

CHAPTER III EXPERIMENTAL

3.1 Materials

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer. Anhydrous ferric chloride, FeCl_3 (AR grade, Riedel-delHean) was used as the oxidant. Chloroform, CHCl_3 (AR grade, Lab-Scan) and methanol, CH_3OH (AR grade, Lab-Scan) were dried over CaH_2 for 24 hours under the nitrogen atmosphere and then distilled. The perchloric acid dopant, HClO_4 (AR grade, AnalaR) was used as received. The dispersing phase was silicone oil (AR grade, Dow corning) with density 0.96 g/cm^3 and kinematic viscosity of 100 cSt, and was vacuum-dried and stored in a dessiccator prior to use.

3.2 Polymerization Procedure

Poly (3-thiopheneacetic acid), PTAA was synthesized by oxidative-coupling polymerization according to the method of Kim *et al.* (Kim *et al.*, 1999). 10.0 g of 3-thiopheneacetic acid was refluxed for 24 hours in 50 ml of dry methanol with 1 drop of concentrated H_2SO_4 , to protect against the oxidative decomposition of the carboxylic acid group of monomer during polymerization. The methanol was evaporated, and the residue was extracted with diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO_4 , and then filtered. The diethyl ether was evaporated from the filtrate by rotating evaporator.

A solution of 10 mmol of protected monomer in 20 ml of chloroform was added dropwise to a solution of 40 mmol of ferric chloride in 30 ml of chloroform under nitrogen atmosphere. The reaction was carefully maintained at $0 \text{ }^\circ\text{C}$ ($\pm 0.5 \text{ }^\circ\text{C}$) for 24 hours. The reaction mixture was precipitated, by pouring into a large excess amount of methanol. The precipitate was repeatedly washed with methanol and deionized water. The precipitate was hydrolyzed, by heating 0.5 g precipitate in 50 ml of 2.0 M NaOH solution for 24 hours at $100 \text{ }^\circ\text{C}$. The PTAA obtained was

neutralized and precipitated with a dilute HCl solution. The PTAA was washed several times with deionized water before vacuum drying at room temperature for 2 days.

To examine the effect of particle conductivity on the electrorheological properties, PTAA particles having different conductivity values were prepared by doping with perchloric acid (Chen *et al.*, 2000). The HClO₄ doped PTAA was prepared by stirring ground PTAA (~7.04 mmol) with HClO₄ aqueous solution at room temperature for 3 days. The amounts of acid used were 7.04 ml of ~0.1 M aqueous acid and 176 ml of ~4.0 M aqueous acid for low and high doping ratios of 1.09×10^{-3} and 0.255, respectively. The HClO₄ doped PTAA particles were filtered and vacuum-dried for 24 hours before grinding with a mortar and pestle and then passed through a 38 μm sieve shaker to control the particle size distribution.

3.3 Preparation of ER fluids

The electrorheological, ER, fluids were prepared by dispersing HClO₄ doped PTAA particles in silicone oil (density 0.96 g/cm³ and kinematic viscosity 100 cSt) with ultrasonicator for 30 minutes at 25 °C. The prepared ER fluids were then stored in a dessiccator prior to use and redispersed before each measurement.

3.4 Characterization Methods

Fourier Transform Infrared (FT-IR) spectra were obtained using a FT-IR spectrometer (Bruker, Equinox 55/FRA 1065) operated in the transmission mode with 32 scans and a resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavenumber range of 4000-400 cm^{-1} using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PTAA was intimately mixed with dried KBr at a ratio of PTAA:KBr = 1:20.

$^1\text{H-NMR}$ spectra in solution state were recorded at 25 ± 1 °C using a 300 MHz Digital NMR spectrometer (Bruker, DPX-300). Deuterated dimethyl sulfoxide was used as the standard solvent.

The UV-Visible spectrum of the synthesized PTAA powder, dissolved in DMSO, was recorded with a UV-Vis spectrometer (Perkins Elmer, Lambda 10), at a scan speed of 240 mm/min, and a slit width of 2.0 nm, using a deuterium lamp as the light source, at wavelengths between 190-800 nm.

