

# CHAPTER IV

## EXPERIMENT



In the present study, the influences of various layers hyperbranch polyether grafted on synthesized polyimide were examined. The experiments were divided into six parts which can be explained as below,

- (i) Materials and chemicals
- (ii) Equipments
- (iii) Polyimide polymerization
- (iv) Preparation of 1-3 layers hyperbranch polyether on polyimide
- (v) Preparation of polyimide films
- (vi) Characterization of all polyimide films

The details of the experiments can be explained as followed.

### 4.1 Materials and chemicals

The chemicals used in these experiments were analytical grade, but only crucial materials were specified as followed:

1. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6 FDA) purchased from Aldrich chemical Company, Inc .
2. 3,3'-Dihydroxy-4,4'-diamino biphenyl (DHBP) purchased from Chriskev Company, Inc.
3. 3,4'-Oxydianiline (ODA) purchased from Aldrich chemical Company, Inc.
4. Phthalic anhydride (PA) purchased from Merck KGaA Germany.
5. N-Methyl-2-pyrrolidinone (NMP) purchased from Merck KGaA Germany.
6. Toluene commercial grade was donated from Exxon Chemical Ltd., Thailand. This solvent was dried over dehydrated  $\text{CaCl}_2$  and distilled over sodium/benzophenone under argon atmosphere before use.
7. Methanol (Commercial grade) was purchased from SR lab.
8. Silicone Oil purchased from Merck KGaA Germany.
9. MonoChloroIsobutyl-POSS (POSS-Cl) purchased from Hybrid plastic company.
10. 3,5-Dihydroxybenzyl alcohol purchased from Aldrich chemical Company,

Inc.

11. Argon gas (Ultra high purity grade, 99.999 %) was purchased from Thai Industrial Gas Co.,Ltd.(TIG) and further purified by passing through columns packed with copper catalyst, NaOH, P<sub>2</sub>O<sub>5</sub> and molecular sieve 4A to remove traces of oxygen and moisture.
12. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) purchased from Ajax Finechem.
13. Acetone (Analytical grade) was purchased from SR lab.
14. Carbon tetrabromide (CBr<sub>4</sub>) purchased from Merck KGaA Germany.
15. Triphenylphosphine (PPh<sub>3</sub>) purchased from Aldrich chemical Company, Inc.
16. Tetrahydrofuran (THF) (Analytical grade) was purchased from SR lab.

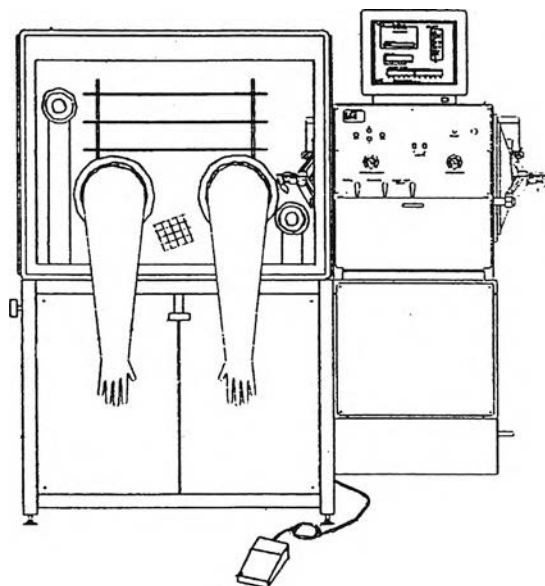
## 4.2 Equipments

The equipments, which used during the polymerization of polyimide, and the procedures to synthesize various layers of the polyether grafted on polyimide, are listed as below:

### 4.2.1 Polyimide synthesis part

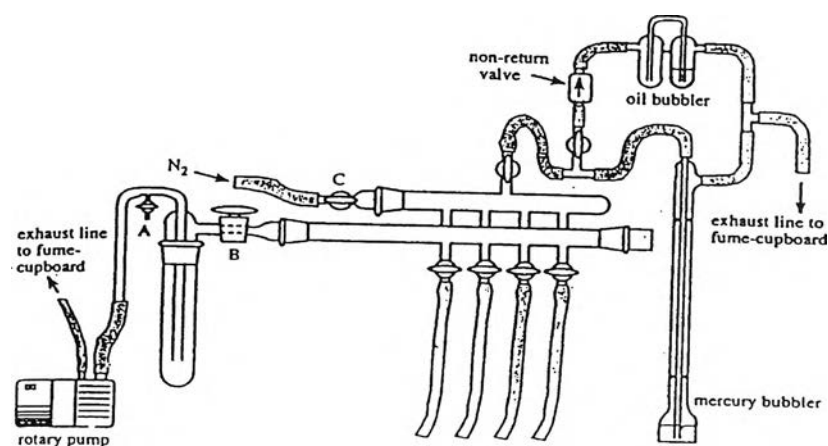
Since most of the reagents were very sensitive to the oxygen and moisture therefore the special techniques were taken during the handling of reagents and the loading of ingredient into the reactor. Such equipments utilized for this purpose are listed as follows:

**(a) Glove box** (Vacuum Atmospheres) with oxygen and moisture analyzer for handling solid reagents under inert atmosphere and for storing air-sensitive reagents. Inside the glove box, oxygen and moisture levels are normally controlled to below 2 ppm. The glove box is shown in Figure 4.1.



**Figure 4.1** Glove box

(b) **Schlenk line** included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 4.2.



**Figure 4.2** Schlenk line

(c) **Schlenk tube** for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line. Schlenk tube is the tube with a ground joint and a side arm which connected with three ways glass valve. The Schlenk tube picture is shown in Figure 4.3.

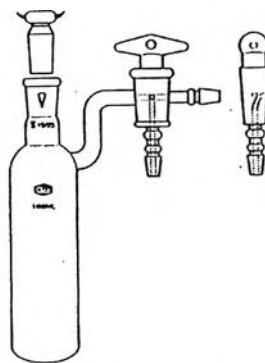


Figure 4.3 Schlenk tube

(d) The inert gas (argon) from the cylinders was passed through columns of oxygen trap (BASF catalyst, R3-11G), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentoxide ( $P_2O_5$ ) in order to purifying the argon gas to obtain ultra high purity argon which was used in Schlenk line and solvent distillation column. The inert gas supply system can be shown in Figure 4.4.

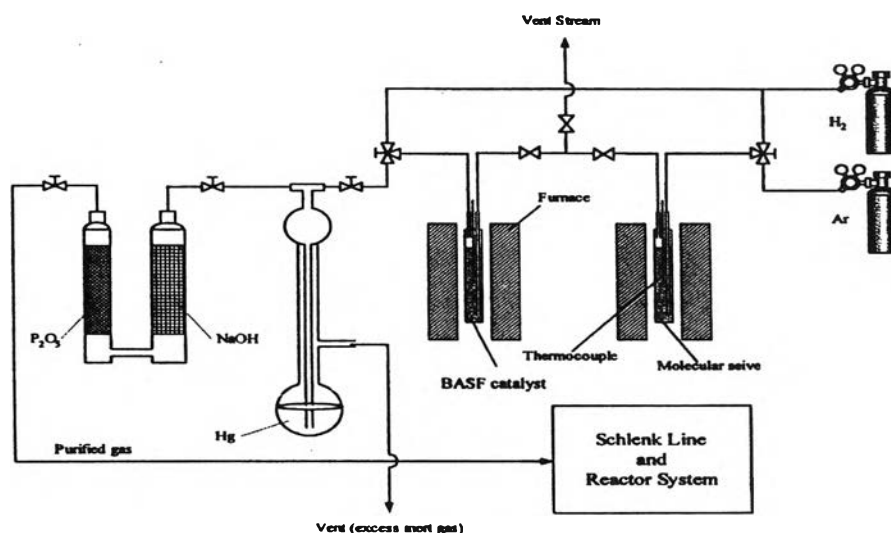
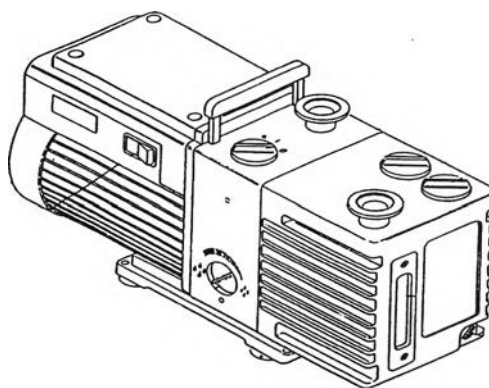


