

CHAPTER III

EXPERIMENTAL

3.1 Materials

In this study, natural rubber films used as the matrix for graft copolymerization with PPV and OPV was provided by Rubber Research Institute, 60% DRC. For the synthesis of PPV, the precursor polymer, α , α' xylene chloride (assay $\geq 98\%$), which is commercially available (Aldrich Chemical Co. Ltd.) was used directly. The chemical reagents for OPV preparation OPV were 10-bromo-1-decene (assay $\geq 98\%$), 4-hydroxy-benzyl cyanide (assay $\geq 98\%$), potassium carbonate (assay $\geq 99\%$), dimethylformamide (assay $\geq 99.9\%$), Magnesium sulfate (assay $\geq 99.5\%$), 1,4-dimethoxybenzene (assay $\geq 98\%$), HBr/AcOH 33%, potassium hydroxide (assay $\geq 85\%$), hexamethylenetetramine (assay $\geq 99\%$), sodium metabisulfide (assay $\geq 97\%$), formaldehyde solution (40 %), 2,5-dimethoxy tetraphthalaldehyde (assay $\geq 50\%$ in water), potassium tert-butoxide (assay $\geq 98\%$), 2-(tert-butylamino)ethanol (assay $\geq 99\%$). All of them were purchased from Aldrich Chemical Co, Ltd. In the grafting method, the natural rubber, dyes at various concentrations (0.5, 1, 2, 3, and 4% by weight of natural rubber), and 2,2'-azoisobutyronitrile (AIBN) 0.3% weight of natural rubber were placed under nitrogen gas, stirred and warmed at 70°C for 40 hours. The solution was cast on the glass in air for 40 hours to get copolymer films.

3.2 Equipment

3.2.1 Thermogravimetric Analysis (TGA)

The PPV, OPV, and copolymer films were analyzed by TGA using a Perkin-Elmer Pyris Diamond TG/DTA instrument under N₂ flow of 200 ml/min. The samples were weighted at 5-12 mg and put them in the platinum pan. The heating process was conducted from 30-700°C at a rate of 10°C/min. The stability and decomposition temperature of samples will be tested.

3.2.2 Differential Scanning Calorimeter (DSC)

The crystallization and melting behaviors of the dyes grafted on natural rubber samples were measured with a Perkin-Elmer DSC 7 analyzer. The heat flow and temperature of the instrument were calibrated with standard material, indium. Nitrogen was consistently purged into the equipment during the scan to prevent specimens from thermal degradation. Samples were weighted at 5-10 mg and put in aluminium pan. During the crystallization experiment, the specimens were first melted 250°C, and then cooled to room temperature at constant rate of 10°C/min. The specimens were subsequently heated at 10°C/min for the corresponding melting behaviour investigations. Moreover, miscibility of the samples defined by the shifting of the glass transition temperature is investigated.

3.2.3 Fourier Transform Infrared Spectrometer (FT-IR)

The FT-IR spectra of natural rubber grafted by dyes film samples were collected by using a Nicolet Nexus 670 FT-IR spectrometer over a wavenumber range of 4,000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} .

3.2.4 Lloyd Universal Testing Machine

Tensile test of natural rubber film with dimension 20×100 mm (thickness 0.3-0.8 mm) was carried out by Lloyd Universal Testing Machine with crosshead speed of 500 mm/min and gauge length of 50 mm under room temperature. This test followed ASTM D882-91. The Test was repeated 3 times.

3.2.5 Compression Molding Machine

Either PPV or OPV grafted on natural rubber films (thickness 1-2 mm) were prepared by a Wabash V50H 50 ton compression molding machine. The film was heated at 50°C, and compressed under pressure 10 tons for 10 minutes. After that the molding was cooling under pressure. All of films were used to measure properties by TGA, DSC, FT-IR, SEM, fluorescence spectrometer, and GPC.

3.2.6 Centrifugal Ball Mill

PPV films were ground by FRITSCH Pulverisette 6 Centrifugal Ball Mill with rotational speed of 450 rpm in milling and reverse directions for 1 hr. The particle size of the powder was less than 44 μm .

3.2.7 Scanning Electron Microscope (SEM)

Copolymer films had to study the morphology. The samples were broken by immersing samples in liquid nitrogen then they were broken. The broken surface was used to see by JEOL JSM-5200 scanning electron microscope (SEM). They were adhered on the brass stubs by using adhesive tape. All of them were coated with gold were observed by SEM with magnification of 1500/20 kV. Homogeneity and morphology of samples were investigated.

