CHAPTER III
EXPERIMENTAL

3.1 Equipment and Chemicals

Divinylbenzene (DVB) used as a monomer in preparation of polyHIPE, hexylamineand 1,3-diaminopropane used for functionalization with 4-vinylbenzyl chloride (VBC), potassium persulfate ($K_2S_2O_8$) used as an initiator for polymerization reaction were purchased from Merck, Germany. 4-Vinylbenzyl chloride (VBC) was purchased from Aldrich. 1, 3-Diaminopropane (99%) used for functionalization with 4 - vinylbenzyl chloride and sorbitanmonooleate (SpanR80) used as surfactant in an oil phase to stabilize an emulsion were purchased from Sigma-Aldrich Co., USA. Triton X-100 used as surfactant in an aqueous phase to stabilize the emulsion system was purchased from Sigma-Aldrich Co., Switzerland. Toluene (analytical grade) and ethanol (analytical grade) were purchased from Labscan Asia Co., Ltd., Thailand.

3.2 Experimental Procedures

3.2.1 PolyHIPE

PolyHIPE was done by the oil in water emulsion system (o/w) which is more potential to improve the CO_2 adsorption ability than water in oil emulsion system (w/o), for example, the polyHIPE from w/o showed lower amine loading in the structure, the high surface area polyHIPE from w/o system is a consequence of the interconnection void in the monolith structure unlike polyHIPE from o/w showed high surface area from size of spheres and size of void on the surface. Water in oil polyHIPE preparation procedure consisted of two parts, oil and aqueous phases. The first part was the oil phase composing of monomers (DVB and VBC), surfactant (Triton X 100), and poragens (toluene) thoroughly mixed in a flask for 30 minutes. The aqueous phase were composed of the initiator $K_2S_2O_8$, SpanR80, and water. Then, the aqueous phase was dropped into the oil phase and stirred thoroughly at room temperature for 30 minutes to obtain the emulsion. After that, the emulsion was poured into the mold and placed in an oil bath at 70°C for 24 hours at which the polyHIPE solid was formed. Eventually, polyHIPE solid was extracted by ethanol using soxhlet apparatus for 6 hours and then dried in a vacuum at 70°C, as a schematic diagram of the preparation shown in Figure 3.1.

