

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

The CO₂ concentration in the atmosphere led to change in global average temperature, climate change, and sea level. Furthermore, CO₂ is harmful to the body. The concentration of carbon dioxide has increased dramatically from 280 part per million (ppm) in pre-industrial time to 400 ppm in 2013, representing 43 percent points increase (Medlyn *et al.*, 2013). Therefore, researchers are interested in the developing technologies for the efficient capturing and sequestration of the large quantities of CO₂. Figure 2.1 presents the uncomplicated path of CO₂ capture technology such as sorbent, solvent, and membrane (Li *et al.*, 2013).

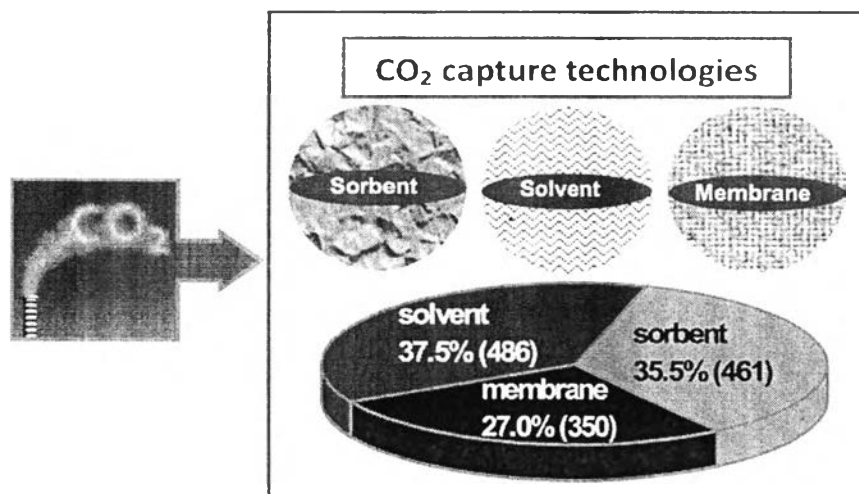


Figure 2.1 Schematic diagram of CO₂ production and capture

The varieties of CO₂ sorbents materials have been studied such as high porous materials (polyHIPE) (Pakeyangkoon *et al.*, 2009), active carbon (Quicker *et al.*, 1987), zeolites (Sumin *et al.*, 2009), alkali metal oxides (Lan *et al.*, 2010), silver oxide (Verykios *et al.*, 1980), lithium oxide, lithium silicate, carbonates, silica gel, alumina, and amine solid sorbents. The outstanding properties of polyHIPE are

lightweight, open structure, high surface area, and high porosity (Gokmen *et al.*, 2009) so it suitable to CO₂ absorption.

2.2 High Internal Phase Emulsion Polymer (PolyHIPE)

PolyHIPE is highly porous polymer synthesized from high internal phase emulsion. The high internal phase emulsion has an aqueous phase (or internal phase) volume that is greater than 74 % and can be greater than 90 % (Lumelsky *et al.*, 2008). PolyHIPE is based on the polymerization of hydrophobic monomers and crosslinking comonomer within organic (continuous) phase of water-in-oil (w/o). Water in oil emulsions are sometime called 'inverted emulsion'. The organic phase is less than 26 % of the total volume generally consisting of monomer, crosslinking comonomer, emulsifier (surfactant), and solvent (Silverstein *et al.*, 2014). The amount of surfactant for stabilization reaches up to 30 wt% of organic phase.

