



CHAPTER IV

PROTON DONOR AND ACCEPTOR POLYMER CHAINS UNDER LAYERED-BY-LAYERED STRUCTURE OF POLYMER ELECTROLYTE MEMBRANCE FUEL CELL (PEMFC)

4.1 Abstract

In order to improve the proton transfer channel efficiency and hydrogen bond network for enhancing the proton conductivity of membrane under anhydrous system at high temperature, the membrane is proposed under the concept of Layered-by-Layered (LBL) proton donor-acceptor with uniform molecular arrangement of heterocycles. In our system, poly (acrylic acid) as acid polymer and bezimidazole branching as basic polymer are designed as LBL structure whereas sulfonated poly (ether ether ketone) (SPEEK) is a substrate based on sulfonated aromatic hydrocarbon. The increment of proton donor-acceptor layers can be observed from scanning electron microscope (SEM) and thickness and weight changed. The highest proton conductivity is 1.378×10^{-5} S/cm at 130 °C for 4 bilayers (MPEI₄ / PAA₄).

Keywords: Layered-by-Layered Membrane, Proton Donor-Acceptor, Polymer Electrolyte Membrane

4.2 Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is an alternative energy source for using in many applications such as transportation, portable devices and power generators (Neburchilov *et al.*, 2007). Nafion[®] is the most reliable commercial membrane for PEMFC. However, the operation at high temperature state is limited due to evaporation of water clusters inside the membrane. Heterocyclic molecules are reported about the proton via hydrogen bond network (Munch *et al.*, 2001). Up to present, many researchers have reported about heterocyclic molecules such as benzimidazole, imidazole, pyrazole (Smitha *et al.*, 2006). Copolymers of 4,5-vinylimidazole and acrylic acid have been investigated with the concept of a single polymer chain with proton acceptor and donor groups (Jithunsa *et al.*, 2008). In addition, copolymer membrane gave the proton conductivity around 10^{-4} S/cm at 150 °C. Totsatitpaisan.P *et al.* (2008) proposed the systematic heterocyclic molecules from mono- to tri- functional benzimidazole units as the model compounds in order to investigate the relationship between the ordered structure and hydrogen bond network. The increase of number of benzimidazole units results in the more ordered structure and hydrogen bond which lead to enhancing proton conductivity.

It is important to note that the ordered structure of heterocyclic compounds and proton-donor acceptor play an important role to transfer the proton for PEM. Based on our knowledge, to enhance proton conductive performance of PEM, the proton transfer channel efficiency and hydrogen bond network are improved. Therefore, the concepts of proton donor-acceptor with uniform molecular arrangement are proposed. Layered-by-Layered (LBL) technique is the one of many approaches that can assemble the membrane to obtain ordered structure polymer membrane. Normally, this technique provides the uniform alternating layers, which can form the interaction between the layers with secondary forces such as hydrogen bond, electrostatic force, and stereocomplex (Zhang *et al.*, 2007). To increase proton conductivity of PEM, the hydrogen bond network and proton transfer channel is the key point. This work focuses on development of proton transfer efficiency of PEM under anhydrous system at high temperature state. In our system, it consists of poly (acrylic acid) as a proton donor and branching polybenzimidazole as a proton

acceptor, which lay on sulfonated poly (ether ether ketone) (SPEEK) membrane as a backbone part. The increment of proton donor-acceptor layers results in the proton transfer via hydrogen bond network efficiently which lead to the high proton conductivity.

4.3 Materials and Methods

4.3.1 Materials

Branched polyethylenimine (*bPEI*) (MW 25000 g mol⁻¹), 2-(chloromethyl) benzimidazole (MBz), were obtained from Aldrich Co (USA). Poly (ether ether ketone) powder was a gift from JJ-Degussa Chemical (Thailand) Ltd., Poly (acrylic acid) (PAA) was obtained from Fluka Chemical (Buchs, Switzerland). Potassium hydroxide (KOH), and dimethyl sulfoxide (DMSO) were purchased from Acros Co (Thailand). Hydrochloric acid (HCl) was bought from Labscan Co (Thailand).

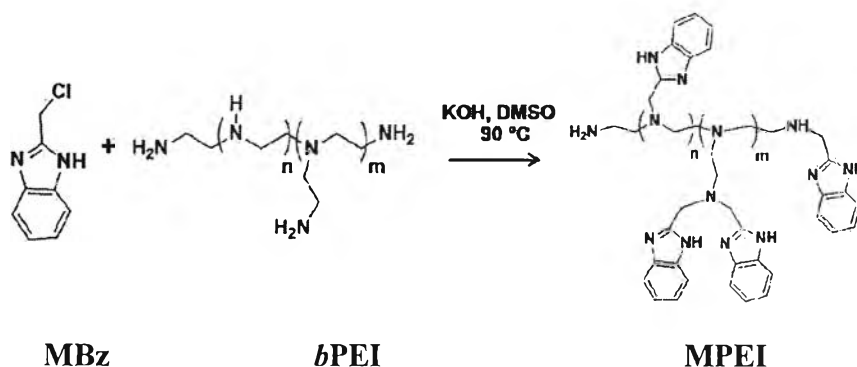
4.3.2 Polymer Syntheses and Membrane Preparation

4.3.2.1 Sulfonated Poly (Ether Ether Ketone) (SPEEK)

Poly (ether ether ketone) PEEK was dried in a hot air oven at 70 °C overnight before dissolving in 400 ml of concentrated sulfuric acid (96%) at room temperature under strong agitation for 24 hours. The polymer solution was precipitated into an excess amount of ice-cold water. The precipitates were collected and washed several times with deionized water until pH 7. The sediment was dried in an oven at 70 °C for 24 hours to obtain the yellow powder (SPEEK).