Figure 4.4 Inert gas supply system

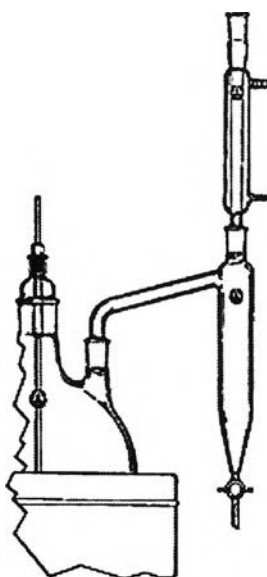
(e) The vacuum pump model 195 from Labconco Corporation was used. The produced low pressure of  $10^{-1}$  to  $10^{-3}$  mmHg was adequate for utilizing as the vacuum supply to the vacuum line of the Schlenk line. The vacuum pump is shown in Figure 4.5.



**Figure 4.5** Vacuum pump

**(f) Synthesized reactor**

The polymerization reactor was a 250 ml. three-neck flask. The reactor was equipped with several fittings for injecting the chemicals and purging with argon gas. A three-necked, round bottom flask equipped with an argon inlet, a thermometer, a magnetic stir bar and a condenser with a Dean-stark trap, was used as the reaction vessel which can be shown in Figure 4.6.



**Figure 4.6** Reactor

**(g) Magnetic Stirrer and Hot Plate**

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

**(h) Cooling System**

The cooling system in the solvent distillation is needed in order to condense the freshly evaporated solvent from the reactor during the synthesis.

**(i) Syringe, Needle**

The syringe used in these experiments had a volume of 50 and 10 ml and the cooperated needles were of No. 17 and 20, respectively.

**4.2.2 Film preparation Part****(a) Vacuum oven**

A Cole-Parmer vacuum oven model 282A was used for removing solvent from freshly cast films. This vacuum oven can be programmed. All functions can be set from digital panel and display their status on LCD. The temperature, pressure and time are controllable variables.

