

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Synthesis Poly(3-Thiopheneacetic acid)

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer. Anhydrous ferric chloride, FeCl_3 (AR grade, Riedel-de Haën), was used as the oxidant. Chloroform, CHCl_3 (AR grade, BDH), and methanol, CH_3OH (AR grade, CARLO ERBA) dried over molecular sieve for 24 hours under the nitrogen atmosphere and then distilled, were used as solvents. The perchloric acid dopant, HClO_4 (AR grade, AnalaR) was used as the dopant. Sulfuric acid, H_2SO_4 was used to protect the oxidative decomposition of monomer. Diethyl ether and deionized water were used to extract materials. Sodium hydroxide, NaOH was used as the hydrolyzing agent.

3.1.2 Acrylonitrile-butadiene rubbers (NBR)

Several commercial grades of Acrylonitrile-butadiene rubber (NBR) [Nipol NBR[®] DN101L, Nipol NBR[®] DN 2850, Nipol NBR[®] DN401L (Zeon Advanced Polymix, Thailand), Krynac[®] 3345 F, and Krynac[®] X7.50 (Bayer) having bound acrylonitrile contents and specific gravities of 42.3%;1, 28%;0.97, 18.5%;0.94, 33%0.97, and 26.5%;0.99 respectively were used as the polymeric matrices.

3.2 Methodology

3.2.1 Polymerization Procedure

3.2.1.1 *Preparation of 3-Thiophene Methyl Acetate (TMA)*

The reaction was by the oxidative-coupling polymerization according to the method of 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 in order to protect the oxidative decomposition of the carboxylic acid group of

monomer during oxidative-coupling polymerization. The methanol was evaporated, and the residue was extracted with fresh 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 a rotating evaporator. TMA product was obtained.

3.2.1.2 *Synthesis of Poly(3-Thiophene Methyl Acetate) (PTMA)*

In a 100 ml three-necked flask, 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 dissolved in 30 ml of dry chloroform under nitrogen atmosphere. The molar ratio of the oxidant to monomer was 4:1 in all cases. 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 (1 L) to obtain PTMA. The product was repeatedly washed with methanol and deionized water.

3.2.1.3 *Synthesis of Poly(3-Thiopheneacetic acid) (PTAA)*

PTMA was hydrolyzed by adding 0.5 g of PTMA in 50 ml of 2.0 M NaOH solution and heating for 24 hours at $100\text{ }^{\circ}\text{C}$. The mixture was filtered, neutralized and precipitated with a dilute HCl solution ($\sim 0.5\text{ M}$) to obtain the polymer product. The P3TAA was washed several times with deionized water before vacuum drying at room temperature for 2 days. PTAA were ground with mortar and passed through a $38\text{ }\mu\text{m}$ sieve to control the particle size.

Flow Chart for Synthesis route of PTAA (Kim *et al.*1999)

The synthesis procedure of Poly(3-Thiopheneacetic acid) (PTAA) was categorized into 3 steps.

1. Preparation 3-thiophene methyl acetate(3TMA)

10.0 g of 3-thiopheneacetic + 50 ml of dry MeOH +1 drop of conc H_2SO_4 , refluxed for 24 hr.

methanol was evaporated, then the residue was extracted with diethyl ether

The extract was washed with deionized water and dried with anhydrous $MgSO_4$

The diethyl ether was evaporated from the filtrate by rotating evaporator

3TMA

2. Preparation Poly(3-thiophene methyl acetate), P(3TMA)

10 mmol of 3TMA in 20 ml of chloroform was added dropwise to a solution of 40 mmol of $FeCl_3$ in 30 ml of chloroform under nitrogen atmosphere

