

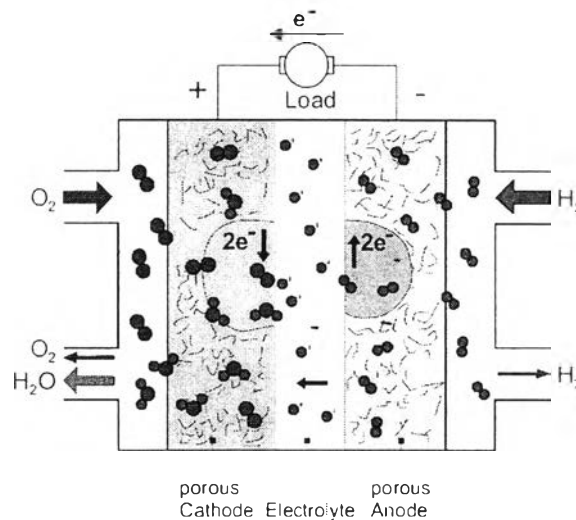
## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Fuel Cell

Fuel cells are electrochemical devices for electrical energy production by using redox reaction of fuels i.e., hydrogen, natural gas or other hydrocarbon-based fuels and oxidant. Fuel cell has been considered to be one of the most promising alternative energies because of low pollution and high efficiency of the energy system for using in several applications such as automotive, portable devices, and stationary powers. The increasing concerns about environmental problems are the main factors that have motivated the development of fuel cell.

The main components of a single fuel cell consist of an electrolyte sandwiched between two electrodes which are anode and cathode as shown an example of hydrogen/oxygen fuel cell in Figure 2.1. In principle, the operation of fuel cell is similar to battery. They produce electrical energy from electrochemical reactions (Kirubakaran *et al.*, 2009).



**Figure 2.1** Schematic draw of a single fuel cell components and operations based on hydrogen/oxygen fuel cell (Carrette *et al.*, 2001).

In general, fuel cells are classified into six main types based on electrolyte and fuel used in the cell which are alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), and direct methanol fuel cell (DMFC). An overview of the fuel cell types is given in Table 2.1.

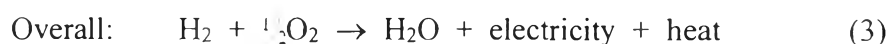
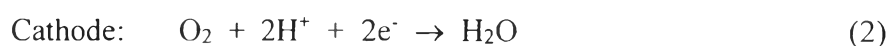
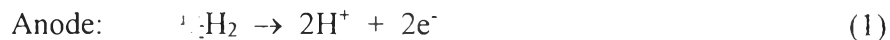
**Table 2.1** Characteristics of different types of fuel cell (Carrette *et al.*, 2001; Kirubakaran *et al.*, 2009)

Fuel Cell type	Fuel	Electrolyte	Charge carrier	Operating Temperature (°C)	Realised Power	Applications
Alkaline fuel cell (AFC)	pure H <sub>2</sub> , or hydrazine	Potassium hydroxide (KOH)	OH <sup>-</sup>	< 100	Small plants 5-150kW modular	Transportation, space, military, energy storage systems
Polymer electrolyte membrane fuel cell (PEMFC)	H <sub>2</sub>	Polymer, proton exchange membrane	H <sup>+</sup>	60-120	Small plants 5-250kW modular	
Direct methanol fuel cell (DMFC)	CH <sub>3</sub> OH	Polymer, Proton exchange membrane	H <sup>+</sup>	60-120	Small plants 5kW	
Solid oxide fuel cell (SOFC)	CH <sub>4</sub> , H <sub>2</sub> , CO	Stabilised zirconia and doped perovskite	O <sup>2-</sup>	800-1000	Small power plants 100-250kW	Combined heat and power for stationary decentralized systems and for transportation (trains, boats, etc)
Molten carbonate fuel cell (MCFC)	CH <sub>4</sub> , H <sub>2</sub> , CO	Molten salts such as nitrate, sulphate, carbonates	CO <sub>3</sub> <sup>2-</sup>	600-800	Small power plants 100kW-2MW	
Phosphoric acid fuel cell (PAFC)	H <sub>2</sub>	Phosphoric acid	H <sup>+</sup>	160-220	Small - medium sized plants 50kW	Combined heat and power for decentralized stationary power systems

## 2.2 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Among the various types of fuel cell, PEMFC is the most promising candidate fuel cell system because PEMFC has several attractiveness such as light weight, the compactness, including the high power density and is considered to be suitable for portable electrical devices and automotives (Andújar and Segura, 2009).

The electrochemical reactions in PEMFC occur on both anode and cathode of the cell by applying hydrogen as a fuel and oxygen or air as an oxidant. At the anode, hydrogen is oxidized by a catalyst on the surface of membrane for generating protons and electrons. The protons pass through the polymer electrolyte membrane and were reduced and recombined by oxygen and electron to generate water and heat as by products. In this state, the electrons flow through wire generating electrical current. The reactions are as following:



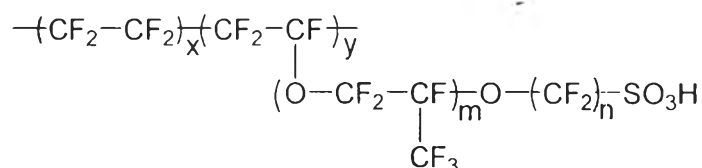
Theoretically, the electrical potential difference between cathode and anode is equal to 1.229 V (at 25 °C and 1 atm) when pure hydrogen and pure oxygen are used as fuel and oxidant, respectively. In practice, the energy losses are always found in the fuel cell, as a consequence, the cell potential difference is not ideal and diminishes to be ~ 0.7-0.8 V for the optimal fuel cell performance (Li, 2006).

One of the most important parts in PEMFC systems is the polymer electrolyte membrane (PEM) which works as a proton exchanging part as well as a barrier for fuel and oxidant. There are several requirements of PEM as PEMFCs for example high proton conductivity, excellent electronic insulator, good mechanical and chemical stabilities, low fuel crossover, and low cost (Alberti *et al.*, 2001; Devanathan, 2008). Consequently, several polymer membranes have been developed for the use as electrolytes in PEMFC. Typically, based on the type of proton

conductive species, PEMs are classified into two main systems: hydrous-based membrane system (e.g., protons transport through water molecules) and anhydrous-based membrane system (e.g., protons transport through other species such as heterocycles).

### 2.2.1 Hydrous-based Membrane System

At present, perfluorosulfonic acid (PFSA) polymer is the key material for polymer electrolytes. Nafion<sup>®</sup> developed by DuPont was firstly applied in 1966 and is still the most widely used as ion-exchange membrane in PEMFC prototypes (Figure 2.2). Nafion<sup>®</sup> chain consists mainly of a poly(tetrafluoroethylene) (PTFE) backbone, which statistically forms segments of several units in length, and a few perfluorinated vinyl polyether branches. The branches, functioning as a flexible pendant, combine the PTFE backbone which carries a terminal acidic group supporting water molecules as a water cluster for proton transferring. As a consequence, proton can be transferred through the membrane. This results in an excellent proton conductivity of PFSA membranes e.g.,  $9 \times 10^{-3} \text{ S cm}^{-1}$  -  $1.2 \times 10^{-1} \text{ S cm}^{-1}$  at 80 °C in a relative humidity (RH) range of 34-100 % (Alberti *et al.*, 2001).



