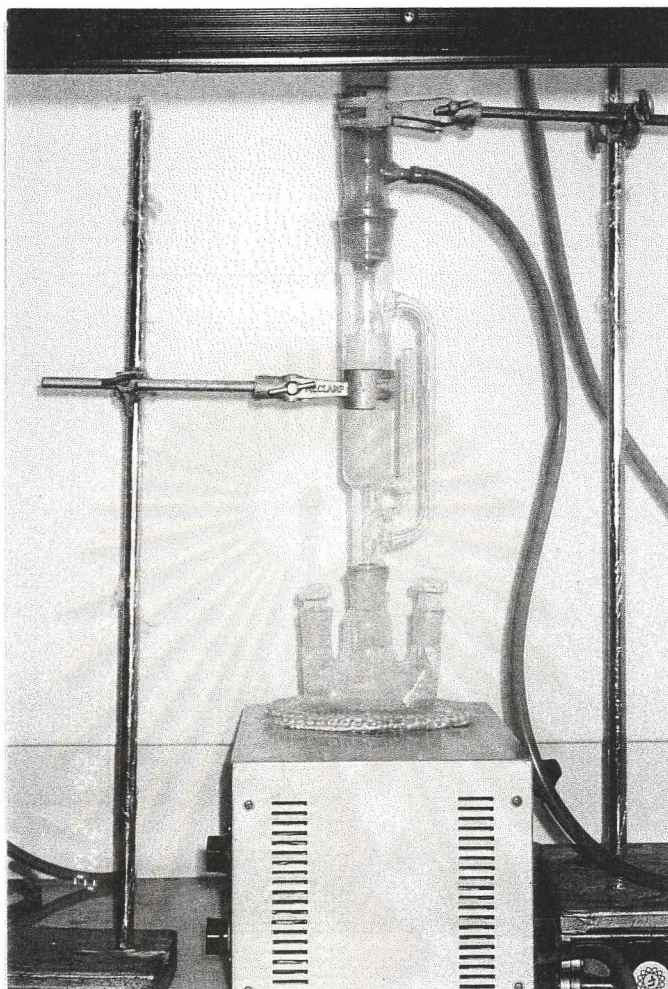


Figure 3.6 Synthesis equipment for Section B.

3.2.1.3 Acid Hydrolysis of Graft Copolymer

In a 250 cm³ Erlenmeyer flask equipped with a condenser (Figure 3.7), the starch-*g*-polystyrene copolymer was weighed and stirred in 200 cm³ of 1.5 N HCl. The mixture was refluxed for 2 hours. The water-insoluble polymer was filtered and washed with distilled water until pH was approximately 7. Then it was dried in an oven at 60°C for 24 hours. The product was kept in a desiccator for one hour before weighing.