4.3.3 Multibenzimidazole Branched Polyethylenimine (MPEI)

Branched polyethylenimine (*bPEI*) (2 g, 46 mmol) was dissolve in DMSO (10 ml) and KOH (0.521 g, 9.3 mmol) was further added. The solution was stirred and heated at 90 °C for 30 min and DMSO solution (20 ml) containing 2-(chloromethyl benzimidazole) (MBz) (1.549 g, 9.3 mmol) was added dropwisely. After stirring at 90 °C under nitrogen atmosphere for 24 hours, the reaction mixture was cooled down to room temperature and neutralized with 1 M HCl. The product obtained was dialyzed in deionized water several times followed by freeze-drying to obtain multibenzimidazole branched polyethylenimine (MPEI).



Scheme 4.1

4.3.4 Preparation of SPEEK Membrane

A solution of SPEEK in DMSO (5% w/w) was cast on a glass mold which was constantly heated at 80 °C for 48 hours to obtain the membrane. The membrane was immersed in H₂SO₄ solution (1.0 M) at room temperature for 24 hours and dried in an oven at 60 °C for 24 hours.

4.3.5 Preparation of Basic Polymer Solution (MPEI)

MPEI was dissolved in methanol with concentration of 5% w/v and vigorously stirred at room temperature to obtain homogeneous solution.

4.3.6 Preparation of Acid Polymer Solution (PAA)

Poly (acrylic acid) was dissolved in methanol with concentration of 5% w/v and vigorously stirred at room temperature to obtain homogenous solution.

4.3.7 Layered-by-Layered Membrane Fabrication

SPEEK membrane was doped with 1M sulfuric acid (H₂SO₄) at room temperature for 24 hours. The membrane was cut in the dimension of 3 cm × 2 cm and was alternatively immersed in both basic and acid polymer solution followed by drying at room temperature to obtain multilayer polymer membrane. The membrane obtained was kept in the desiccators to control the humidity prior to use.

4.4 Characterizations

4.4.1 FTIR

The chemical structure of proton donor-acceptor polymer solution were recorded on a Thermo Nicolet Nexus 670 Fourier Transform Infrared Spectroscopy in range 4000 cm^{-1} - 650 cm^{-1} with 64 scans and a resolution of 4 cm^{-1} , ZnSe was used as the background material. ATR-FTIR mode was applied to the LBL SPEEK membrane so as to analyze the interaction between proton donor layers and proton acceptor layers. Spectra collection was performed using OMNIC program.

4.4.2 $^1\text{H-NMR}$

Nuclear magnetic resonance (NMR) spectra were obtained from a Bruker Avance 500 MHz NMR spectrometer. The samples were measured using DMSO-d₆ as a solvent to determine the degree sulfonation of SPEEK and analyze the chemical structure.

4.4.3 Layered-by-Layered Observation

4.4.3.1 *Thickness Gauge and Balance*

SPEEK membrane was measured and weighed by thickness gauge and four-digit balance every time after immersing in acid-base polymer solution to observe the change of membrane.

4.4.3.2 *Contact Angle*

The hydrophobic and hydrophilic properties of LBL SPEEK membrane at each step in the LBL assembly was measured by KRUSS DSA 10-MK2 Germany contact angle. Water dropped onto the membrane surface was interpreted by drop shape software.

4.4.3.3 *SEM*

The morphology of the LBL SPEEK membrane was investigated using a scanning electron microscope. The cross-section fractures of LBL SPEEK membrane were vacuum sputtered with a thin layer of platinum prior to the analysis.

4.4.4 Conductivity Measurement

The proton conductivity of LBL SPEEK membrane was measured by the impedance spectroscopy technique in the frequency range of 500000 Hz. Alternating current under the temperature range from 30 °C to 170 °C without humidity was applied. The conductivity (σ) of the sample was calculated from the impedance data by using the relation between $(\sigma) = d / RS$ where d and S are thickness and face area of the sample, respectively. R is the low intersect of the high frequency semi-circle on complex impedance.

4.5 Results and Discussion

4.5.1 Structural Characterization

4.5.1.1 *MPEI Structure*

In our system, MPEI was prepared from branched polyethylenimine and chloromethyl benzimidazole and the chemical structure was confirmed by FTIR technique and $^1\text{H-NMR}$. **Fig. 4.1** demonstrates the important peak of hydrogen bonded N-H at $3500\text{-}2400\text{ cm}^{-1}$, C-H stretching at 2936 cm^{-1} and 2819 cm^{-1} , C=N deformation at 1621 cm^{-1} , N-H deformation at 1537 cm^{-1} and C-H bending at 744 cm^{-1} . Moreover, NMR technique is also used to identify the MPEI structure. **Fig. 4.2** shows the $^1\text{H-NMR}$ spectrum of MPEI. The position of chemical shifts is 7.5 ppm (s, ArH), 7.1 ppm (s, ArH), 3.9 ppm (br, N-CH₂), and 2.3-2.9 ppm (br, N-CH₂).