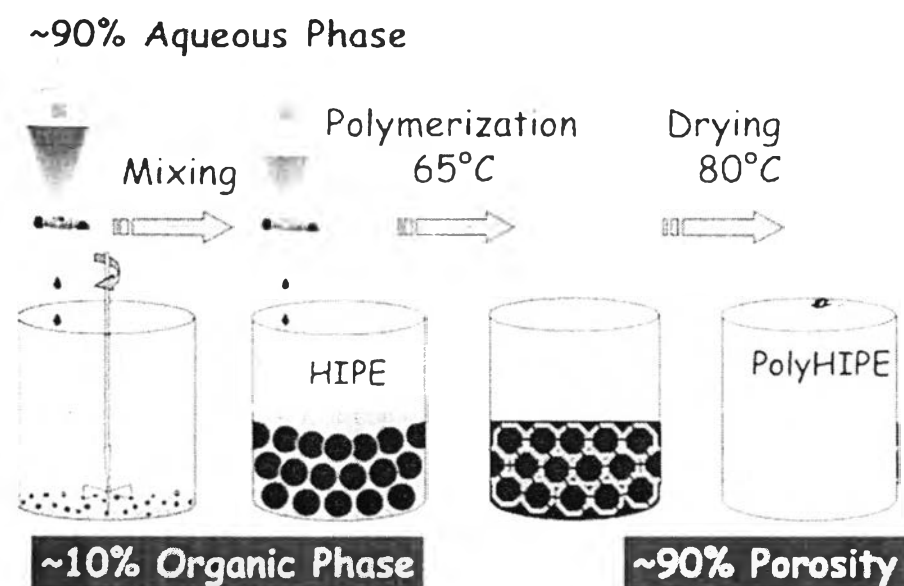


Figure 2.2 PolyHIPE preparation.

The preparation of porous polymers from water soluble or miscible monomers, oil-in-water HIPE must be used. Firstly, aqueous phase was slowly added in the organic phase of monomer mixture, under mechanical stirring, forming uniform water-in-oil (W/O) HIPE providing in Figure 2.2. Then, polyHIPE was

washed by Soxhlet extraction. Finally, solid foams were dried in oven. Figure 2.3 (Hayward *et al.*, 2013) provides information about the characteristic structure of polyHIPE porous foam. The monomer styrene (S) and divinylbenzene (DVB) have been most widely used on W/O emulsion system of organic phase because their monomer were obtained good properties of polyHIPE such as small pore and high surface area (William *et al.*, 1990). Furthermore, the organic phase consists of porogenic solvent and mixture surfactant due to increasing emulsion stability of system.

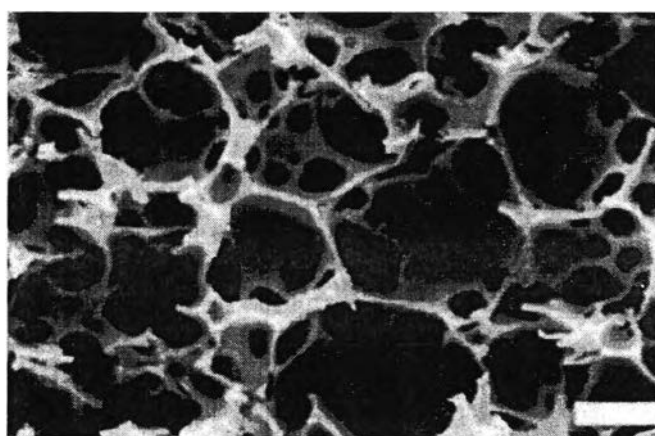


Figure 2.3 Characteristic structure of a polyHIPE

Emulsion stability is strongly influenced by the composition of each phase. The emulsion may become unstable in 4 different ways which are shown in Figure 2.4.

1. Coalescence is the process of the fusion of two or more drops to form a larger drops.
2. Ostwald ripening is process of molecular diffusion transfer of oil from the smaller to the large drop and is driven by chemical potential differences.
3. Sedimentation is due to the density difference between the two immiscible.
4. Flocculation occurs when the drops stick to each other and form aggregates due to the action of the colloidal forces.

