

CHAPTER III

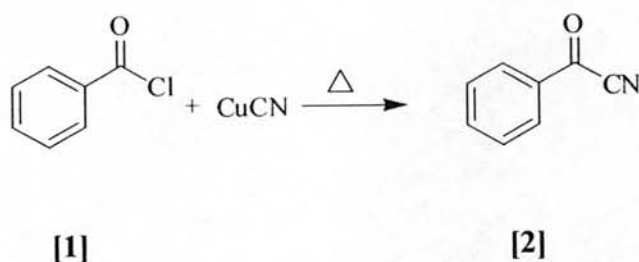
EXPERIMENTAL SECTION

3.1 General materials and instruments

All reagents were purchased from Aldrich Chemical Co. and Fischer Chemical Co. Potassium carbonate and cuprous cyanide were ground and dried at 100°C under reduced pressure overnight before use. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Toluene was dried with magnesium sulfate overnight and distilled before use. Carbon tetrachloride was dried by simple distillation before use, rejecting the first 10 % percent of distillate; until the distillate is clear (bp. 77°C). The inhibitor was removed from the methylmethacrylate (MMA) by washing twice with equal amount of 10% NaOH solution. The MMA was then washed with distilled water until the base had been removed. The MMA was then dried over sodium sulfate anhydrous and evaporated under reduced pressure.

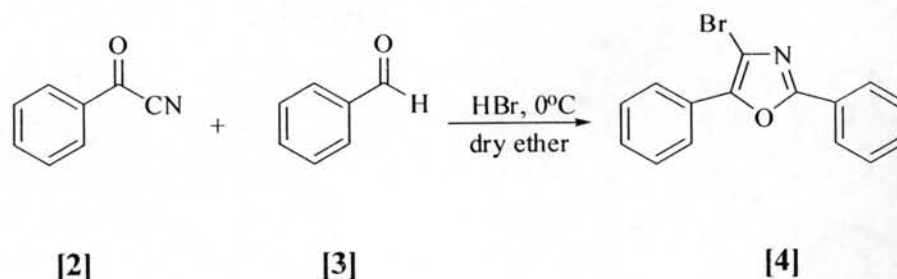
¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury 400 MHz spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) were reported in parts per million (ppm) relative to the residual signals of this solvent (δ 7.24 for ¹H and δ 77.0 for ¹³C). Infrared spectra were acquired using an Impact 410 Nicolet FT-IR spectrometer as a solid suspended in a potassium bromide disk between 600 and 3500 cm⁻¹ in transmittance mode. UV-vis absorption spectra were recorded on a Varian Carry Eclipse using 1 cm path length quartz cells. Fluorescence emission spectra were measured using Varian Cary Eclipse. The fluorescence quantum yield (ϕ_f) was determined at 298 K in tetrahydrofuran against anthracene in ethanol as the standard (0.27). Gel permeation chromatography (GPC) was carried out on a Jasco 880-PU system with Jasco UV-970 Detector. Calibration was done with standard polystyrene samples. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min⁻¹ at 28°C. Thermogravimetric analyses (TGA) were carried out under nitrogen at a heating rate of 10°C/min using a TA instrument model 2950 thermogravimetric analyzer.

3.2 Preparation of benzoyl cyanide [2]



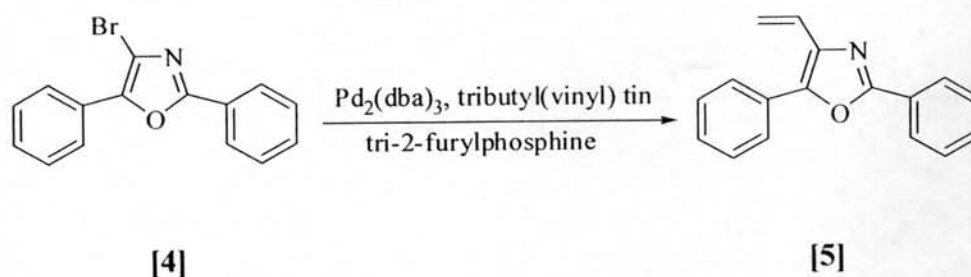
Benzoyl chloride [1] 19 mL (21 g, 150 mmol) and copper cyanide 15.2 g (170 mmol) were added to a round bottom flask equipped with condenser. The mixture was heated at 200°C for 48 hours. The remaining mixture was distilled at 150°C. The product was purified by distillation under reduced pressure to give 12.8 g of benzoyl cyanide [2] as a colorless liquid with 65% yield; FT-IR spectrum (KBr pellet): ν 3068 (CH), 2222 (CN), 1685 (C=O) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 7.56 (t, 1H, $J = 6$ Hz), 7.77 (t, 2H, $J = 2$ Hz) and 8.10 (d, 2H, $J = 2$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 112.8, 128.5, 129.6, 130.3, 133.3, 136.9 and 167.9. ppm.