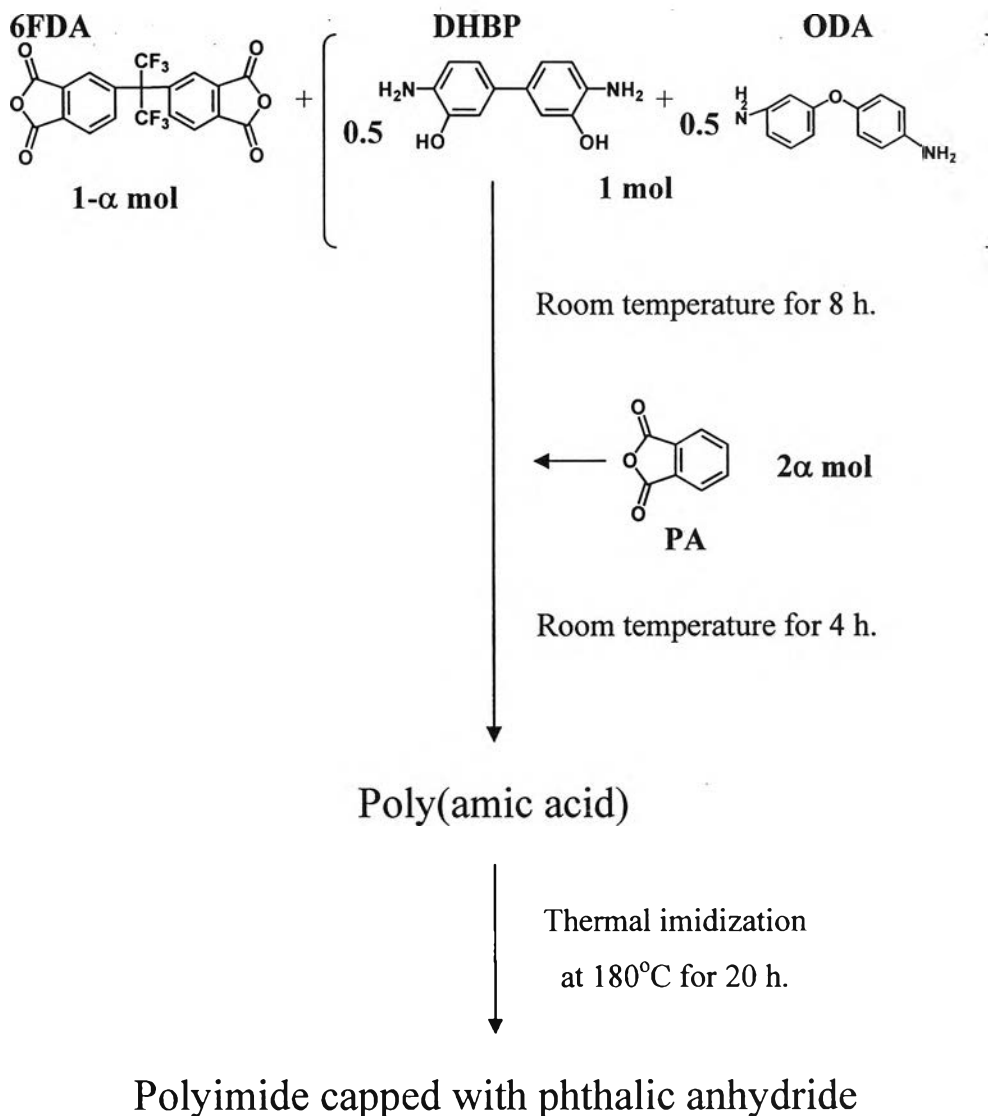
**(b) Temperature controlled oven**

A Carbolite LHT5/30 (201) Temperature controlled oven was utilized in these experiments. The maximum working temperature of this machine is 500°C. The equipment was used for thermal treated the film polyimide.

**4.3 Polyimide polymerization**

Various hydroxyl concentrations of polyimide capped with non-reactive end groups were prepared by the reaction of 6FDA, with diamine mixtures of DHBP and 3,4'-ODA and PA in NMP. The synthesized figure can be shown in figure 4.7. The content of hydroxyl groups in the polyimide was controlled by adjusting the mole ratio of diamine monomers DHBP and 3,4'-ODA.

Here, coded polyimides of PI25, PI50, PI75 and PI100 indicated the percent of DHBP in total diamine mixtures of the synthesized polyimides that varied from 25, 50, 75 and 100% respectively.



**Figure 4.7** Preparation of polyimide capped with non-reactive end groups

As a typical example, the preparation of PI50 can be explained as follow. A three-necked, round bottom flask equipped with the purified argon inlet, a thermometer, a magnetic stir bar and a condenser with a Dean-stark trap was used as the reaction vessel. DHBP (1.5039 mmol, 0.3248 g), 3,4'-ODA (1.5039 mmol, 0.3008 g) and 6 mL of NMP were added to a reaction vessel. The mixture was stirred at ambient temperature until both diamines were completely dissolved. Next, 6FDA (3.0000 mmol, 1.3326 g) solution in NMP with about 10% solids (w/w) was added. This solution was stirred under argon atmosphere for 8 h at room temperature. Subsequently, PA (0.0154 mmol, 0.0023g) was added and reacted and stirred for other 4 h to obtain the PA end capped poly(amic acid). Toluene 20 mL was added to the reaction solution to remove water from condensation polymerization by azeotropic

distillation. This required approximately 20 h at 180°C to complete the reaction. After cooling down, the solution was precipitated in 500 mL of a 1:1 methanol/deionized water mixture. The precipitated polyimide was filtered and dried in vacuum oven at 150°C for 15 h and the PI50 obtained was kept for further grafted with polyethers.

