

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Reagent

Propionyl chloride (98%, Fluka), AlCl₃ (97%, Fluka), Nitrobenzene (98%, Merck), Tin(II) 2-ethylhexanoate (stannous octoate, SnOct₂, 95%, Aldrich), LiAlH₄ (95%, ACROS), Dichloromethane (99.8%, Lab Scan), Tetrahydrofuran (99.8%, Lab Scan), Toluene (99.5%, Lab Scan), Ethanol (99.9%, Aldrich), Dicumyl peroxide (98%, Fluka), ϵ -caprolactone (99%, Fluka), DL-lactide (Aldrich), Polystyrene (PS) and Caprolactam were used as received. All syntheses were carried out under purified nitrogen gas.

3.1.2 Starting Polymers

Polystyrene chains (MW=334,492) were cut by dicumyl peroxide 0.5% (w/w) in dichloromethane at room temperature for 30 minutes and frozen in refrigerator.

3.2 Equipments

3.2.1 FTIR/HATR Spectroscopy

FTIR spectra were obtained with a Thermo Nicolet spectrometer (NEXUS 670 FT-IR). The spectra were collected in the wave number range 4000-400 cm⁻¹ and using KBr pellets.

3.2.2 NMR Spectroscopy

¹H NMR spectra were measured in CDCl₃ in 5-mm glass tubes using a Bruker DPX 300 spectrometer at frequencies 300.13 MHz of frequency and 16 number of scan.

3.2.3 Gel Permeation Chromatography (GPC)

All polymers were characterized by GPC (SHIMADZU ClassVP) in THF at room temperature at flow rate of 0.8 ml/min using a set of Water Styragel[®]

HT4 columns. Polystyrene standards for PS/THF system were used to calculate apparent values of molecular weights.

3.2.4 Scanning Electron Microscope (SEM)

The morphology of electrospun fibers was observed by using scanning electron microscope (SEM; JSM-6400, JEOL) at voltage of 15 kV. The specimen for SEM were prepared by cutting an aluminum sheet covered with the as-spun fibers and attaching on a SEM stub. Each specimen was gold-coated for 4 mins.

3.2.5 Differential Scanning Calorimetry (DSC)

The melting temperature were determined by differential scanning calorimetry. The melting points were defined as the peak of the endothermal curve. The DSC measurements were carried out with a Perkin-Elmer DSC7 differential scanning calorimeter under N₂ purge, at heating rate 10°C/min. The temperature and heating flow calibration were performed with indium. The scanning range was from 30-250°C

3.2.6 Thermal Gravimetry – Dynamic Temperature Analysis (TG-DTA)

Thermal Gravimetry – Dynamic Temperature Analysis technique was used to determine thermal stability and the decomposition temperature of graft copolymers. Perkin-Elmer thermal gravimetry – dynamic temperature analyzer characterize graft copolymers at heating rate 10°C/min under the nitrogen purge with a purge rate of 200 ml/min. The mass change with increasing temperature was monitored and recorded. The decomposition temperature (Td) was obtained from the derivative TG-DTA thermogram. The sample were in solid state.

3.2.7 X-ray Diffractometer (XRD)

XRD spectra were recorded by using a D/MAX-2000 series of Rigaku/X-ray Diffractometer that provides X-ray of Cu K-alpha at 40 kV/30 mA. The experiment was operated at scan speed 5 degree/min with the 0.02-degree 2 θ -stepwise increment.

3.3 Methodology

3.3.1 Synthesis of Ring-Acylated Polystyrene (polymer A)

A dichloromethane solution (180 ml) of polystyrene which was cut (20 g, MW=269,356, 0.074 mmol) was added under nitrogen to a stirred solution of propionyl chloride (10 ml, 0.576 mol), AlCl₃ (12 g) in nitrobenzene (20 ml) (0.09 mol of AlCl₃) and dichloromethane (140 ml). The mixture was stirred for 5 h. at room temperature and then precipitated into acidified 80% ethanol (v/v, 1000 ml; 15 ml of HCl). The resulting product was reprecipitated from THF into 80% ethanol and dried at 40 °C under vacuum Yield: 18.12g (white powder). GPC: MW=325,380.

3.3.2 Synthesis of Polystyrene Ring Substituted with 1-hydroxypropyl Group (polymer B)

A solution of polymer A (20 g, MW=325,380, 0.061 mmol) in dry THF (160 ml) was added to a suspension of LiAlH₄ (10 g, 0.26 mol) in dry THF (340 ml) under nitrogen gas. The mixture was refluxed for 5 h and, after that water (5 ml) was gently added to decompose residual LiAlH₄. The mixture was then precipitated into acidified water (1350 ml; 150 ml of HCl), filtered, washed with water and dried. The product was reprecipitated from THF into water and finally dried at 40 °C under vacuum. Yield: 10.03g (white powder). IR (KBr, cm⁻¹): 3415 (broad; ν_{OH}) GPC: MW=338,798.

3.3.3 Synthesis of Polystyrene-Graft-Poly(ε-caprolactone)

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (3 g, MW=338,798, 0.01 mmol), and ε-caprolactone (9 g, 30 g, and 60 g; ratio 1:3, 1:10 and 1:20, respectively) in toluene was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (3 ml, 0.9 mmol of SnOct₂) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum. Yield (PS:Caprolactone): 16.45g (1:3), 30.74g (1:10), 55.35g (1:20) (white powder). FTIR (KBr, cm⁻¹): 1727(ν_{C=O}) GPC: MW=689,493 , 642,860, and 622,882, respectively.

3.3.4 Synthesis of Polystyrene-Graft-Polycaprolactam

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 0.003 mmol), and caprolactam (1 g, 2 g, and 3 g; ratio 1:1, 1:2 and 1:3, respectively) in toluene (10, 20 and 30 ml, respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3 mmol of SnOct₂) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum. Yield (PS: caprolactam): 1.4444g (1:1), 1.8385g (1:2), 2.4058g (1:3) (pale yellow powder). FTIR (KBr, cm⁻¹): 1653 ($\nu_{C=O(\text{amide})}$). GPC: MW=264,824, 228,859, and 149,131, respectively.

3.3.5 Electrospinning Process

Polymer solution were prepared for electrospinning at different concentrations. Chloroform and toluene were used as the solvent for PS-g-PCL and PS-g-Nylon respectively. Polymer solution was placed in a 5ml syringe fitted with a needle. Nanofibers were fabricated by electrospinning process at different applied voltage using a positive high voltage power supply (Gamma High Voltage Research). The collection plate of aluminum foil was located at a fixed distance 20 cm from the needle tip. The tilt angle of syringe was 45° from the horizontal baseline. The polymer solution formed Taylor cone at the tip of the needle by combination of gravitational force and electrostatic force. The charged jet ejected to form nanofibers and grounded on the aluminum foil target. As-spun nanofibers were dried under vacuum at room temperature over night.