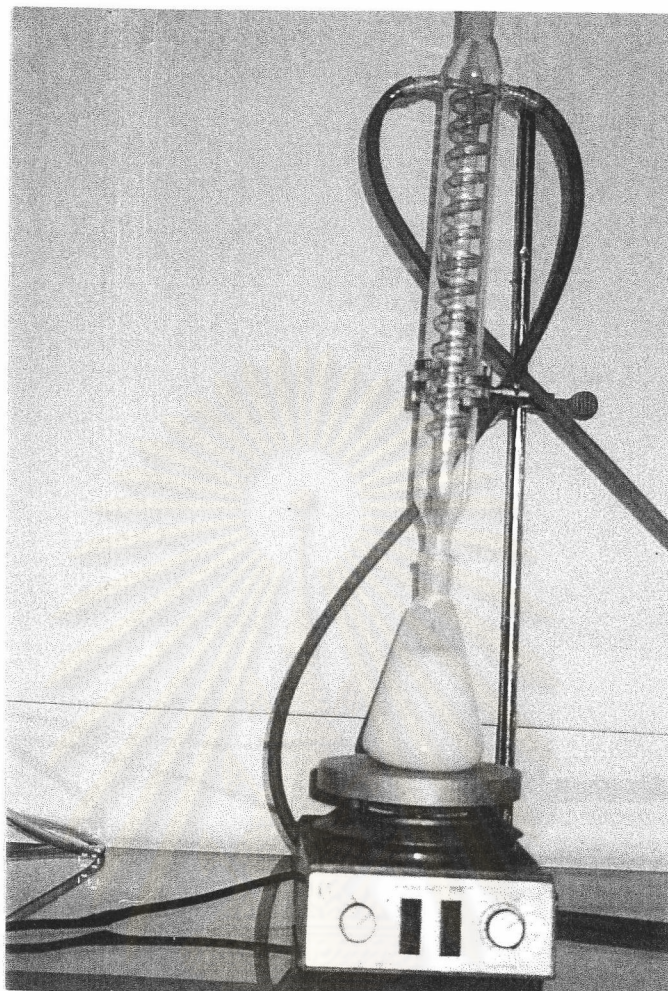


Figure 3.7 Synthesis equipment for Section C.

3.2.2 Effects of Reaction Parameters

For further study, the mixing method C using purified BPO (as mentioned in section 3.2.1.1 (c)) was employed.

3.2.2.1 Initiator Concentration

Several solutions of purified BPO in 10 cm³ of acetone were prepared. The weights of BPO used in each solution were 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, and 2.0 g. The synthesis was carried out using reaction temperature of 80°C, reaction time of 2 hours, and the ratio of starch and styrene monomer of 5:5 (g:g).

3.2.2.2 Reaction Time

To determine an appropriate reaction time, the grafting reaction time was varied in a range of 1, 2, and 3 hours. The synthesis was performed using the ratio of starch and styrene monomer of 5:5 (g:g), 0.5 g of purified BPO, and the reaction temperature of 80°C.

3.2.2.3 Reaction Temperature

To determine an appropriate reaction temperature, the grafting reaction temperature was varied as: 70, 80, and 90°C. The synthesis was performed using the ratio of starch and styrene monomer of 5:5 (g:g), 0.5 g of purified BPO, and the reaction time of 2 hours.

3.2.2.4 Ratio of Starch and Styrene Monomer

Different ratios of starch and styrene monomer, as presented in Table 3.1, were used in order to investigate the effect of ratio of reactants on grafting reaction. The synthesis was performed using 0.5 g of purified BPO with reaction temperature of 80°C and reaction time of 2 hours.

Table 3.1 The ratios of starch and styrene monomer

Starch (g)	1	2	3	4	5	6	7	8	9
Styrene Monomer (g)	9	8	7	6	5	4	3	2	1

3.3 Characterization of Graft Copolymer

3.3.1 Determination of Percent Add-on or Percent Grafting [15, 65]

It is referred to as the weight percent of synthetic polymer in the pure graft copolymer and it can be determined as follows:

$$\% \text{ add-on} = \frac{\text{weight of grafted polymer } (w_6)}{\text{weight of the pure grafted copolymer } (w_5)} \times 100$$

3.3.2 Determination of Percent Conversion of Monomer [15, 65]

It is used to describe the degree of polymerization of the monomer, which gives graft copolymer and homopolymer. It can be evaluated by the following expression.

$$\% \text{ conversion} = \frac{\text{weight of homopolymer } (w_4 - w_5) + \text{weight of grafted polymer } (w_6)}{\text{weight of styrene monomer } (w_3)} \times 100$$

3.3.3 Determination of Homopolymer Formation [15, 65]

It is used to describe the percent of homopolymer formed which is related to grafting efficiency. It can be calculated as:

$$\% \text{ homopolymer formation} = \frac{\text{weight of homopolymer } (w_4 - w_5)}{\text{weight of grafted polymer } (w_6) + \text{weight of homopolymer } (w_4 - w_5)} \times 100$$

3.3.4 Determination of Grafting Efficiency [15, 65]

It is defined as the percentage of total synthetic grafted polymer. High grafting efficiencies indicate that the formation of grafted polymer is more preferable than the formation of homopolymer. It can be calculated as:

$$\% \text{ grafting efficiency} = \frac{\text{weight of grafted polymer } (w_6)}{\text{weight of grafted polymer } (w_6) + \text{weight of homopolymer } (w_4 - w_5)} \times 100$$

3.3.5 Determination of Grafting Ratio [15, 65]

It is defined as the percentage ratio of the polymer grafted starch with respect to the starch. It can be calculated by the following expression:

$$\% \text{ grafting ratio} = \frac{\text{weight of grafted polymer } (w_6)}{\text{weight of starch } (w_1)} \times 100$$

