



## CHAPTER IV

### Highly Porous Polymeric Foam of Poly(DVB) Filled with Maleimide-Terminated Poly(arylene ether sulfone) Oligomers via High Internal Phase Emulsion

#### 4.1 Abstract

Maleimide-terminated poly(arylene ether sulfone) oligomers were synthesized by the nucleophilic step-growth polymerization of bisphenol A phenolates with activated halides at about 150 °C and a required amount of Bis-(4-chlorophenyl)-sulfone. This method was accomplished by reacting the terminate amine with maleic anhydride. The obtained maleimide-terminated poly(arylene ether sulfone) oligomers were characterized by IR, NMR, and DSC. PolyHIPEs, using divinylbenzene filled with maleimide-terminated poly(arylene ether sulfone) oligomers (0, 2.5, 5, and 10 %) were prepared using SPAN80:DDBSS:CTAB (6.3:0.4:0.3) as the surfactant. The obtained polyHIPEs were characterized for their phase morphology, surface area, thermal properties, and mechanical properties using SEM, BET, TG/DTA, and a Universal Tensile Testing machine, respectively. The prepared polyHIPEs will be used for adsorbing the CO<sub>2</sub> produced during the gasification process to increase the heating value of syn gas.

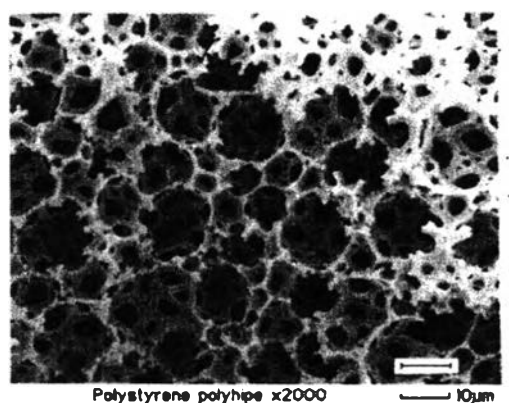
Keywords: Poly(DVB)HIPEs, Mixed surfactants, Polysulfone, CO<sub>2</sub> gas adsorption

#### 4.2 Introduction

One of the most important problems in the atmosphere is high levels of CO<sub>2</sub> gas which comes from many different sources, mainly release by industrial activities and gasification processes. Therefore, it is very important to design polyHIPE on adsorbent materials that would adsorb CO<sub>2</sub> gas before being liberated into the environment.

Polymerization of the monomeric continuous phase of a high internal phase emulsion(HIPE) prepared highly porous crosslinked polymer materials. The monomer system which has received the most attention in PolyHIPE studies is

styrene/divinylbenzene (DVB). A lot of effort was invested to determine the factors which affect the cellular structure and cell size of the resulting porous polymers, and in 1997, Neil R. C. *et al.* have described the production of PolyHIPE materials with high internal surface areas, employing methodologies similar to those used in porous polymer bead preparation. Scanning electron microscopy (SEM) can clearly see the foamlike morphology of open-cellular Poly-HIPE materials (Figure 4.1).



**Figure 4.1** Scanning electron micrograph (SEM) of poly-(styrene/DVB) PolyHIPE.

The open-cell polymers are characterized by an extremely low dry bulk density, less than  $0.1 \text{ g cm}^{-3}$ , which is due to complete interconnection between all neighboring cells. Their mechanical properties are similar to gas-blown polystyrene foams, although the smaller cell sizes and higher degree of cellular spherical symmetry of the emulsion-derived foams produces higher compressive strengths. However the inherent brittleness of polystyrene and the characteristic low density of PolyHIPE polymers, monolithic materials derived from styrene/DVB tend to fragment into particles rather easily under mechanical stress. Moreover, they possess the low thermooxidative stability and low selective property. This could be rectified by the addition of a high-performance polymer such as polysulfone to get good mechanical properties and good selectivity.

In this work we will attempt to produce highly porous polymeric foam of poly(DVB) filled with maleimide-terminated poly(arylene ether sulfone)oligomers via high internal phase emulsion for selective retention of carbondioxide gases, mainly

released by industrial activities and gasification processes, which are harmful to the environment.

## 4.3 Experimental

### 4.3.1 Materials

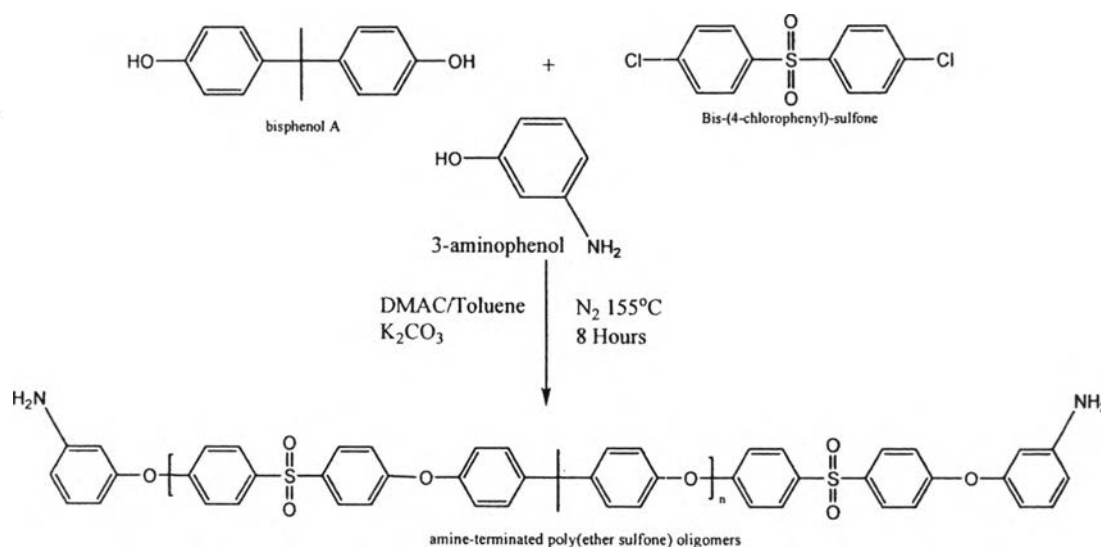
Bis-(4-chlorophenyl)-sulfon 98% ( $(\text{ClC}_6\text{H}_4)_2\text{SO}_2$ ) was supplied by Chemical Express Co., LTD. Divinylbenzene (DVB) was supplied by Merck. 3-Aminophenol, Maleic anhydride 99%, Dimethylacetamide (DMAC), Isopropanol, N-cyclohexylpyrrolidone (CHP), methanol, ethanol, and Chloroform ( $\text{CHCl}_3$ ) and Bisphenol A 97% (Bis-A) were supplied by Etalma (Thailand) Co., LTD. Toluene (T) was supplied by Lab Scan. Sorbitan monooleate (SPAN80) and Dodecylbenzenesulfonic acid, sodium salt (DDBSS) were supplied by Sigma. Cetyltrimethylammonium  $[\text{C}_{16}\text{H}_{31}\text{N}^+(\text{CH}_3)_3]$  bromide (CTAB), Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), Calcium chloride dehydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) and Potassium carbonate anhydrous were supplied by Fluka. B was supplied by Thai Nippon (BN)entonite Chemical Industry Co., Ltd. B of (CEC)The cation exchange capacity T Nis 43 g/100/mmol of clay.  $\text{N}_2$  UHP was supplied by The Petroleum and Petrochemical College.

