CHAPTER III
EXPERIMENTAL

3.1 Materials

Fumed silica, 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol were purchased from Aldrich Chemical Co., Inc. (USA), used without purification and kept under nitrogen atmosphere. Triethylenetetramine (TETA) was also purchased from Facai Polytech. Co., Ltd. used as received and as a catalytic base. Sodium hydroxide and potassium hydroxide were purchased from Merck Company Co., Ltd., used as received and as co-catalyst.

Ethylene glycol and acetonitrile were purchased from Lab-Scan Company Co., Ltd., purified by standard methods under nitrogen atmosphere and kept in sealed bottoms. Methanol was purchased from J.T. Baker Company Co., Ltd., and purified by distillation over magnesium activated with iodine. Phenol was purchased from Ajax Laboratory Chemical Company Co., Ltd., and used as received. Formaldehyde was purchased from Merck Company Co., Ltd., used as received and as a starting material for the synthesis of new benzoxazines.

1,4-Dioxane agent was purchased from Carlo Erba Reagenti s.r.l. mentedson group and 2,2,4-trimethylpentane (isooctane) was purchased from Labscan Co., Ltd., both were purified by distillation over calcium hydride and kept in sealed container.

3.2 Equipment

3.2.1 Fourier Transform Infrared Spectroscopy (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 4000-400 cm^{-1} was observed using a deuteriated triglycinesulfate detector (DTGS) with specific detectivity of D*, of 1×10^{9} cm $\times$ $Hz^{1/2}$ $\times$ W^{-1}. Both neat techniques on ZnSe plate and KBr pellet were used.

3.2.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H-NMR and ^{13}C-NMR were performed on a Brüker 400 MHz spectrometer at room temperature. The samples were pulsed at 400 MHz for proton and 200 MHz for carbon NMR with a spin rate of 21 rpm. A relaxation delay time was 1 sec with a sweep width of 3105 Hz or about 15 ppm, using a pulse of 45 μsec. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent. 16 scans were run for ^{1}H while ^{13}C samples were pulsed for more than 2 hrs or more than 400 scans. Tetramethylsilane (TMS) was used as the reference for chemical shift measurements in both proton and carbon NMR.

3.2.3 Thermogravimetric Analysis (TGA)

TGA thermograms were carried out on a Du Pont instrument, Du Pont TGA 2950 and used platinum pan. Samples size was typically 5-10 mg. and experiments were studied under nitrogen atmosphere at a flow rate of 25 ml/min. The temperature program was started from room temperature to 750°C, with a heating rate of 10°C/ min.

3.3 Methodology

3.3.1 Synthesis Method

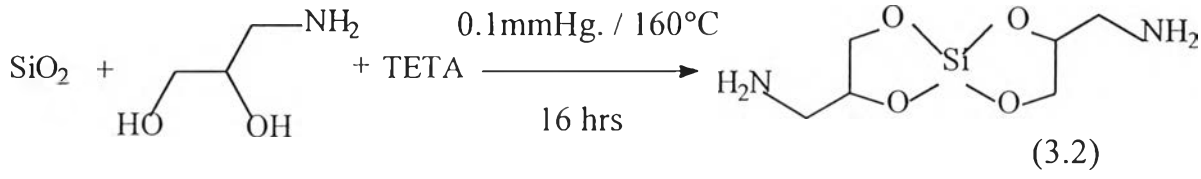
3.3.1.1 Synthesis of Spirosilicate from Silica and Ethylene Glycol

Spirosilicate was synthesized (Sun, 2000) from fumed silica and excess amount of ethylene glycol, using triethylenetetramine (TETA) as a catalyst and small amount of sodium hydroxide as a co-catalyst, see eq. (3.1). The reaction was run under nitrogen atmosphere at the boiling point of ethylene glycol (200°C) for 8 hr. The product was precipitated by using acetonitrile. Due to the moisture absorption property of the product, it was kept under nitrogen atmosphere.

$$SiO_2 + EG + TETA + NaOH \xrightarrow[N_2 \,/\, 8\ hrs]{200°C} \text{spirosilicate} \qquad (3.1)$$

3.3.1.2 Synthesis of Aminospirosilicate (C3) from Silica and 3- Amino-1,2-propanediol

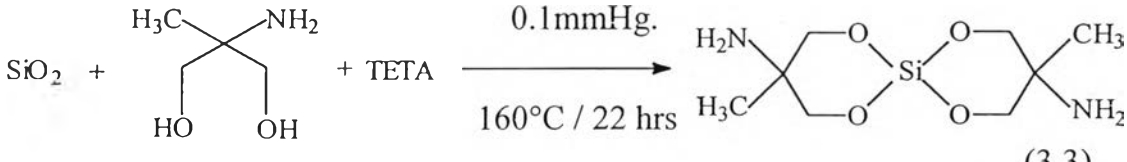
The aminospirosilicate product (C3) was synthesized (Sun, 2000) from fumed silica and 3-amino-1,2-propanediol, using triethylenetetramine (TETA) as both solvent and catalyst under vacuum (1 torr) at 160°C for 16 hr. The product was precipitated by using trace amount of methanol in acetonitrile, and kept under nitrogen atmosphere for further use as a starting material in the step of benzoxazine derivative synthesis. Chemical reaction is shown in equation (3.2).