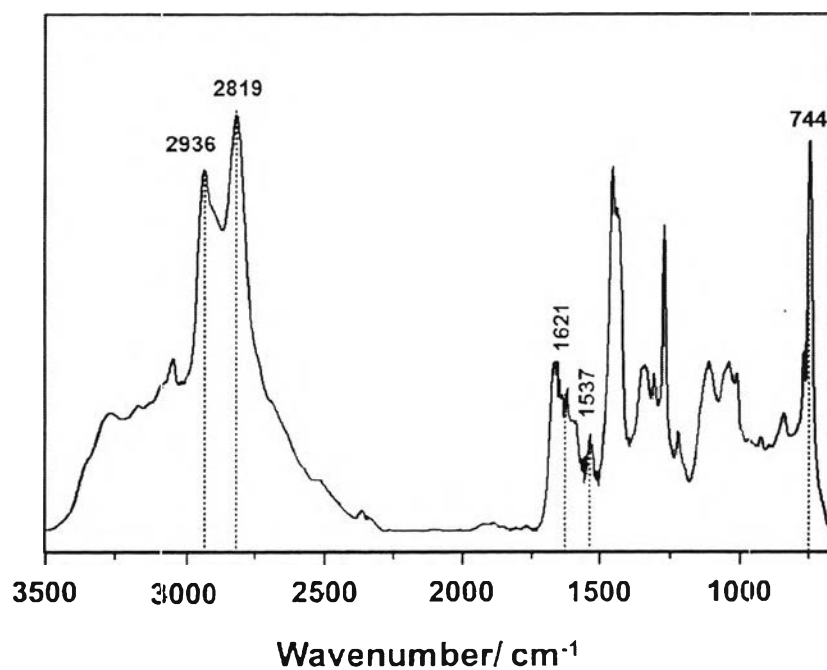


Figure 4.1 FTIR spectrum of multibenzimidazole branched polyethylenimine (MPEI).

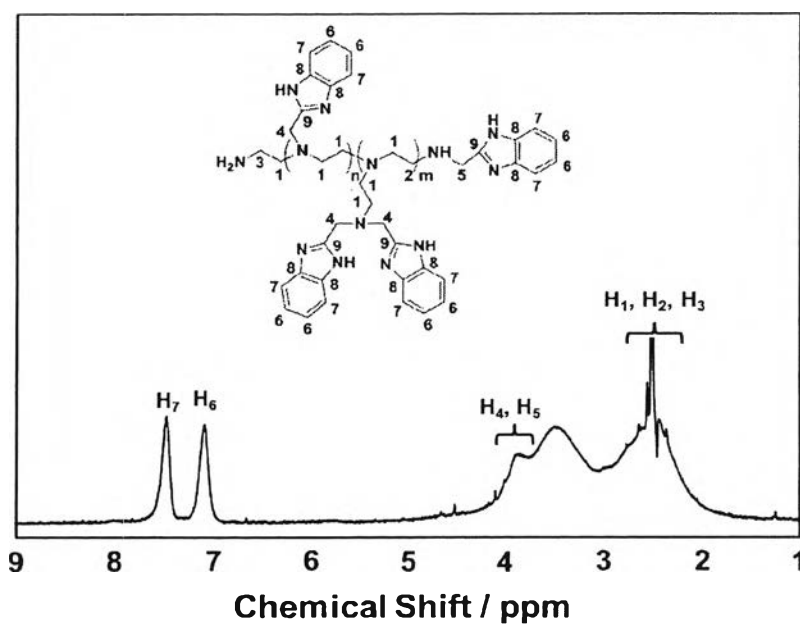


Figure 4.2 $^1\text{H-NMR}$ spectrum of MPEI.

4.5.1.2 SPEEK Structure

The FTIR spectra of SPEEK are shown in **Fig. 4.3** with peak assignment for the various functional groups. The important peaks of SPEEK are the asymmetric O=S=O stretch at 1217 cm^{-1} , the symmetric O=S=O stretch at 1073 cm^{-1} , S=O stretch at 707 cm^{-1} . Moreover, the absorption bands around 1468 cm^{-1} are aromatic C=C stretch while the absorption at 1642 cm^{-1} is assigned to be carbonyl groups.