### 4.3.2 Methods

#### 4.3.2.1 *Preparation of Amine terminated PSO-Oligomer. (using procedure adopted from Lyle G. D. et al., 1988)*

The stoichiometry of the reactants were varied according to the Carrothers equation to achieve the various molecular-weight oligomers. A four-neck roundbottomed flask were fitted with a Dean Stark trap, mechanical stirrer, thermometer and nitrogen inlet. The activated halide Bis-(4-chlorophenyl)-sulfone (57.434 g) were added to the flask followed by bisphenol A (43.388 g) and m-aminophenol (2.272 g). A total of  $600 \text{ cm}^3$  of DMAC were added to the flask. Dried potassium carbonate (34 g) and toluene ( $150 \text{ cm}^3$ ) were added next and the reaction were refluxed at  $145^\circ\text{C}$ . After all the water were removed from the reaction flask ( $\sim 4$  h), toluene were drawn from the Dean Stark trap until the temperature increased to

155°C. The reaction were allowed to proceed for 8 h, after which the solution were cooled and filtered to remove the inorganic salts, then it coagulated in an excess of rapidly stirred methanol. The polymer were purified by redissolving in chloroform and coagulating in methanol again, prior to vacuum drying at 80°C to a constant weight.( see scheme 1 )



Scheme 1

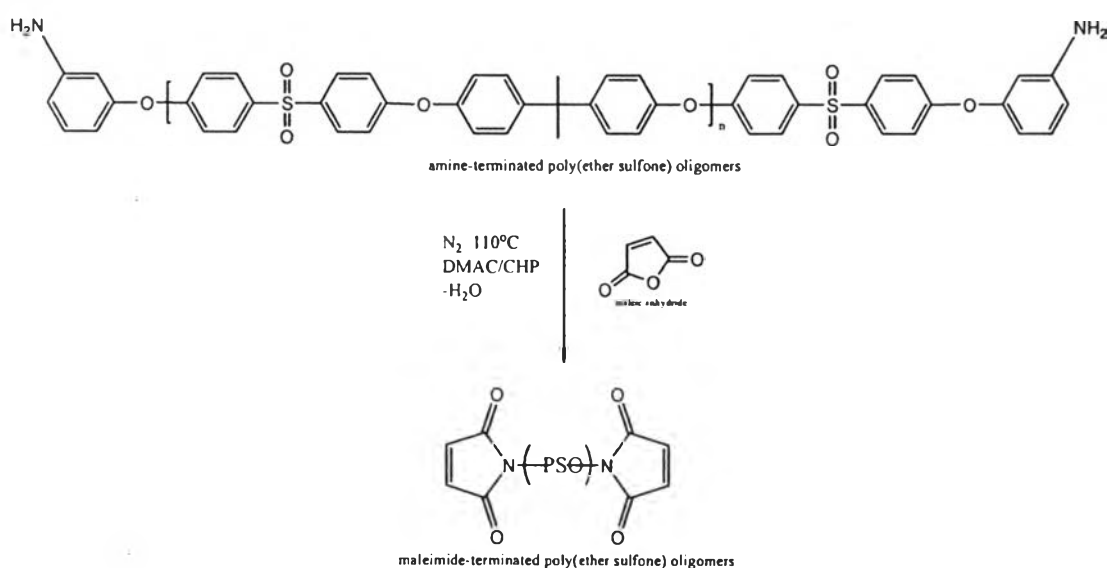
#### 4.3.2.2 Characteristics of Amine-terminated PSO-Oligomers.

- a. Identified compounds or investigated Amine terminated PSO-Oligomers composition by Infared Spectroscope (IR)
- b. Characterized the structure of Amine terminated PSO-Oligomers by  $^1\text{H}$ - Nuclear magnetic resonance ( $^1\text{H}$ -NMR)
- c. Determined Molecular Weight by Gel Permeation Chromatography (GPC)
- d. Determined Glass transition temperature of PSO-Oligomers by Differential Scanning Calorimetry (DSC)

#### 4.3.2.3 Preparation of Maleimide terminated PSO-Oligomer.(using procedure adopted from Lyle G. D. et al., 1988)

For the two-step procedure, the amine-terminated poly(ether sulfone) oligomers were determined the number-average molecular weight before imidization. For example, amine-terminated oligomers(10.804 g, MW=3485) were

added to a three-neck 500 cm<sup>3</sup> roundbottomed flask equipped with a nitrogen inlet, a mechanical stirrer and a Dean Stark trap. DMAC (200 cm<sup>3</sup>) and CHP (40 cm<sup>3</sup>) were added to the flask to dissolve the polymer. Maleic anhydride (MA) (0.97g) were added and the solution were stirred for 6h. Subsequently, the nitrogen flow were increased, and the temperature were raised to 130°C and maintained at this temperature for up to 24 h. The polymer solution were coagulated at room temperature in water/methanol (30/70) and vacuum dried at 80°C to a constant weight. ( see scheme 2 )



Scheme 2

#### 4.3.2.4 Characteristics of Maleimide terminated PSO-Oligomers.

- a. Identified compounds or investigated Maleimide terminated PSO-Oligomers composition by Infrared Spectroscope (IR)
- b. Characterized the structure of Maleimide terminated PSO-Oligomers by <sup>1</sup>H- Nuclear magnetic resonance (<sup>1</sup>H-NMR)
- c. Determined Glass transition temperature of PSO-Oligomers by Differential Scanning Calorimetry (DSC)

#### 4.3.2.5 Preparation of Poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers and Poly(DVB)HIPE filled with Acid-treated Clay.