3.2.8 Fluorescence Spectrometer

Influence of either PPV or OPV to fluorescent properties is studied by varying concentrations of dyes by using Fluorescence spectrometer Perkin Elmer LS65 precisely in range 200-900 nm, and scan speed 200 (nm/min). The fix excitation wavelength of each sample was determined by using the pre scan mode. The emission spectra of copolymers were collected under excitation wavelength with excitation and emission slits set to 15 nm. The copolymer films had to have the same thickness (2 mm). All PL experiments conducted at room temperature and were measured on free-standing films with detection from the front of films. Moreover, the influence of stress or strain to photoluminescent properties of samples is studied by varying stress or strain that put on the samples.

3.2.9 Size Exclusion Chromatography (SEC or GPC)

GPC is a chromatographic technique that separates polymeric chains following their molecular weight, and therefore it allows the determination of the molecular weight and molecular weight distribution of a polymeric sample. The GPC solution of copolymers was prepared by dissolving 10 mg of the copolymer into 5 ml of THF, the solution was agitated and then filtered with a microfilter. The average molecular weight was determined by using GPC operated at 30-40°C with Styragel column (Walters) in THF solvent. Inject sample solution of 20 μl was passed through the column using UV detector. The mobile phase is THF flow at 0.6 ml/min. The calibration curve can be seen in Appendix A.

3.3 Methodology

3.3.1 Synthesis of Poly(p-phenylene vinylene) (PPV)

The bis-sulfonium salt 16 g (45.5 mmol) was dissolved in the mixture of 80 ml of water and 45 ml of methanol. The solution was purged with nitrogen for one hour, and cooling to 0 °C. 91 ml of nitrogen purged NaOH (45.5 mmol) are added at once with rapid stirring. After stirring for 120 min at 0°C the polymerization is quenched by addition of 0.5 M HCl until pH 6-7 was reached. The neutralized solution was dialyzed against a minimum of 50 l deionized water for 2 days in order to separate the polymer from monomer residues, sodium chloride and oligomeric compounds. The solution from the dialyzed tube was used to prepare free standing films by cast on glass plates in air. Thin films of the precursor polymer were converted to PPV by heating in a vacuum oven at 200°C for 16 hours. PPV films were used to measure properties by TGA, DSC, FT-IR, SEM, and fluorescence spectrometer.

3.3.2 Preparation of PPV Graft on the Natural Rubber by Free Radical

Polymerization

The natural rubber, PPV at various concentrations (0.5, 1, 2, 3, and 4% by weight of natural rubber), and AIBN 0.3 wt% of natural rubber were put in a vessel that was placed under nitrogen gas, stirred and warmed at 70°C for 40 hours. The solution was cast on the glass to get NR-g-PPV film. All of films were used to measure properties by TGA, DSC, FT-IR, and SEM. The average molecular weight was determined by using GPC operated at 30-40°C with special column in THF solvent. The copolymers solution was prepared by dissolving 10 mg of the copolymer into 5 ml of THF. The copolymer films had to have the same thickness (2 mm) by using compression molding machine. All PL experiments conducted at room temperature and were measured on free-standing films with detection from the front of films. Moreover, the influence of stress or strain to photoluminescent properties of samples is studied by varying stress or strain that put on the samples.

3.3.3 Synthesis Oligo(para-phenylene vinylene)

3.3.3.1 *Synthesis of (4-Dodecyloxyphenyl) acetonitrile*

A suspension of K_2CO_3 (4.05 g, 29.2 mmol) in dimethylformamide (15 mL) was purged with N_2 for 15 min and heated to 80 °C, and 4-hydroxyphenylacetonitrile (1.47 g, 11.0 mmol) was added. After stirring at 80 °C for 10 min, 10-bromododecene (3.54 g, 14.2 mmol) was slowly added and the suspension was stirred at 70 °C under N_2 for another 4 h. After this time a pale yellow precipitate had formed. The reaction was terminated by pouring the suspension into ice-water (150 mL) and $CHCl_3$ (50 mL) was added to dissolve the precipitate. The organic layer was separated off and the aqueous phase was extracted with $CHCl_3$ (3 x 50 mL). The combined organic layers were washed with H_2O and saturated aqueous NaCl, respectively. The organic phase was dried with $MgSO_4$ and filtered, and the solvent was evaporated in vacuum to yield a pale yellow powder (3.30 g). Recrystallization from EtOH (50 mL) afforded (4-dodecyloxyphenyl) acetonitrile in the form of white crystals.