**Figure 2.2** Structure of commercial PFSA polymers, Nafion<sup>®</sup>:  $m=1$ ;  $n=2$ ;  $x=5-13.5$ ;  $y=1$ , Flemion<sup>®</sup>:  $m=0,1$ ;  $n=1-5$ ;  $x=5-13.5$ ;  $y=1$ , Aciplex<sup>®</sup>:  $m=0$ ;  $n=2-5$ ;  $x=1.5-14$ ;  $y=1$ , Dow<sup>®</sup>:  $m=0$ ;  $n=2$ ;  $x=3.6-10$ ,  $y=1$  (Heitner-Wirguin, 1996).

Although PFSA membranes are currently intensively used in PEMFC as they meet the requirements of high proton conductivity ( $9-120 \text{ mS cm}^{-1}$  at 80 °C in RH range of 34-100 %) (Alberti *et al.*, 2001), outstanding chemical stability (in H<sub>2</sub>O<sub>2</sub> at temperature up to 80 °C) (Heitner-Wirguin, 1996; Kinumoto *et al.*, 2006), and longevity (60,000 h at 80 °C) (Kerres, 2001), there are several major drawbacks for

example high cost, special cautions required in manufacturing process, system complication, working temperature limitation under 100 °C, and fuel crossover.

As a result of phase separation between hydrophobic fluorocarbon backbone and water-surrounded hydrophilic end groups of sulfonic acid species, water cluster networks (liquid state) with narrow channels connected were formed (Eikerling *et al.*, 1997). For hydrous membrane, proton conductivity critically depends on the degree of membrane hydration (Kreuer *et al.*, 2008). The higher the amount of water inside the membrane, the higher the proton conductivity.

To overcome the drawbacks of the conventional PFSA hydrous-based polymer especially the Nafion<sup>®</sup> membrane, various approaches have been made, i.e., adding additives to retain water, enhance proton conductivity and increasing PEMFC working temperature with auto-humidification to accelerate proton movement (Hogarth and Benziger, 2006).

Additives improve water retention, thermal stability, preventing fuel crossover, and proton transfer efficiency. Up to present, various types of additives for example acids, i.e. Brønsted acids (Savinell *et al.*, 1994), polymer, i.e. PTFE (Finsterwalder and Hambitzer, 2001), inorganic, i.e. metal oxide (Adjemian *et al.*, 2002; Adjemian *et al.*, 2006), and clay including organic, i.e. heterocyclic compounds have been investigated.

Savinell and coworkers reported that by adding phosphoric acid, the performance of Nafion<sup>®</sup> 117 membrane was enhanced (Savinell *et al.*, 1994). The reaction kinetics accompanied by high proton conductivity ( $<0.05 \Omega^{-1} \text{ cm}^{-1}$ ) up to 200 °C as well as lower methanol crossover as compared to Nafion<sup>®</sup> 117 membrane were achieved.

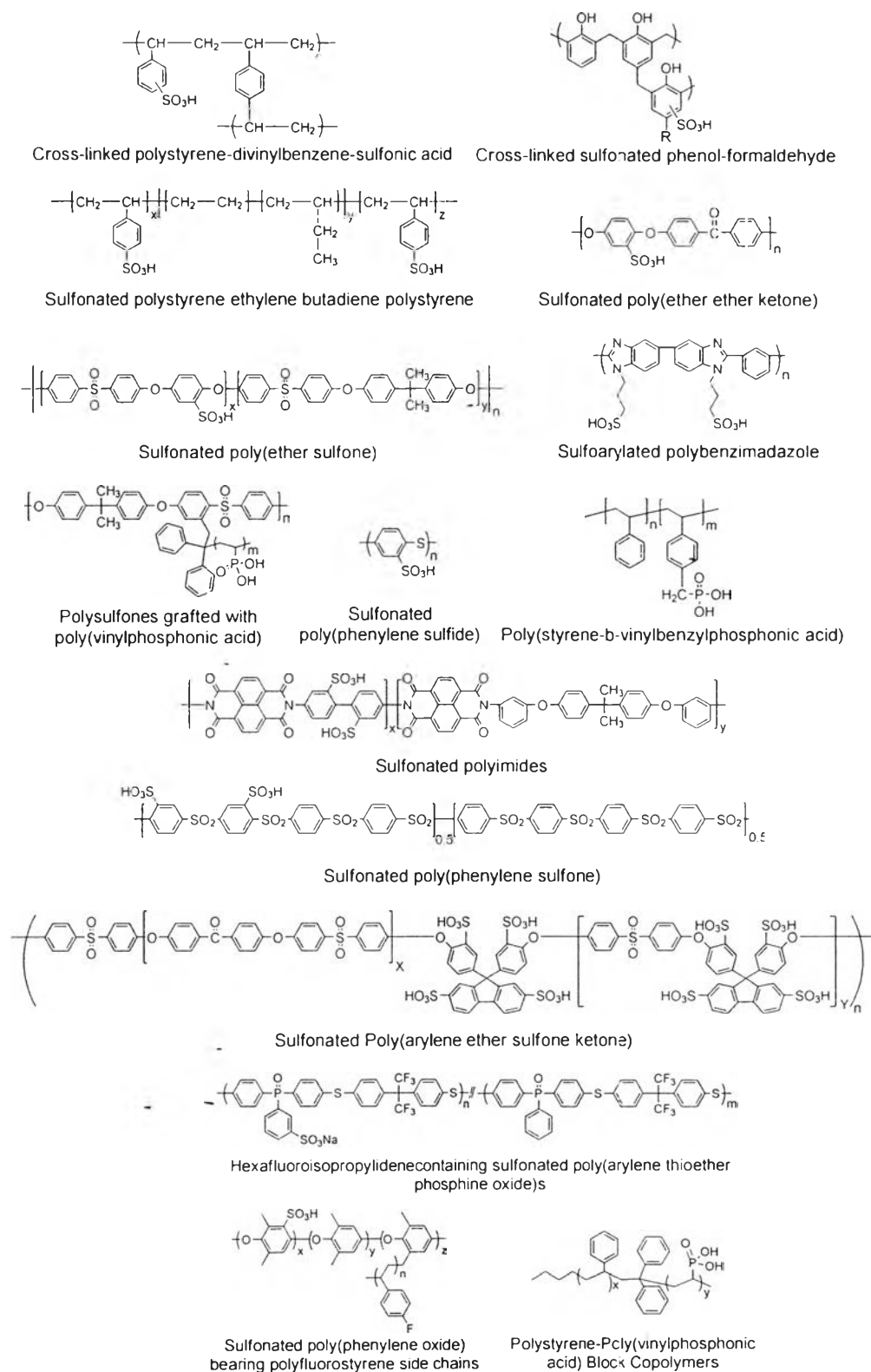
Moreover, dispersion of other inorganic materials such as silicon dioxide (SiO<sub>2</sub>) (Adjemian *et al.*, 2002; Adjemian *et al.*, 2006), titanium dioxide (TiO<sub>2</sub>) (Adjemian *et al.*, 2006; Jian-hua *et al.*, 2008; Zhengbang *et al.*, 2011), zirconium dioxide (ZrO<sub>2</sub>) (Saccà *et al.*, 2006), and zirconium phosphate (ZrP) (Bauer and Willert-Porada, 2005; Arbizzani *et al.*, 2010), etc. in the PTFE membranes not only retain water at elevated temperature but also improve mechanical properties were investigated. A significant improvement in proton conductivity at elevated temperature was found in PFSA incorporating perfluorinated ionomers and

