



CHAPTER II

LITERATURE REVIEW

2.1 Polydiphenylamine Synthesis and Derivatives

Bangheni *et al.* (1998) developed the copolymer of polydiphenylamine by copolymerizing diphenylamine (DPA) and benzidine (BZ) to improve their electro activity. Poly(Diphenylamine-*co*-Benzidine) was synthesized via the electrochemical polymerization in an aqueous solution. The solution contained 0.5 M NaClO₄, 0.5 M HClO₄, 1 mM DPA and 1mM BZ monomers. A three-electrode includes an Ag/AgCl electrode as a reference, a glassy carbon, and a Pt plate. The later two electrodes were used as the working and counter electrodes, respectively. They were immersed into the solution. Polymer was formed on the working electrode under acidic solutions by cyclic potential sweeping method continuously between -0.1 and 1.0 V and followed by raising the polymer-deposited electrode with distilled water. They found that the copolymer, which was formed under optimum conditions, was much more electroactive than the corresponding homopolymers and could be altered by variation of comonomer feed ratios. In addition, the copolymer formation was much higher than homopolymerization.

Wen *et al.* (2002) studied methane sulfonic acid (MeSA) doped with polydiphenylamine (PDPA) and soluble in various solvents. Diphenylamine (DPA) was polymerized by electrochemical polymerization which was performed in a single compartment reaction cell fitted with a Pt disk as working electrode, a Pt wire counter electrode, and Ag/AgCl reference electrode. The reaction was carried out by using aqueous 30 mM solution of DPA in 3M MeSA, added reversibly cycling the potential between 0.0 and 1.0 V (for 50 cycles) at a constant scan rate of 100 mV/s and dried. They found that PDPA was synthesized in MeSA doped and soluble in THF, DMF, NMP and DMSO. The doped polymer showed a doping level of 0.37, as obtained from TGA. Redox transitions from reduced PDPA structure to diphenosemiquinone imine and diphenoquinone diimine could be observed after polymerization.

Polydiphenylamine (PDPA) is known as an *N*-substituted, similar to polyaniline (PANI); it was conceived that PANI film can be pH sensors for different ranges of pH through sensitivity of *N*-substituted. Tsai *et al.* (2003) worked on these characteristics of PDPA. They prepared PDPA, PANI and copolymer of DPA and ANI to study the tuning for the optimal sensing of pH by PDPA. They synthesized the polymers by the electrochemical polymerization, which was performed by applying a constant potential (0.8 V) via a three-electrode cell, with Ag/AgCl electrode as the reference and Pt wires as counter electrode, and ITO used as the working electrode. The potential was applied into a solution, having DPA and ANI or mixture of DPA and ANI in 1 M HClO₄. Polymer films could be seen on ITO-coated glass surface. The films were washed with 1 M HClO₄ and dried. After pH measurement, the reversibility test and the response time measurement, they found that the pK_a of PDPA for the imine protonation/deprotonation equilibrium, which was higher (8.70) than PANI (6.80), became possible to tune the pK_a and pH sensitivity by making a copolymer of DPA with ANI. The copolymers possessed pK_a a value of about 7.0. Furthermore, PDPA and its copolymers with aniline had a reproducible pH behavior which was similar to PANI. PDPA had a shorter response time (7.0 s) than PANI. This work showed that PDPA can be doped by an acidic solution.

Hua and Ruckenstein (2003) synthesized poly (ethylene oxide)-grafted polydiphenylamine which was a water-soluble conductive copolymer. First, they synthesized polydiphenylamine (PDPA) by a chemical oxidation method of diphenylamine in a 3 N aqueous HCl solution using ammonium persulfate as the initiator. Diphenylamine (6.0 g, 0.0354 mol), 120 mL of 3 N HCl solutions, and 150 mL of ethanol were introduced into a 500 mL round-bottom flask. The system was subjected to intensive magnetic stirring for a few minutes and then cooled to 5 °C in an ice-water bath. Ammonium persulfate (3.01 g, 0.0132 mol) was dissolved in 15 mL of 3 N HCl solution and added dropwise into the flask. The color of the reaction solution changed from transparent to green, indicating the start of polymerization. The system was subjected to intensive stirring for 16 h. A green precipitate, PDPA, was separated by using a supercentrifuge at 3500 rpm for 30 min. The PDPA particles were washed with ethanol/water mixtures (3/1, v/v) a few times (30 mL

each time), until no green supernatant was identified, and finally dried under vacuum at room temperature for at least 24 h. The yield was 35%. PDPA product was HCl-doped form which possessed the high conductivity of 0.37 S/cm, and could attain 0.45 S/cm at 55°C as a result of thermal active effect.

