

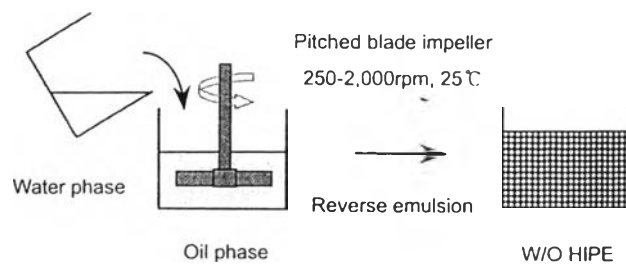
## CHAPTER II

### LITERATURE REVIEW

#### 2.1 High Internal Phase Emulsion (HIPEs)

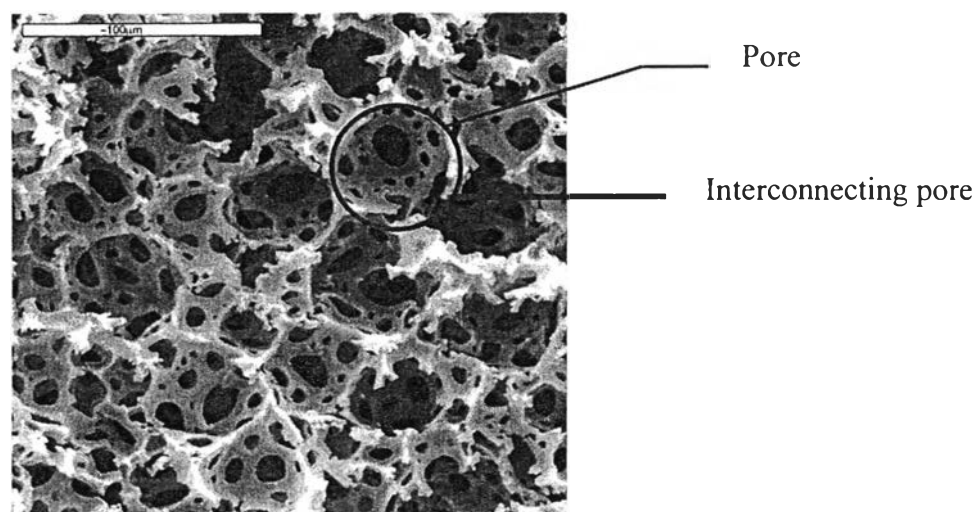
High internal phase emulsion (HIPEs) were porous materials. Following the Unilever patent by Barby and Haq in 1982. Classifications as emulsions with an internal phase or disperse phase volume above 74.05% for monomer disperse of the total volume more close-cell porous structure. The internal (disperse) phase typically consists of water, initiator, and stabilizer. The external (continuous) phase less than 26% of the total volume generally consists of monomer, crosslinking comonomer, emulsifier (surfactant) and solvent (Seong Jae Lee *et al.*, 2004).

The emulsion droplets during polymerization and crosslinking, forming holes that connect the discrete droplets and creating a continuous aqueous phase. The aqueous phase could be removed following polymerization or remove by drying in convection oven, leaving voids connected by holes. The result was a polymer with a highly interconnected porous structure (Michael S. Silverstein *et al.*, 2008).



**Figure 2.1** Schematic diagram for the preparation of water-in oil HIPE system.

This produces a highly porous and permeable materials, it was instructive to define some terms will be used. First, 'voids' or 'pore' were referred to the spherical cavities in the materials. Secondly, the small holes between each void and its neighbors were referred to 'interconnecting pore' (Cameron *et al.*, 2005).



**Figure 2.2** SEM picture showing typical structure of polyHIPE pores and interconnected pores.

The oil phase consists of monomers, viscosity improver and surfactant. The aqueous phase consists of initiator and distilled water (DI). The oil phase stands in beaker and mechanically stirred at a speed. The aqueous phase was adding droplet in oil phase at the same time stirred machine. Total time was 30 min. The emulsion mixture was sealed with parafilm for water evaporation and polymerization 48 h in convection oven at 60 °C. The polymerized was removed water and residual (Seong Jae Lee *et al.*, 2004).