3.3 Synthesis of 4-bromo-2,5-diphenyloxazole [4]



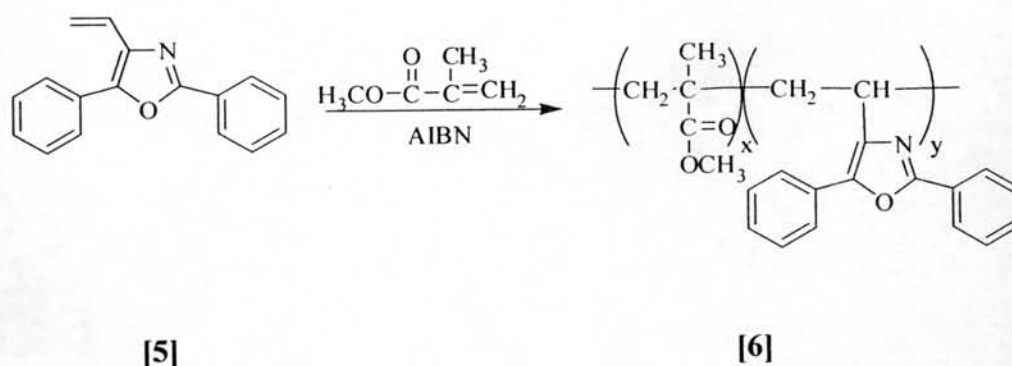
Benzoyl cyanide **[2]** 4.26 mL (4.71 g, 36 mmol) and benzaldehyde **[3]** 3 mL (3.18 g, 30 mmol) in 20 mL dry diethyl ether were contained in reaction flask. The reaction flask was then connected to a HBr gas generator. The reaction mixture was allowed to cool in an ice-NaBr cooling bath and then dry HBr gas passed into the solution flask until the HBr gas was no longer absorbed by the reaction mixture, tested by ammonia at the outlet of the reaction flask. At this stage, the reaction flask was quickly sealed and kept at 0°C for 2 days. The reaction mixture was then poured onto an ice with continuous stirring and the precipitate was collected by filtration. Recrystallization from ethanol gave pure white crystal of 4-bromo-2,5-diphenyloxazole **[4]** 5.85 g with 65% yield, m.p. 72-73°C; FT-IR spectrum (KBr pellet): ν 3057 (CH), 1604, 1448 (C=C), 1580 (-NCO), 983 (C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.11-8.08 (m, 2H), 7.95 (d, 2H, $J = 7$ Hz), 7.51-7.48 (m, 5H) and 7.39 (t, 1H, $J = 7$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 125.0, 126.4, 126.4, 126.5, 126.9, 128.7, 128.8, 128.9, 130.9, 143.9 and 158.9 ppm.