The cellular materials were prepared by first dissolving organic phase containing 5 mL of DVB monomer, 5 mL of toluene, required amounts of

Maleimide terminated PSO-Oligomers and acid-treated clay, and a mixture of nonionic, anionic, and cationic surfactants: SPAN80, DDBSS, and CTAB was added to the mixture, stirred for 10 min. While 90 mL of distilled water containing 0.2 g of potassium persulfate and 1 g of calcium chloride dihydrate were added dropwise. After all the water has been added, the emulsion was further stirred for 20 min and placed in a glass bottle. The obtained emulsions were capped and put in a convection oven at 70°C for 24 h to polymerize (Barbetta *et al.*, 2004). After polymerization, the cellular materials were removed from the glass bottles and washed by soxhlet for 6 h with Iso-propanol. Then the cellular materials were returned to vacuum oven to dry at 70°C for 48 h (Pakeyangkoon *et al.*, 2008).

4.3.2.6 *Characteristics of Poly(DVB)HIPE filled Maleimide terminated PSO-Oligomers and acid- treated clay.*

a. Thermal properties characterizing: The thermal properties of poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers were studied using TG/DTA.

b. Morphology characterizing: The morphology of poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers was studied using SEM.

c. Mechanical properties analysis: The mechanical properties of poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers were studied using LLOYD/LRX.

d. Surface area analysis: The surface area of poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers was analyzed using Autosorb-1.

e. Adsorption analysis: Study of carbondioxide gases adsorption properties of poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers comparing with poly(DVB)HIPE filled with acid-treated clay were carried out using a pilot gasification unit at the Faculty of Chemical Technology Chulalongkorn university.

### 4.3.3 Equipment

#### 4.3.3.1 *Gel Permeation Chromatography (GPC)*

The number-average molecular weight of amine-terminated polysulfone oligomers were obtained by SHIMADZU GPC-RID10A, HT 6E THF Waters brand of 7.8 × 300 nm column, PS standard, flow rate 1.00 mL/min.

#### 4.3.3.2 *Surface Area Analyzer SAA*

196-desorption isotherms were obtained at -adsorption  $2N^{\circ}C$  on a Quantachrome Autosorb-1. Samples were degassed at 100°h in a 12C during e calculated using the BET Surface areas wer .vacuum furnace prior to analysis Joyner and ,The pore size distributions were constructed based on Barrett .equation .method using the adsorption branch of the nitrogen isotherm (BJH)Halenda

#### 4.3.3.3 *Fourier Transform Infrared Spectroscopy (FT-IR)*

The FT-IR spectra of BTN, organo BTN and organo acid-treated BTN were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400  $cm^{-1}$  with 32 scans at a resolution of 2  $cm^{-1}$ . KBr pellet technique was applied in the preparation of powder samples. The incorporation of organic group into silicate network is investigated by using FTIR.

#### 4.3.3.4 *$^1H$ -Nuclear magnetic resonance ( $^1H$ -NMR)*

The  $^1H$ -NMR spectra of amine-terminated polysulfone oligomers and maleimide-terminated polysulfone oligomers were obtained using  $^1H$ -Nuclear magnetic resonance at the Chemistry Department, Faculty of Science, Naresuan university.

#### 4.3.3.5 *Thermogravimetric Analysis (TGA)*

Thermo-gravimetric analysis (TGA) was performed to measure the thermal stability of the Poly(DVB)HIPE filled Maleimide terminated PSO-Oligomers. TGA of Poly(DVB)HIPE filled Maleimide terminated PSO-Oligomers was performed using a Mettler Toledo TGA/SDTA 851e instrument. Experiment was carried out under nitrogen gas atmosphere. Sample was cut into a small piece weigh about 2–5 mg. Then the sample was loaded on the platinum pan and heated to 600°C from 40°C at a heating rate of 10°C/min. One steps degradation was observed during testing, and the decomposition temperature was recorded corresponding to 50% decomposition of the material.

#### 4.3.5.6 *Differential Scanning Calorimetry (DSC)*

The glass transition temperature of polysulfone was determined using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 250°C and cooled down at a rate of 10°C/min under a N<sub>2</sub> atmosphere with a flow rate of 10 mL/min. The sample was then reheated to 250°C at the same rate.

#### 4.3.3.7 *Scanning Electron Microscope (SEM)*

Scanning electron microscopy was performed on JEOL/JSM 5200 Model to observe surface morphology of Poly(DVB)HIPE filled Maleimide terminated PSO-Oligomers. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

#### 4.3.3.8 *Universal Testing Machine (LLOYD)*

A Lloyds Universal Testing Machine (Lloyds/LRX) equipped with a 500 N load cell was used to measure mechanical properties in compression. The samples were loaded at a rate of 1.27 mm/min. Samples of 25.4 mm in diameter and 25.4 mm in height were used for tested of each poly(DVB)HIPEs filled Maleimide terminated PSO-Oligomers. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached.

#### 4.3.3.9 *CO<sub>2</sub> Gas Adsorption*

Study of CO<sub>2</sub> gas adsorption capacities of poly(DVB)HIPEs filled Maleimide terminated PSO-Oligomers was carried out using a pilot gasification unit at the Chemical Technology Department, Faculty of Science, Chulalongkorn university. Samples were cut into small pieces weigh about 1–2 g. Then the samples were loaded into sample tube 2×25 cm. CO<sub>2</sub> 3 mL/min and He 17 mL/min were flowed through the sample at room temperature. The residue of CO<sub>2</sub> was measured by a Gas Chromatography instrument, column used Shimadzu 2014, flow rate 35 mL/min.