PolyHIPEs had many properties, such as highly porosity, surface area up to 700m<sup>2</sup>/g, low density down to 0.03 g/cm<sup>3</sup> high permeability and highly absorb large amount of liquid (Michael S. Silverstein *et al.*, 2008). Application macro porosity is necessary for convective mass transfer. The use of high internal phase emulsion for preparation of polystyrene membranes for separation of mixture of solvent. Their low density, high absorbency capabilities, microstructural and open cell were HIPE foam (Menner *et al.*, 2006). High surface area could increase capture efficiency (Pacharakhorn *et al.*, 2012).

PolyHIPE was synthesized by using divinylbenzene (DVB) and styrene (S) as continuous phase, aqueous phase containing potassium persulphate and calcium chloride dihydrate, a mixture of surfactant (emulsion) (span 20, CTAB, DDBSS) and toluene as a porogen. polyHIPE sample vary ratio of DVB/S (80:20, 100:0) and

polymerization time for 24-48 h. High surface area was  $431 \text{ m}^2/\text{g}$  when polymerized a ratio of (DVB/S:100/0) and 24 h (Cetinkaya *et al.*, 2006).

The surfactant employed from sorbitan monoolate (SPAN 80) to 3 component mixture of cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (DDBSS) and sorbitan monolaurate. Those surfactant mixture, surface area values were much higher in almost every case than span 80. The mixture surfactant improved of ionic and non-ionic surfactant, leading to enhanced emulsion stability (Barbetta *et al.*, 2004).

Synthesis of emulsion-templated porous materials had been most extensively studied involves a W/O emulsion. The average void diameter in polyHIPEs materials could be varied over a range from  $1 \mu\text{m}$  to  $100 \mu\text{m}$ . It was observed that increasing the DVB/S ratio in the S/DVB HIPE, from 0 to 100% DVB, caused a small but significant decrease in average void diameter from  $15$  to  $5 \mu\text{m}$ . DVB was more hydrophobicity compare to styrene, which causing decrease in void diameter by a decrease in HIPE droplet diameter. A result of increased emulsion stability presence of increasing levels of DVB, which increasing stability smaller average droplet size. An increase in surfactant concentration also decreases in average void diameter. Therefore lead to a more stable emulsion with a smaller average droplet diameter (Cameron R. *et al.*, 2005). The amount of DVB was increased surface area. PolyHIPE was focused because it contains many advantages, i.e., one of the important properties of adsorbent was very high surface area. (Pacharakhorn *et al.*, 2012).

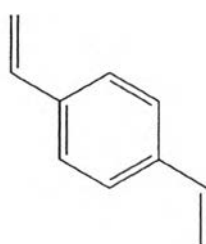
### 2.1.1 Application of PolyHIPE

These structural factors was allow polyHIPE to rapidly large absorb of liquid through capacity increasing porosity could adding a porogen to the monomer, relatively high surface area (Kulygin *et al.*, 2007). Good solvents for polystyrene, such as toluene greatest effect on surface area a 1:1 mixture of toluene to total monomers. a concomitant high level of cross linker (80%), produces materials with surface areas up to  $350 \text{ m}^2 \text{ g}^{-1}$ , very low bulk density ( $<0.1 \text{ gcm}^{-3}$ ) and very high pore volume (90%) (Cameron *et al.*, 1996). In order to achieve a stable emulsion, a surfactant must be low the interfacial tension between two phase. Ionic surfactant stabilizes through electrostatic repulsion and nonionic surfactant stabilizes through steric hin-

drance the interfacial was enhanced by the ability of surfactant to pack closely able to pack more effectively.