heteropolyacids such as phosphotungstic acid, phosphomolybdenic acid, phosphotriphosphoric acid, and cesium hydrogen salt of heteropolyacids (Xu *et al.*, 2005; Ramani *et al.*, 2006). Tazi and Savadogo prepared the composite membrane of Nafion<sup>®</sup> 117 with the incorporation of silicotungstic acid (SA) or thiophene (TH) in order to enhance the ionic conductivity and power density (Tazi and Savadogo, 2000). The highest current density of 810 mA cm<sup>-2</sup> at 600 mV was achieved from TH incorporated Nafion<sup>®</sup> 117 while that of Nafion<sup>®</sup> 117 was only 640 mA cm<sup>-2</sup>.

It is important to note that the addition of additives might induce phase separation, pores, roughness, etc., resulting in defects of membranes. Gosalawit and coworkers demonstrated an approach to develop miscibility between silica and Nafion<sup>®</sup> (Gosalawit *et al.*, 2006). The fact that the structure of Krytox is similar to Nafion<sup>®</sup>, a coupling reaction between silica and Krytox brought not only well-dispersed silica in the membrane without phase separation but also an enhancement of water retention and thermal stability. An addition of 5 wt% Krytox-Si in Nafion<sup>®</sup> was found to maintain the proton conductivity at 10<sup>-3</sup> S cm<sup>-1</sup> at 130 °C.

Currently, acid-functionalized aromatic membranes, e.g. sulfonated poly(ether ether ketone) (Zaidi *et al.*, 2000), sulfonated poly(ether sulfone) (Wang *et al.*, 2002), polysulfones grafted with poly(vinylphosphonic acid) (Parvole and Jannasch, 2008), sulfoarylated polybenzimidazole (Kawahara *et al.*, 2000), sulfonated polyimides (Genies *et al.*, 2001), and sulfonated poly(phenylene sulfide) (Miyatake *et al.*, 1996) (Figure 2.3) have been widely investigated for PEM owing to their good thermal, mechanical, and chemical stabilities with affordable cost and wide availability.

Sulfonated poly(ether ether ketone) (SPEEK) is one of the most successful aromatic PEMs due to its good performance in conducting protons and reducing methanol crossover. SPEEK composite membranes blended with heteropolyacids, i.e., tungstophosphoric acid (TPA) and molybdophosphoric acid (MPA) were reported about their significant thermal stability ( $T_d$  above 250 °C) and mechanical stability with good proton conductivity either at room temperature (10<sup>-2</sup> S cm<sup>-1</sup>) or above 100 °C (10<sup>-1</sup> S cm<sup>-1</sup>) (Zaidi *et al.*, 2000). It should be noted that the proton conductivity of SPEEK depends on the degree of sulfonation (Gosalawit *et al.*, 2009).



**Figure 2.3** Aromatic polymers (Miyatake *et al.*, 1996; Kawahara *et al.*, 2000; Zaidi *et al.*, 2000; Genies *et al.*, 2001; Wang *et al.*, 2002; Parvole and Jannasch, 2008).

### 2.2.2 Anhydrous-based Membranes

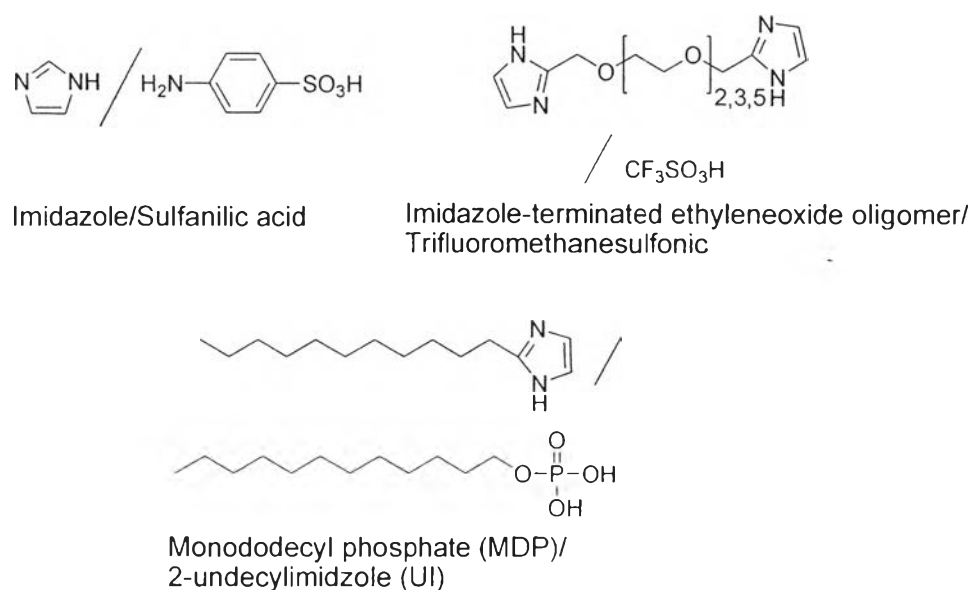
As well known, an increase of operating temperature to more than 120 °C leads to a significant improvement in CO tolerant of electrode catalysts, especially platinum, resulting in applicability of hydrogen gas obtained from reforming process (Yang *et al.*, 2001). Proton movement acceleration at higher temperature also provides a higher proton conductivity. However, evaporation of water inside the-membrane limits working temperature to be lower than 100 °C. This leads to a limitation of hydrous-based membrane, therefore many researchers focus on alternative polymers for PEMFC which functions in water-free or anhydrous conditions (Beuscher *et al.*, 2005).

Heterocycles are potential compounds as proton transfer channels due to (i) amphoteric behavior which can either donate or accept protons and (ii) high thermal stability leading to a development of heterocycles to use as proton conductive species instead of water in anhydrous system. Kreuer and coworkers investigated the use of heterocycles i.e., imidazole, and pyrazole as acidic proton transfer species (Kreuer *et al.*, 1998). Imidazole is one of the simplest heteroaromatic compounds that have been successively studied as proton conductive species due to its melting point and boiling point at 90 °C and 256 °C, respectively. Proton transfer mechanism of the neat imidazole was reported by Münch *et al.*, 2001. The mechanism involved with a diffusion of excess protons in the form of proton transfer and local cooperative reorientation was proposed. Consequently, investigations of heterocycles based PEMFC, e.g., mixing imidazole derivatives as a proton conductive additive, conjugating on polymer backbone (imidazole side chain) and heterocycles on polymer backbone proved that imidazoles effectively function in proton conductivity. The fact that imidazole and other derivatives for anhydrous PEM mostly require protonic sources to initiate proton transfer.