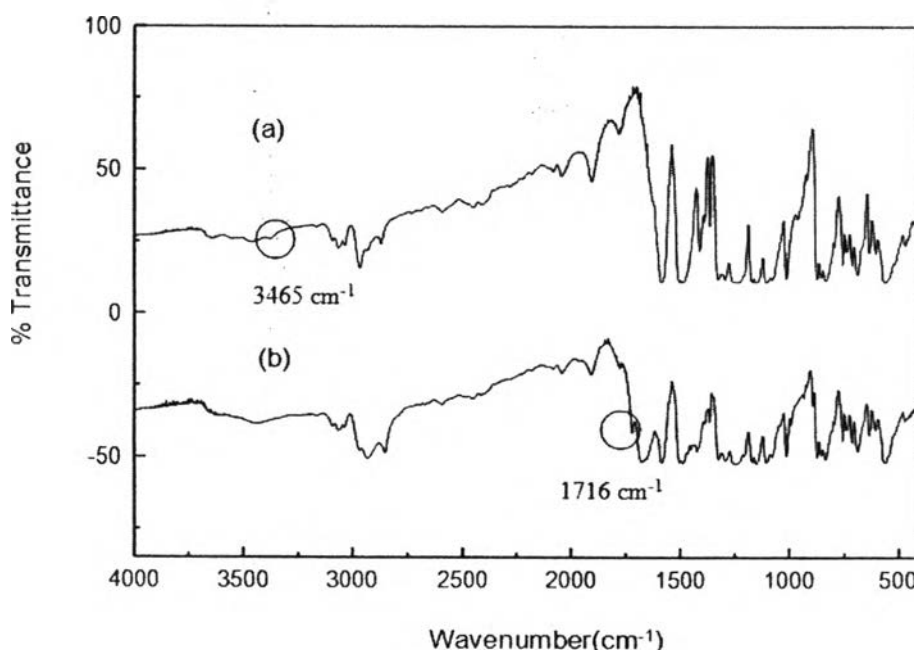
## 4.4 Results and Discussion

### 4.4.1 Synthesis and characterization of amine-terminated and maleimide-terminated polysulfone oligomers

Functionalized terminal oligomers, such as amine-terminated PSO-oligomers were synthesized via Scheme 1, Bisphenol A was reacted with the sulfone-containing



monomer (Bis-(4-chlorophenyl)-sulfone). Amine-terminated PSO-Oligomers were characterized and then converted to the corresponding maleimide materials by solution imidization at moderate temperatures using a solvent/azeotroping agent system. DMAC was normally used as the solvent and CHP as the azeotroping agent. The role of the CHP was to assist in the efficient removal of water from the reaction solution. CHP is miscible with water only up to about 80°C and higher temperatures produce an efficient azeotroping system. Moderate temperatures were necessary to achieve ring closure and also to prevent premature free-radical crosslinking from occurring (Scheme 2). The only change is the substitution of a maleimidophenol for an aminophenol as the end-capper. Of course, the reaction fails if the endcapper is not incorporated. The incorporation of the maleimide end-group was demonstrated by FTIR and NMR spectroscopy. When comparing the FTIR spectra of an amine-terminated 3500 MW (analyzed by GPC) oligomers with that of a maleimide-terminated 3500 MW oligomers, the only differences observed were the absence of the amine stretching band at  $\sim 3400\text{ cm}^{-1}$  and the appearance of an imide carbonyl band at  $1716\text{ cm}^{-1}$  (Figure 4.2).



**Figure 4.2** FTIR spectra of (a) amine-terminated polysulfone oligomers and (b) maleimide-terminated polysulfone oligomers

The  $^1\text{H}$ -NMR spectra of the amine-terminated and maleimide-terminated PSO-oligomers in the same solvent (deuterated chloroform) are compared in Figure 4.3 and 4.4, respectively. A and B represent different protons of maleimide-endcap. From the large structure of maleimide-terminated PSO-oligomers effects diamagnetic anisotropy<sup>3</sup>, the protons (A,B) of maleimide-terminated PSO-oligomers are shields. Resulting peaks appear at low chemical shift (2-3 ppm) instead of high chemical shift (4-6 ppm).

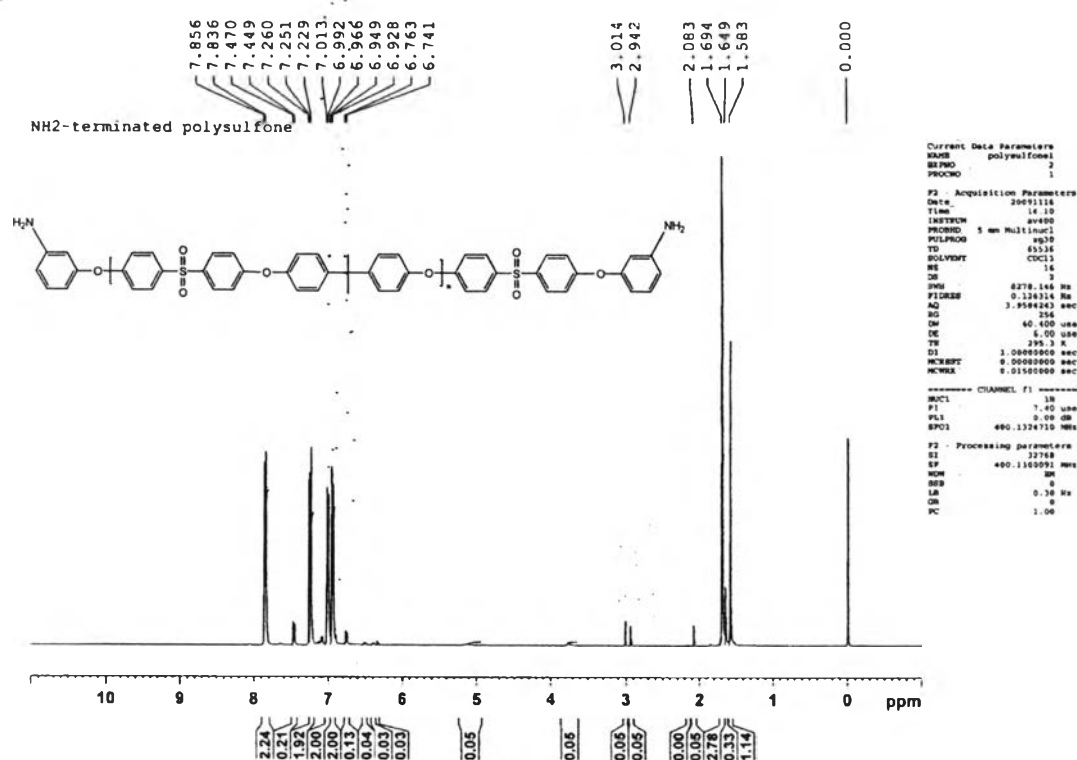
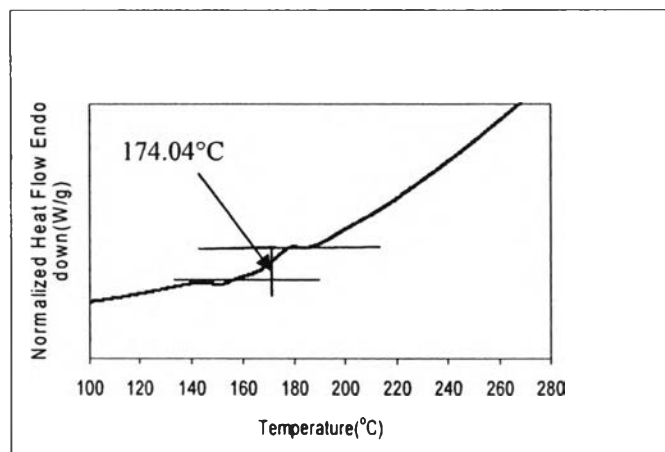
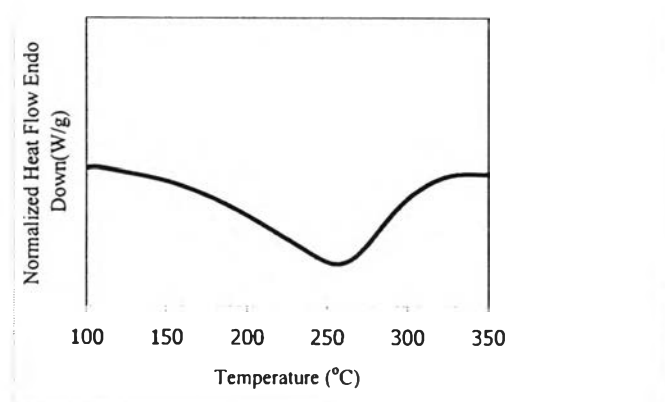


