CHAPTER III
EXPERIMENTAL

3.1 Materials

1,2-Phenylenediamine (99.5 wt%) and 5-aminoisophthalic acid (94 wt%) were purchased from Aldrich, Germany. Terephthaloyl chloride was purchased from Nacalai tesque, Kyoto, Japan. 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) was the product of TCI, Japan. Triphenylphosphite, phthalic Anhydride and 1-methyl-2-pyrrolidone (NMP) were purchased from Fluka. Sodium hydrogen carbonate was the product of Riedel-de Haën. Hydrazine hydrate and sulphuric acid were purchased from Carlo Erba. Poly(ether ether ketone) (PEEK) was a gift from J.J.- Degusa company, Germany. All other chemicals and solvents were analytical grade and were used without further purification.

3.2 Instruments and Equipment

3.2.1 Fourier Transform Infrared (FTIR) Spectrophotometer

Fourier transform infrared (FTIR) spectra were recorded on KBr and ZnSe window by using a Thermo Nicolet/Nexus 670 with 32 scan at a resolution of 2 cm^{-1} in a frequency range of 4000-400 cm^{-1} equipped with deuterated triglycerinesulfate detector (DTGS) with specific detectivity of 1 x 10^9 $cm \cdot Hz^{1/2} \cdot w^{-1}$.

3.2.2 Nuclear Magnetic Resonance (NMR)

NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer (USA). The deuterated solvent used was DMSO-d_6 and the internal reference for ^1H NMR was tetramethylsilane.

3.2.3 MALDI-TOF Mass Spectrometer (MALDI-TOF MS)

Mass spectra were collected by using a microflex (Bruker Daltomics) MALDI-TOF mass spectrometer. The spectra were obtained based on doubly recrystallized α-cyano-4-hydroxy cinnamic acid (CCA) matrix.

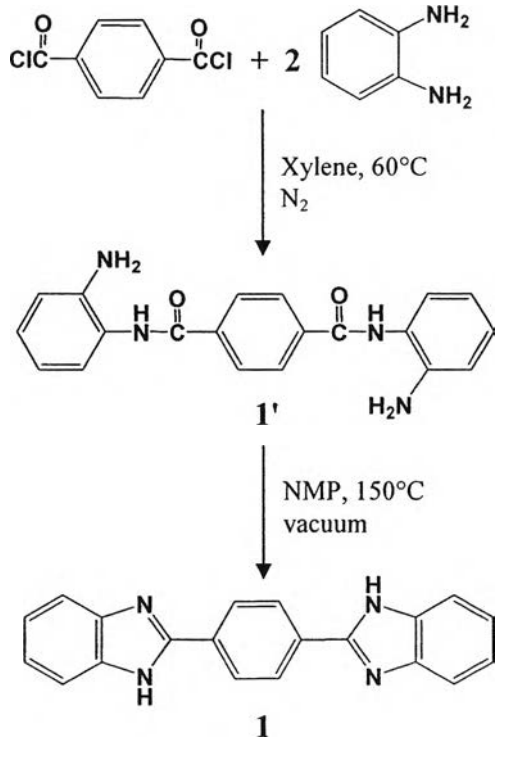
3.2.4 Elemental Analyzer (EA)

Elemental analyse was done by a PerkinElmer series II CHNS/O Analyzer 2400.

3.3 Methodology

3.3.1 Synthesis of 1,4-di(1*H*-benzo[*d*]imidazol-2-yl)benzene, 1

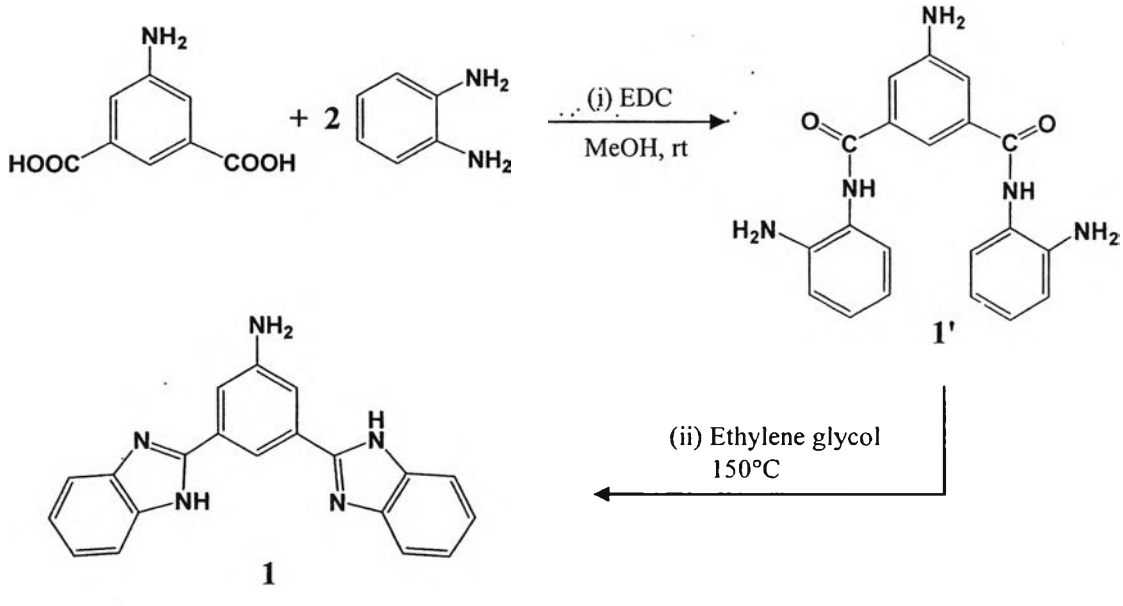
Terephthaloyl chloride (6.6 mmole, 1.34 g) in xylene 150 ml was dropwisely added into a vigorously stirred solution of 1,2-phenylenediamine (2.88 g, 2.64×10^{-2} mol) in xylene (10 ml) at 60°C under nitrogen atmosphere. The reaction was proceeded for 12 hours obtaining the brown precipitate in yellow solution. The precipitate was collected and then dried at 60°C before washing by methanol. The precipitate obtained was dissolved in NMP (80 ml). After refluxing under vacuum at 150°C for 24 h, the white precipitate was obtained. The crude product was dried at 100°C under vacuum for 6 h.