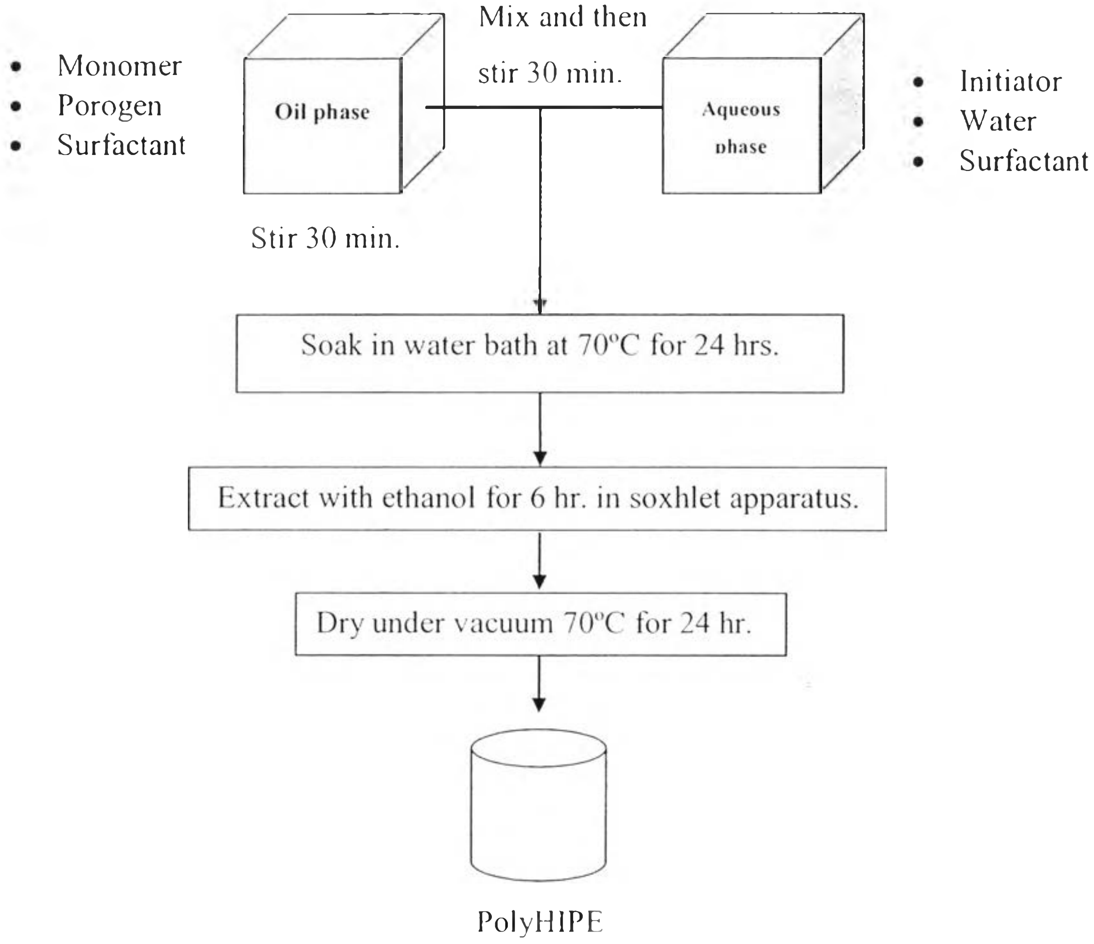

Figure 3.1 Methodology flow diagram.

3.2.2 PolyHIPE Preparation with Amine Compounds

Amine compounds (Hexylamine, 1,3-diaminopropane) was initially added to react with VBC at ratio 1:1.07 (Appendix B), 65°C for 15 minutes and then addition of DVB, toluene, spanR80 altogether with stirring for 30 minutes. Then, the aqueous phase was added into the oil phase and stirring at room temperature for 30 minutes to form the emulsion. After that, the procedure was repeated as described previously.

To avoid an effect of amine on a change of emulsion formation condition deviating from the polyHIPE reference condition, so that the effect of amine loading can be compared with the reference, the volume ratio of DVB to VBC was fixed at 9:1, the volume ratio of monomers (DVB plus VBC) to poragen (toluene) was 1:1, and the ratio of the initiator to monomer was 1:25 g/mL. Only the surfactant ratio (oil soluble surfactant to water soluble surfactant) was varied because both surfactants play the important role to stabilize the emulsion system. The oil soluble surfactant causes void and fracture on the surface appearance whilethe water soluble surfactant causes the spherical shape of polyHIPE appearance.

3.2.3 Effect of Surfactants on PolyHIPE

To form the emulsion with good stability, the emulsion system needs to be stabilized by the surfactants both in oil and aqueous phases. The ratio of SpanR80 to Triton X 100 was varied from 1to 4 (recipes 1- 6) for a reference condition, 1.20 to 1.71 (recipes 7-10) for hexylamine added polyHIPEs and 0.72-0.93 (recipes 11-15) for 1,3diaminopropane added polyHIPEs as shown in the Table 5.1.

Table 3.1 PolyHIPE preparation at various conditions

Recipe	DVB (mL)	VBC (mL)	Amine (mL)	Toluene (mL)	SpanR80 (g)	Water (mL)	$K_2S_2O_8$ (g)	Triton x-100 (g)	Surfactant ratio
1	0.900	0.100	-	1.000	0.20	18.0	0.04	0.20	1.00
2								0.17	1.18
3								0.15	1.33
4								0.13	1.54
5								0.10	2.00
6								0.05	4.00
7	1.800	0.200	0.200	2.000	0.60	36.0	0.08	0.50	1.20
8								0.45	1.33
9								0.40	1.50
10								0.35	1.71
11			0.126		0.65			0.90	0.72
12								0.85	0.76
13								0.80	0.81
14								0.75	0.87
15								0.70	0.93

3.3 Characterization of PolyHIPE

3.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (Hitachi S-4800, Japan) was used to observe the morphology of polyHIPEs. Each sample was coated by platinum for 230 seconds. The magnifications of the images were 10K, 20K, 50K, and 100 K.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (Thermo Nicolet Nexus 670, USA) was used to characterize the reaction of VBC and amine.

3.3.3 Surface Area of PolyHIPE

The Brunauer, Emmett, and Teller (BET) technique was used to perform on the Autosorb-1MP (Quantachrome, USA). The polyHIPE were dried in a vacuum oven overnight at 70°C before out gassing at 110 °C. The specific surface area of the polyHIPEs was performed using nitrogen adsorption.

3.3.4 Amine Loading of PolyHIPE

The polyHIPE was measured for the amount of amine by CHN analyser (Truespec CHNSO, LECO, USA). The sample (0.08 g) was wrapped by CHN foil and burned in the furnace at 850 °C under O_2 and He ambient. The weight percent of elements of carbon, hydrogen and nitrogen is calculated and reported.