Figure 4.3  $^1\text{H}$  NMR spectra and structure of amine-terminated polysulfone oligomers





**Figure 4.5**  $T_g$  of amine-terminated polysulfone oligomers



**Figure 4.6** Curing temperature of maleimide-terminated polysulfone oligomers

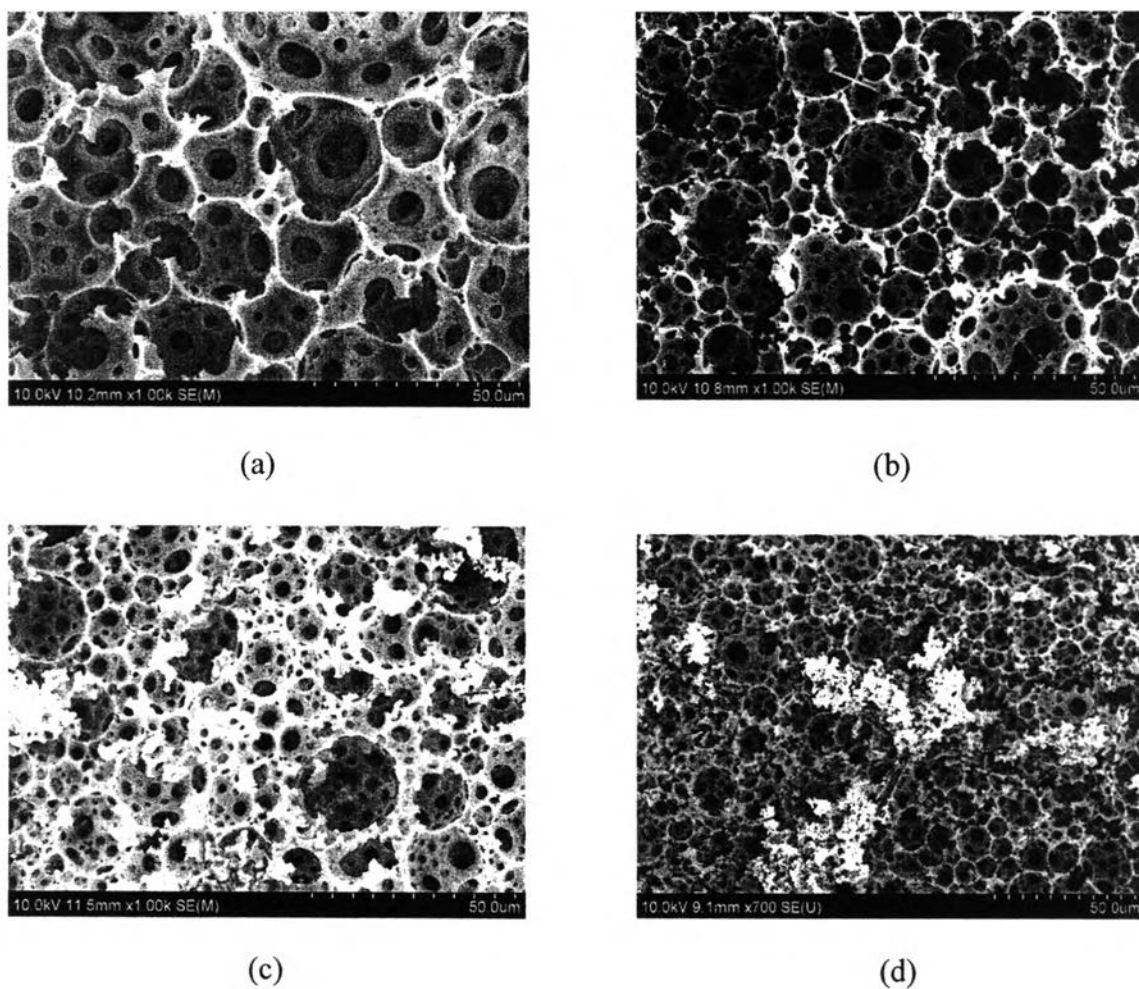
#### 4.4.2 Characteristics of Poly(DVB)HIPE filled Maleimide terminated PSO-Oligomers.