Orlov *et al.* (2005) studied the kinetics of the oxidative polymerization of diphenylamine by using three different polymerization conditions; they were for polymerization in a solution of sulfuric acid, a 0.1 M solution of diphenylamine in 5 M H₂SO₄, and a 0.125 M solution of ammonium persulfate in 5 M H₂SO₄ (1/4 based on the total volume). For polymerization in a H₂SO₄—*tert*-butanol mixture, a 0.2 M solution of diphenylamine in a mixture of 4 M H₂SO₄ and *tert*-butanol (equal volumes) and a 0.25 M solution of ammonium persulfate in the same solvent (1/4 based on the total volume) were prepared. For the interfacial polymerization, a 0.2 M solution of diphenylamine in toluene and a 0.25 M solution of ammonium persulfate in the same volume of a 1 M solution of HCl were prepared. The solutions of monomer and oxidizer were cooled to -2-0°C and mixed together, the reaction was carried out under intense stirring, and temperature maintain at -2 - 0°C at 2-4 h. The reaction mixture was precipitated into either a 5-fold excess of ice water (polymerization in H₂SO₄ and the H₂SO₄—*tert*-butanol mixture) a 5-fold excess of isopropyl alcohol cooled to -2 - 0°C (the interfacial polymerization), precipitate polymer was filtered and washed by distilled water many times until they was neutral form. They found that the interfacial polymerization resulting in the highest molecular weight and yield.

2.2 Doping

Hua and Ruckenstein. (2003) improved solubility properties of polydiphenylamine by grafting the backbone with poly (ethylene oxide). Polydiphenylamine (PDPA) was synthesized through a chemical oxidation method of using diphenylamine in 3 N HCl solutions. They found that the polymer, after first synthesized without neutralization, contained polarons and bipolarons. Its electrical conductivity was 0.37 S/cm. Based on this result, polydiphenylamine was doped by HCl.

Thanpitcha *et al.* (2005) studied preparation and characterization of blended polyaniline/chitosan film. Polyaniline was prepared through the chemical oxidative polymerization of distilled aniline monomer in HCl solution which obtained a dark green precipitated. The mixture was neutralized by distilled water and methanol until the solution was colorless. By considering doped times and doped concentration, they found that the electrical conductivity of the films was increased by adding HCl-doped from 0.1 to 1 M, but decreased with 2-6 M HCl solution. This result came from the over-protonation of PANI chains causing a decrease in the delocalization length of PANI. Moreover, the doping times from 0.5 to 10 h resulted in an electrical conductivity increase but a decrease after 10 h. This work was interesting because polyaniline had *N*-substituted polymer like a polydiphenylamine in which HCl-doped would affect its *N*-substituted.

Hua and Ruckenstein. (2005) improved pH response of polydiphenylamine by introducing sulfonate groups in their side chains. The resulting polymer could respond to pH above 7 and below pH 7. Above pH 7, doping mechanism was according to the sulfonate side chains, but below pH 7 the doping was dependent on HCl doped. The electrical conductivity measured was 3.7×10^{-2} S/cm.

2.3 Preparation of Styrenic Triblock Copolymer

Winter *et al.* (1993) studied ordering of Styrene-Isoprene-Styrene copolymer (SIS) films near their order-disorder temperature. They cast the films, giving an equilibrium microphase-separated morphology which was hexagonally packed cylinders of polystyrene (PS) in a polyisoprene (PI) matrix by using SIS with %styrene content of 24.3%. The films were cast from 10 wt % toluene solution at room temperature for 1 week. To further remove toluene and reduce stresses from solvent evaporation, the films were vacuum-dried at 120 °C or 24 h. The initial morphology after solution casting consisted of hexagonally packed cylinders of PS in a PI matrix.

Matsushita *et al.* (1994) introduced tricontinuous double-diamond structure by casting films of styrene-isoprene-2-vinylpyridine triblock copolymer with a variety of monomer volume ratios. The films were prepared by solvent-casting from

3 to 5% solutions of THF, annealed under vacuum at 120°C for a week. The morphology was observed by TEM. They found that copolymer with styrene/isoprene/2-vinylpyridine volume ratio was 0.31/0.43/0.26 (SIP-2). The film was formed three-phase four-layer lamella morphology.

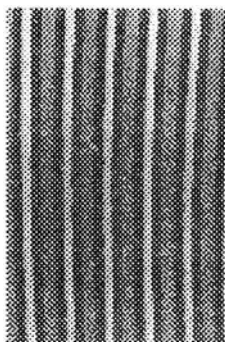


Figure 2.1 Electron micrograph of SIP-2 showing the three phase four-layer lamellar structure (Matsushita *et al.*, 1994).