(3.2)

3.3.1.3 Synthesis of Aminospirosilicate (C4) from Silica and 2-Amino-2- methyl-1,3- propanediol

The aminospirosilicate product (C4) was synthesized (Sun, 2000) from fumed silica and 2-amino-2-methyl-1,3-propanediol, using triethylenetetramine (TETA) as both catalyst and solvent and small amount of potassium hydroxide as a co-catalyst. The reaction was done under vacuum (1 torr) at 160°C for 22 hr. The product was precipitated by using trace amount of methanol in acetonitrile. It was then kept under nitrogen atmosphere to use as a starting material in the step of benzoxazine derivative synthesis. Product structure is shown below,



(3.3)

3.3.2 Determination of Curing Conditions

To determine the density of monomers in order to compare with their corresponding polymers, the suitable time and temperature for curing monomers to obtain fully crosslinked polymers was first investigated.

3.3.2.1 Variation of Curing Temperature

The optimum curing temperature was obtained by fixing curing time at 1 hr and varying temperature from 80° to 180°C in vacuum oven. %Ceramic yield data from TGA was used to clarify the amount of crosslinking, meaning that the higher %ceramic yield, the higher crosslinking. The suitable curing temperature was the point that the % ceramic yield started to approach constant.

3.3.2.2 Variation of Curing Time

Like-wise, the optimum curing time was obtained by fixing the selected temperature and varying the time in range of 1 to 5 hrs in vacuum oven. The suitable time was again the point that the %ceramic yield started to approach constant.

3.3.3 Density Measurement

The volumetric property of each product was obtained by comparing the densities of monomer and its corresponding polymer. The density results were determined using a 25 mL pycnometer (for power form product) and distilled isooctane as media. In the process, as shown in Figure 3.1, the pycnometer bottle was weighed and tarred. The purified product in the bottle was weighed in the range of 0.5-1.0 g. The media was added to the bottle until covering the product. The bottle-containing sample was then

sonicated in an ultrasonic bath to eliminate bubbles and left to cool to room temperature. The sample was incubated at 25°C for 2 hrs. The media was then added to the bottle until it reached the marked point. The bottle was wiped and covered it with the cap having a thermometer. The weight was measured and the density of the sample was finally calculated.

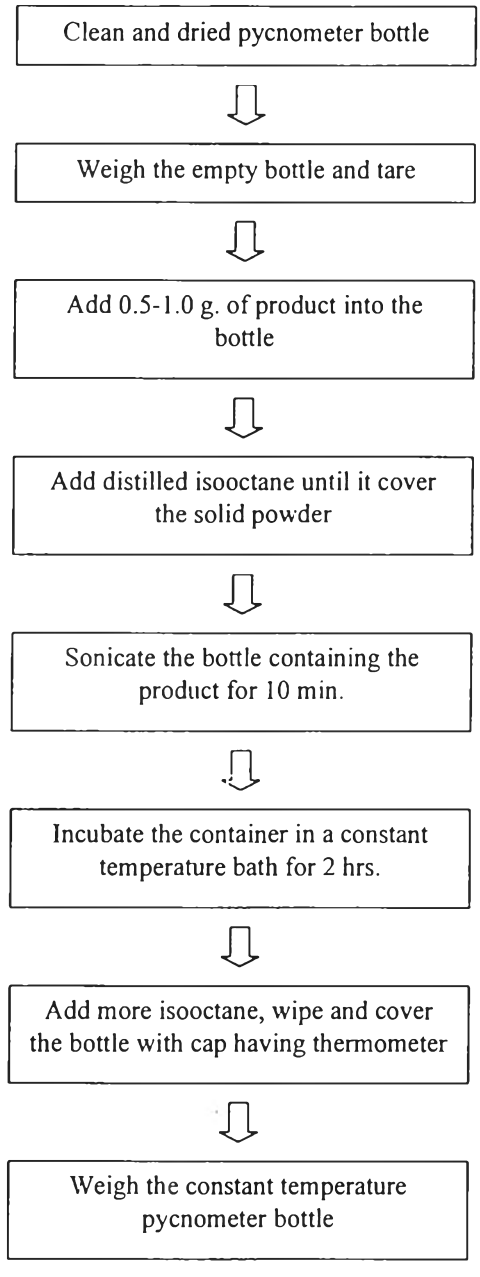


Figure 3.1 Step of Density Measurement.