##### 4.4.2.1 *Morphologies and surface areas*

SEM micrographs (Figure 4.7) show morphological characteristics of poly(DVB)HIPE prepared using a surfactant mixture of 6.3 wt% of SPAN80, 0.4 wt% of DDBSS, and 0.3 wt% of CTAB (S80DCI) filled with different maleimide terminated PSO-Oligomers content.

The surface areas of the obtained materials were found to decrease 70% with increasing content of maleimide terminated PSO-Oligomers (see Table 4.1).

This could be due to PSO-oligomers agglomerate, were observed in SEM micrographs of the obtained polyHIPE (see Fig 4.7)

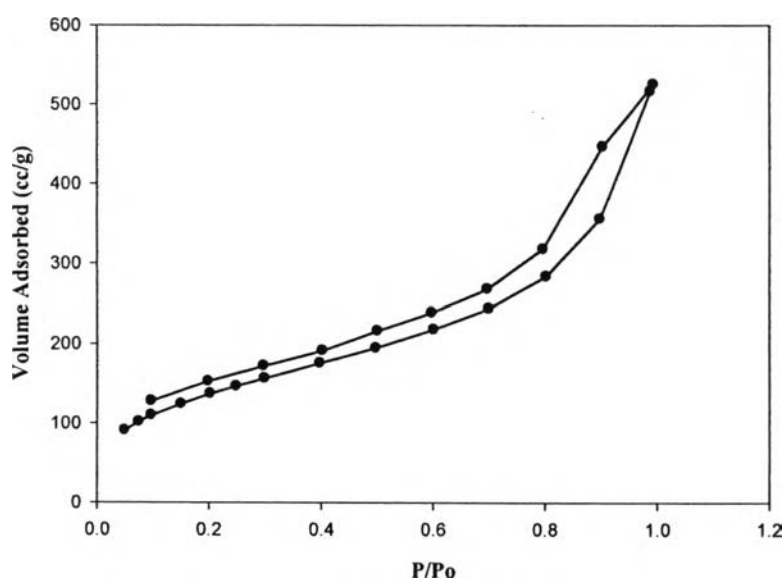


**Figure 4.7** SEM micrographs of Poly(DVB)HIPE filled with different maleimide terminated PSO-Oligomers content (wt%); (a) 0; (b) 2.5; (c) 5; and (d) 10.

**Table 4.1** Surface areas of Poly(DVB)HIPE filled with different amount of Maleimide terminated PSO-Oligomers content (wt%)

Sample	Surface areas (m <sup>2</sup> /g) <sup>a</sup>
0 wt%	550 ± 11
2.5wt%	440 ± 10
5 wt%	239 ± 13
10 wt%	165 ± 10

<sup>a</sup> From BET treatment of N<sub>2</sub> adsorption data.



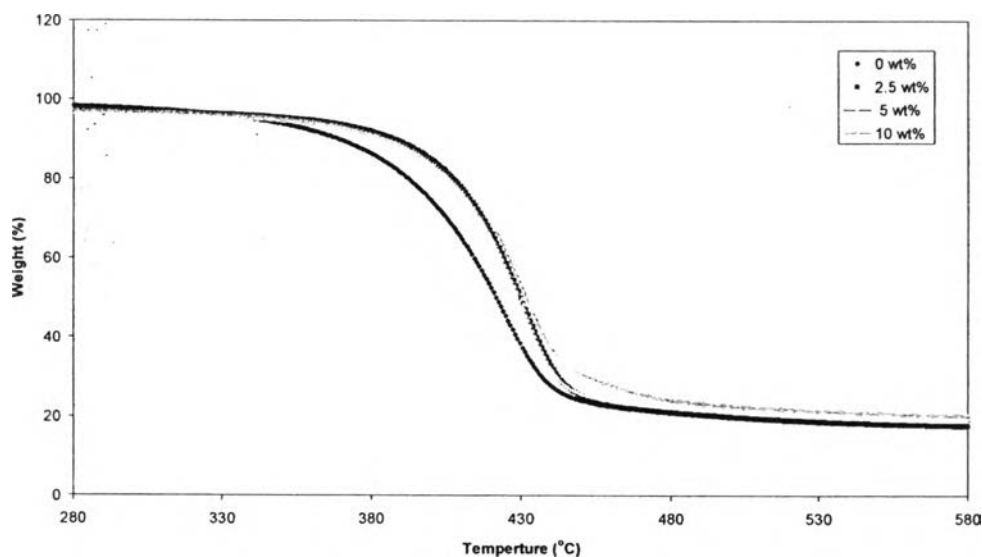
**Figure 4.8** Typical example of N<sub>2</sub> sorption isotherm for poly(DVB)HIPE samples in Table 4.1.

A typical example of the type of N<sub>2</sub> sorption isotherm for poly(DVB)HIPE filled with maleimide-terminated poly(arylene ether sulfone) oligomers is presented in Figure 4.8, N<sub>2</sub> sorption isotherms of all poly(DVB)HIPE

samples listed in Table 4.1 are of mesoporous materials (type IV). BET isotherm according to the BDDT classification.

#### 4.4.2.2 Thermal properties

TG analysis of poly(DVB)HIPEs, prepared from different mixture of surfactants with different amount of maleimide-terminated poly(arylene ether sulfone)oligomers content, was carried out to measure thermal stability of the poly(DVB)HIPEs with the temperature range between 40-600°C and heating rate of 10°C/min. TGA thermogram of temperature against percent weight loss are shown in Figure 4.9. It was observed from the thermogram that decomposition behaviors of all poly(DVB)HIPE were in the form of a one step degradation process, and hence decomposition temperature reported the temperature corresponding to 50% decomposition of the material. The thermal decomposition temperature ( $T_d$ ) and residue yield (%) were listed in the Table 4.2, and the DTG curves of samples as shown in Figure. 4.9.