Nagata *et al.* (2005) prepared and characterized a multi-block copolymer of styrene-isoprene copolymers by casting of SI films from 5 wt% dilute polymer solutions of THF, dried under vacuum at 25°C. The films were annealed at 150°C for 4 days. The films which was cast from dilute solution of SIS, giving gyroid micro-domain with M.w. $[M_w]$ 4.14×10^4 , styrene content 68 wt%. The lamellar morphology was obtained from casting dilute solution of SISISISISIS copolymer with 27.5×10^4 , styrene content of 70%. Moreover, the lamellar morphology can be prepared from casting of SI copolymer solutions with styrene contents of 38%, 55% and 42% but obtaining different sizes in the micro-domains.

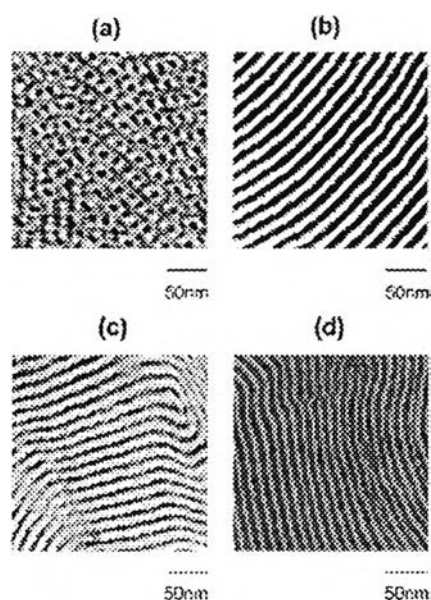


Figure 2.2 Transmission electron micrographs of multiblock copolymers: (a) pre-3, (b) pre-5, (c) pre-7, (d) pre-9 (Nagata *et al.*, 2005).

Hotta *et al.* (2002) studied polystyrene-polyisoprene-polystyrene (SIS), where the microphase-separated PS blocks acted as physical cross-links for the PI elastic network in the stress relaxation in transient networks. They prepared micellar-structure and cylindrical-structure by using of SIS with styrene content 14% and 17%, respectively. Those microphase structures were obtained from melt casting. The results from the experiment can conclude that the phase separation created an energy barrier, which holded the segment in the (molten) spherical and cylindrical micelles and thus created an effective cross-link for polyisoprene network. At higher temperatures, this energy barrier became weak and insufficient to resist the elastic force. This was one of the obvious reasons for the transitions on raising the temperature.

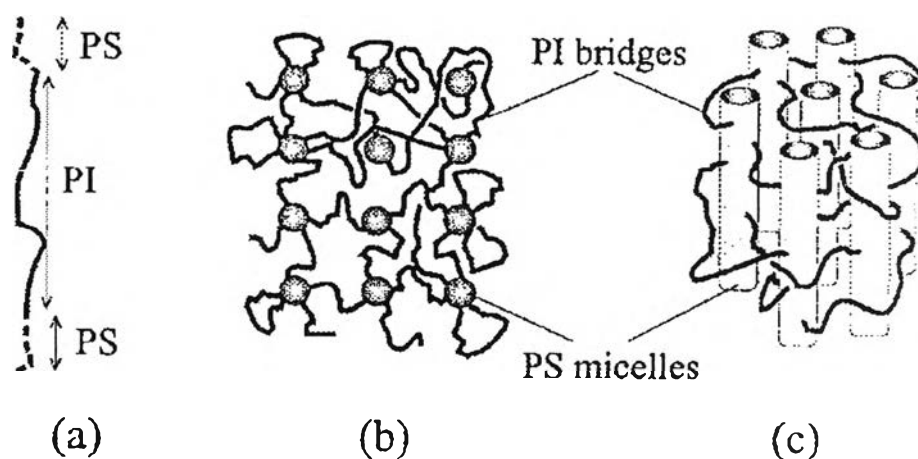


Figure 2.3 Sketch of SIS triblock copolymer (a); the morphology of its phase separation: the cubic phase of spherical micelles in the 14% PS material (b); and the hexagonally packed phase of cylindrical micelles in the 17% PS material (c). Long PI bridges interconnect the PS micelles, making an elastomer network with effective multifunctional cross-links (Hotta *et al.*, 2002).

2.4 Electroactive Polymers

Puvanattvattana *et al.*, (2007) found that, in the system of polythiophene/polyisoprene suspensions, the storage modulus (G') of the suspensions increases dramatically by 3–4 orders of magnitude as the electric field strength was increased from 0 to 2 kV/mm. The suspensions exhibited a transition from a fluid-like to a solid-like behavior as the field strength is increased, as evidenced by the crossovers between the scaling exponents n' and n'' , and the finding that G' becomes greater than G'' . The influences of particle conductivity and particle concentration appeared to be more evident at intermediate field strength of 0.5 kV/mm. Higher particle conductivity and particle concentration resulted in thicker fibrillar structures formed and in the lower critical electric field strengths for the sol-to-gel transition to occur.