3.4 Synthesis of 2,5-diphenyl-4-vinyloxazole [5]



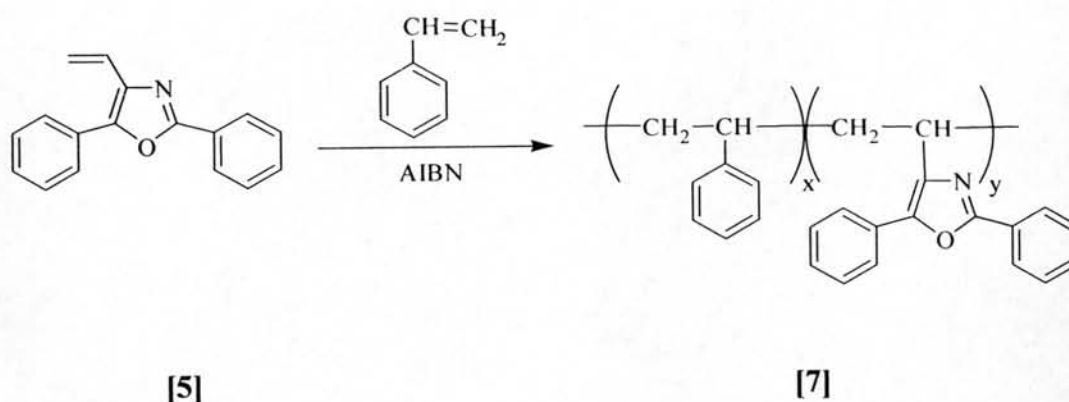
4-Bromo-2,5-diphenyloxazole [4] 3 g (10.0 mmol), tris(dibenzylideneacetone)dipalladium(0) 230 mg [0.25 mmol (50 mol % Pd)], and tri-2-furylphosphine 460 mg [2 mmol (200 mol % ligand)] were stirred in 1-methyl-2-pyrrolidinone (100 mL) for 15 min. Tributyl(vinyl)tin 3.51 mL (3.81 g, 12.0 mmol) was added, and the resultant mixture was heated to 65 °C and stirred for 16 hour, after which time blackening of the mixture had occurred. The reaction mixture was then stirred with a 10% aqueous solution of potassium fluoride (75 mL) and diethyl ether (25 mL) for 1 h before being filtered through a pad of Celite. The pad of Celite was rinsed with a further portion of diethyl ether (25 mL). The aqueous phase was separated and extracted with a further portion of diethyl ether (25 mL). The combined organic extracts were washed with a saturated aqueous solution of ammonium chloride (4 × 25 mL), dried over magnesium sulfate, and concentrated to dryness by evaporation under vacuum. The mixture was further purified by column chromatography using 4% diethyl ether in hexanes gave pure white solid of 2,5-diphenyl-4-vinyloxazole [5] 1.24 g (50% yield), mp 70-71 °C; FT-IR spectrum (KBr pellet): ν 3052 (CH), 1640 (C=C) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.09-8.14 (m, 2H), 7.64-7.69 (m, 2H), 7.30-7.48 (m, 6H), 6.79 (d, 1H, $J = 7.0$ Hz), 6.28 (d, 1H, $J = 7.0$ Hz), 5.47 (d, 1H, $J = 7.0$ Hz) ppm.

3.5 Synthesis of 2,5-diphenyl-4-vinyloxazole-co-methyl methacrylate polymer [6]



The aqueous phase was comprised of 0.1M NaCl 50 ml. The organic phase contained MMA 2.375 g, 2,5-diphenyl-4-vinyloxazole [5] 125 mg (5 wt.% to the total monomer) and polyvinyl alcohol 131 mg were mixed together with 25 mg of 2,2'-azobisisobutyronitrile (AIBN) in 2.5 ml of toluene. The mixture was added to a three-neck round bottom flask equipped with condenser and nitrogen inlet. The solution was heated at 65°C during stirring at 300 rpm for 10 hours. After the reaction, the beads were filtered under suction and washed with distilled water and ethanol. The product was dried in a vacuum oven.

3.6 Synthesis of 2,5-diphenyl-4-vinyloxazole-co-styrene polymer [7]



125 mg of 2,5-diphenyl-4-vinyloxazole (5 wt.% to the total monomer), 2.375 g of styrene monomer and 25 mg (1 wt% to the total monomer) of 2,2'-azobisisobutyronitrile (AIBN) were dissolved in 20 mL of toluene. The mixture was added to a three-neck round bottom flask equipped with condenser and nitrogen inlet. The solution was heated at 65°C during stirring at 300 rpm for 48 hours. The solution was cooled and slowly poured with vigorous stirring into methanol to precipitate the polymer. After filtering, the product was washed with methanol and dried in a vacuum oven.

3.7 Characterization of polymers

3.7.1 Determination of molecular weight

The molecular weights of the polymers used in this work were determined using gel permeation chromatography (GPC). A UV detector was used to provide data that was analyzed to determine the molecular weights of the polymer materials. Samples were prepared as solution of 0.1 wt% in THF. Monodisperse polystyrene standards were used for calibration of the molecular weights. Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were calculated for each sample from the output of the UV detector

3.7.2. Determination of thermal properties

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the approximate glass transition temperature (T_g) and decomposition temperature (T_d) of the polymer samples. To determine T_g , two lines are drawn parallel to the baseline above and below the inflection at T_g . The midpoint of the departure from the left and the intersection with the baseline nearest T_g on the right is determined by the instrument. This midpoint is taken as the glass transition temperature. T_d was determined at 5% weight losses.

3.7.3 Polymer solubility

The samples were dispersed in the solvents at concentration in the range 5-20 g/L. The dispersions were maintained under stirring overnight at room temperature. The solubility was determined by the residual mass after centrifugation.

3.8 UV absorption and fluorescence emission analysis

All UV absorption spectra were recorded at wavelengths between 200-500 nm at room temperature (25°C) with air-saturated solutions. The fluorescence emission were recorded at wavelength between 300-600 nm. 1 cm Pathlength quartz cuvettes were used for both UV and emission spectra.