PolyHIPE was generally hydrophobic polymer to synthesize with water in oil (W/O). PolyHIPE could be make hydrophilic and hydrogel for application such as support drug delivery, and tissue engineering. The synthesis can easily make hydrophilic polyHIPE. There were two procedures that can do. The first method was directly synthesized of an oil in water (O/W). Unfortunately, these were limited of (O/W) polyHIPE i.e. poor stability, low porosity, poor interconnectivities. The second synthesize type (W/O) polyHIPE that good more than (O/W) polyHIPE. Advantage of (W/O) polyHIPE such as high stability, high porosities, and high interconnectivities. According to (W/O) polyHIPE as hydrophobic can modified to enhance hydrophilicity. Modification by add a functional of comonomer, such as vinylbenzyl chloride (LIVSHIN *et al.*, 2009)

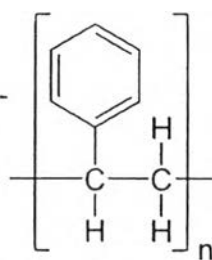
### 2.1.2 Materials for polyHIPE Polymer



**Figure 2.3** The structure of Divinylbenzene (DVB).

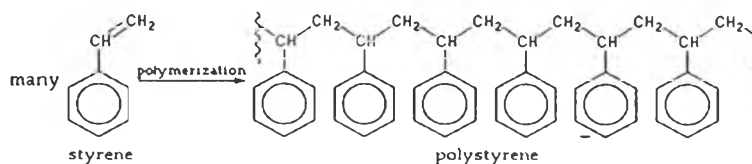
Divinylbenzene (DVB) consists of a benzene ring bonded to two vinyl groups. It was related to styrene (vinylbenzene) by the addition of a second vinyl group. Divinylbenzene, as it is usually encountered, is a 2:1 mixture of *m*- and *p*-divinylbenzene, containing also the corresponding ethylvinylbenzene isomers. It is manufactured by the thermal dehydrogenation of isomeric diethylbenzenes. Under synthesis conditions, *o*-divinylbenzene converts to naphthalene and thus is not a component of the usual mixtures of DVB.

When reacted together with styrene, divinylbenzene can be used as a reactive monomer in polyester resins. Styrene and divinylbenzene react together to form the copolymer styrene-divinylbenzene, S-DVB or Sty-DVB. The resulting cross-linked polymer is mainly used for the production of ion exchange resin. Density is 0.914 g/mL.



**Figure 2.4** The structure of polystyrene.

Polystyrene was synthesized from aromatic polymer. The structure was containing a long chain hydrocarbon alternating carbon centers that attached to phenyl group (aromatic ring benzene). Polystyrene was thermoplastic polymer as solid state at room temperature that above a glass temperature about 100°C it became softened or flowed and form rigid again. Widely properties of Polystyrene were clear, hard, brittle, poor barrier oxygen and water vapor, transparent, good resistance and good insulator. Materials was not expensive.

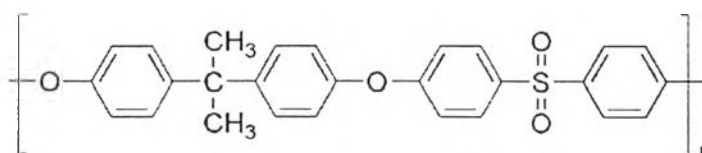


**Figure 2.5** Polymerization reaction of polystyrene.

## 2.2 Surface Modification

### Polysulfone

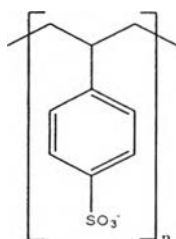
Polysulfone described a family of thermoplastic polymers. These polymers were known for their toughness and stability at high temperatures. They contained the subunit aryl-SO<sub>2</sub> aryl, the defining feature of which was the sulfone group. Polysulfones were introduced in 1965 by Union Carbide. Due to the high cost of raw materials and processing, polysulfones were used in specialty applications and often were a superior replacement for polycarbonates.



**Figure 2.6** Polysulfone repeating unit.

### Polystyrenesulfonate (PSS)

Polystyrenesulfonate (PSS) are polystyrene sulfonic acid polysalts, usually in form of sodium and calcium. PSS is polyanion, white powder, readily soluble in water, and insoluble in lower alcohols. They used as ion-exchange resins.