Scheme 3.1 Preparation of **1**.

3.3.2 Synthesis of 3,5-di(1*H*-benzo[*d*]imidazol-2-yl)benzenamine, **2** via pathway A

Methanol (100 ml) solution containing 5-aminoisophthalic acid (5 mmole, 0.9649 g) was dropwisely added into the methanol solution (10 ml) containing 1.20 g (11 mmole) of 1,2-phenylenediamine and 2.15 g (11 mmole) of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC-HCl) in methanol. The mixture was stirred overnight at room temperature. The white powder obtained was filtered and washed several times by methanol. The white powder was dried in vacuum at 80°C for 6 h, dissolved in ethylene glycol (100 ml) and refluxed under vacuum at 150°C for 24 h. The solvent was removed and the crude product was dried in vacuum at 80°C for 6 h.



Scheme 3.2 Preparation of **2** via pathway A.

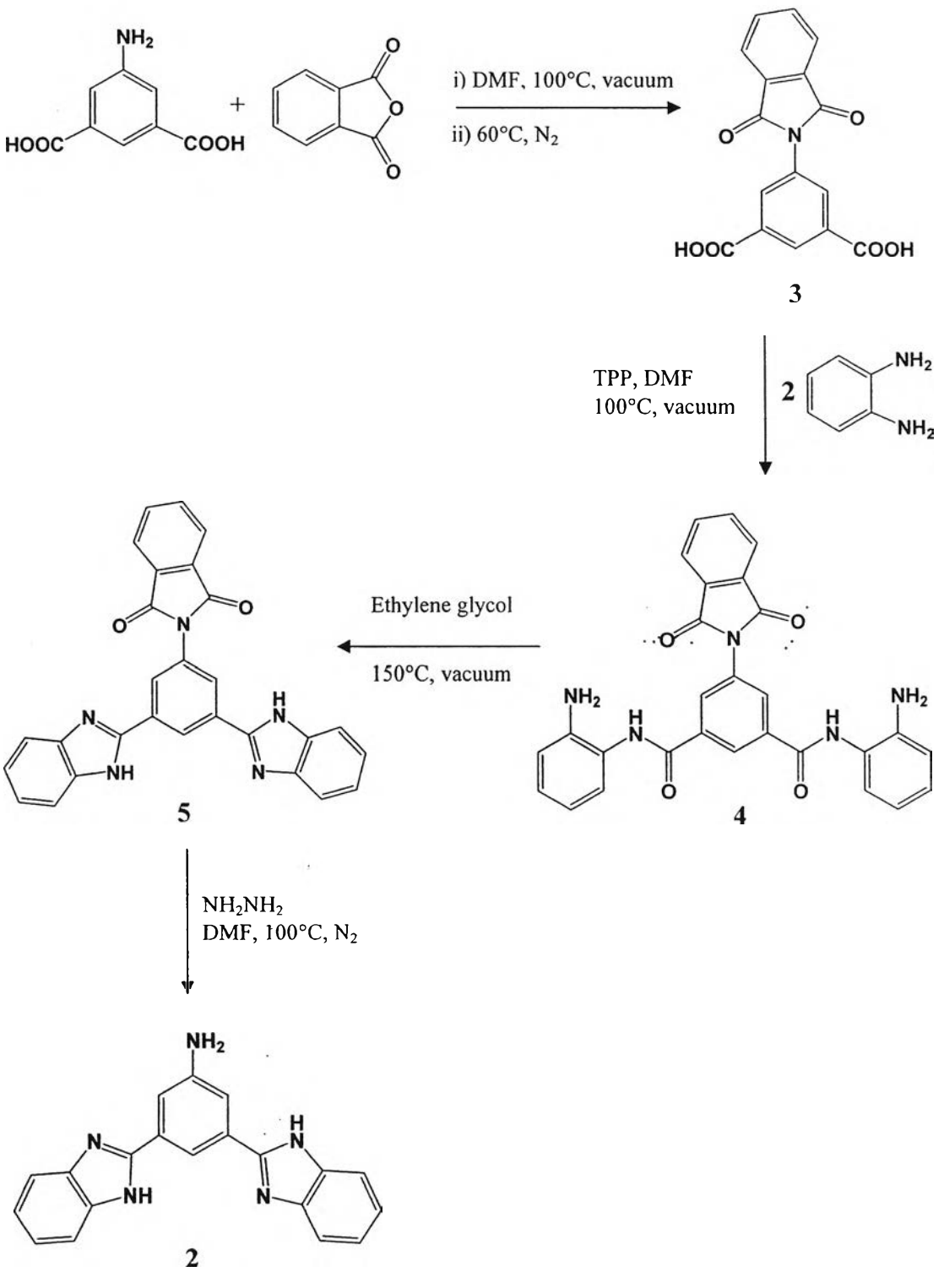
3.3.3 Synthesis of 3,5-di(1*H*-benzo[*d*]imidazol-2-yl)benzenamine, **2** via pathway B