3.3.3.2 *Synthesis of 1,4-Bis(Bromomethyl)-2,5-dimethoxybenzene*

To stirred solution of 150 g (1.1 mol) of 1,4-dimethoxybenzene in 750 ml of glacial acetic acid, 65 g (2.2 mol) of paraformaldehyde and 425 ml of HBr/AcOH (33%) were added slowly. The reaction mixture was heated for 1 hour at 50°C and hydrolysed in 3000 ml of water after cooling to room temperature. The residue was filtered off and suspended in 750 ml of $CHCl_3$. This suspension was refluxed for 10 min and filtered off again after cooling to room temperature. The residue was finally dried at 0.1 torr with KOH.

3.3.3.3 *Synthesis of 1,4-Dimethoxy-2,5-dicarbaldehyde*

To a stirred solution of 87 g (0.6 mol) of hexamethylenetetramine in 2000 ml of toluene, 100 g (0.3 mol) of 1,4-Bis(Bromomethyl)-2,5-dimethoxybenzene was added and refluxed for 4 hours. After cooling to room temperature the yellowish salt was filtered off and dissolved in 1000 ml of $CHCl_3$. The residue was filtered off and dried in vacuum oven. This salt was dissolved in 3000 ml of water. After the addition of 180 ml of formaldehyde solution (40 %), the reaction mixture was refluxed for 3 hours. After cooling to room temperature, the crude compound was filtered off and purified by conversion to the bisulfite adduct. The crude product was suspended in 2000 ml of water. $Na_2S_2O_5$ (250

g, 1.3 mol) was added to the stirred suspension. The reaction mixture was refluxed for 30 min and filtered off to separate by-products. To the stirred solution of the bisulfite adduct, 600 ml (7.4 mol) of conc. HCl was added dropwise. The yellow dialdehyde precipitated and was separated by filtration. Compound was dissolved in 1000 ml of water, filtered off again, and dried at 0.1 torr with P_2O_5 .

3.3.3.4 *Synthesis of 1,4-Bis (R-cyano-4-dodecyloxystyryl)-2,5-dimethoxybenzene*

2,5-Dimethoxyterephthaldehyde (146 mg, 0.75 mmol) and (4-dodecyloxyphenyl) acetonitrile (500 mg, 1.66 mmol) were dissolved at 70 °C in a mixture of t-BuOH (11 mL) and THF (5 mL). t-BuOK (0.11 mL of a 1 M solution in THF, 0.11 mmol) and n-Bu₄NOH (1 mL of a 1 M solution in MeOH, 1 mmol) were added quickly and an orange precipitate started to form immediately. The mixture was stirred for 15 min at 70 °C, cooled to RT, and poured into acidified methanol (50 mL containing 1 drop of concentrated acetic acid). The resulting precipitate was filtered off, excessively washed with MeOH, and dried in vacuum at 50 °C to yield in the form of orange crystals which is called OPV. OPV were used to measure properties by TGA, DSC, FT-IR, UV/Vis spectrometer, and SEM. The average molecular weight was determined by using GPC operated at 30-40°C with special column in THF solvent. The copolymers solution was prepared by dissolving 10 mg of the copolymer into 5 ml of THF. The copolymer films had to have the same thickness (2 mm) by using compression molding machine. All PL experiments conducted at room temperature and were measured on free-standing films with detection from the front of films. Moreover, the influence of stress or strain to photoluminescent properties of samples is studied by varying stress or strain that put on the samples.

3.3.4 Preparation of OPV Graft on the Natural Rubber by Free Radical Polymerization

The natural rubber, OPV at various concentrations (0.5, 1, 2, 3, and 4% by weight of natural rubber), and AIBN 0.3 wt% of natural rubber were placed under nitrogen gas in vessel, stirred and warmed at 70°C for 40 hours. The solution was cast on the glass in air for 40 hours to get NR-g-PPV film. All of films were used to measure properties by TGA, DSC, FT-IR, SEM, and fluorescence spectrometer.

The average molecular weight was determined by using GPC operated at 30-40°C with special column in THF solvent. The copolymers solution was prepared by dissolving 10 mg of the copolymer into 5 ml of THF.