**Figure 4.9** TGA thermograms of poly(DVB)HIPE filled with different amount of maleimide terminated PSO-oligomers content (wt%)

**Table 4.2** Thermal decomposition temperature ( $T_d$ ) and residue yield (%) of poly(DVB)HIPE filled with different amount of maleimide terminated PSO-oligomers content (wt%)

content	Poly(DVB)HIPE filled with maleimide terminated PSO-oligomers	
	$T_d$ (°C)	Residue Yield (%)
0 wt%	421.66	16.1
2.5 wt%	430.05	16.6
5 wt%	430.32	16.9
10 wt%	431.93	18.4

It was observed that the decomposition temperature of poly(DVB)HIPE filled with maleimide-terminated poly(arylene ether sulfone) oligomers shifted to a slight high temperature i.e. from 421°C in the neat polyHIPE to 430°C for polyHIPE filled with PSO-oligomers. This result, indicated that the incorporation of maleimide-terminated poly(arylene ether sulfone) oligomers into poly(DVB)HIPE offers a stabilizing effect against decomposition: protecting from thermal degradation by keeping the polydivinylbenzene chains and the original molecular structure intact which results in increasing decomposition temperature and residue yield of the obtained polyHIPEs<sup>12</sup>.

#### 4.4.2.3 Mechanical properties

##### 4.4.2.3.1 Compressive Response

Mechanical properties analysis of poly(DVB)HIPEs, prepared from different amount of maleimide terminated PSO-Oligomers, were carried out. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached. The compressive modulus and compressive strength of the samples were listed in the Table 4.3.



**Table 4.3** Compressive modulus (MPa) and Compressive strength of poly(DVB)HIPEs and poly(DVB)HIPEs filled with different amount of maleimide terminated PSO-oligomers content (wt%)

content	Poly(DVB)HIPE filled with maleimide terminated PSO-oligomers	
	Compressive Modulus (MPa)	Compressive Strength (MPa)
0 wt%	2.21±0.15	0.13±0.04
2.5 wt%	2.87±0.15	0.16±0.04
5 wt%	2.99±0.14	0.21±0.03
10 wt%	3.22±0.16	0.24±0.01

Poly(DVB)HIPEs without added maleimide terminated PSO-oligomers showed compressive modulus and compressive strength of 2.21 and 0.13 MPa, respectively. The compressive modulus and compressive strength of poly(DVB)HIPEs filled with 0 to 10 wt% maleimide terminated PSO-oligomers content, increased from 2.21 to 3.22 and 0.13 to 0.24 MPa, respectively. The compressive modulus and compressive strength increased 46 % and 85 % when compared with neat poly(DVB)HIPEs.

It is observed that both the compressive modulus and compressive strength are slightly higher for poly(DVB)HIPE filled with maleimide terminated PSO-oligomers. Poly(DVB)HIPE filled with maleimide terminated PSO-oligomers exhibited improvement in the mechanical properties of the resulting materials such as compressive modulus and compressive strength when compare to the neat poly(DVB)HIPEs.

#### 4.4.2.4 Adsorption capacities

CO<sub>2</sub> gas adsorption of poly(DVB)HIPE, prepared from different mixture of surfactants with different amount of maleimide terminated PSO-

Oligomers content (wt%), was carried out using a pilot gasification unit at the Department Chemical Technology Department, Faculty of Science, Chulalongkorn University with CO<sub>2</sub> flow rate of 3 mL/min and Ar 17 mL/min through the sample at room temperature. The CO<sub>2</sub> gas adsorption capacities were listed in Table 4.4.

**Table 4.4** CO<sub>2</sub> gas adsorption capacity (mmol/g) of Poly(DVB)HIPE filled with different amount of Maleimide terminated PSO-Oligomers content (wt%)

Sample	CO <sub>2</sub> gas adsorption capacity (mmol/g)
0 wt%	3.1
2.5 wt%	3.2
5 wt%	3.3
10 wt%	3.5

Poly(DVB)HIPE without added maleimide terminated PSO-oligomers showed CO<sub>2</sub> gas adsorption capacity of 3.1 mmol/g. The CO<sub>2</sub> gas adsorption capacity of Poly(DVB)HIPE filled with maleimide terminated PSO-oligomers was found to remain the stand with increasing content of Maleimide terminated PSO-Oligomers added.

Table 4.5 shows surface area and CO<sub>2</sub> gas adsorption of poly(DVB)HIPEs before and after filled with different amount of maleimide terminated PSO-oligomers content.

**Table 4.5** surface area ( $\text{m}^2/\text{g}$ ) and  $\text{CO}_2$  gas adsorption capacity ( $\text{mmol/g}$ ) of Poly(DVB)HIPE filled with different amount of Maleimide terminated PSO-Oligomers content (wt%).

Sample	Surface areas ( $\text{m}^2/\text{g}$ )	$\text{CO}_2$ gas adsorption capacity ( $\text{mmol/g}$ )
0 wt%	$550 \pm 11$	3.1
2.5wt%	$440 \pm 10$	3.2
5 wt%	$239 \pm 13$	3.3
10 wt%	$165 \pm 10$	3.5

Poly(DVB)HIPE filled with maleimide terminated PSO-oligomers. The surface area was found to decrease about 70% with increasing content of maleimide terminated PSO-oligomers added. From the result, it indicates that when increasing content of maleimide terminated PSO-oligomers, the emulsion stability of poly(DVB)HIPEs decreases (emulsion stability drops) because of PSO's agglomerating. But  $\text{CO}_2$  gas adsorption capacities of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers showed remain about the same in maleimide terminated PSO-oligomers have S=O functional group which are a basic property<sup>4</sup>. Gases such as  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , which are acidic in nature, are expected to be more soluble in polymers containing basic moieties than in polymers without such groups<sup>5</sup>. Therefore, large numbers of maleimide terminated PSO-oligomers (large numbers of S=O groups) can maintain the adsorption of  $\text{CO}_2$  gas of poly(DVB)HIPEs to a certain rate.

**Table 4.6** Comparing the characterizations of neat Poly(DVB)HIPE, Poly(DVB)HIPE filled with 10 wt% maleimide terminated PSO-oligomers and Poly(DVB)HIPE filled with 10 wt% acid treated clay.