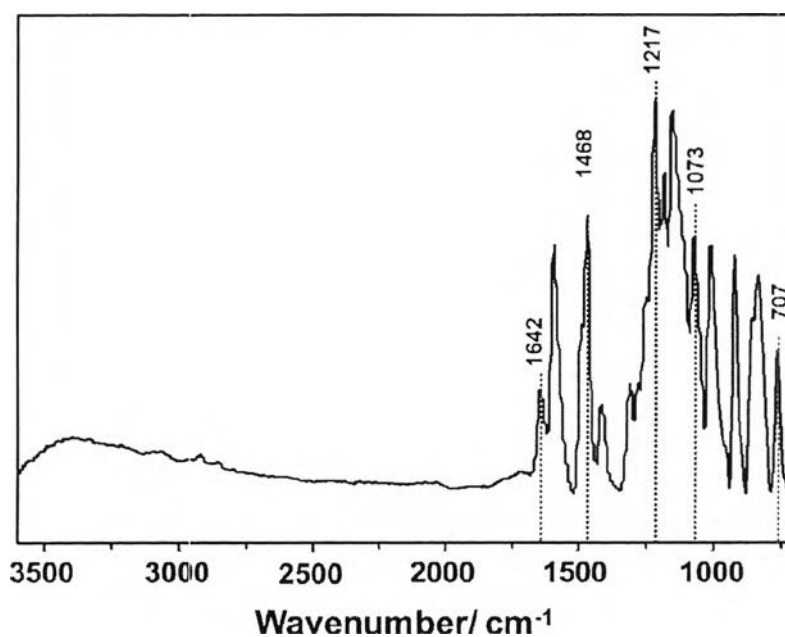


Figure 4.3 FTIR spectrum of sulfonated poly(ether ether ketone) (SPEEK).

4.5.1.3 Degree of Sulfonation

The degree of sulfonation can be controlled by reaction time and temperature. The degree of sulfonation is evaluated by $^1\text{H-NMR}$ technique. **Fig. 4.4** shows $^1\text{H-NMR}$ spectrum of SPEEK that the integration was used to determine the degree of sulfonation (DS) by using Eq (1).

$$DS (\%) = 100 \times [A_{H13} / [(A_{H5-H12} / 4) + A_{H1-H4} + A_{H13}] \times 3] \quad (1)$$

According to Eq. (1), this formula was calculated by proton species based on aromatic ring in SPEEK unit and PEEK unit. The degree of sulfonation was found to be 45% DS. In our system, the proton conductivity of SPEEK was studied by impedance spectroscopy. Alternating current under the temperature range from 30 °C to 170 °C without humidity was applied. The conductivity at 90 °C of SPEEK for 45% DS is 8.86×10^{-6} S/cm. An increase in temperature results in a significant reduction of the proton conductivity. This might be due to the dehydration of SPEEK membrane was occurred at the temperature above 90 °C

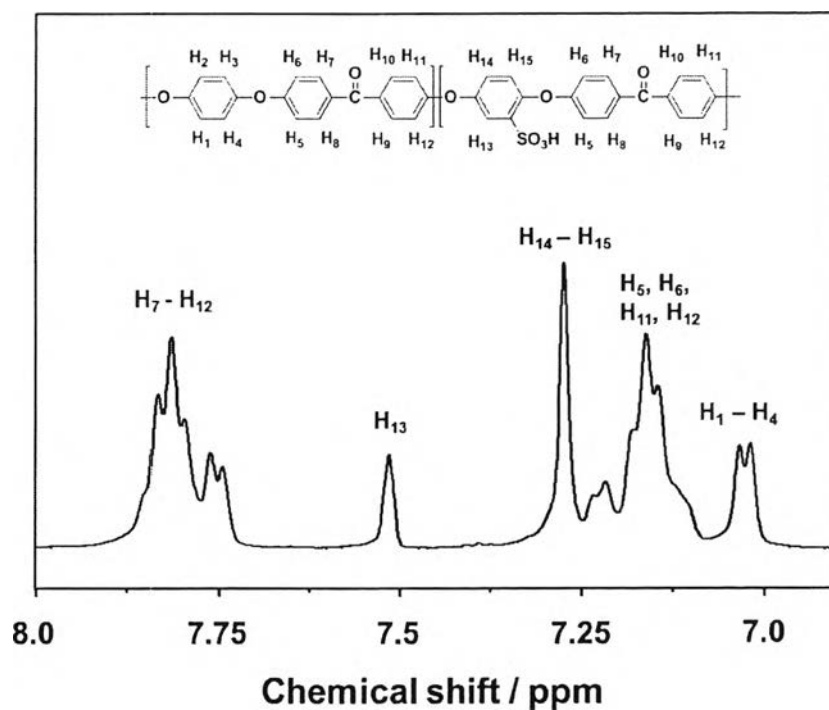


Figure 4.4 ^1H -NMR spectrum of SPEEK.

4.5.2 Layered-by-Layered Observation

4.5.2.1 Increment of Thickness and Weight

The multilayer of SPEEK membrane can be prepared by dipping cycle process. To prove the multilayer membrane formation, normally, the thickness and weight measurement by using thickness gauge and balance is the simple approaches. Herein, the multilayer of SPEEK membrane, which is immersed in poly (acrylic acid) (PAA) and MPEI solution with varied numbers of alternative layers, contains 1 layer (MPEI₁), 2 layers (MPEI₁ / PAA₁), 3 layers (MPEI₂ / PAA₁), 4 layers (MPEI₂ / PAA₂), 5 layers (MPEI₃ / PAA₂), 6 layers (MPEI₃ / PAA₃), 7 layers (MPEI₄ / PAA₃), 8 layers (MPEI₄ / PAA₄), respectively. **Fig. 4.5** and **Fig. 4.6** display the relation between the thickness and weight increment of LBL SPEEK membrane with varied number of proton donor-acceptor layers. This indicates that when the SPEEK membrane is immersed in acid-base polymer solution so as to form a layer, the thickness and weight of LBL SPEEK membrane is increased. It can be proved that the LBL SPEEK membrane formation is successful.