For type I (Figure 2.4), imidazole derivatives mixed with acids were studied to understand how proton transfer occurs through heterocyclic structure. Kreuer and coworkers showed that imidazole acts as proton donor-acceptor in the proton transfer process as observed its conductivity increased with temperature up to 120 °C ( $\sim 2 \Omega^{-1} \cdot \text{cm}^{-1} \cdot \text{K}$ ) (Kreuer *et al.*, 1998). When acids protonated imidazoles formed, it allows an enhancement of proton conductivity. Schuster and coworkers



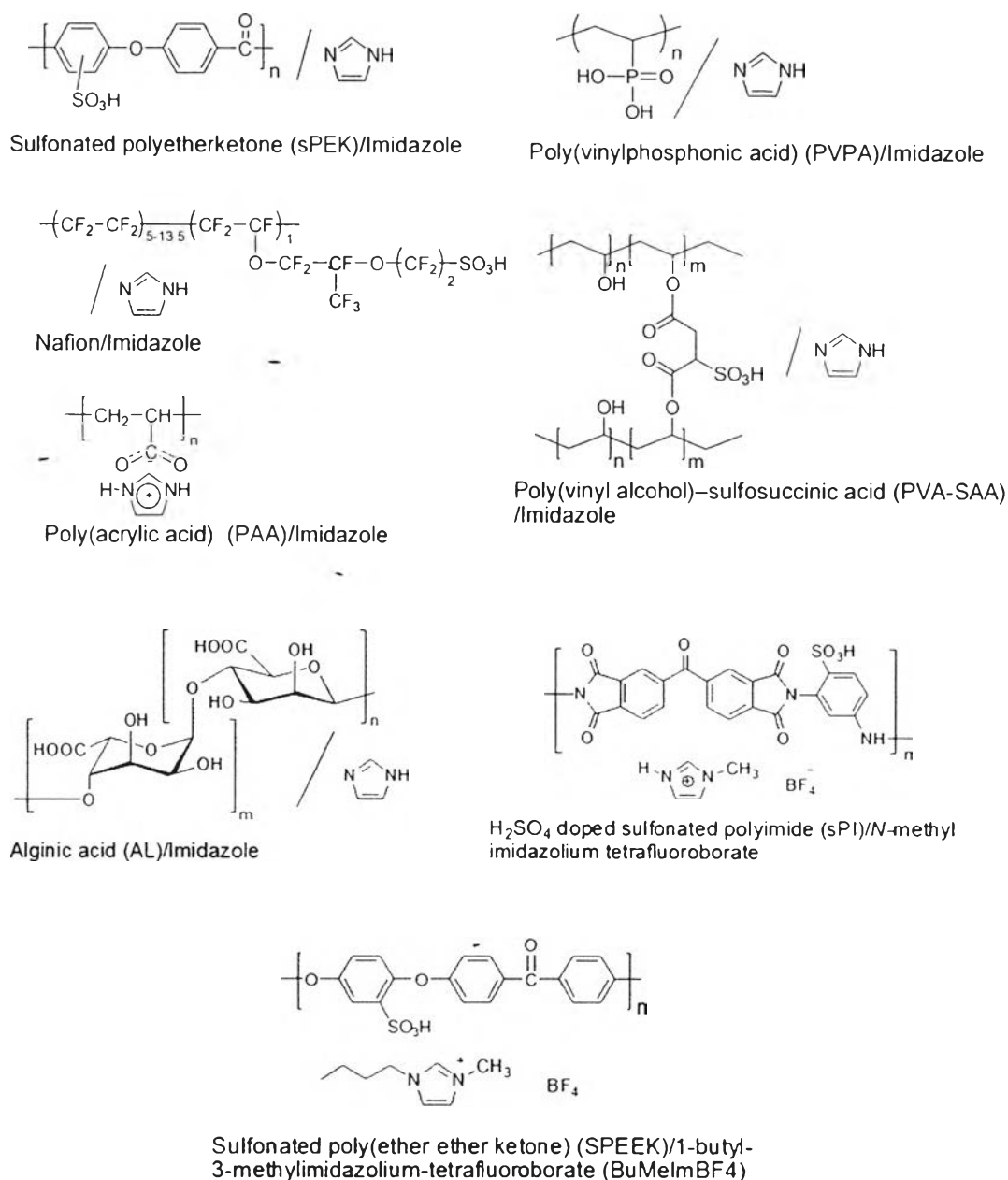
functionalized imidazoles onto ethylene oxide oligomers and demonstrated proton transfer of immobilized heterocycles along hydrogen bond pattern as a result of local dynamics of aggregated structures (Schuster *et al.*, 2001). Proton conductive pathway of self-assembled acid-base composite was investigated through a case study of acidic surfactant monododecyl phosphate (MDP) and basic surfactant 2-undecylimidzole (UI) system (Yamada and Honma, 2004). The ordered molecular arrangement of UI-MDP resulted in-lamellar packing structure with two-dimensions of proton conducting pathway.



**Figure 2.4** Imidazole-based compounds for PEMFC: type I-mixing imidazole derivatives with other species.

In the case of type II (Figure 2.5), as reviewed in Table 1, imidazole derivatives were developed as anhydrous membranes by incorporated in the polymer matrices, for example, sulfonated poly ether ketone (SPEK), Nafion<sup>®</sup>, poly(acrylic acid) (PAA), poly(vinylphosphonic acid) (PVPA), poly(vinyl alcohol)-sulfosuccinic acid (PVA-SAA), alginic acid (AL), sulfonated poly(ether ether ketone) (SPEEK), and sulfonated polyimide (SPI). The blend membranes showed the maximum proton conductivities in the range of  $10^{-1}$ - $10^{-3}$  S  $\text{cm}^{-1}$  at high temperature ( $>120$  C $^{\circ}$ ). The properties of imidazole as solvent for acidic proton transfer in polymer matrix of