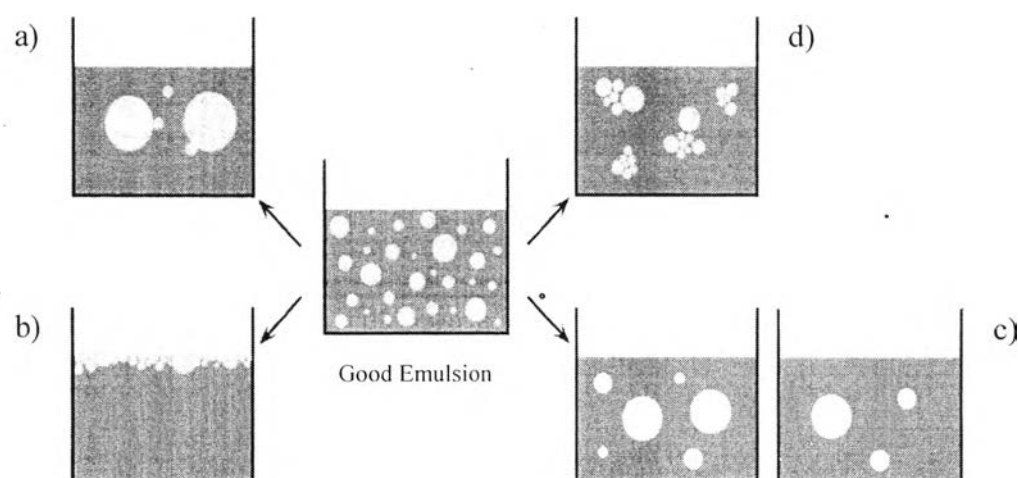


Figure 2.4 Different type of unstable emulsion

a) Coalescence, b) Sedimentation, c) Ostwald ripening, and d) Flocculation

Differences in the properties of each phase might affect emulsion stability of different mechanisms. We must concern about composition of continuous phase (hydrophobic monomer and crosslinking comonomer (Styrene and DVB)), surfactant concentration, type of surfactant, salt concentration in aqueous solution, and porogenic solvent (toluene). For example, increasing amount of DVB in system, the size of large voids decreased and the emulsion phases to become more stable (Williams *et al.*, 1990).

In addition, the effect of surfactant on emulsion stability can form a thin interfacial film between the two liquids and maintain minimizing contact of emulsion, coalescence, and aggregation of the dispersed phase. At 20 percent of surfactant, polyHIPE shows smooth surface with no defect and produce open cell with small interconnected (William *et al.*, 1990).

In 2004, Cameron and co-worker studied porogenic solvent leading to reduce electrical repulsion between head group of system. As a result, the porogenic solvent were increasing emulsion stability and surface area (Barbetta *et al.*, 2004).

Furthermore, during 2008, Pakeyangkoon and co-worker studied the surfactant system on morphology and property of polyHIPEs. They used porogenic solvent (toluene) and mixture surfactant namely span 20, cetytrime tylammonium bromide (CTAB), and dodecyl-benzolsulfonic acid sodium salt (DDBSS). In conclusion, the surface area of the porous material tended to increase from 10.49

(span 20, CTAB and DDBSS) to 568.7 (span 20, CTAB, DDBSS and toluene) m^2/g providing in Figure 2.5 (Pakeyangkoon *et al.*, 2008).

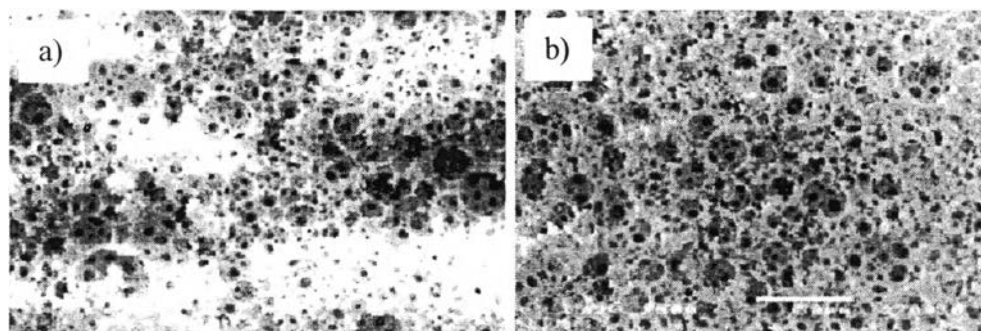


Figure 2.5 Morphology of polyHIPEs.;

a) Sample was using span20 mix surfactant without toluene and b) Sample was using span20 mix surfactant with toluene

Another effect of emulsion stability is salt concentration. Salts can enhance the ability of surfactants to pack into a more stable structure. In 1992, Pons and co-worker found that the addition of NaCl can enhance the rigidity of the interfacial film in water in oil (W/O) HIPEs (Pons *et al.*, 1992). Furthermore, It also increase the emulsion stability by hindering Ostwald ripening, a process by which smaller droplets form to larger droplets. In addition, salts can reduce the solubility of the aqueous phase in the oil phase, thus reducing the attractive forces between the droplets leading to small cells in emulsion system (Kizling *et al.*, 2006).

