

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Materials

All reagents and solvents were of analytical grade quality. Zinc (II) acetate dihydrate, triethylenetetramine, salicylaldehyde, hexamethylene diisocyanate, polycaprolactone diol ( $M_n = 530$ ), polycaprolactone triol ( $M_n = 300$ ), polypropylene glycol ( $M_n = 1000$ ), dioxane, methyl red indicator, *n*-butylamine, dibutyltin dilaurate and hydrochloric acid were obtained from Fluka and Sigma-Aldrich Company. All Chemicals were used without further purification.

#### 2.2 Analytical Procedures

The IR spectra were recorded on a Nicolet Impact 410 IR spectrometer using potassium bromide (KBr) method. Liquid crystalline properties were observed by an Olympus SC 35 polarizing optical microscope equipped with a Mettler FP5 heating stage. All the samples were placed between glass slides and heated to the isotropic melt. The morphology of polymer was observed by JEOL JSM-5410LV and JOEL JSM-5800LV scanning electron microscope. The analyses of dynamic mechanical behaviors were obtained by Perkin Elmer DMA7e. Variable temperature X-ray powder diffraction was measured using Cu K $\alpha$  radiation on an Bruker D8 GADDS system.

#### 2.3 Synthetic Procedures

##### 2.3.1 Preparation of ZnL complex.

The preparation of ZnL was carried out according to the method reported in the literature.<sup>19</sup> A cool (0-10°C) solution (10 mL) of triethylenetetramine (1 mL, 6.70

mmol) in methanol (10 mL) was added dropwise to a stirred cool solution of salicylaldehyde (1.18 g, 9.66 mmol) and zinc (II) acetate dihydrate (1.05 g, 4.84 mmol) in methanol (15 mL). The mixture was neutralized by a 2M sodium hydroxide solution (5 mL, 10 mmol) and stirred for another 30 minutes. The yellow crystals of ZnL precipitated from the solution upon standing at room temperature for 10 hours. The crystal was collected by filtration and dried in vacuo (1.86 g, 93%) : m.p. 220°C. IR (KBr,  $\text{cm}^{-1}$ ); 3646 (NH), 3300, 3000, 2800, 1634(C=N), 1600, 1448, 1200, 930, 870.

### 2.3.2 Preparation of Prepolymer

#### 2.3.2.1 HDI / PCL diol prepolymer

Into a 100 mL round bottom flask equipped with a magnetic bar and a reflux condenser, PCL diol (0.762 g, 1.437 mmol) and HDI (235  $\mu\text{L}$ , 1.453 mmol) were mixed and stirred. The reaction mixture was refluxed with stirring under nitrogen atmosphere and heated at 60°C for 1.5, 2, 2.5, 3, 5, 8 hours, respectively. Prepolymer was allowed to cool to room temperature. IR spectrum of synthesized prepolymer was obtained by casting the prepolymer on NaCl discs. IR (neat,  $\text{cm}^{-1}$ ); 3400 (NH), 2935, 2860, 2272 (NCO), 1729 (C=O).

#### 2.3.2.2 HDI / PCL triol prepolymer

The experiment was performed according to the procedure described in experiment 2.3.2.1 employing PCL triol (0.431 g, 1.437 mmol) and PCL triol (0.287 g, 0.957 mmol) instead of PCL diol. IR spectrum of synthesized prepolymer was obtained by casting the prepolymer on NaCl discs. IR (neat,  $\text{cm}^{-1}$ ); 3300-3500 (NH), 2930, 2862, 2272 (NCO), 1713 (C=O).

#### 2.3.2.3 HDI / PP glycol prepolymer

The experiment was performed according to the procedure described in experiment 2.3.2.1 employing PP glycol (1.437 g, 1.437 mmol) instead of PCL diol.



IR spectrum of synthesized prepolymer was obtained by casting the prepolymer on NaCl discs. IR (neat,  $\text{cm}^{-1}$ ); 3470 (NH), 2965, 2928, 2863, 2272 (NCO), 1713 (C=O).