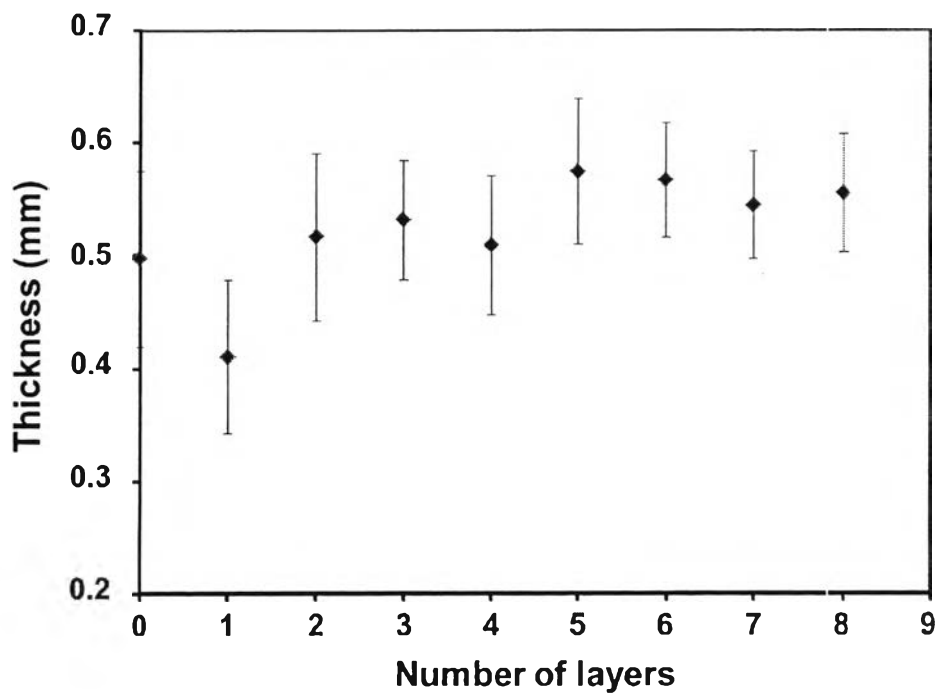


Figure 4.5 Thickness of LBL SPEEK membrane with varied number of layers.

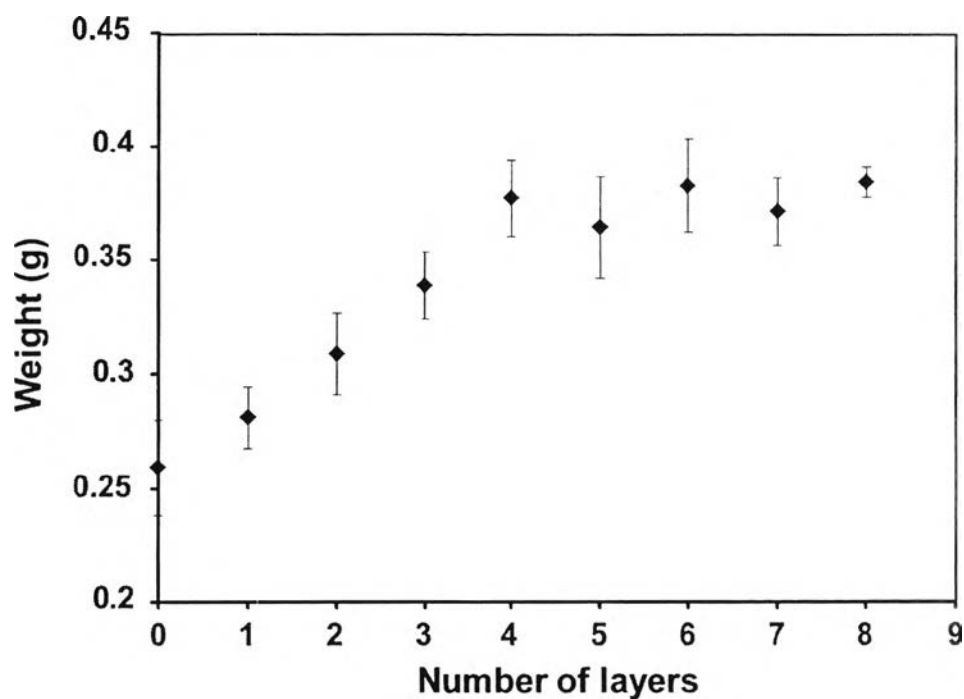


Figure 4.6 Weight of LBL SPEEK membrane with varied number of layers.

4.5.2.2 Contact Angle

The difference of hydrophobic and hydrophilic property between proton donor layers and proton acceptor layers is applied to prove the formation of LBL SPEEK membrane. **Fig. 4.7** demonstrates the plot of the LBL SPEEK membrane between poly (acrylic acid) as a proton donor layers and MPEI as a proton acceptor layers. It was found that the mean angle of MPEI as a proton acceptor layers is $75.8^\circ \pm 1.05$ while that of poly (acrylic acid) as a proton donor layers is $94.3^\circ \pm 1.35$. The angle changed in a zigzag pattern indicates that the formation of LBL SPEEK membrane can be successful by different chemical components.