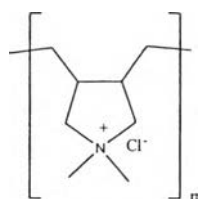


**Figure 2.7** The Structure of Polystyrenesulfonate (PSS).

### Poly(diallyldimethylammonium chloride) (PDADMAC)

Polydiallyldimethylammonium chloride (shortened polyDADMAC or polyDDA) is a homopolymer of diallyldimethylammonium chloride (DADMAC). The molecular weight of polyDADMAC is typically in the range of hundreds of thou-

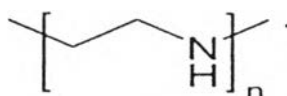
sands of grams per mole, and even up to a million for some products. PolyDADMAC is usually delivered as a liquid concentrate having a solids level in the range of 10 to 50%. It is a high charge density cationic polymer. The charge density makes it well suited for flocculation. PolyDADMAC is used in waste water treatment as a primary organic coagulant which neutralizes negatively charged colloidal material and reduces sludge volume compared with inorganic coagulants.



**Figure 2.8** The structure of Poly(diallyldimethylammonium chloride).

### Polyethylenimine (PEI)

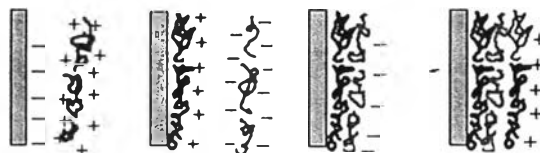
Polyethylenimine (PEI) is a polymer with repeating unit composed of the amine group and two carbon aliphatic  $\text{CH}_2\text{CH}_2$ . Linear polyethylenimines contain all secondary amines, in contrast to branched PEIs which contain primary, secondary and tertiary amino groups. Totally branched, dendrimeric forms were also reported. PEI is produced on industrial scale and finds many applications usually derived from its polycationic character. Linear and branched polyethylenimine has been used for  $\text{CO}_2$  capture which impregnated over a porous material. Adsorbent materials led to higher  $\text{CO}_2$  adsorption capacities when using PEI impregnated materials to adsorb  $\text{CO}_2$  from the air.



**Figure 2.9** The structure of Polyethylenimine.

### Layer-by-Layer Technique

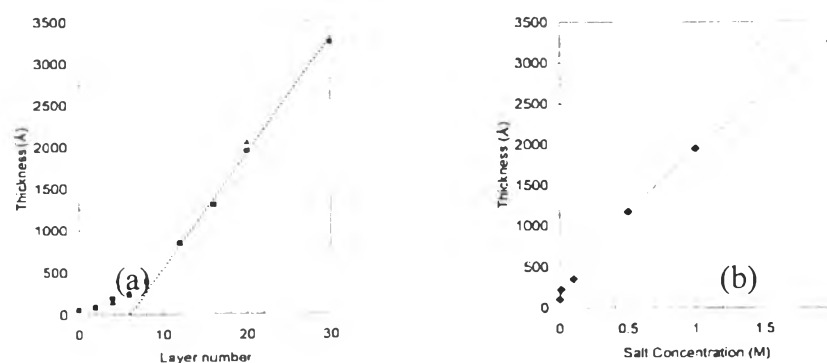
Layer-by-layer used alternative adsorption for opposite charged by dipping of solid substrate into solutions that containing a cationic and anionic. Polycationic such as poly(ethylenimin) PEI, poly(dimethyldiallylammonium chloride) PDDA and poly(allylamine) PAH. Poly anions such as polystyrenesulfonate PSS, poly(vinylsulfate) PVS and polyacrylic acid, PAA). Layer by layer find widely application surface modifications, nanoreactors, pharmacy, electronics, sensor layer and bioreactors (Hua *et al.*, 2008).



**Figure 2.10** Schematic of the layer by layer self-assembly, alternated adsorption of polycations and polyanions on the solid substrate.