### 2.3.3 Titration for Calculate Amount of Isocyanate in Prepolymer

*n*-Butylamine reagent (20 mL) was added to prepolymer HDI / PCL diol prepolymer in experiment 2.3.2.1. The mixture was allowed to stir at room temperature for 15 minutes under nitrogen atmosphere. A very few samples may require heating for a few minutes to complete the addition of the *n*-Butylamine to diisocyanate. All heating should be done under reflux to prevent loss of *n*-Butylamine. The condenser was rinsed with water. The unreacted amine was titrated with 0.1N HCl using methyl red as an indicator. The same experiment to investigate percentage of isocyanate was done in case of HDI / PCL triol prepolymer and HDI / PP glycol prepolymer in experiments 2.3.2.2 and 2.3.2.3, respectively.

### 2.3.4 Preparation of polyurethane

#### 2.3.4.1 Preparation of PCL diol polyurethane-1 from the reaction between ZnL, HDI and PCL diol

Into a 100 mL round bottom flask equipped with a magnetic bar and a reflux condenser, PCL diol (2.283 g, 4.307 mmol) and HDI (705  $\mu\text{L}$ , 4.359 mmol) were mixed and stirred. Nitrogen was kept flowing through the system continuously. After 3 hours, the mixture was stirred and degassed under vacuo for 30 minutes, then ZnL, (0.309 g, 0.740 mmol) was added to prepolymer. The degassed mixture was cast into a mold and degassed under vacuo for 8 hours. Allow the reaction to go to completion by placing mold in oven at 60°C for 8 hours. The mold was then allowed to cool to room temperature and the polymer was removed. IR (neat,  $\text{cm}^{-1}$ ); 3366 (NH), 2935, 2865, 1729 (C=O), 1638 (C=N), 1536, 1251, 1164, 777.

#### **2.3.4.2 Preparation of PCL diol polyurethane-2 from the reaction between ZnL, HDI and PCL diol**

PCL diol (0.762 g, 1.437 mmol) was dissolved in 15 mL of dried  $\text{CH}_2\text{Cl}_2$  in two-necked round-bottom flask with a reflux condenser, magnetic stirrer, thermometer and addition funnel charged with HDI and dried  $\text{CH}_2\text{Cl}_2$ . Nitrogen was kept flowing through the system continuously. HDI (235  $\mu\text{L}$ , 1.453 mmol) was added dropwise to the solution. The solution was stirred and heated at  $40^\circ\text{C}$  under nitrogen atmosphere. After 3 hours, 2 drops of dibutyltin dilaurate was added, and a solution of ZnL (0.103 g, 0.247 mmol) dissolved in 10 mL of dried  $\text{CH}_2\text{Cl}_2$  was added to the solution. The solution was kept stirring for another 8 hours to ensure the complete reaction. The polymer was standing at room temperature. The product was dried in vacuo. The progress of the reaction was followed by using IR spectroscopy. IR (neat,  $\text{cm}^{-1}$ ); 3366 (NH), 2935, 2865, 1729 (C=O), 1638 (C=N), 1536, 1251, 1164, 777.

#### **2.3.4.3 Preparation of PCL triol polyurethane-1 from the reaction between ZnL, HDI and PCL triol**

Into a 100 mL round bottom flask equipped with a magnetic bar and a reflux condenser, PCL triol (1.724 g, 5.747 mmol) and HDI (940  $\mu\text{L}$ , 5.812 mmol) were mixed and stirred. Nitrogen was kept flowing through the system continuously. After 2 hours, the mixture was stirred and degassed under vacuo for 15 minutes, then ZnL (0.315 g, 0.755 mmol) was added to prepolymer. The degassed mixture was cast into a mold and degassed under vacuo for 8 hours. Allow the reaction to go to completion by placing mold in oven at  $60^\circ\text{C}$  for 8 hours. The mold was then allowed to cool to room temperature and the polymer was removed. IR (neat,  $\text{cm}^{-1}$ ); 3390-3360 (NH), 2934, 2862, 1713 (C=O), 1638 (C=N), 1536, 1460, 1259, 1050, 777.