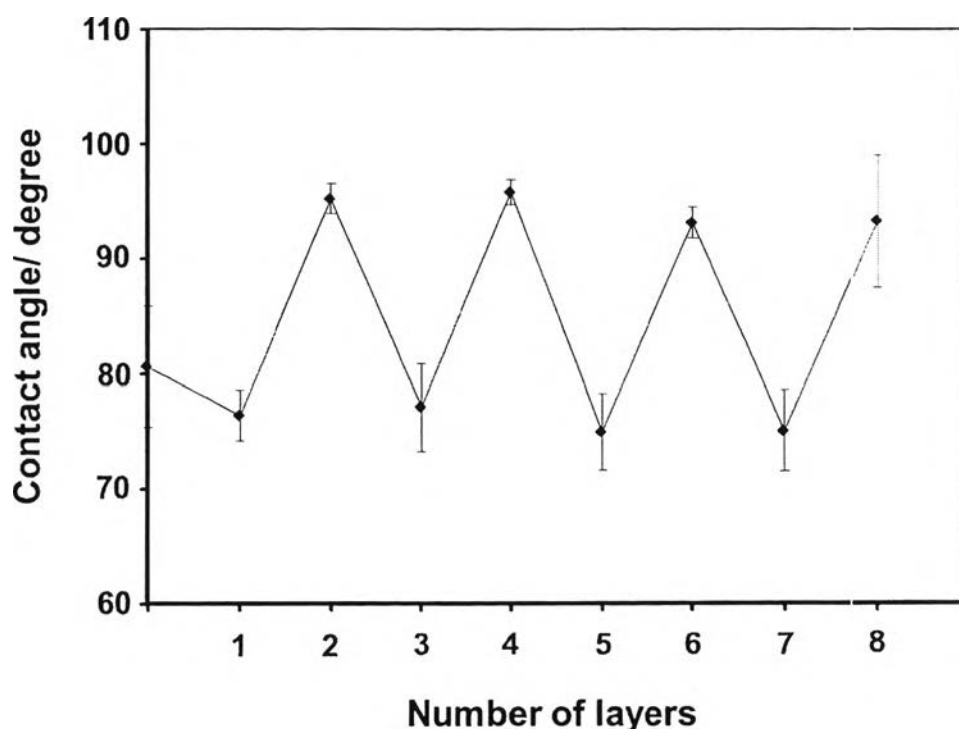


Figure 4.7 Plot of contact angle between MPEI layers and PAA layers.

4.5.2.3 Morphology of LBL SPEEK Membrane

The morphology of the LBL SPEEK membrane, which is covered with alternating proton donor-acceptor layers, has been investigated by scanning electron microscope (SEM). The SEM micrograph of the cross-section LBL SPEEK membrane is presented in **Fig. 4.8**. It was found that the proton donor-acceptor layers are capable of forming layer on SPEEK membrane as a substrate via dipping cycle process. The thickness of LBL SPEEK membrane can be manipulated by controlling the number of immersion times of the membrane in the acid-base polymer solution and concentration of acid-base polymer solution. From this micrograph, the LBL SPEEK membranes containing no layer coating, 1 bilayer (MPEI₁ / PAA₁), 2 bilayers (MPEI₂ / PAA₂), 3 bilayers (MPEI₃ / PAA₃) and 4 bilayers (MPEI₄ / PAA₄) are observed. The cross-section of LBL SPEEK membranes, which can observe from SEM technique, shows some evidence so as to confirm the LBL formation.

The comparison between no layer and layer shows the different thickness of cross-section. It might be implied that the LBL formation can be occurred.

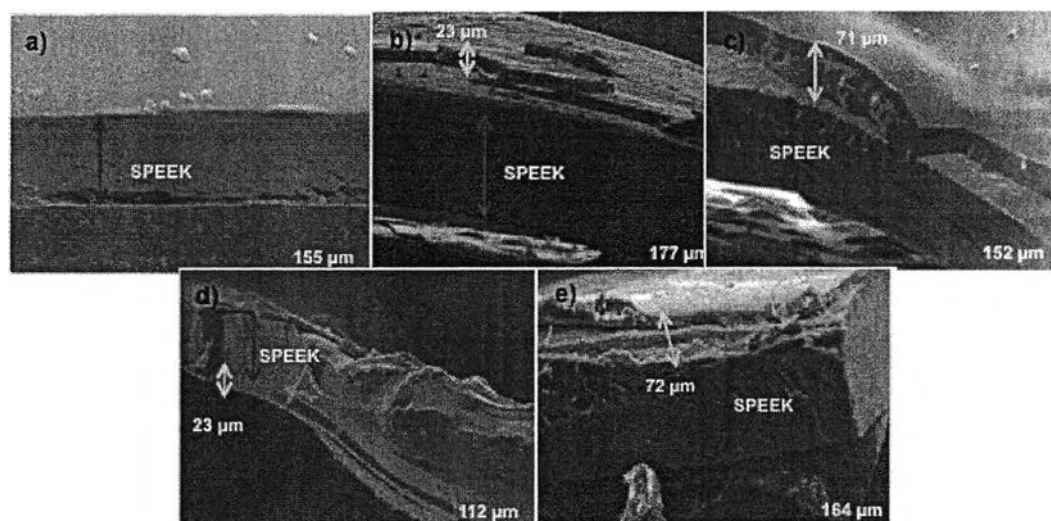


Figure 4.8 Cross-section of a) no layer coating, b) 1 bilayer, c) 2 bilayers, d) 3 bilayers and e) 4 bilayers.