<b>Characterizations</b>	<b>neat Poly(DVB) HIPE</b>	<b>Poly(DVB)HIPE filled with 10% PSO</b>	<b>Poly(DVB)HIPE filled with 10% acid treated clay</b>
<b>Surface area</b>	550 m <sup>2</sup> /g	165 m <sup>2</sup> /g (-70%)	346 m <sup>2</sup> /g (-37%)
<b>Compressive modulus</b>	2.21 MPa	3.22 MPa (46%)	2.80 MPa <sup>14</sup> (27%)
<b>Decomposition temperature</b>	421.66 °C	431.93 °C	428.26°C <sup>14</sup>
<b>CO<sub>2</sub> gas adsorption capacities</b>	3.125 mmol/g	3.459 mmol/g	1.754 mmol/g

From table 4.6, the surface areas of the Poly(DVB)HIPE were found to decrease 70% with increasing content of Maleimide terminated PSO-oligomers because PSO-Oligomers agglomerate which can be seen in SEM micrographs. The decomposition temperature of poly(DVB)HIPE filled with maleimide-terminated Poly(arylene ether sulfone) Oligomers shifted to a high temperature. The compressive modulus increased 46% from neat poly(DVB)HIPEs. There is no change in the CO<sub>2</sub> gas adsorption capacities of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers, this could be resulted from large numbers of maleimide terminated PSO-oligomers (large numbers of S=O groups) can maintain the adsorption of CO<sub>2</sub> gas of poly(DVB)HIPEs to certainly rate.

Addition, Poly(DVB)HIPE without added acid-treated clay showed CO<sub>2</sub> gas adsorption capacity of 3.125 mmol/g when increased acid treated clay to 10 wt% content the CO<sub>2</sub> gas adsorption capacity of Poly(DVB)HIPE filled with acid-treated clay was found to decrease. The surface areas of the Poly(DVB)HIPE were found to decrease 37% with increasing content of acid-treated clay because acid-treated clay agglomerate. The decomposition temperature of poly(DVB)HIPE filled

with acid-treated clay slightly shifted to a high temperature. The compressive modulus increased 27% from neat poly(DVB)HIPEs.

#### 4.5 Conclusions

Poly(DVB)HIPE filled with maleimide terminated PSO-oligomers were successfully prepared. The decomposition temperature of poly(DVB)HIPE filled with maleimide-terminated poly(arylene ether sulfone)oligomers shifted to a high temperature. The compressive modulus and compressive strength of poly(DVB)HIPEs filled with 0 to 10 wt% maleimide terminated PSO-oligomers content increased about 46% and 85%, respectively. The surface areas of the obtained materials were found to decrease about 70% with increasing content of maleimide terminated PSO-oligomers because PSO-Oligomers agglomerate which can be seen in SEM micrographs. From the result, indicates when increases content of Maleimide terminated PSO-Oligomers, the emulsion stability of Poly(DVB)HIPEs decreases (emulsion stability drops) because of PSO's agglomerating. There were little no change in the CO<sub>2</sub> gas adsorption capacities of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers. This could be due to maleimide terminated PSO-oligomers have S=O functional group which are a basic property<sup>4</sup>. Gases such as CO<sub>2</sub> and H<sub>2</sub>S, which are acidic in nature, are expected to be more soluble in polymers containing basic moieties than in polymers without such groups<sup>5</sup>. Therefore, large numbers of maleimide terminated PSO-oligomers (large numbers of S=O groups) can maintain the adsorption of CO<sub>2</sub> gas of poly(DVB)HIPEs to certainly rate.

#### 4.6 References

- (1) Neil, R. C.; Sherrington D.C. *Macromolecules* **1997**, 30(19), 5860-5869.
- (2) Lyle, G. D.; Senger, J. S.; Chen, D. H.; Kilic, S.; Wu, S. D.; Mohanty, D. K.; McGrath, J. E. *Polymer* **1989**, 30, 978-985
- (3) Silverstein, R.M., Clayton B.G., *Spectrometric identification of organic compounds* **1991**, 5, 174-177
- (4) Elmes, A. R.; Hammond, K.; Sherrington, D. C. *European Patent Application* 88 303 675.8. **1988**.
- (5) Ghosal, K.; Chern, R. T; Freeman, B. D. *Macromolecul* **1996**, 29, 4360-4369
- (6) Barby, D.; Haq, A. *European Patent Application* 0 060 138. **1982**.
- (7) Walsch, D.C.; Stenhouse J.I.T.; Kingsbury L.P.; Webster E.J. *J. Aerosol Sci.* **1996**, 27, 629.
- (8) Barbetta, A.; Cameron, N. R. *Materials chemistry* **2000**, 10, 2466.
- (9) Barbetta, A.; Cameron, N. R. *Macromolecules* **2004**, 37(9), 3202.
- (10) Clem, E. P.; Greg, G. Q. *Membrane Science* **2006**, 279, 1-49.
- (11) Feng, L.; Zhen, W.; Huili, Y.; Lianxun, G; Mengxian, D. *polymer* **2005**, 12, 937-945.
- (12) Mills, G.A.; Holmes, J.; Cornelius, E.B. *Journal of Physical and Colloid Chemistry* **1950**, 54, 1170.
- (13) Pakeyangkoon, P., Magaraphan, R., Malakul, P., Nithitanakul, M. *Macromol. Symp.* **2008**. 264, 149.
- (14) Pannak, P., Magaraphan R., Malakul, P. and Nithitanakul, M. *Master of thesis book*. **2009**.
- (15) Venaruzzo, J.L.; Volzone, C.; Rueda, M.L.; Ortega, J. *Microporous and Mesoporous Materials* **2002**, 56, 73.
- (16) Volzone, C. *Applied Clay Science* **2007**, 36, 191-196.
- (17) Scamehorn, J.F. *American Chemical Society* **1986**, ACS Symposium Series 311, 1
- (18) Dekany, I., Turi, L., Fonseca, A., Nagy, J.B. *Applied clay science* **14** **1999**, 141-160.

- (19) Saha, M.C., Kabir, Md.E., Jeelani, S. *Materials Science and Engineering A* **2008**, 479, 213–222
- (20) Shim, S. E., Yang, S., Jung, H., Choe, S. *Macromolecular research* **2004**, 12 (2), 233.
- (21) Silverstein, R.M., Clayton B.G., *Spectrometric identification of organic Compounds* **1991**, 5, 174-177
- (22) Menner, A., Powell, R., Bismarck, A. *Soft matter* **2006**, 2, 337.
- (23) Jin, J. M., Lee, J.M., Ha, M. H., Lee, K., Choe, S. *Polymer* **2007**, 48, 3107.
- (24) Srinath, G., Gnanamoorthy, R. *J Mater Sci* **2005**, 40, 2897.
- (25) Jo, C., Naguib, H. E. *J Cell Plast* **2007**, 43, 111.