CHAPTER III
EXPERIMENTAL SECTION

3.1 Polymerization

3.1.1 Apparatus

The polymerization equipment used in this study is as follows;

- 366 nm, 4 watt power mineral light lamp of Cole Parmer (model E-97604-00)
- 365 nm, 100 watt power high pressure mercury lamp of Cole Parmer (model E-97600-05)
- Gel Permeation Chromatography: Perkin-Elmer with column containing Waters Styragel HR5E, and tetrahydrofuran (THF) as the eluent. Refractive index (Perkin-Elmer series 200) detector was used.

3.1.2 Raw materials

- Styrene monomer : The styrene monomer was supplied by Dow & Siam Cement joint venture companies (Thailand), and washed with an aqueous solution of 1 mol NaOH, followed by distillation under vacuum.
- Sterile water : It was injection grade from General Hospital Products, and filtrated two times with 0.2 μm cellulose nitrate filters, Whatman.
- Di (2-ethylhexyl) phosphate : Minimum 95% purity from Sigma Chemicals.
- Sodium hydroxide : AR grade from Baker Analyzed.
- Methanol : AR grade form Baker Analyzed.

3.1.3 Polymerization procedure

Di (2-ethylhexyl) phosphate (HDEHP) was neutralized to sodium diethylhexyl phosphate (NaDEHP) by making a mixture with equimolar sodium hydroxide (NaOH) in the 2 dram vial. After adding 5 ml sterile water, the mixture was shaken for 30 minutes. Then, the distilled styrene monomer was added. The mixture was settled for 15 hours to reach equilibrium. The sample was exposed to UV light from the 4 watt or 100 watt lamps. During the polymerization period, the temperature was preset to 25 °C. A small amount of methanol was used to terminate the reaction. The polymer sample was dried in the oven at 60 °C for 24 hours. The molecular weight average, molecular number average, and polydispersity index of the polystyrene product were measured by gel permeation chromatography.

Experiments were conducted with the following conditions;

- Initiation by UV lamps either 4 or 100 watts
- Percentage of styrene monomer at 0.5, 1, 2, and 3 %
- Sodium diethylhexyl phosphate concentration at 0.5, 1 and 1.5 mmol

Base composition was 5ml water, 0.5 mmol NaDEHP (0.02g NaOH, 0.1697g HDEHP), and 3% styrene monomer (0.2322g).

3.2 Characterization

3.2.1 Chemicals

- Tetrahydrofuran : HPLC grade form J.T. Baker (filtrated with 0.45 μm nylon membrane filters of Gelman Sciences.)

3.2.2 Gel permeation chromatography

Gel permeation chromatography (GPC) makes use of the size exclusion principle. GPC has developed into one of the most useful methods to measure of average molecular weights (MWs) and polydispersity indexes (PDIs) of linear polymers. Being combined with on-line microprocessor based data handling facilitates the calculation of the molecular weight averages from the size distribution chromatograms. It is the most effectiveness of analyses polymer samples. In addition, only very small sample sizes are required.

GPC is a form of liquid chromatography in which the molecules are separated according to their molecular size. The procedure involves injecting a dilute solution of a polydisperse polymer into continuous flow of solvent passing through a column containing tightly packed microporous gel particles. The gel has particle sizes in the range of 5-10 μm in order to give efficient packing and typically posses a range of pore sizes from 0.5 to 10^5 nm, which correspond to the effective size range of polymer molecules. Typically GPC columns are 30-60 cm. in length. The main column is usually divided in tubes, each packed with a different pore size gel. Alternately, a mixed pore size column may be employed. Most of the column materials in use today are cross-linked polystyrene. These particles are fairly rigid and do not swell in the solvent.

Separation of the molecules occurs by preferential penetration of the different sized molecules into the pores: small molecules are able to permeate more easily through the pores, as compared to the larger sized molecules so that their rate of passage through the column is correspondingly slower. The continuous flow of solvent leads to separation of the molecules according to size, with the larger molecules being eluted first and the small

Separation of the molecules occurs by preferential penetration of the different sized molecules into the pores: small molecules are able to permeate more easily through the pores, as compared to the larger sized molecules so that their rate of passage through the column is correspondingly slower. The continuous flow of solvent leads to separation of the molecules according to size, with the larger molecules being eluted first and the small molecules, which have penetrated more deeply into the pores, requiring longer elution times.

Consequently, section of the column packing material to have the appropriate pore size distribution is crucial and different columns are usually required for polymers having widely different molecular weight distributions. The recent availability of gels of mixed pore sizes which can separate over four decades of molecular weight has made this a less demanding requirement (Campbell and While, 1989).