#### 4.4 Preparation of 1-3 layers hyperbranch polyether on polyimide

##### 4.4.1 Preparation of the first layer

Various amounts of POSS-Cl (0.03g, 0.3247 mmol for the PI50 case) were directly reacted with 10% reactive hydroxyl groups of polyimide (prepared by the reaction of 6FDA, diamine mixtures of DHBP and 3,4'-ODA and PA). The contents of hydroxyl groups in the polyimide were controlled by adjusting the ratio of diamine monomers of DHBP that contain two hydroxyl groups and 3,4'-ODA that contain no hydroxyl groups. The first layer was prepared according to the following procedure. The polyimide was dissolved in NMP to give a 15% solution while POSS-Cl was dissolved in THF to give a 15% solution. Then, POSS-Cl solution was slowly added into polyimide solution and stirred for 3 h to obtain POSS-PI nanocomposite (PI50-L1). The solution obtained was directly cast into film shape on clean glass plate.

##### 4.4.2 Preparation of the second layer

###### (a) Synthesis of dendritic Benzyl Alcohols [G-1]OH

A mixture of the appropriate POSS-Cl (2.00 equiv), 3,5-dihydroxybenzyl alcohol (1.00 equiv), dried potassium carbonate (2.50 equiv) in dry toluene/acetone was heated, refluxed and stirred vigorously under argon atmosphere for 48 h. The mixture was allowed to cool and evaporated to dryness. The residue product was washed with deionized water for three times, dried in vacuum oven at 100°C for 3 h.

###### (b) Synthesis of dendritic Benzyl Bromides [G-1]Br

A mixture of the appropriate of [G-1]OH (1.00 equiv) and carbon tetrabromide (1.25 equiv) in the tetrahydrofuran (10%w/v) required to dissolve the above reagents was made. Next, triphenylphosphine (1.25 equiv) was added and the reaction mixture



was stirred under argon for 1 h. The mixture was evaporated to dryness. The residue was washed with acetone for three times. The product was dried in vacuum oven at 67°C for 3 h.

### **(c) Preparation of dendrimer polyimide-ether (layer 2)**

Various amounts of [G-1]Br (0.03g, 0.3247 mmol for the PI50 case) were reacted with 10% hydroxyl groups of polyimide (prepared by the reaction of 6FDA, diamine mixtures of DHBP and 3,4'-ODA and PA). The content of hydroxyl groups in the polyimide was controlled by adjusting the ratio of diamine monomers DHBP and 3,4'-ODA. The second layer branch polyether grafted polyimide was prepared according to the procedure as described below. The selected polyimide was dissolved in NMP to give a 15% solution while [G-1]Br was dissolved in THF to give a 15% solution. Then, [G-1]Br solution was slowly added into polyimide solution and stirred for 3 h. The solution obtained was directly cast into film shape on clean glass plate.

## **4.4.3 Preparation of the third layer**

### **(a) Synthesis of dendritic Benzyl Alcohols [G-2]OH**

A mixture of the appropriate [G-1]Br (2.00 equiv), 3,5-dihydroxybenzyl alcohol (1.00 equiv), dried potassium carbonate (2.50 equiv) in dry THF was heated, refluxed and stirred vigorously under argon for 48 h. The mixture was allowed to cool and evaporated to dryness. The residue was washed with deionized water for three times. The product was dried in vacuum oven at 100 °C for 3 h.

### **(b) Synthesis of dendritic Benzyl Bromides [G-2]Br**

A mixture of the appropriate of [G-2]OH (1.00 equiv) and carbon tetrabromide (1.25 equiv) in the tetrahydrofuran (10%w/v) required to dissolve the above reagents. Next, triphenylphosphine (1.25 equiv) was added and the reaction mixture was stirred under argon for 1 h. The mixture was evaporated to dryness. The residue was washed with acetone for three times. The product was dried in vacuum oven at 67°C for 3 h.