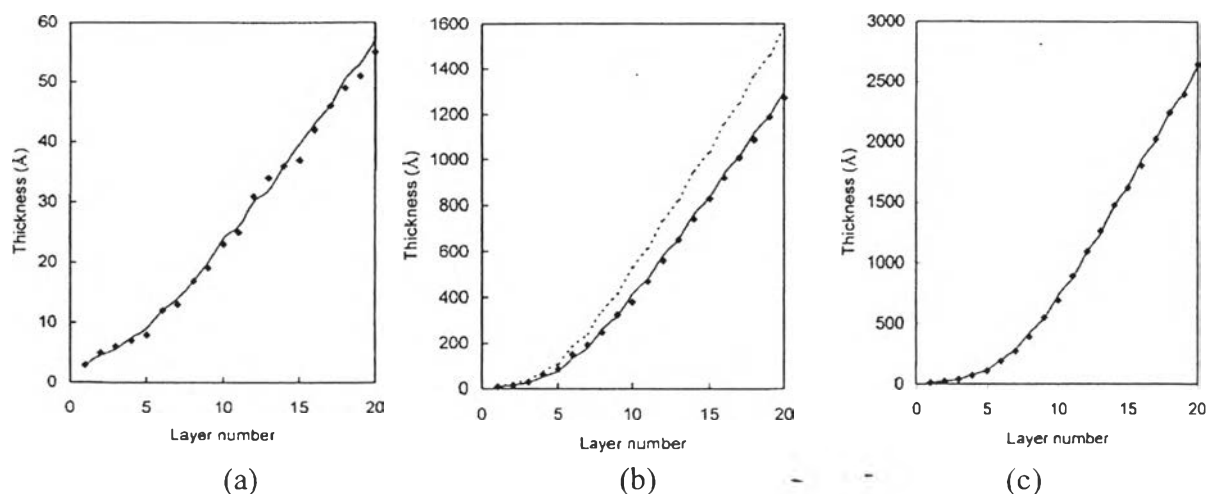
Films dip-cycled multilayers of PSS/PDADMAC as number of deposited cycles, the layer number does not dependence layers thickness as show in Figure 2.4. Thickness as a function of the number of layers for PSS/PDADMAC multilayer that deposited on silicon wafer from 0.1 M NaCl<sub>(aq)</sub>. Even layers of PSS and odd layers of PDADMAC. Polymer concentration 1 mM and deposited hydrodynamic at 600 rpm. Time deposition is 5 min and rinse 3 times between layers by water. The sample dried between layers (squares) or left in contact with solution (triangle). Figure 2.4.(a) (Dubas *et al.*, 1999). However the layer thickness depends on salt concentration in Figure 2.4 (b)





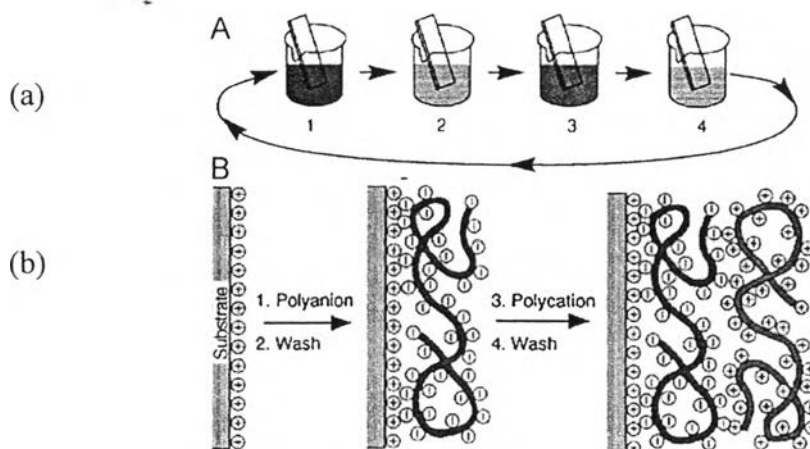
**Figure 2.11** (a) Schematic of Thickness vs. Salt Concentration, (b) Film thickness vs. salt concentration.

A polyelectrolyte deposited a hydrophilic substrate by using polyanions and polycations. The analyze of PSS/PDADMAC system mechanism of charge balance in surface and buildup of multilayers Polystyrenesulfonate (PSS) and Poly(diallyldimethylammonium chloride (PDADMAC). The adsorption of polyelectrolyte was prepared by dipping or aid of robot. Two polymer solutions, there were three rinse of fresh water that rinsed approximately 50 mL each. The deposition time for each layer was 5 min. Polymer concentration were 1 mM. The concentration of salt was 0 to 10 M. Figure 2.5 multilayer for PDADMAC/PSS film thickness as a function of layer number of deposition solutions that containing 0, 0.05, and 1 M salt (multilayer with 14 PSS, 15 PDADMAC). Therefore a thickness vs layer number determined salt concentration for amount of adsorption by controlling surface charge. (Schlenoff *et al.*, 2001).