Thus, emulsion system of polyHIPE is a flexible and easily controlled method for the fabrication of macroporous materials by polymerizing the continuous phase of a high internal phase emulsion consisting of significant ratio of monomer, surfactant, porogenic solvent, and salt concentration (Zhang *et al.*, 2005).

Finally, polyHIPEs can apply to various application, such as separation/column filtration, supporting for catalysis, tissue engineering, and biotechnology (Feuerabendt *et al.*, 2014).

2.3 Polystyrene (S)

Polystyrene is made from petroleum, produced from free radical vinyl polymerization of petroleum based styrene monomers, a hydrocarbon material. Its structure consists of a long hydrocarbon chain with phenyl groups (aromatic rings) besides, along the chain show in Figure 2.6.

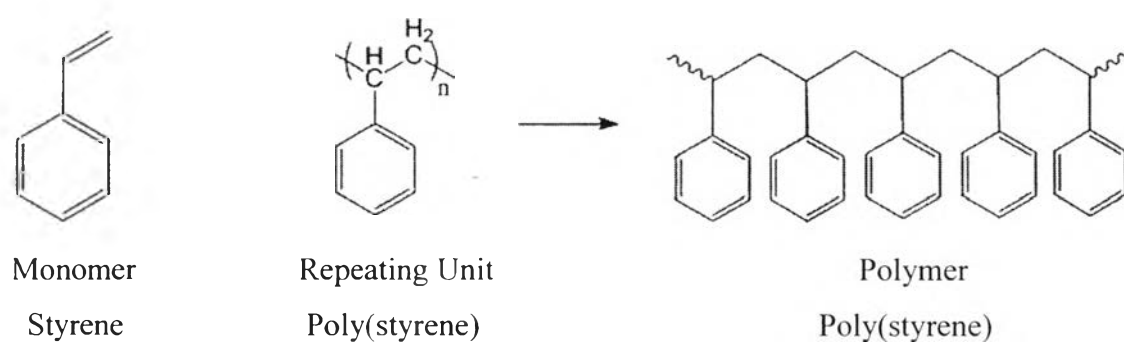


Figure 2.6 The structure of polystyrene

As a thermoplastic polymer, polystyrene is in a solid (glassy) state at room temperature but flows if heated above about 100 °C, its glass transition temperature. It becomes rigid again when cooled. Due to the many aromatic rings in its structure, polystyrene is a material that possesses high fire resistance, good resistance to acids and bases, good electric insulating properties, high shock-resistance, and excellent surface characteristics.

Application of polystyrene such as packing peanuts, CD/DVD cases, containers (such as clamshells), lids, bottles, trays, tumblers, disposable cutlery, and high porous material (such as polyHIPEs and foam packaging).

In 2012, polyHIPE was prepared by polystyrene and polyethylene glycol dimethacrylate used as scaffold in tissue engineering. PolyHIPE was modified surface by atmospheric pressure plasma treatment. As a result, polyHIPE had highly porous structure and good mechanical strength. (Pakeyangkoon *et al.*, 2013)

2.4 Divinylbenzene (DVB)

Divinylbenzene (DVB) was used for cross-linking agent that also improves polymer properties. Divinylbenzene consists of a benzene ring bonded to two vinyl groups show in Figure 2.7. Divinylbenzene can be used as a reactive monomer in polyester resins such as styrene. Styrene and divinylbenzene react together to form the copolymer styrene-divinylbenzene, S-DVB or Sty-DVB. In 1990, Williams and co-worker studied emulsion stability of S-DVB system. The resulting cross-linked polymer was necessary to obtain small pore size and good property (Williams *et al.*, 1990).

Furthermore, during 2013, He and co-worker studied effect of crosslinking of polystyrene and divinylbenzene particle, they found that mechanical property depend on cross-linking (He *et al.*, 2013).