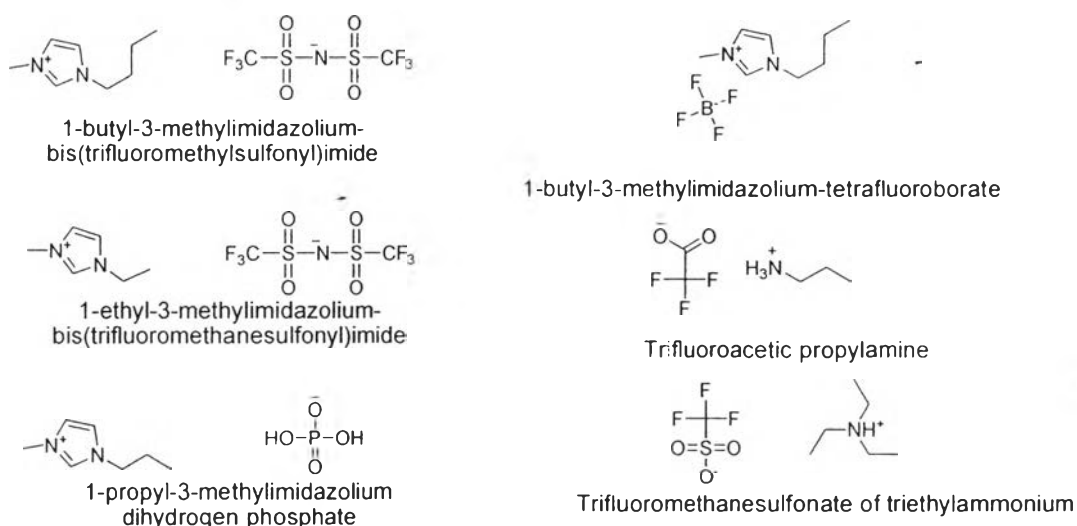
sulfonated poly ether ketone were studied (Kreuer *et al.*, 1998). It was found that imidazole, acting as proton donor and acceptor, performed similar behavior to water in proton transfer process. The proton conductivity of the system increased with an increase of imidazole concentration and temperature. Up to 150 °C, sulfonated poly (ether ketone) with the mole number of imidazole for 6.7 times to that of SO<sub>3</sub>H showed a higher conductivity than the pure sulfonated poly ether ketone saturated with water. This indicated that the ionic conductivity was based on intermolecular proton transfer reactions rather than self diffusion belonging to all protons of imidazole including acid protons.



**Figure 2.5** Imidazole-based compounds for PEMFC: type II-incorporating into polymer matrices.

Recently, ionic liquids, liquid salts at room temperature consisting of organic cation and inorganic anion, as thermally stable charge carrier to initiate proton conductivity in high temperature PEM under anhydrous condition have received much more attention. Imidazolium salts (*N*-methyl imidazolium

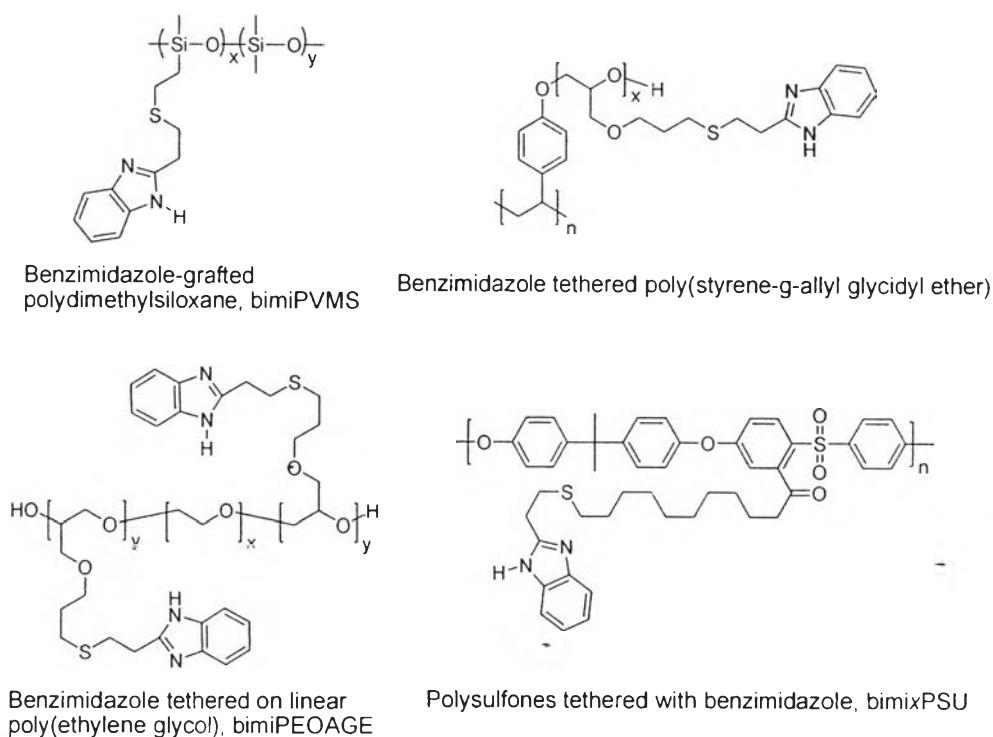
tetrafluoroborate (MeIm-BF<sub>4</sub>) (Deligöz and Yılmazoğlu, 2011), 1-butyl-3-methylimidazolium-tetrafluoroborate (BuMeImBF<sub>4</sub>) (Li *et al.*, 2012), 1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (BMI-BTSI) (Subianto *et al.*, 2009), 1-ethyl-3-methylimidazolium-bis(trifluoromethanesulfonyl) imide (EMI-TFSI) (Lakshminarayana and Nogami, 2010), and 1-propyl-3-methylimidazolium dihydrogen phosphate) (Ye *et al.*, 2008) and ammonium salts (trifluoroacetic propylamine (Che *et al.*, 2008) and trifluoromethanesulfonate of triethylammonium (TEA-TF) (Di Noto *et al.*, 2010)) are examples of ionic liquids used in PEM (Figure 2.6). Noto and coworkers proposed the use of TEA-TF in Nafion<sup>®</sup> membrane improved mechanical and thermal properties including water uptake (Di Noto *et al.*, 2010). Composite SPEEK membranes containing BuMeImBF<sub>4</sub> were found to show the highest ionic conductivity ( $1.04 \times 10^{-2}$  S cm<sup>-1</sup> at 170 °C under anhydrous conditions) when using *N,N'*-dimethylformamide (DMF) for casting the membranes compared to other solvents, i.e. *N,N'*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP) (Li *et al.*, 2012). At that time, DMF might induce the formation of inter-microchannel connected ionic clusters to facilitate proton transfer.



**Figure 2.6** Imidazole-based compounds for PEMFC: type III-ionic liquids.

Persson *et al.* developed various types of benzimidazole tethered polymer chains (Type III) via thiol-ene coupling reaction, i.e. benzimidazole-grafted