**Figure 2.12** Schematic of Thickness vs. layer number vary concentration of salt (a) 0 M (b) 0.05 M and (c) 1 M.

Polyelectrolyte film fabrication by successive dipping of polycation and polyanion solutions compared to classic dipping. Figure 2.6 The poly(styrene sulfonate)/poly(allylamine hydrochloride). Step of adsorption of polyanion, washing, polycation and washing, respectively that film dried during multilayer with nitrogen gas/air flow. It is found that film deposited by dipping. The thickness of the multilayer grows linearly with the number of deposition (Iost *et al.*, 2001).



**Figure 2.13** Schematic of the film deposition process.

### 2.3 CO<sub>2</sub> Adsorption Capacity of PolyHIPEs

The increasing of greenhouse effect mainly caused come from industrial process, the combustion of fossil fuels. The most important greenhouse gas is carbon dioxide (CO<sub>2</sub>). Therefore, it is very important to design adsorbent materials for solving.

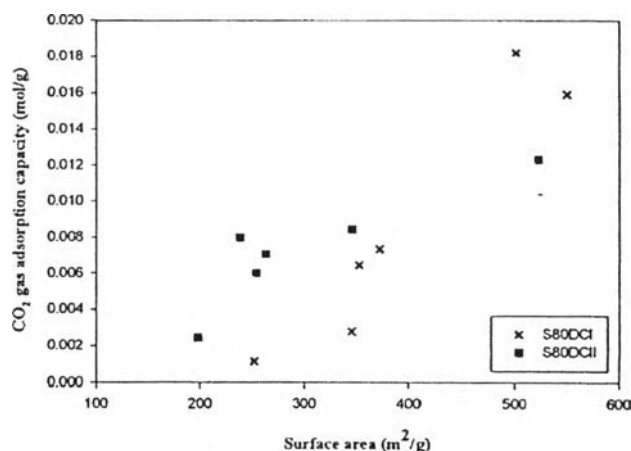
The best CO<sub>2</sub> capture technique is using amine solution but have some problem thus have been developed for adsorption. A requirement adsorbents using activated carbon, zeolites and polymer. The polymer obtained from High Internal phase Emulsion (HIPE), one of important properties of adsorbent is high surface area, very flexible. Increasing efficiency can used amine functional group on the adsorbent, focusing on polyethylene imine (PEI). The polymer has an amine group in structure that it can capture CO<sub>2</sub> (Dejburum *et al.*, 2012).

The polymerization of High internal phase emulsion (HIPEs) of maleimide-terminated aryl ether sulfone oligomer (MAPES) was copolymerized with divinylbenzene (DVB) in continuous phase. A method using mix surfactant system i.e. sorbitan monoleate (Span 80), cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (DDBSS). Preparing two different ratio; (Span 80, CTAB, and DDBSS; 6.3,0.4, and 0.3 wt%) and (Span 80, CTAB, and DDBSS; 11.3,0.4, and 0.3 wt%). All HIPE were characterized CO<sub>2</sub> adsorption that test was obtained materials showed higher adsorption (Thanamongkollit *et al.*, 2012).

Study of clay, zeolites and carbons used as adsorbent for capture that different type between inorganic and organic solution. The structure properties are adsorbent capacities, that the clays could be improved after modifications. The CO<sub>2</sub> gas retention at 25°C and 0.1 MPa and CO<sub>2</sub> gas may be controlled environment. The modifications improved the capacity of clays for gas adsorptions. The retaining of CO<sub>2</sub> gas equal to 0.437-0.602 mmol/g by modify clays (Volzone *et al.*, 2006).