The thermal stability of PTAA was investigated using a thermogravimetric analyzer (Perkin Elmer, TGA7) in the temperature range 25 to 750 °C at a heating rate of 10 °C/min.

The particle size distribution of PTAA powder was determined using a particle size analyzer (Malvern, Master Sizer X).

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, JSM-5200-2AE) using an acceleration voltage of 20 kV and a magnification of 1,000.

3.5 Specific Conductivity Measurement

To determine the electrical conductivity, HClO_4 doped polythiophene disks (25 mm diameter and ~ 0.2 mm thickness) were prepared by molding with a hydraulic press. Electrical conductivity was measured using a custom-built four-point probe. The specific conductivity, σ (S/cm), was obtained, by measuring the resistance, R and using the following relation: $\sigma = (l/Rt)(l/K)$, where t is the film thickness and K is the geometric correction factor. A geometric correlation factor was calibrated by using standard silicon wafer sheets with known specific resistivity values. The measurements were performed in the linear Ohmic regime i.e. the specific conductivity values were independent of the applied DC current. The measurements were carried out at 27 °C and repeated at least two times.

3.6 Electrorheological Properties Measurement

3.6.1 Electrorheological Properties Measurement under Oscillatory Shear

A fluids rheometer (Rheometrics, ARES) was used to investigate the rheological properties. It is fitted with a custom-built copper parallel plates fixture (diameter of 25 mm) attached to insulating plexiglass sheets. A DC voltage was applied with a DC power supply (Tektronic, PS280) and a custom-built DC power supply, which can deliver an electric field strength to 2 kV/mm. A digital multimeter (Tektronic, CDM250) was used to monitor voltage and current.

When evaluating the steady state ER response, the electric field was applied for 10 minutes to ensure formation of an equilibrium agglomerate structure before measurements was taken. Each measurement were carried out at a temperature of 25 ± 0.1 °C and repeated at least two or three times.

3.6.2 Electrorheological Properties Measurement under Steady Shear

Rheological properties were carried out using a rotational rheometer (Carrimed, CR50) with 4 cm diameter parallel plate geometry at 25 ± 0.1 °C. The gap for the geometry used was 0.1 mm for each measurement. A DC voltage was applied during the rheological measurements using a high voltage power supply (Bertan Associates Inc., Model 215). The electric field was applied for 10 minutes to ensure the formation of equilibrium agglomerate structure before a measurement was taken. Each measurement was carried out at a temperature of 25 ± 0.1 °C and repeated at least two or three times. The static yield stress was measured using the controlled shear stress mode (CSS) as the highest stress value prior to the onset of flow in the presence of an electric field of specified magnitude. CSS experiments were also applied to investigate the dependence of viscosity on shear stress above the yield point. In the CSS experiments, the shear sweep was always applied at a sweep rate of 40 Pa/min.

3.6.3 Creep and Recovery Behaviors Measurement

The creep and recovery behaviors were carried out using a stress-controlled rheometer (Carrimed, CR50) with 4 cm diameter parallel plate geometry at 25 ± 0.1 °C. The gap for the geometry used was 0.1 mm for each measurement. A DC voltage was applied during the measurements using a high voltage power supply (Bertan Associates Inc., Model 215). For initial conditioning, the suspensions were subjected to a steady shearing at 300 s^{-1} and then electrified in a quiescent state for 5 min to ensure the formation of equilibrium agglomerate structure before a measurement was taken. A constant stress was then instantaneously applied, maintained for 180 s, and suddenly removed. The time dependent of strain was measured at various electric field strengths. Each measurement was carried out at a temperature of 25 ± 0.1 °C and repeated at least two or three times.

3.7 Morphological Observation

The morphology of the PTAA particles was characterized using scanning electron microscopy (JEOL, JSM-5200-2AE), using an acceleration voltage of 20 kV and a magnification of 1,000. The formation of particle chain structures in the electric field under stationary conditions was observed with an optical microscope (B&B Microscopes, Ltd., Olympus BX60) equipped with a camera (Diagonostic Instrument Inc., model # 3.2.0). ER fluids were placed between stationary thin copper foil electrodes attached to glass slides. External electric fields were applied to the suspensions using a DC power supply (Bertan Associates Inc., Model 215).