#### **2.3.4.4 Preparation of PCL triol polyurethane-2 from the reaction between ZnL, HDI and PCL triol**

PCL triol (0.431 g, 1.437 mmol) was dissolved in 15 mL of dried  $\text{CH}_2\text{Cl}_2$  in two-necked round-bottom flask with a reflux condenser, magnetic stirrer, thermometer and addition funnel charged with HDI and dried  $\text{CH}_2\text{Cl}_2$ . Nitrogen was kept flowing through the system continuously. HDI (235  $\mu\text{L}$ , 1.453 mmol) was added dropwise to the solution. The solution was stirred and heated at  $40^\circ\text{C}$  under nitrogen atmosphere. After 2 hours, 2 drops of dibutyltin dilaurate was added, a solution of ZnL (0.079 g, 0.189 mmol) dissolved in 10 mL of dried  $\text{CH}_2\text{Cl}_2$  was added to the solution. The solution was kept stirring for another 8 hours to ensure the complete reaction. The polymer was standing at room temperature. The product was dried in vacuo. The progress of the reaction was followed by using IR spectroscopy. IR (neat,  $\text{cm}^{-1}$ ); 3390-3360 (NH), 2934, 2862, 1713 (C=O), 1638 (C=N), 1536, 1460, 1259, 1050, 777.

#### **2.3.4.5 Preparation of PP glycol polyurethane-1 from the reaction between ZnL, HDI and PP glycol**

Into a 100 mL round bottom flask equipped with a magnetic bar and a reflux condenser, PP glycol (2.395 g, 2.395 mmol) and HDI (385  $\mu\text{L}$ , 2.380 mmol) were mixed and stirred. Nitrogen was kept flowing through the system continuously. After 2 hours, the mixture was stirred and degassed under vacuo for 1 hour, then ZnL (0.546 g, 1.308 mmol) was added to prepolymer. The degassed mixture was cast into a mold and degassed under vacuo for 8 hours. Allow the reaction to go to completion by placing mold in oven at  $125^\circ\text{C}$  for 15 hours. The mold was then allowed to cool to room temperature and the polymer was removed. IR (neat,  $\text{cm}^{-1}$ ); 3500-3350 (NH), 2970, 2923, 2870, 1713 (C=O), 1635 (C=N), 1541, 1465, 1251, 1100.

### 2.3.4.6 Preparation of PP glycol polyurethane-2 from the reaction between ZnL, HDI and PP glycol

PP glycol (1.437 g, 1.437 mmol) was dissolved in 15 mL of dried  $\text{CH}_2\text{Cl}_2$  in two-necked round-bottom flask with a reflux condenser, magnetic stirrer, thermometer and addition funnel charged with HDI and dried  $\text{CH}_2\text{Cl}_2$ . Nitrogen was kept flowing through the system continuously. HDI (235  $\mu\text{L}$ , 1.453 mmol) was added dropwise to the solution. The solution was stirred and heated at  $40^\circ\text{C}$  under nitrogen atmosphere. After 2 hours, 2 drops of dibutyltin dilaurate was added, a solution of ZnL (0.333 g, 0.798 mmol) dissolved in 10 mL of dried  $\text{CH}_2\text{Cl}_2$  was added to the solution. The solution was kept stirring for another 8 hours to ensure the complete reaction. The polymer was standing at room temperature. The product was dried in vacuo. The progress of the reaction was followed by using IR spectroscopy. IR (neat,  $\text{cm}^{-1}$ ); 3500-3350 (NH), 2970, 2923, 2870, 1713 (C=O), 1635 (C=N), 1541, 1465, 1251, 1100.



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