

CHAPTER III EXPERIMENTAL

3.1 Materials

Poly(vinyl alcohol) with 97.5-99.5 % degree of hydrolysis and degree of polymerization of 1600 (MW = 72,000), trimethylsilylchlorosulfonate, 3-aminopropyl triethoxysilane and glutaraldehyde solution (50%w/w), *N,N'*-dimethylacetamide and dimethylsulfoxide, were obtained from Fluka Chemicals, Switzerland. *N,N'*-carbonyldiimidazole was from TCI, Japan. Methanol, ethanol, benzene and cyclohexane were purchased from J.T. Baker, USA. 1,4-Dioxane and diethyl ether were obtained from Lab-Scan, Thailand. All chemicals were used without further purification.

3.2 Instruments

3.2.1 Fourier transform infrared spectrophotometer (FTIR)

FTIR spectra were obtained on a VECTOR 3.0 BRUKER Spectrometer with 32 scans at a resolution of 2 cm^{-1} . A frequency range of $4000\text{-}400\text{ cm}^{-1}$ was observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D^* , of $1 \cdot 10^9\text{ cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$.

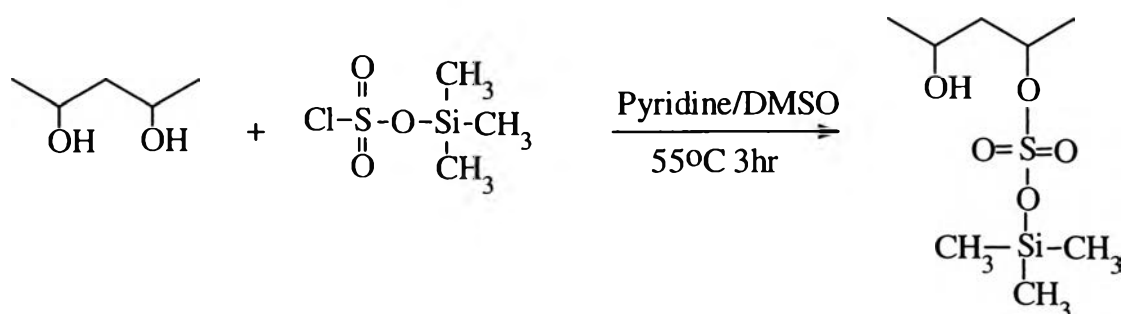
3.2.2 Proton Nuclear Magnetic Resonance Spectrometer ($^1\text{H-NMR}$)

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained from Fourier Transform NMR Spectrometer ACF 200 MHz of Bruker, Switzerland. Sample was dissolved in deuterated dimethylsulfoxide with tetramethylsilane as an internal standard.

3.3 Methodology

3.3.1 Modification of Poly(vinyl alcohol)

3.3.1.1 *Coupling with Trimethylsilylchlorosulfonate(TMSCS)*

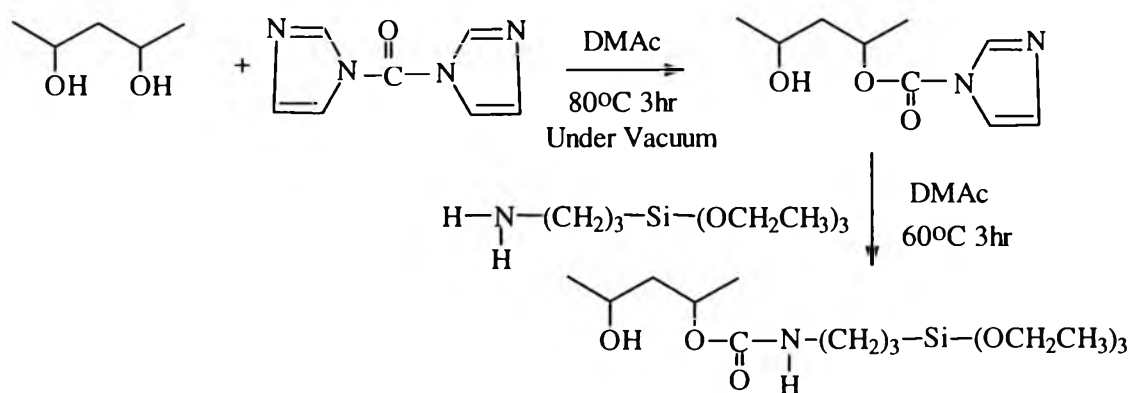


Scheme 3.1 Reaction of trimethylsilylchlorosulfonate(TMSCS) with PVA.