### (c) Preparation of dendrimer polyimide-ether (layer3)

Various amounts of [G-2]Br (0.26g, 0.3247 mmol for the PI50 case) were reacted with 10% hydroxyl groups of polyimide (prepared by the reaction of 6FDA, diamine mixtures of DHBP and 3,4'-ODA and PA). The content of hydroxyl groups in the polyimide was controlled by adjusting the ratio of diamine monomers DHBP and 3,4'-ODA. The third layer polyether grafted to polyimide can be prepared according to the following procedure. The polyimide was dissolved in NMP to give a 15% solution while [G-2]Br was dissolved in THF to give a 15% solution. Then, [G-2]Br was slowly added into polyimide solution and stirred for 3 h. The solution obtained was directly cast into film shape on clean glass plate.

## 4.5 Preparation of the polyimide films

Various layers polyimide solutions were cast on a well cleaned glass substrates and the remained solvent was evaporated under vacuum at 50°C for 10 h. The cast film were thermally treated at 100°C (1h), 150°C and 200°C for 0.5 h each in a temperature controlled oven. After the thermal treatment the films were removed from the glass substrate by immersing into water and dried at 100°C for 24 h. All prepared films were obtained as transparent, dark brown to yellow colored and flexible.

## 4.6 Characterization Instruments

### 4.6.1 Infrared Spectroscopy (FTIR)

Infrared survey spectra were recorded with Nicolet 6700 FTIR spectrometer. The scanning ranged from 400 to 4000  $\text{cm}^{-1}$  with scanning 64 times.



**Figure 4.8** Fourier transform infrared spectroscopy (FT-IR) Equipment

#### 4.6.2 Thermogravimetric analysis (TGA)

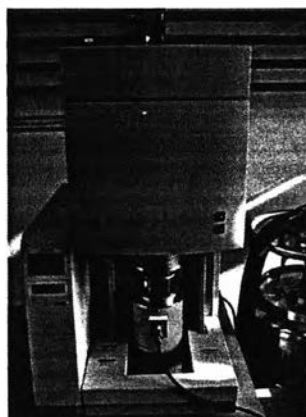
Thermogravimetric analysis (TGA) thermograms were performed using a SDT Analyzer Model Q600 from TA Instruments, USA. The sample weights were 3-10 mg. The temperature range of 50-600°C at a heating rate of 10°C/min with oxygen and nitrogen purge flow rate 100 ml/min.



**Figure 4.9** Thermogravimetric analysis (TGA) Equipment

#### 4.6.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of all polyimide products were determined by using Dynamic Mechanical Analysis (DMA) with a Perkin-Elmer Pyris Diamond DMA. The samples were cut for standard DMA samples (10x25 mm). Condition and parameters were shown in the Table below.