Figure 2.7 Structure of divinylbenzene

2.5 Surface Modification Using Layer-by-Layer Technique

Layer-by-Layer technique of formation of thin film is employed for its simplicity in methodology. The concept was popularized in the 1990's by Gero Decher's group at the Universite Louis Pasteur and CNRS in France. They used polycation (e.g. polyethylenimine (PEI), tetraethylenepentamine (TEPA)) and polyanion (e.g. polystyrene sulfonate (PSS), polyacrylic acid (PAA)) on a polyHIPE. These amine-multilayered sorbents had much faster CO₂ desorption rates compared to sorbents prepared using the current PEI-impregnation approach (Jiang *et al.*, 2011). Moreover, Gong and co-worker found that the compression degree of PSS/PDADMAC multilayers is as high as 70-90 percent depending on number of layer and concentration of NaCl (Gong *et al.*, 2009). In addition, salt concentration controls the thickness and stability of layers (Dubas *et al.*, 1999).

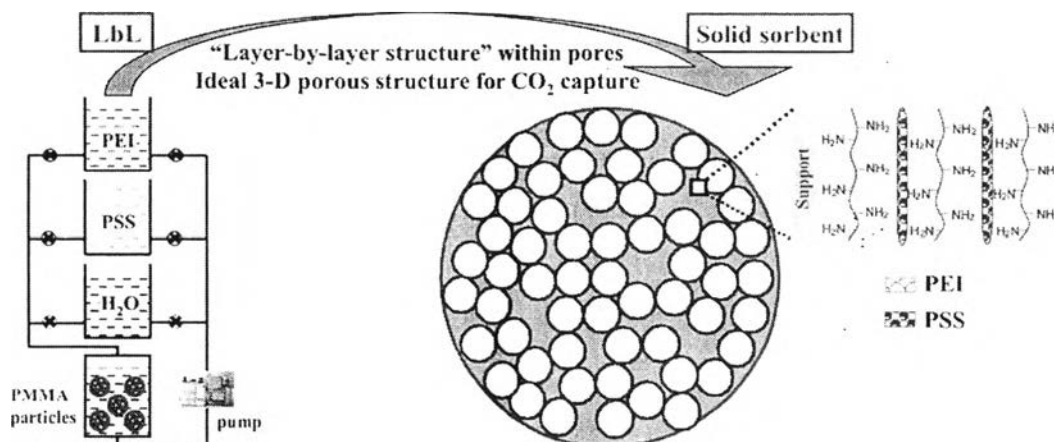


Figure 2.8 Preparation of amine multilayered on PMMA microparticles

Preparation of PEI-multilayered (Figure 2.8) was used a vacuum pump to remove air and to run solutions through the interior pores of sorbent supports. A positively-charge polymer (PEI, TEPA or PAH) solution was run through sorbent support, then the samples were rinsed with deionized water. Next, the samples were rinsed with a negative-charge polymer and deionized water again. Finally, the samples were dried under vacuum at 80 °C overnight.

Another method, dipping a cleaned sample into a solution of positively charged polyelectrolyte (polycation) results in adsorption of first layer. A washing steps are necessary to remove supernatant material. Now the surface potential is positive and a polyanion is adsorbed and thus two layers is formed. Washing step is shown in Figure 2.9 (Dey *et al.*, 2008).

Layer-by-Layer technique can apply to many applications, such as increasing hydrophilic for water absorption, corrosion control, biomedical application, and CO₂ adsorption. According to research, the amine-multilayers sorbents using layer-by-layer technique via alternate deposition of CO₂ adsorbing amine polymer and an oppositely charged polymer. More polymer (i.e. PEI and PSS) were deposited with increasing number of PEI/PSS bilayer show in Table 2.1. The capacity decreased from 1.7 mol CO₂/(kg sorbent) of (PEI/PSS) PMMA to a little adsorption, i.e. 0.1 mol CO₂/(kg sorbent) of (PEI/PAA) of PMMA 10 layer (Jiang *et al.*, 2011). Furthermore, Jiang and co-worker used amino acid for CO₂ sorbents.

They found that the type of amino acid, complex loading capacity and ratio of amino acid could have significant effect on CO₂ adsorption. The result found that arginine improved amino acid water solubility and save higher CO₂ adsorption capacity (Jiang *et al.*, 2013).