3.4 Carbon Dioxide Adsorption

The experimental setup is shown in Figure 3.2. A premixed 15 % CO_2/N_2 and pure N_2 gases from the two gas cylinders, which are controlled by mass flow controllers are mixed in the mixing chamber to obtain 4 % CO_2. The mixed gas is then controlled to a fixed pressure for ventilation and enabling small quantity of 4% CO_2 gas to pass through the rotameter which the flow rate is adjusted to 3 mL/min and determined by the bubble flow meter. The adsorption column is a tubular glass flow adsorber with the dimension of 4mm id x 6mm od x 39 cm length vertically oriented for the evenly distribution of the adsorbent. The column is wounded with an insulator of 40 cm long to maintain constant room temperature (25 °C) throughout the whole experiment. From the top 18.5 cm of the column, the adsorbent (0.25 g) is packed and emplaced with the glass wool at the top and the bottom to support the adsorbent, so the feed can be running against gravity.

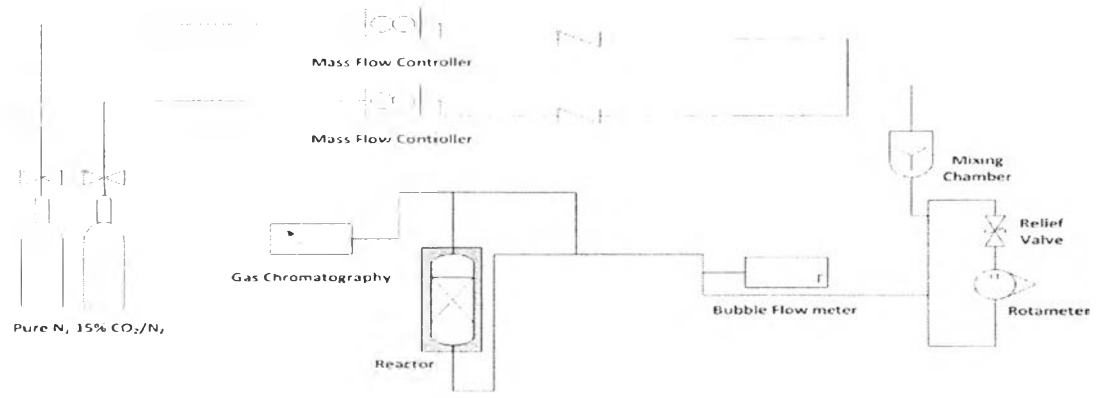

Figure 3.2 Schematic flow diagram for CO_2 adsorption (Kangwanwatana W. et al., 2013).

For gas chromatography-thermal conductivity detector (GC-TCD) operation, Rt®-Q-BOND column with 0.53 mm id x 20 μm film thickness x 30m length was used to operate at an isothermal temperature of 40 °C. The GC injection port was heated to 100 °C with the spilt flow of 8 mL/min and helium as a carrier gas. In typical CO_2 adsorption, 0.25 g of adsorbent in the column was pre-dried at 60 °C for 1 hr while purging with N_2 gas at 113 mL/min. Then, 4 % premixed CO_2 of dry gas at 3 mL/min was allowed to flow into the packed bed adsorber to carry out the experiment at room temperature and atmospheric pressure until the CO_2 concentrations of the feed gas at the outlet of adsorber reached equilibrium. The concentrations of CO_2 in the downstream in terms of chromatogram were continuously monitored with a computer program, WiniLab III V4.6. The dynamic adsorption capacity of the adsorbent (Q_{ads}) was calculated with Eq (1),

$$Q_{ads} = \frac{FC_{in}t_{st}}{M} \qquad (1)$$

where F (mol/min) is the total molar flow of feed gas, C_{in} is the CO_2 concentration of the inlet stream, M is the mass of solid adsorbent loaded in the column, and t_{st} (min) is the stoichiometric time which was determined from the breakthrough curve according to Eq (2) via MATLAB software.

$$t_{st} = \int_0^t (1 - \frac{C_{ou}}{C_{in}})dt \qquad (2)$$

Where C_{in} and C_{out} are the CO_2 concentrations of inflow and outflow gas stream of the column, respectively.

The CO_2 adsorption was run under dried and moisturized condition. For the moisturized condition, the polyHIPE containing hexylamine sample was initially dried for 6 hours at 100 °C, and then equilibrated in a water saturated chamber at room temperature for 12 hours. Different weight before and after the equilibration was measured. Finally, the sample was taken to measure the CO_2 adsorption capacity.