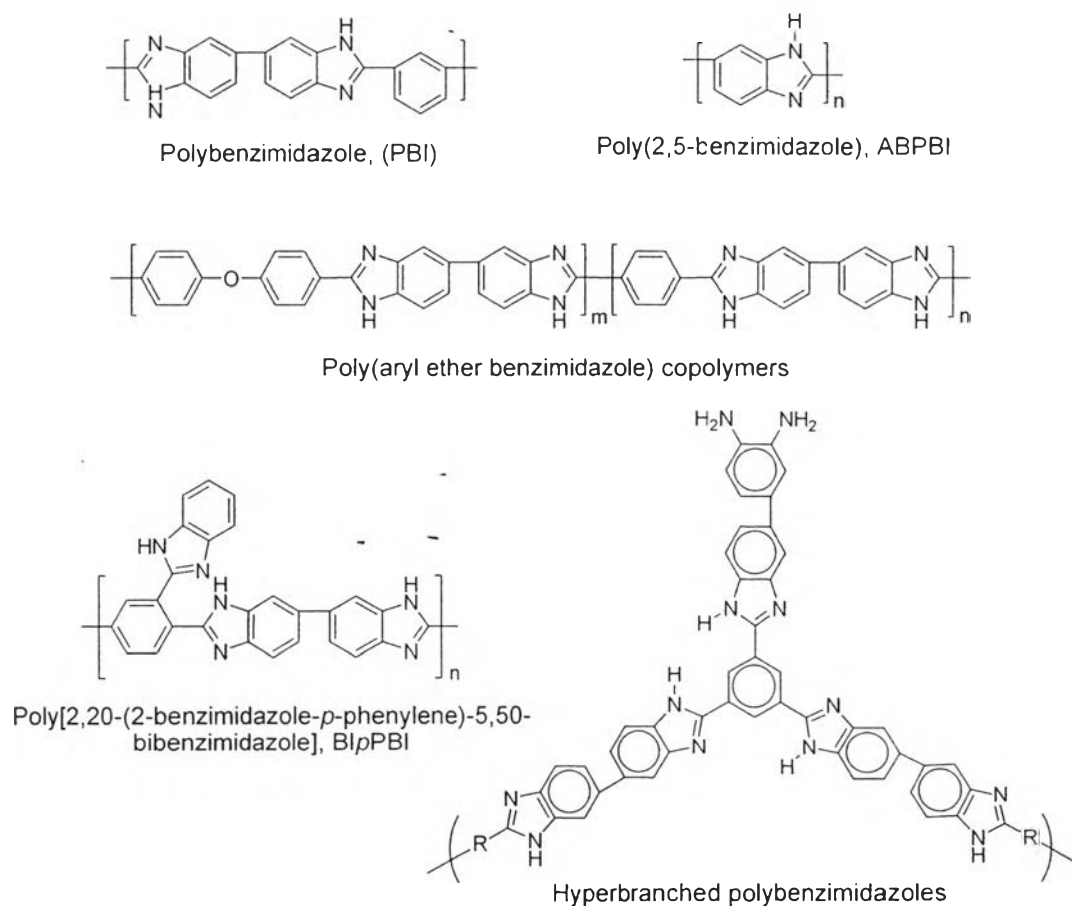
on polydimethylsiloxane (bimiPVMS) (Persson and Jannasch, 2005), benzimidazole tethered on linear poly(ethylene glycol) (bimiPEOAGE) (Persson and Jannasch, 2006), benzimidazole tethered poly(styrene-g-allyl glycidyl ether), (bimiPSAGEx) (Persson and Jannasch, 2006), and polysulfones tethered with benzimidazole (bimixPSU) (Figure 2.7) (Persson *et al.*, 2006). Considering bimiPVMS with various degrees of benzimidazole functionalities, it was found that the glass transition temperature ( $T_g$ ) increased because of inter- and intramolecular hydrogen bonds among benzimidazole units (Persson and Jannasch, 2005). Proton transfer efficiency of the bimiPVMS membranes was found to be promoted when the polymers showed high segmental mobility (low  $T_g$ ) at low temperature (60 °C) and high benzimidazole concentration at high temperature (140 °C). However, thermal stability of the bimiPVMS membrane was limited at 165 °C. The study of bimiPEOAGE triblock copolymer membranes also showed that both segmental mobility and benzimidazole concentration were the main factors controlling proton conductivity with an improvement of the thermal stability as high as 210 °C (Persson and Jannasch, 2005). Persson and coworkers also reported that bimiPSAGE7.0 with lower  $T_g$  ( $T_g = 50$  °C) showed a higher proton conductivity than bimiPSAGE2.4 ( $T_g = 57$  °C) especially at low temperature (Persson and Jannasch, 2005). For bimixPSU systems, it was found that their proton conductivities increased with increasing benzimidazole substitution. However, as a result of low concentration of benzimidazole units, the percolation of hydrogen bond network was not high enough to allow an efficient proton transfer, resulting in proton conductivity of  $\sim 10^{-9}$  S cm<sup>-1</sup> at 180 °C.



**Figure 2.7** Imidazole-based compounds for PEMFC: type III-side chain structures.

For type IV (Figure 2.8), polybenzimidazole (PBI) which is a commercial available membrane frequently used in high temperature or anhydrous PEMFC since it illustrates high thermal, chemical, oxidative, and mechanical stabilities as well as good proton conductivity ( $\sim 10^{-1}$  S cm $^{-1}$  under acid treatment even at temperature up to 200 °C) (Wainright *et al.*, 1995; Bouchet and Siebert, 1999; Xiao *et al.*, 2005). PBI was synthesized from polycondensation of 3,3',4,4'-biphenyltetramine and terephthalic acid or isophthalic acid in polyphosphoric acid (PPA) to obtain *p*PBI and *m*PBI, respectively (Lee *et al.*, 2010). Phosphoric acid-doped PBI is the most successful one as it showed the proton conductivity as high as  $10^{-1}$  S cm $^{-1}$  at the temperature more than 100 °C. When the polymer was mixed with acid, protonation of PBI was accomplished under strong hydrogen bond formation between PBI and acid. Its proton conductivity according to Arrhenius behavior under the temperature in the range of 25 °C to 130 °C indicated the proton transfer under Grotthuss mechanism (Lee *et al.*, 2010). Jiang and coworkers suggested a significant role of tridecyl phosphate (TP) in increasing proton conductivity with less migration

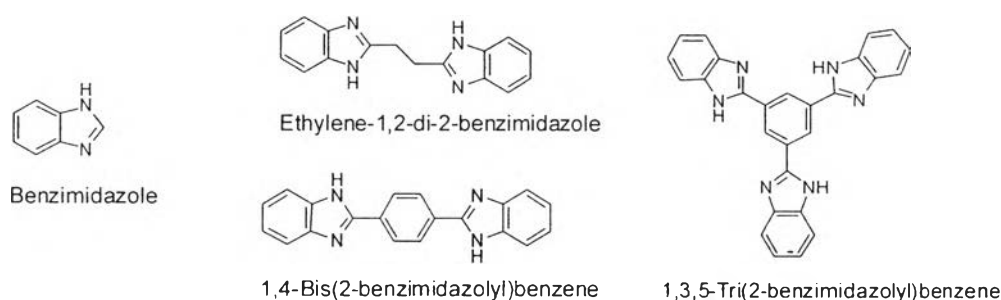
as compared to that of  $\text{H}_3\text{PO}_4$  in PBI. For example, it was found that the blending content of TP and  $\text{H}_3\text{PO}_4$  for 1.8 mol per PBI repeating unit brought the proton conductivity for  $10^{-4} \text{ S cm}^{-1}$  and  $10^{-5} \text{ S cm}^{-1}$  at  $140 \text{ }^\circ\text{C}$ , respectively (Jiang *et al.*, 2008). Although PBI, especially acid-doped one showed a good performance in proton conduction at high temperature, some drawbacks were reported e.g. the difficulty of the preparation of high molecular weight PBI, the polymer solubility, the membrane durability, the limitation of acid doping amount, and the retention of acid during operation, etc. Modified PBIs such as sulfonated PBI (SPBI) (Mader and Benicewicz, 2010), epoxy-based cross-linked PBI (Wang *et al.*, 2011), poly(aryl ether benzimidazole) copolymers (Kim *et al.*, 2008), poly[2,20-(2-benzimidazole-*p*-phenylene)-5,50-bibenzimidazole] (BIpPBI) (Kim *et al.*, 2009), and hyperbranched polybenzimidazoles (HBPBI) (Xu *et al.*, 2007) were reported as alternative materials