**Figure 4.10** Dynamic Mechanical Analysis (DMA) Equipment

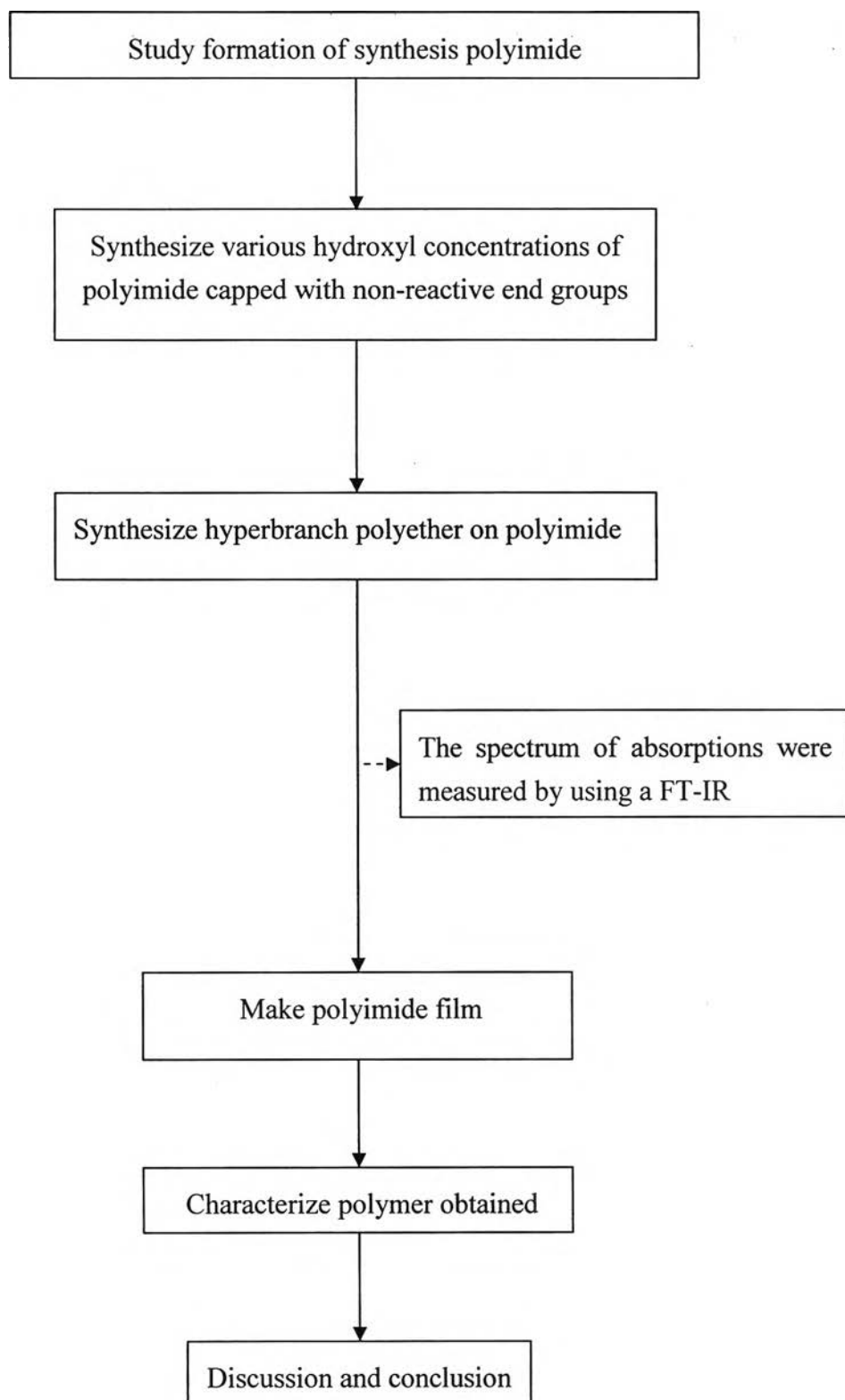
**Table 4.1** Conditions and parameter for running DMA

Conditions and parameter	Value
Sample size(w x l) (mm)	10 x 20
DMS Measurement Mode	Tension
Temperature Control Mode	Ramp (5.0 °C/min)
DMS frequency (Hz)	1.0, 5.0, 10.0
Temperature range	50 to 400 °C
L Amplitude (μm)	10
Minimum Tension/Compression Force(mN)	200
Tension/Compression Force gain	1.5
Force Amplitude Default Value (mN)	4000
Nitrogen as carrier gas (ml/min)	100

#### 4.6.4 Dielectric properties

The dielectric properties of the polyimide films were obtained via the capacitance method and were measured at room temperature and 500 mV with Agilent E 4980A Precision LCR Meter. The films for dielectric properties analysis were coated with gold layer by JEOL JFC-1100E ion sputtering device on both sides to provide electrical contact to the specimens. The specimens size were 1.5 x1.5 (cm).

**Figure 4.11** LCR Meter Equipment



**Figure 4.12** Flow diagram of research methodology