Phthalic anhydride (4 mmole, 0.62 g) and 5-aminoisophthalic acid were dissolved in dimethylformamide (20 ml) and stirred at 100°C under vacuum for 8 h. The crude product, **3**, was obtained by removing the solvent followed by washing with methanol. The solution of **3** in dimethylformamide was dropped wisely

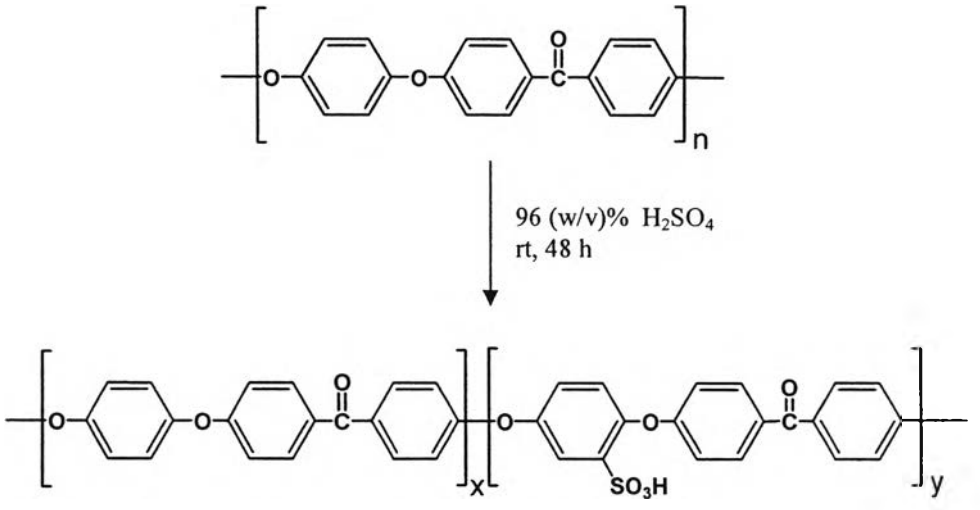
into the mixture of 1,2-phenylenediamine (4 mmole, 0.44 g) and triphenyl phosphite (4 mmole, 2 ml) in dimethylformamide (50 ml) and stirred at 100°C under vacuum for 6 h. The solvent was removed and the product was dried in vacuum at 80°C for 6 h. The product obtained was dissolved in dichloromethane before extracting with saturated $NaHCO_3$ aqueous solution. The organic layer was treated with Na_2SO_4. The solvent was removed to obtain **4**. Compound **4** was dissolved in ethylene glycol (50 ml) and refluxed at 150°C under vacuum for 24 h to obtain **5** after removing solvent and washing with methanol. Compound **5** was stirred in dimethylformamide and heated to 100°C under nitrogen. Hydrazine monohydrate was added and stirred for 1 h. After solvent removing, light pink solid was obtained and recrystalized by ethyl acetate to give the colorless crystal.

3.3.4 Sulfonation of poly(ether-ether-ketone) (PEEK)

The sulfonation was carried out as follows. An amount of PEEK (6g) was gradually added into 96% sulphuric acid (300 ml) and vigorously stirred for 48 h at room temperature. The solution was precipitated in a large excess of ice water and washed with deionized water until neutral. The precipitates were dried in a vacuum at 70°C for 24 h.



Scheme 3.3 Preparation of **2** via pathway B.



Scheme 3.4 Sulfonation of poly(ether ether ketone).