**Figure 2.8** Imidazole-based compounds for PEMFC: type IV-main chain structures.

### 2.3 Fundamental Study of Model Compounds Based on Heterocycles Related to Proton Conductivity

To understand proton conductivity performance based on structure, Totsatitpaisan et al. studied a series of benzimidazole model compounds with varied numbers of benzimidazole units, i.e. mono-, di-, and tri-functional benzimidazole model compounds to investigate how the structures develop their hydrogen bond systems to favor the proton transfer (Totsatitpaisan *et al.*, 2008; Pangon *et al.*, 2011). Single crystal analysis revealed that hydrogen bond systems of the model compounds were developed from lamella hydrogen bond network in the case of mono- and di-functional benzimidazoles to columnar hydrogen bond network in the case of tri-functional benzimidazole. Proton conductivities of the model compounds were evaluated by doping them with PPA to find that the proton conductivity was the highest for tri-functional type ( $7.8 \times 10^{-2} \text{ S cm}^{-1}$  at  $170 \text{ }^\circ\text{C}$ ). By blending this tri-functional compound (15 phr) to the SPEEK, the conductivity became as high as  $8.1 \times 10^{-4} \text{ S cm}^{-1}$  at  $120 \text{ }^\circ\text{C}$  or 1.3 times higher than the pure one (Figure 2.9).

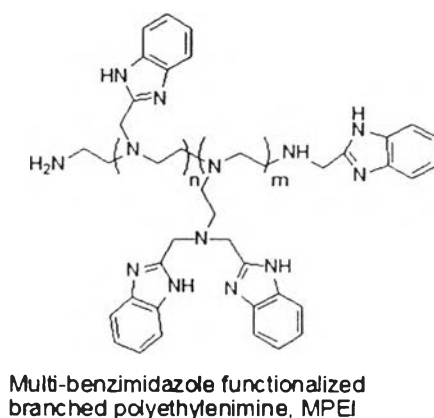


**Figure 2.9** Series of benzimidazole model compounds with varied numbers of benzimidazole units (Totsatitpaisan *et al.*, 2008; Pangon *et al.*, 2011).

Based on this research, Pangon and coworkers developed benzimidazoles branched (MPEI) with varied benzimidazole substitution for 19.7-90.5% and found that proton conductivity was enhanced through a higher molecular mobility of the polymer chain under hydrogen bond network (Figure 2.10). They found that MPEI with a benzimidazole content for 19.7% allowed preferable proton conductivity as



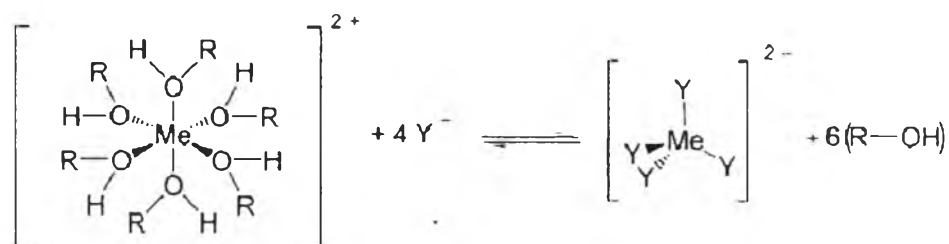
high as  $10^{-4}$  S  $\text{cm}^{-1}$  at 190 °C. Therefore, they concluded that this level of benzimidazole substitution brought a good balance between hydrogen bond and chain mobility to favor the proton movement (Pangon *et al.*, 2011).



**Figure 2.10** Structure of multi-benzimidazole functionalized branched polyethylenimine (MPEI) (Pangon *et al.*, 2011).

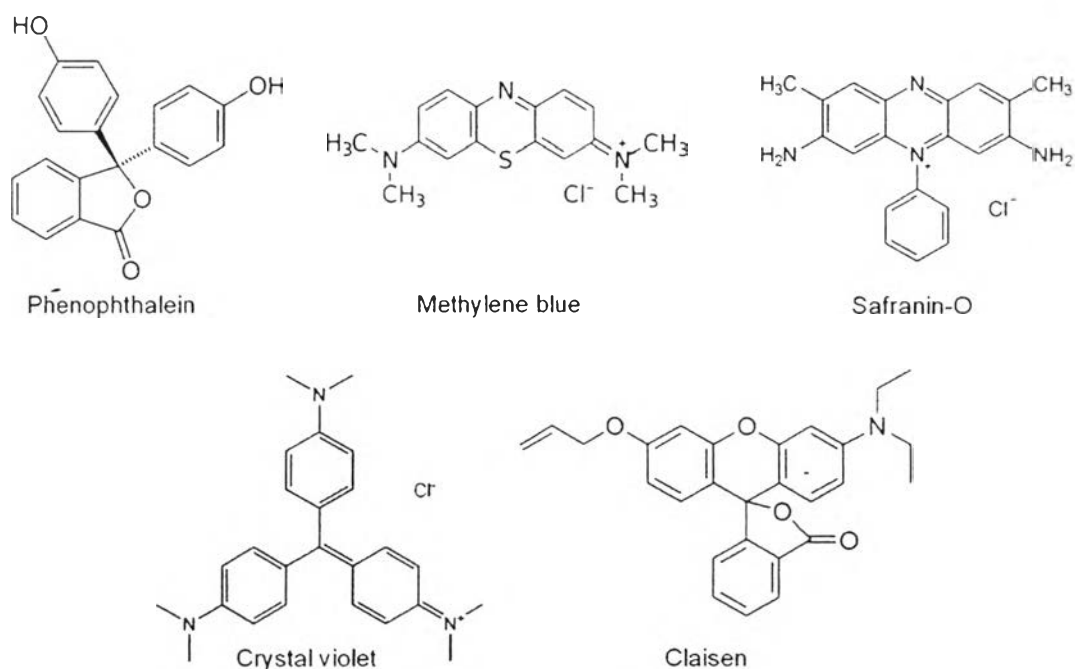
## 2.4 Thermochromic Polymer

Thermochromic polymers are the materials that can change visible optical properties related to temperature. With this property, thermochromic materials have been applied in sensors and actuators applications (Wilson *et al.*, 2007; Kar *et al.*, 2009). Among a various types of materials, interaction of molecules inside materials is a main factor providing this property.  $\Pi$ - $\pi$  interaction is significant interaction to generate color for thermochromic materials (M. Raimundo Jr and Narayanaswamy, 1999; Baron and Elie, 2003). For small molecules, thermochromic property has been approached by ligand exchange system and leuco-dye compounds. Thermochromic activity of ligand exchange system results in a reversible change in absorbance of electromagnetic radiation as a function of temperature (Figure 2.11) (Patel *et al.*, 1979; Druy and Seymour, 1983; Wenz *et al.*, 1984; Baron and Elie, 2003; Zhao and Wang, 2007; Seeboth *et al.*, 2010).