Shiga *et al.*, (1993) examined the electroviscoelastic effect of silicone elastomers having lightly doped conjugated polymer particles. The semiconducting polymers used experimentally were poly(*p*-phenylenes) lightly doped with CuCl_2 or FeCl_3 making PPP particles attained dc conductivities of 10^{-10} - 10^{-7} S/cm. The increments of G' and of G'' of the specimens which contained the particles content over 10.8% were induced by an electric field. They reported an effect of particle dispersion that the straight lines of particles aligned to electric fields were more effective in comparison with the random dispersion of particles, for a large electroviscoelastic effect to occur.

Gazotti *et al.*, (1999) studied the electrical, mechanical and thermal behaviours of a conductive polymer blend which was prepared by combining the elastomer poly(epichlorohydrin-co-ethylene oxide), which was of ionic conductivity when containing LiClO_4 , and a soluble derivative of polyaniline, poly(*o*-methoxyaniline) doped with *p*-toluene sulfonic acid. With an increase in concentration of the electronic conducting polymer up to 10% (w/w), the electrical conductivity of the elastomer increased by three orders of magnitude, with no changes in its mechanical properties. TGA results indicated that the presence of the rubber inhibited the degradation of the conducting polymer.

Carpi *et al.* (2003) studied an extension of electromechanical characterization of dielectric elastomer actuators. Planar actuators were realized with a 50 μm -thick film of an acrylic elastomer coated with compliant electrodes. The isotonic transverse strain, the isometric transverse stress, and the driving current due to a 2 s high voltage impulse, were measured from four electrode materials (thickened electrolyte solution, graphite spray, carbon grease and graphite powder). Carbon grease, graphite powder, and thickened electrolyte solution were smeared on the two sides of the strip, while graphite spray electrodes were realized as follows. They showed an electrode resistance per unit length; the graphite powder had the highest value, 50 Ω/cm by applying a certain voltage V across the definite thickness z_0 of a prestretched actuator. The result showed an electrostatic pressure generated a strain depending on the square of the applied electric field.

Kim *et al.*, (2004) prepared a copolymer of poly(acrylic acid) and poly(vinyl sulfonic acid), PAAc/PVSA, to study swelling ratios at various temperatures and pH, and deformation ratio in an electrical field. The copolymer was prepared by sodium vinylsulfonate and *N,N'*-methylenebisacrylamide, crosslink agents, were dissolved in deionized water, then ammonium peroxydisulfate (APS) was added. The stored in a dry oven and heated at 50 °C for 2 days. Swelling properties of the PAAc/PVSA copolymer showed a temperature dependent swelling behavior in pure water and also pH-dependent swelling behavior. An applied electric field caused a contraction of the PAAc/PVSA copolymer hydrogels in the buffered solutions at various pH. The contraction of the hydrogel in an applied dc electric field was due to the voltage-induced motion of ions, and the association state of the ionic groups within the polymer, which in turn, was due to the association/dissociation of the hydrogen bonds of the -COO- groups of the PAAc and the $\text{-SO}_3\text{-}$ groups of the PVSA in the hydrogels.

Moschou *et al.*, (2004) prepared a novel artificial muscle material based on an acrylic acid/acrylamide hydrogel blended with a conductive polypyrrole/carbon black composite. After curing at 80 °C, the hydrogels were preconditioned in the NaCl test solution for at least 24 h. The material was optimized in terms of its electroactuation response by varying the acrylic acid content, the blending concentration of the conductive composite, and the intensity of the electric field. The higher the acrylic acid content, the higher the bending angle of the hydrogel was obtained. An additional parameter that was investigated when optimizing the artificial muscle composition was the incorporation of a conductive polymer such as polypyrrole on carbon black. They found that the hydrogel, composed of 4% (w/w) carbon black alone, presented a significantly lower response than its PPy/CB counterpart. The application of higher potentials (2 and 3 V) showed an expected improvement in the response of the material.

Ma and Cross (2004), studied electric field induced transverse-strain response in dielectric acrylic elastomer at 1 Hz. The strain was observed to be proportional to square of the electric field strength within the measurement range (0 to 2MV/m). Elastic compliance of the elastomer was measured as a function of frequency and was found to exhibit strong frequency dependence between 1 and 10

Hz. It was indicated that the field-induced-strain response in the acrylic elastomer originates primarily from the Maxwell stress effect.