$0^\circ C$ ($0.5^\circ C$) for 24 hours

Blue-Black solution

Pour the reaction mixture into 1 L MeOH

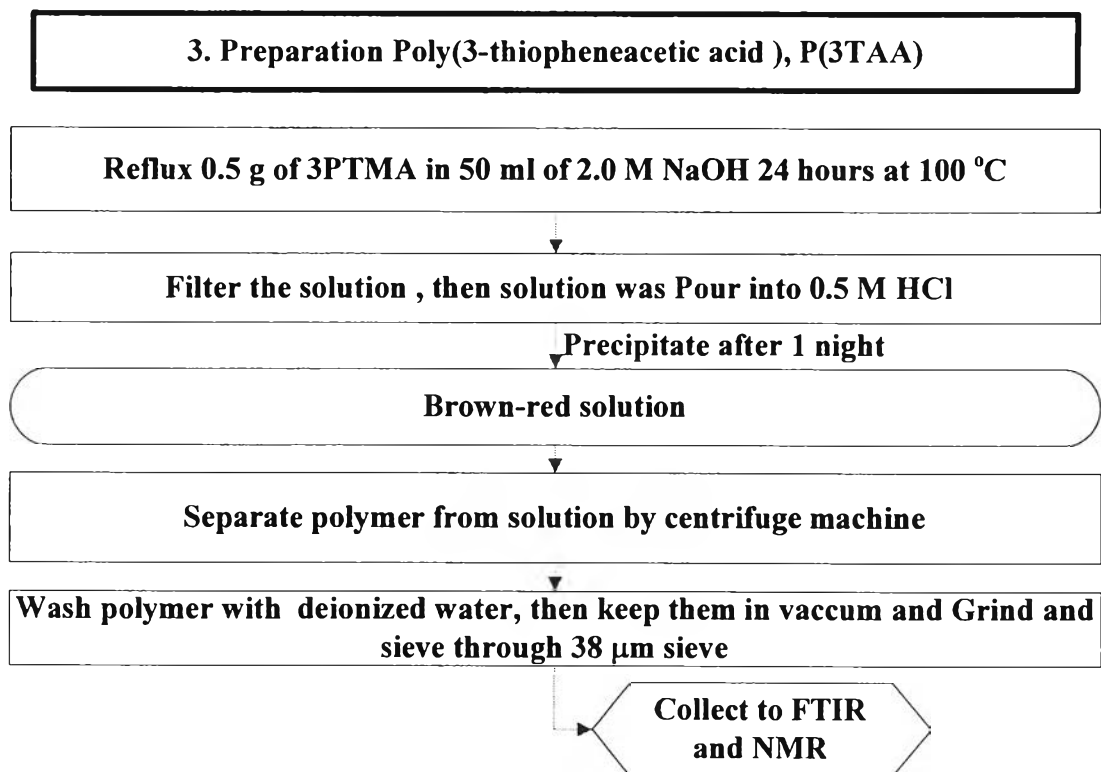
Precipitate after 1 night

Brown-red

The reaction was filtered, and wash with MeOH follow by deionized water
* Repeat until disappear yellow solution

P3TMA, brown-red

Collect to FTIR and NMR



3.2.2 Preparation of Pure Acrylonitrile-butadiene rubber

Crude acrylonitrile-butadiene rubbers were purified by dissolving in CHCl_3 (AR grade, BDH) and coagulating in methanol, and then they were subsequently dried (Vallim *et al.*, 1999). Purified rubbers were dissolved in CHCl_3 to obtain rubber solution prior casting into films thickness around 1 mm. Then they were placed in atmosphere at room temperature overnight and taken into vacuum to remove remaining solvent.

Table 3.1 Summary of specification data of Acrylonitrile-butadiene rubber various acrylonitrile contents

Type	Code	Bound acrylonitrile (%)	Mooney viscosity*1	Specific gravity	Note
DN101L	NBR1	42.3	62	1.00	-
KRYNAC® 3345 F	NBR2	33.0	45	0.97	-
DN2850	NBR3	28.0	50	0.97	-
DN401L	NBR4	18.5	66	0.94	-
Krynac® X7.50	NBR5	26.5	46	0.99	Carboxylic 7.16%

*1 ML-4 at 100°C (212°F)

3.2.3 Preparation of the P3TAA/Acrylonitrile-butadiene rubber blends

The blends were prepared by mechanical blending of undoped synthesized polythiophene at various particle concentrations (5%, 10%,15%, 20%, and 30%vol./vol.) into acrylonitrile-butadiene rubbers. The solutions were magnetically stirred for ~24 hr at 27 °C. Bubbles were removed in atmosphere at room temperature of 27 °C overnight prior casting into the films. Then they were taken into vacuum to remove remaining solvent.