Table 2.1 CO₂ capture capacity of amine-multilayered PMMA solid sorbents under pure CO₂ atmosphere

Sample	CO ₂ Capture Capacity		
	mol CO ₂ / (kg Sorbent)	mol CO ₂ / (kg PEI)	mol CO ₂ / (mol N)
(PEI/PSS) 5 layer	0.8	12.8	0.56
(PEI/PSS) 10 layer	1.7	17.4	0.77
(PEI/PAA)10 layer	0.1	1.8	0.08

Furthermore, the layer-by-layer of polyelectrolyte multilayers (PDADMAC and PSS) was deposited on multiwall carbon nanotubes surface from first to the sixth layer. This sample was used for drug delivery application (Iamsamai *et al.*, 2011).

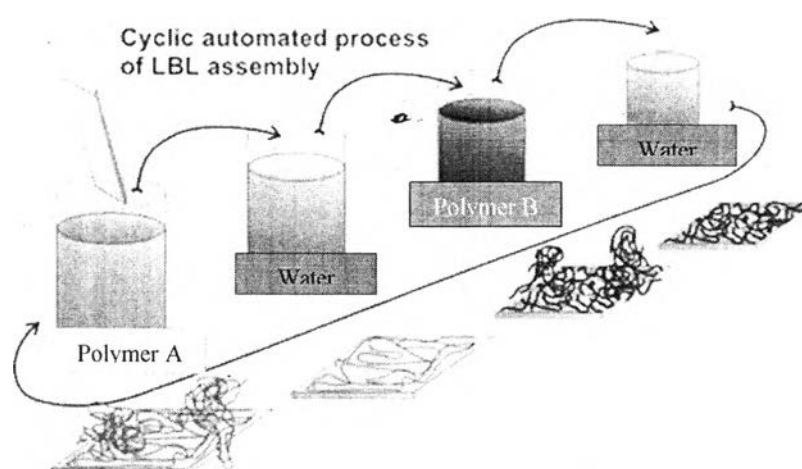


Figure 2.9 Schematic of layer-by-layer adsorption of polyelectrolyte multilayers.

2.6 Polystyrenesulfonate (PSS)

Polystyrenesulfonate (PSS) is polyanion containing sulfonic acid or sulfonate functional groups. The material is prepared by sulfonation of polystyrene. The structure of polystyrenesulfonate is shown in Figure 2.10. This polymer is classified as polysalts and ionomers. Polystyrenesulfonate is known for its toughness and stability at high temperatures. In addition, many researchers used PSS for layer-by-layer technique.



Iamsamai *et al.*, (1992) studied surface modification of multiwall carbon nanotube using the layer-by-layer technique. They used polystyrenesulfonate (PSS) and poly (diallyldimethylammonium chloride) (PDADMAC) (Iamsamai *et al.*, 2011). Moreover, Jiang and co-worker (2011) used amine-multilayer (polyethyleneimine (PEI) and polystyrenesulfonate (PSS)) for polycation and polyanion. The result showed high CO₂ capture capacity.

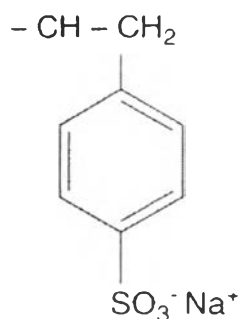


Figure 2.10 Structure of polystyrenesulfonate

2.7 Poly(diallyldimethylammonium Chloride) (PDADMAC)

Poly(diallyldimethylammonium chloride) or PDADMAC shown in Figure 2.11 is high charge density cation polymer. The reaction of allyl chloride with dimethylamine is forming monomer of PDADMAC. Polymerization of polyDADMAC is synthesized by radical polymerization using DADMAC with an organic peroxide as catalyst.

In 2009, Wu and co-worker found that low molecular weight PDADMAC have shown increasing absorption amount (mg/g), while for high molecular weight PDADMAC lower adsorption than low molecular weight PDADMAC. The nominal molecular masses of the low and high PDADMAC have given as 5 k-20 k and 400 k-500 k ranges (Wu *et al.*, 2009).