CO<sub>2</sub> gas adsorption of poly(DVB)HIPE, prepared from different mixture of surfactant with different amount of acid treated clay content. Poly(DVB)HIPE filled with 1 to 5 wt% of or organo clay. CO<sub>2</sub> gas adsorption capacities of poly(DVB)HIPE filled with acid treated clay shows higher. Therefore, Figure 2.6 the CO<sub>2</sub> gas adsorp-

tion of poly(DVB)HIPE increase after acid treatment and to increase the surface area, improving and thermal properties (Pannak *et al.*, 2009).



**Figure 2.14** Surface area and adsorptive capacity of poly(DVB)HIPE filled with acid treated clay.

The greenhouse gas emission in the world has been increasing significantly; carbon dioxide (CO<sub>2</sub>) was the most important greenhouse gas with the largest impact on climate change. A widely developed technology to separate CO<sub>2</sub> from flue gas and natural gas stream is based on absorption using liquid amine. Adsorption of CO<sub>2</sub> was performed with an adsorbent impregnated with piperazine. A maximum piperazine loading of 3.12 wt % was impregnated on the activated carbon and was detected by a gas chromatography-flame ionization detector. The adsorption capacity of 4 % CO<sub>2</sub> on the unmodified activated carbon (Act.C), moisturized adsorbent, and 3.12 wt % piperazine loaded on activated carbon (Pz-Act.C) at room temperature and atmospheric pressure reached 16.47 mg/g, 6.12 mg/g, and 23.17mg/g, respectively. The gas cylinders is controlled by mass flow controllers before mixing premixed 15 % CO<sub>2</sub>/N<sub>2</sub> with pure N<sub>2</sub> in the mixing chamber to obtain 4 % CO<sub>2</sub>. The mixed gas is then controlled to a fixed pressure for 4 % CO<sub>2</sub> gas to pass through the rotameter which the flow rate will be adjusted to 5 mL/min determined by a bubble flow meter. the 4 % CO<sub>2</sub> gas is analyzed by a gas chromatography-thermal conductivity detector (GC-TCD). Activated carbon beds adsorption capacity enhanced significantly after impregnation with piperazine. The highest CO<sub>2</sub> adsorption capacity improvement

reaches as high as 40.73 % for Pz-Act.C in comparison with pure Act.C at room temperature (Kangwanwatana *et al.*, 2013).

Porous adsorbents were prepared as emulsions. These emulsions were prepared by slowly adding an aqueous phase containing water, initiator, and stabilizer into an oil phase containing a vinylbenzylchloride (VBC) monomer and a divinylbenzene (DVB) co-monomer, poragen, and a surfactant under constant agitation for 1h to produce a water-in-oil emulsion. The procedure for amine functionalization was adopted which cut Poly(VBC-co-DVB) pieces and immersed in the amine solution. The resulting mixture was left at room temperature for 1 h and then put into a water bath (80 C°) for 24 h. The capability of the adsorbents was expressed in terms of dynamic adsorption capacity ( $Q_{ads}$ ) which can be calculated by

$$Q_{ads} = \frac{FC_{in}t_{st}}{M}$$

$$t_{st} = \int_0^t \left(1 - \frac{C_{out}}{C_{in}}\right) dt$$

A piece of solid amine-based adsorbent was loaded into the reactor and pretreated in N<sub>2</sub> gas flow (20 mL/min) at 60 C for 1 h before allowing CO<sub>2</sub> to enter the reactor. At room temperature, the N<sub>2</sub> flow was then switched to 4 vol% of CO<sub>2</sub> in N<sub>2</sub> balance at a total flow rate of 5 mL/min. The concentration of CO<sub>2</sub> was measured by gas chromatography

(GC) and the adsorption breakthrough points were determined after the adsorption process reached equilibrium (Muchan *et al.*, 2013).

Objectives of my research were to synthesize polyHIPE in different S/DVB in monomer ratio, to modify surface on polyHIPE by layer by layer and to evaluate CO<sub>2</sub> adsorption.

Scope of this research covers as follow: (1) Synthesis of polyHIPE by using Styrene (S) and Divinylbenzene (DVB) very monomer ratio of S/DVB form 0/100, 20/80, and 80/20. (2) Modification surface using layer by layer technique (3) testing polyHIPE for CO<sub>2</sub> adsorption.