3.2.4 Characterization and Testing

1) Infrared spectra was recorded by using a Fourier transform infrared spectrometer (FTIR, Thermo Nicolet, Nexus 670) in the wave number range of 400-4000 cm^{-1} . The absorbance mode was 32 scans with a resolution resolution of $\pm 4 \text{ cm}^{-1}$. The samples will be prepared by grinding the conductive polymer and with KBr (Carlo Erba Reagent) at a ratio of PTAA:KBr 1:20 and then the mixtures were pressed into pellets.

2) Nuclear Magnetic Resonance; $^1\text{H-NMR}$ (Varian Unity Inova) was used to check the structure of Poly(thiophenemethyl acetate, PTMA) and Poly(thiopheneacetic acid, PTAA) by using duterated DMSO be a solvent.

3) UV-Vis absorption spectrometer (Shimadzu, UV 2550) was used in the absorbance mode in the wavelength range of 200-800 nm. Synthesized PTAA was grinded into a fine powder, dissolved in DMSO at the concentration of 6.0×10^{-5}

M, and pipetted into the sample holder. Scan speed was 240 mm/min with a slit width of 2.0 nm, using a deuterium lamp as the light source.

4) A scanning electron microscope (JOEL, model JSM-5200-2AE) was used with a magnification range between 100-10000 times to examine the morphological structure and conductive polymer dispersion. The samples in pellet form were cut into small pieces and adhered on a brass-stub by using an adhesive tape. Then, they were coated with a thin layer of gold by using JFC-1100E ion-sputtering device prior to observation.

5) A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to study thermal stability, moisture content and decomposition temperature of samples with the temperature scan from 30 to 800 °C at a rate of 10°C/min under air condition. The powder samples were weighted in the range of 5-10 mg and loaded into a platinum pan.

6) Thermogravimetric/differential Thermal Analyzer (Perkin Elmer, Pyris Diamond) was used to study thermal stability, moisture content and decomposition temperature of samples with the temperature scan from 30 to 800 °C at a rate of 10°C/min under nitrogen gas. The samples were weighted in the range of 5-10 mg and loaded into platinum pans.

7) Two-point probe was used to determine electrical conductivity of conductive polymer which it is the inverse of its specific resistivity (ρ). This meter consisted of two probes which were connected to a voltmeter for detect voltage changes and they also were connected to a constant current source system. The voltage changing was converted to the electrical conductivity.

8) The resistivity testing fixture (Keithley, Model 8009) connected to a source meter (Keithley, Model 6517A) was used to determine conductivity of matrix materials and the blended films. A constant voltage source, the resultant current was recorded under the atmospheric pressure, 54-60% relative humidity and 24-25°C. The conductivity of matrixes was calculated following the ASTM standard D257.

9) Melt rheometer (Rheometric Scientific, ARES) was used to measure rheological properties. It was fitted with a custom-built copper parallel plate fixture (diameter of 25 mm). A DC voltage was applied with a DC power

supply (Instek, GFG 8216A), which can deliver electric field strength up to 2 kV/mm. A digital multimeter was used to monitor voltage input. In these experiments, the oscillatory shear strain was applied and the dynamic moduli (G' and G'') were measured as functions of frequency and electric field strength. Strain sweep tests were first carried out to determine the suitable strain to measure G' and G'' in the linear viscoelastic regime.

10) Dielectric measurements were carried out in the frequency range 20 Hz up to 600 kHz under applied voltage 1 volt at 27 ± 0.5 °C by using an LCR meter type (HP, 4284A) which was connected with and controlled by the melt rheometer (Rheometric Scientific, ARES) fitted with a custom-built copper parallel plate fixture (diameter of 25 mm). The samples were covered with silver conductive paint (Electrolube) to protect unreliable data from air that were entrapped in the samples.