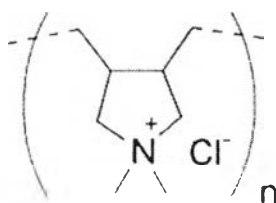


Figure 2.11 Structure of poly(diallyldimethylammonium chloride)

2.8 Polyethylenimine (PEI)

Amine group and two carbon aliphatic are repeating unit of polyethylenimine (PEI). Linear polyethylenimines contains secondary amines, conversely branched PEIs contains primary, secondary, and tertiary amines. Many researchers selected linear and branched polyethyleneimine for CO₂ capture using impregnated or layer-by-layer into porous material. For example, activated carbon was modified by polyethyleneimine using impregnation. Increasing amount of PEI was enhanced CO₂ adsorption capacity (Pipatsantipong *et al.*, 2012).

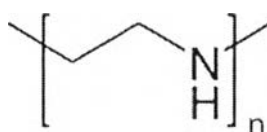


Figure 2.12 The structure of polyethylenimine

2.9 Tetraethylenepentamine (TEPA)

Tetraethylenepentamine (TEPA) occupies five amine groups per molecule to afford more CO₂ affinity sites per gram. Tetraethylenepentamine use as polycation coming from ethylenediamine. Ethylenediamine is the primary member of the so-called polyethylene amines namely, diethylenetriamine (H₂N-CH₂CH₂-NH-CH₂CH₂-NH₂), triethylenetetramine (H₂N-CH₂CH₂-NH-CH₂CH₂-NH-CH₂CH₂-NH₂), and tetraethylenepentamine (H₂N-CH₂CH₂-NH-CH₂CH₂-NH-CH₂CH₂-NH-CH₂CH₂-NH₂). TEPA is used in many applications, such as lubricating oil additive, paint adhesives, fuel additive, and CO₂ adsorption.

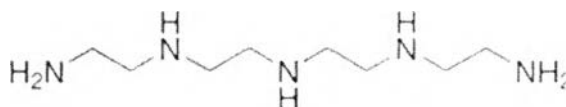


Figure 2.13 Structure of tetraethylenepentamine

In 2011, Qi and co-worker studied CO₂ capture by solid sorbents based on amines (polyethylenimine, PEI and tetraethylenepentamine, TEPA). They found CO₂ capacity up to 7.9 mmol/g (Qi *et al.*, 2011). Moreover, Fisher and co-worker studied TEPA on zeolite exhibiting the highest CO₂ capture capacity. CO₂ adsorbed on TEPA/beta zeolite as weakly bound CO₂ and formed carbonate species at 30 °C. CO₂ desorption regenerates the NH₂ sites of TEPA/beta zeolite sorbent (Fisher *et al.*, 2009) Furthermore, the mesoporous silica KIT-6 was impregnated with TEPA dissolved in ethanol. The dynamic adsorption capacity increases from 1.5 mmol/g-adsorbent to 2.9 mmol/g-adsorbent when the amount of loaded TEPA increases from 10 wt.% to 50 wt.% (Liu *et al.*, 2010).

Remarkably, Yue and co-worker studied CO₂ capture using the tetraethylenepentamine (TEPA) impregnated mesoporous silica. The TEPA-impregnated adsorbents exhibited the CO₂ adsorption capacities as 3.93 mmol/g for a 70 wt% of TEPA loaded onto the as SBA-1. This was probably due to that the template in the pore could prevent TEPA from aggregating to clusters. They further investigated a mixture of TEPA and diethanolamine (DEA) impregnated into the as-

synthesized SBA-15 (Yue *et al.*, 2006). They got the highest CO₂ adsorption capacity as 4.00 mmol/g was obtained at a loading of 35 % TEPA and 15 % DEA, while the maximum CO₂/N ratio around 0.4 was observed at a loading of 30 % TEPA and 20 % DEA under anhydrous pure CO₂.

In 2013, Muchan studied polyHIPEs for CO₂ adsorption. PolyHIPEs were prepared from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) with various amines. They found, the adsorption capacity of the material depended on the type of amine group which decreased in the order of primary > secondary > tertiary amine containing in the adsorbent because primary and secondary amines carry free protons on the nitrogen atom. (Saiwan *et al.*, 2014)

The reason we are interested in TEPA and PEI in my research because TEPA and PEI were used to incorporate with the polyHIPE in order to enhance the adsorption capacity because its structure contained both primary and secondary amine. Both amine increase the stability of the formed carbamate in equation 2 and 3.