4.5.2.4 Interaction between Layers

ATR-FTIR mode is applied to clarify the formation of LBL SPEEK membrane containing proton donor layers as a poly (acrylic acid) solution and proton acceptor layers as a MPEI solution . **Fig. 4.9** reveals the characteristic peak of MPEI layers and poly(acrylic acid) layers in each step of LBL formation. It can be proved that when the SPEEK membrane is covered with either proton donor layers or proton acceptor layers, it shows the important peak of those layers. The function groups of proton donor layers demonstrate the range of carboxylic acid groups at $1710\text{-}1680\text{ cm}^{-1}$ and the significant peaks of proton acceptor layers are C=N at 1656 cm^{-1} , N-H at 1527 cm^{-1} and 1452 cm^{-1} , and benzene ring at 749 cm^{-1} . It means that every dipping step of SPEEK membrane in poly(acrylic acid) solution or MPEI solution in order to form multilayers demonstrates the different formative layer.

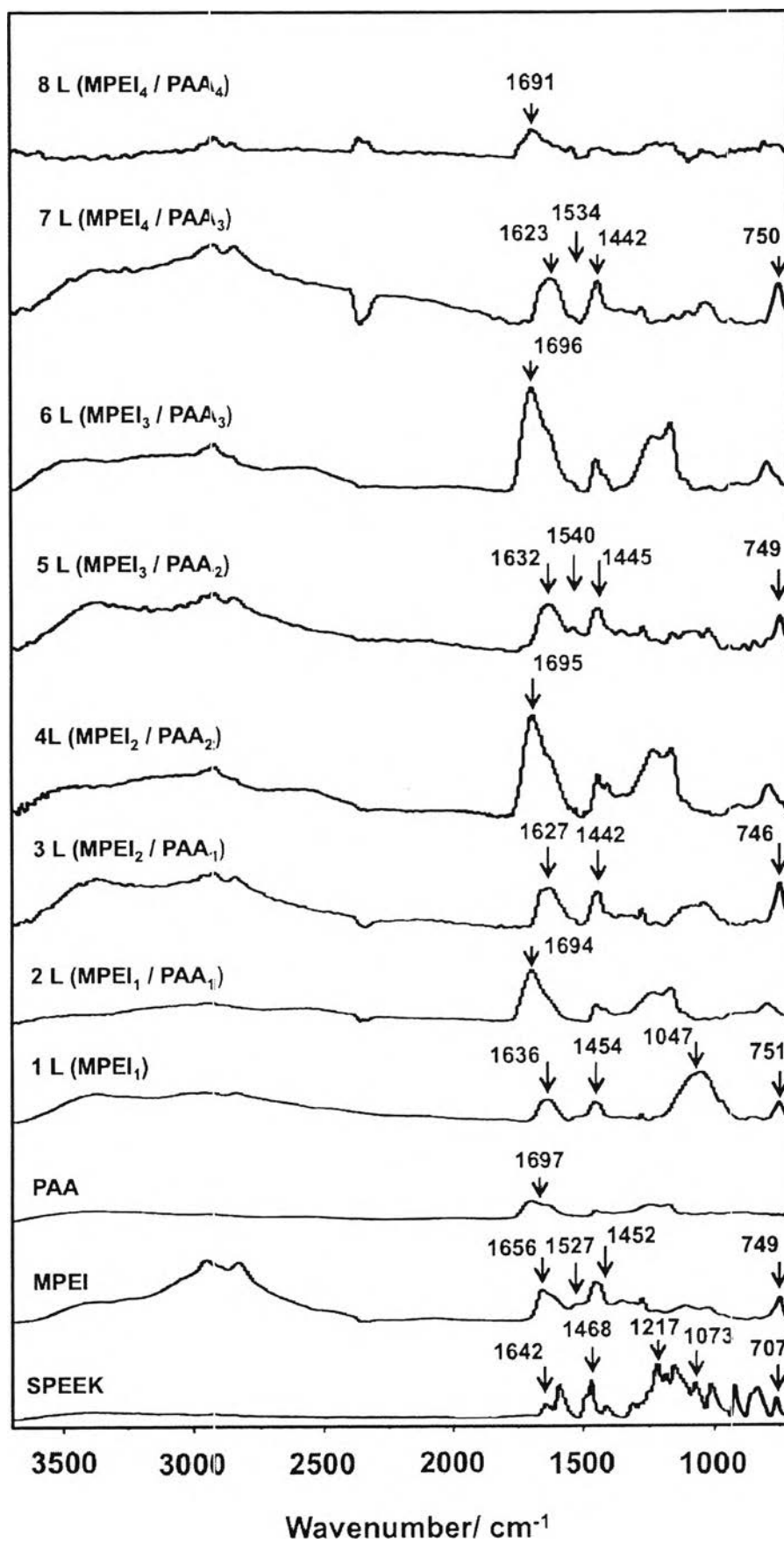


Figure 4.9 FTIR spectrum of LBL formative steps.