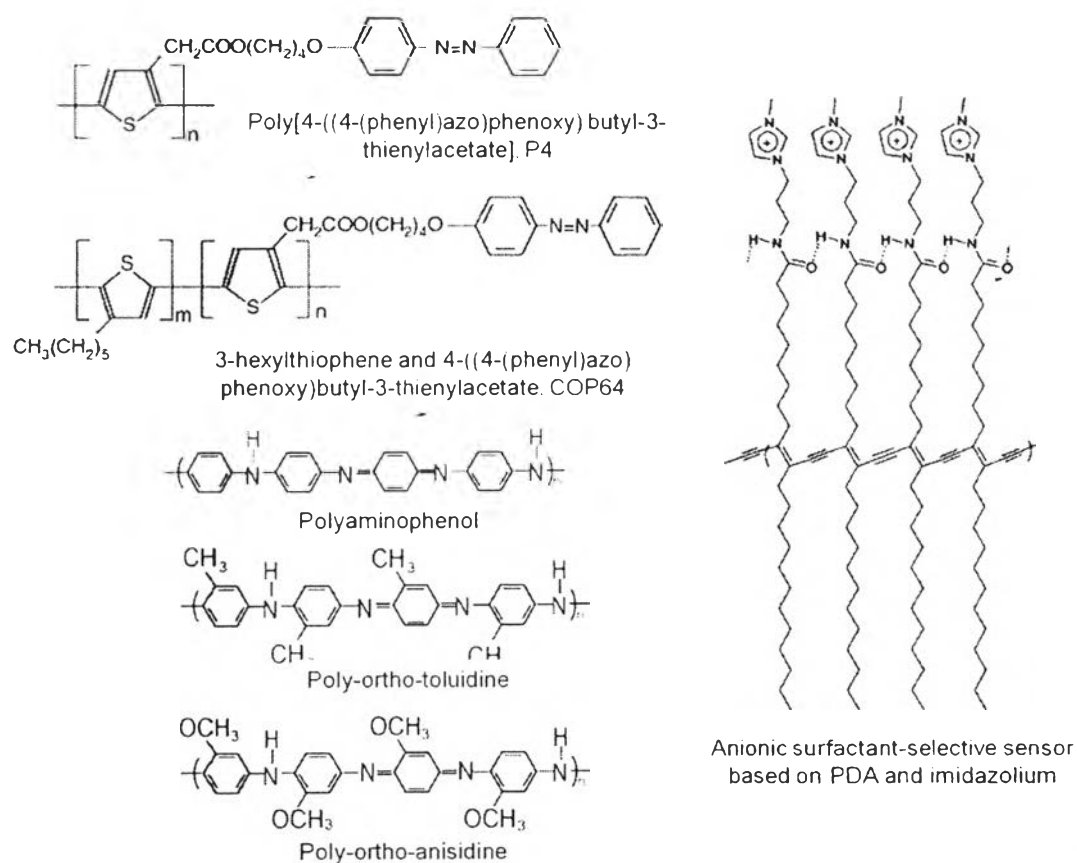
**Figure 2.11** Ligand exchange thermochromic system mechanism (Seeboth *et al.*, 2010).

In addition, there are many reports about using leuco-dye compounds as thermochromic materials such as, rearrangement of claisen, bicomponent systems of leuco-dye and biphenyl compounds, and others (Figure 2.12). These dye compounds performs optical transition with temperature sensitivity combining with acid-base equilibrium (Baron and Elie, 2003; Seeboth *et al.*, 2010).



**Figure 2.12** Leuco dye compounds (Baron and Elie, 2003; Seeboth *et al.*, 2010).

In case of polymer materials, interaction between molecules is also important similar to small molecules. Polymers containing aromatic ring and conjugated bond system are promising polymers performing as thermochromic materials. Polymer containing conjugated bond such as polydiacetylene (Patel *et al.*, 1979; Wenz *et al.*, 1984), polythiophene, and derivatives of polythiophene (Druy and Seymour, 1983; Zhao and Wang, 2007) can show thermochromic property based on interaction of  $\pi$  bond (figure 2.13). It is important to note that polymer electrolyte membrane has been used as thermochromic materials. For example, Nafion<sup>®</sup> membrane as known as polymer electrolyte was mixed with dye compounds such as phenolphthalein, methylene blue, safranin-O, and crystal violet. This blended membrane can perform color by using acid-base equilibrium with temperature sensitivity (M. Raimundo Jr and Narayanaswamy, 1999; Baron and Elie, 2003).



**Figure 2.13** Thermochromic responsive polymer based on aromatic and conjugated polymer (Konopelnik *et al.*, 2005; Zhao and Wang, 2007; Chen *et al.*, 2010).

Considering based on structure related to thermochromic property, aromatic rings and  $\pi$ -conjugated bond are a key factor (Alvey *et al.*, 2010). According to thermochromic properties, it depends on interaction of molecules including hydrogen bond network or/and  $\pi$ - $\pi$  interaction based on structure of compound itself, therefore, thermochromic polymer materials have to have these requirements (Rannou *et al.*, 2002; Konopelnik *et al.*, 2005).

## 2.5 Points of Study

Heterocycles are attractive molecules for using as electrolyte membranes under high temperature. There are several advantages such as their proton conductive behavior and high boiling point compared with water, and ease of molecular design and modification. Although many types of heterocyclic based membranes have been developed for several decades, their conductive properties are still limited for the practical use.

Based on our viewpoint, an understanding of the molecular structures of the materials as well as the factors related to the proton transfer efficiency including hydrogen bond network and molecular mobility would lead us to a fundamental knowledge for PEM development. The present work proposes a molecular design containing alkyl urocanates based on ultimate goal to enhance the proton conductivity of the heterocyclic membrane with a balance of hydrogen bond network and molecular mobility (Chapter III). In this work, a series of alkyl urocanates as model compounds are developed and the factors of hydrogen bond network formation and molecular mobility related to the proton conductivity are clarified. Moreover, we extend our work to the blended systems of their model compounds with an expectation to enhance the proton conductivity of the heterocyclic membrane based on a synergistic effect of water and imidazole molecules with optimization of hydrogen bond and molecular mobility (Chapter IV). In this work, blended systems are prepared and the synergistic effect of water and imidazole molecules based on molecular mobility and hydrogen bond interaction correlated with proton transfer effectiveness are investigated. In addition, our work are also covered another phenomenon of SPEEK as a thermochromic polymer. By specific preparation of SPEEK thin film; this might induce pre-orientation of SPEEK polymer chain to generate reversible thermochromic property under high temperature. In this work, temperature dependence with basic characterization such as FTIR, WAXD and UV-Vis are carried out to understand reversible thermochromic property under high temperature of SPEEK thin film (Chapter V).