3.3.6 Determination of Yield Product [15, 65]

The yield product is described the abilities of raw materials to form starch-g-polystyrene copolymer in section A. It can be calculated by following expression:

$$\% \text{ yield} = \frac{\text{starch - g - polystyrene copolymer with homopolystyrene } (w_4)}{\text{weight of starch } (w_1) + \text{weight of BPO } (w_2) + \text{weight of styrene monomer } (w_3)} \times 100$$

3.4 Chemical Structure Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) technique was performed using a Nicolet Impact 400D to characterize chemical structure of the samples. The dried powder samples were mixed with KBr and pressed into the disc form by the hydraulic

compression. The samples were scanned at the frequency range of 4000-400 cm^{-1} with 32 consecutive scans and 4 cm^{-1} resolution.

3.5 Determination of Molecular Weight Distribution and Grafting Frequency

GPC chromatograms were obtained using a Millifore Waters 150-CV Gel Permeation Chromatography. Solution samples of homopolystyrene and grafted polystyrene were prepared by dissolving polymer in HPLC grade tetrahydrofuran. The molecular weights of samples were calculated using polystyrene standards having molecular weights of 5400 – 1.2×10^6 g/mol as references. For the grafting frequency, i.e. AGU/graft, was calculated from this equation [59]:

$$\text{Grafting frequency} = \frac{(100 - \% \text{add-on}) / 162}{\% \text{add-on} / \text{MW graft}}$$

Where AGU/graft is the number of anhydroglucose (formula weight 162) units per grafting point.

3.6 Thermal Analysis

3.6.1 Thermogravimetric Analyzer (TGA)

Thermal decomposition temperatures were obtained using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. Approximately 5 mg of each sample was heated using a heating rate of 20°C/min from 50°C to 800°C under nitrogen atmosphere. Prior to test, the sample was dried in an oven at 60°C for 24 hours and kept in a desiccator. The onset degradation temperature and the percent weight loss for each sample were recorded.

3.6.2 Differential Scanning Calorimetry (DSC)

Glass transition temperatures were obtained using Perkin-Elmer DSC 7 Differential Scanning Calorimeter. About 10 mg of sample, dried in an oven at 60°C for 24 hours and kept in a desiccator, was placed in a sealed aluminum cell and then sealed. The sample was initially heated using a heating rate of 20°C/min from 50°C to 200°C under nitrogen atmosphere.

For polystyrene, starch-*g*-polystyrene copolymer with and without homopolystyrene, and grafted copolymer, the samples were cooled down to 50°C with a cooling rate of 20°C/min. Then they were heated again using the same condition as the first heating cycle.

3.7 Morphological Analysis

Joel JSM 5800 LV Scanning Electron Microscope was used to observe the sample morphology. Prior to test, the sample was dried in an oven at 60°C for 24 hours 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 in order to improve conductivity and prevent electron charging on the surface. The SEM was operated at 15 kV.

3.8 Solubility Test

0.05 g of sample was put in a 50 cm³ beaker. Then 40 cm³ of the solvent (distilled water, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform, and benzene) was poured into the beaker. The mixture was stirred with magnetic bar at desired temperature (room temperature, 50, 60, 70, 80, 90 and 100°C) for 3 hours. The solubility behavior of sample in solvent was observed.

3.9 Determination of Moisture Absorption

The sample was dried in an oven at 60°C for 24 hours and cooled in a desiccator. The dried sample was then weighed and immediately placed in controlled desiccator (100% humidity atmosphere). After that, the sample was removed, weighed to determine the weight change or moisture uptake periodically, and immediately placed back in controlled desiccator after each measurement. The weight change was measured at every 1 hour for the first 8 hours, and then measured at every 8 hours. The weight of sample was monitored until no further change. The moisture absorption was calculated as the weight difference and reported as percentage of weight increase from the initial weight. The moisture absorption of sample was calculated from the following equation:

$$M(\%) = \frac{W_t - W_0}{W_0} \times 100$$

Where M represents moisture absorption (%). W_t and W_0 are the weight of sample at a specific time and the weight of oven-dried sample, respectively.

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