Poly(vinyl alcohol) (0.15 g) was dried under vacuum at 80°C for 3 hours. Dried poly(vinyl alcohol) was dissolved in 5 ml DMSO and heated to 60°C to obtain a poly(vinyl alcohol) solution. The solution was purged with nitrogen and the temperature was reduced to 55°C. A catalytic amount of pyridine was added to the solution. After stirring for 5 minutes, trimethylsilylchlorosulfonate 0.25 ml was added with a dropper to this solution and reacted for 3 hours. After the reaction, the solvent was removed to obtain a viscous solution. The solution was extracted with chloroform and water. The product was filtered from aqueous phase and was purified by dissolving in 1,4-dioxane, reprecipitation in water, and drying under vacuum at room temperature. The functional groups of the obtained product were qualitatively confirmed by FTIR.

3.3.1.2 Coupling with 3-Aminopropyltriethoxysilane via PVA-CDI

Precursor



Scheme 3.2 Reaction of 3-aminopropyltriethoxysilane and CDI with PVA

Poly(vinyl alcohol) 0.15 g was dried under vacuum at 80°C for 3 hours before dissolving in DMAC 5 ml. *N,N'*-carbonyldiimidazole 0.06 g was added and reacted for 3 hours at 80°C under vacuum. The product was reacted further with 3-aminopropyltriethoxysilane 0.1 ml at 60°C for 3 hours. The solvent was removed and the obtained product was reprecipitated in diethyl ether and dried under vacuum. The product was characterized by FTIR.

3.3.2 Membrane Preparation

3.3.2.1 PVA Membrane

Poly(vinyl alcohol) was dissolved in water at 100°C. The PVA solution was cooled down to room temperature and glutaraldehyde solution was added to the PVA solution followed by the addition of a catalytic amount of HCl. After stirring, the mixture solution was cast on petri dish and dried at

room temperature for 24 hours. The concentration of PVA solution, the concentration of HCl and the concentration of glutaraldehyde were varied to find the best condition for membrane preparation.

3.3.2.2 Modified PVA Membrane

The membrane was prepared with the best condition for PVA membrane but using 1,4-dioxane as a solvent. After the membrane was prepared, its structure and thickness were characterized by FTIR.

3.3.2.3 Membrane Thickness Study

The FTIR spectrum of PVA membrane in the range of 2000-1800 cm^{-1} was expanded to find fringe pattern. The thickness was calculated from the equation 3.1 to obtain the average thickness.

$$\text{Membrane thickness (d)} = \frac{\Delta m}{2n(\nu_1 - \nu_2)} \quad (3.1)$$

Where Δm = number of fringe pattern in the specific region

n = refractive index of polymer film

ν_1, ν_2 = initial and final wave number, respectively

3.3.3 Gas Permeation Study

In the present work, gas permeation study was performed by using liquid cell as a simplified apparatus. The vapor of organic solvent was applied as a model for volatile organic compounds. The system of gas permeation study is shown in Figure 3.1.

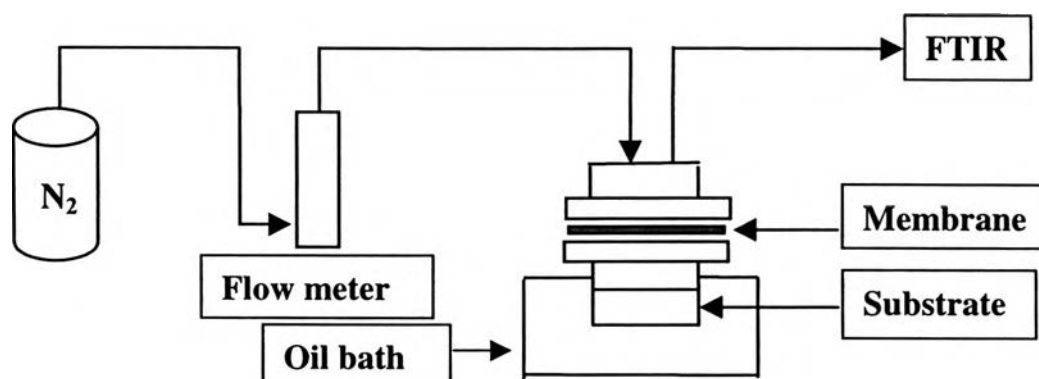


Figure 3.1 Schematic diagram of gas permeation system.

The gas permeation study was done according to the following procedures:

- Clean the cell with acetone and dry in the oven.
- Fill the lower compartment of the cell with organic substrate for 0.1 ml.
- Set the membrane on the fluorinated elastomer gasket to cover the lower compartment.
- Seal the upper side of the membrane with the fluorinated elastomer gasket and tighten the allen screws holding the upper and lower chambers of the cell.
- Immerse the cell in the oil bath.
- Start to measure the permeate amount as a function of time by using FTIR(rapid scan measurement).
- Remove residue organic substrate from the membrane by drying the membrane under vacuum for 1 hour before using the membrane for another measurement.

The substrates used in this study are methanol, ethanol, *iso*-propanol, benzene and cyclohexane. The temperature was maintained at 50°C and nitrogen was used as a carrier gas the flow rate of which was controlled at 113 ml/min. The permeate concentration was measured quali/quantitatively by FTIR.