4.5.2 Proton conductivity of LBL SPEEK Membrane

The proton conductivity is one of the crucial properties for fuel cell membranes. In this case, we expected to improve the proton transfer channel efficiency for enhancing proton conductivity. To increase proton transfer channel, the membrane was designed to be LBL structure membrane containing proton donor-acceptor layers. It was found that the proton conductivity of LBL SPEEK membrane at 130 °C is 5.21×10^{-7} S/cm for 1 bilayer (MPEI₁ / PAA₁), 2.02×10^{-6} S/cm for 2 bilayers (MPEI₂ / PAA₂), 2.96×10^{-6} S/cm for 3 bilayers (MPEI₃ / PAA₃), and 1.378×10^{-5} S/cm for 4 bilayers (MPEI₄ / PAA₄), respectively. It is important to note that the increasing number of proton donor-acceptor layers has an influence on proton conductivity. The enhancement of proton conductive performance might come from the uniform alternating layer of proton conductive species leading to proton transfer via hydrogen bond network efficiently.

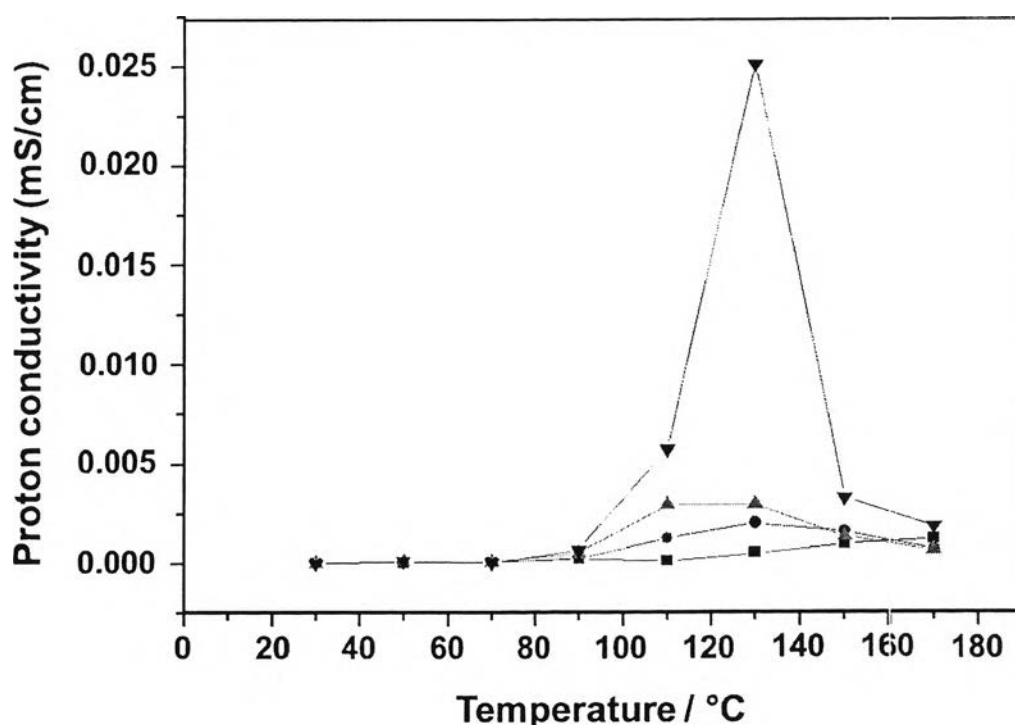


Figure 4.10. Proton conductivity of LBL SPEEK membrane measured in the temperature range from 30 °C to 170 °C at (■) 1 bilayer, (●) 2 bilayers, (▲) 3 bilayers, and (▼) 4 bilayers respectively.

4.6 Conclusions

The LBL SPEEK membranes which contain the uniform alternating proton donor-acceptor layers can be successfully prepared by alternating soaking in poly (acrylic acid) solution as a proton donor layer and MPEI solution as a proton acceptor layer. MPEI demonstrates good properties used in transferring under anhydrous system at high temperature. The LBL SPEEK membrane with varied number of layers consisting of 1 bilayer (MPEI₁ / PAA₁), 2 bilayers (MPEI₂ / PAA₂), 3 bilayers (MPEI₃ / PAA₃), and 4 bilayers (MPEI₄ / PAA₄) respectively, is investigated the proton conductivity under anhydrous system at the temperature range 30 °C to 170 °C. The proton conductivity with increasing number of proton donor-acceptor layers is 5.213×10^{-7} S/cm, 2.02×10^{-6} S/cm, 2.96×10^{-6} S/cm, and 1.378×10^{-5} S/cm, respectively at 130 °C. The LBL technique can provide ordered structure resulting in the strong hydrogen bond network. Consequently, the molecular arrangement of proton conductive species leading to the increment of proton transfer channel efficiency and hydrogen bond network is the key factors for enhancing proton conductivity of LBL SPEEK membrane.

4.7 Acknowledgment

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4.8 References

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