CHAPTER IV

INVESTIGATION OF THE EFFECT OF BENZIMIDAZOLE-BASED MODEL COMPOUNDS ON THERMAL PROPERTIES AND PROTON CONDUCTIVITIES OF SULFONATED POLY(ETHER ETHER KETONE)

4.1 Abstract

The present work shows a strategy to apply a hydrogen bond networked benzimidazole for improvement of proton conductivity and thermal stability of sulfonated poly(ether ether ketone) (SPEEK). A series of benzimidazole derivatives, i.e., mono-, di- and trifunctional benzimidazole, are applied to study the level of hydrogen bond related to the specific properties of SPEEK as proton exchange membrane fuel cell. The benzimidazole-based compounds increase the thermal stability of the SPEEK and, at the same time, improve proton conductivity of SPEEK under dry condition at temperature higher than 80°C. Investigation of structural effect of the model compounds implies that the higher number of benzimidazole unit on the model compound leads to the higher degradation temperature and higher proton conductivity of SPEEK.

Keywords: Benzimidazole, Heterocyclcs, Proton Conductivity, Proton Transfer, PEMFC, Fuel Cell.

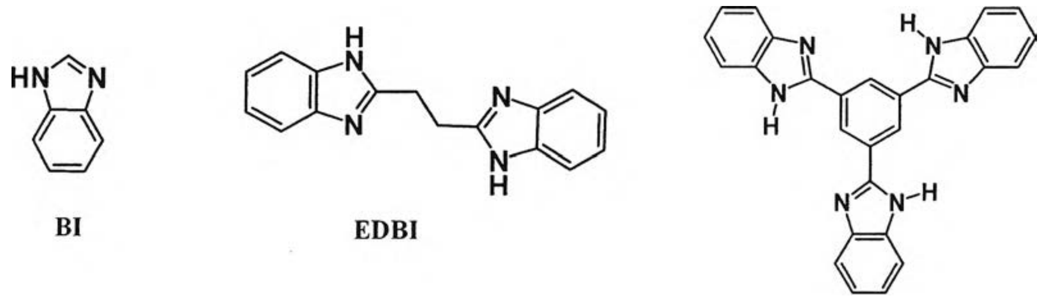
4.2 Introduction

Proton-conducting polymers are the key materials for electrochemical sensors, electrochromic devices, and polymer electrolyte fuel cells (PEMFCs).[1,2] At present, perfluorosulfonic acid polymers, Nafion®, and the related are the most reliable materials for application in PEMFC because of their specific mechanical, chemical, and thermal stability with a high proton conductivity under humidifying conditions.[3,4] As the polymers function under the high mobility of water present in the material under hydrated state, the operating temperature of the PEMFC is essentially limited to temperatures below the boiling point of water.[5] However, the fact that the effective cell performance of the PEMFC system requires the operating temperature at above 120 °C,[5-7] it is attractive to develop new polymeric materials that conduct protons in the absence of water. Therefore, several different approaches have emerged during recent years, and one of the most investigated approaches is based on the proton hopping through the hydrogen-bond network of heterocyclic resonance-structured compounds, e.g., imidazole, benzimidazole and pyrozole.[1,8-13] The example of the works were carried out based on the simple approach of the blend system between the heterocycles, i.e., imidazole, pyrazole and benzimidazole, and the polymer matrices, such as Nafion, sulfonated poly(ether ether ketone) (SPEEK) and polyacrylic acid, etc.[5,8,14] However, most of the researches concerned only about the application of those compounds in polymeric membranes whereas the points about the orientation of the heterocyclic resonance and its consequent hydrogen bond networks, which are the key factors to initiate proton conduction through their possible proton transfer mechanism,[15] are still under investigation. Focusing on this point, although the studies on the proton conductivity of a well-arranged system of the heterocycles have been rarely reported, the attempts to accomplish this concept were carried out by preparing the short and flexible chain coupled with imidazole or benzimidazole group as proposed by Schuster *et. al.* and Persson *et. al.*, respectively.[16-17] The basic information, for example, the self aggregation of the proton carrying groups provided the conductivity in the level of 10^{-3} S.cm^{-1} at temperature above 120 °C.

On this viewpoint, we originally propose a well-defined molecular packing structure with hydrogen bond network based on the heteromatic model compounds not only to understand the role of hydrogen bond network to the proton transfer mechanism of the heterocycles from the fundamental knowledge but also to direct the practical molecular design and synthesis including the application of heterocyclic compound for PEMFC. In previous, we developed a series of heterocyclic model compounds, i.e., mono-, di- and tri-functional benzimidazole molecules as to induce the well-packing structure of heteroaromatic molecules governed by hydrogen bond network. Up to present, it is not yet understand how the hydrogen bond network either its well aligned network structure or the number of the hydrogen bonds contributes the proton transfer and helps in PEMFC efficiency.

The present work, thus, focuses on the effects of hetercylcic-induced hydrogen bond by carrying out a systematical variation of the benzimidazole compounds starting form monofunctional, *benzimidazole,* BI; difunctional, *1,2-ethylenedi-2-benzimidazole*, EDBI; and trifunctional, *1,3,5-benzenetri-2-benzimidazole*, BTBI (Scheme 1). In order to minimize other related factors and clearly identify the effect of hydrogen bond, the compounds were incorporated into polymer matrix and measuring proton conductivity under water-free condition at temperature above 80°C.

Scheme 4.1 Structures of BI, EDBI, and BTBI.



BI **EDBI** **BTBI**

4.3 Experimental

4.3.1 Materials

1,2-Ethylenedi-2-benzimidazole, EDBI, and *1,3,5-benzenetri-2-benzimidazole*, BTBI, were synthesized as reported previously (Chapter III). SPEEK was prepared by modifying the sulfonation procedure reported by Gaowen *et al.*[18] Benzimidazole (BI) was purchased from Aldrich, Germany. All chemicals were analytical grade and used without further purification.

4.3.2 Instruments and Equipments

FT-IR spectra were recorded on a Thermo Nicolet Nexus 670 Fourier transform infrared spectrophotometer at a resolution of 2 cm^{-1} in a frequency range of 4000-400 cm^{-1}, using a deuterated triglycinesulfate detector (DTGS). Temperature dependent FTIR spectroscopy was performed with an in-house temperature-controlled sample holder. Proton nuclear magnetic resonance (^1H NMR) spectra were collected by a Varian Mercury-400BB spectrometer using tetramethylsilane as an internal standard and DMSO-d_6 as a solvent. Wide angle X-ray diffraction (WAXD) measurements were done by using a Rigaku X-ray diffractomer. Thermogravimetric analyses (TGA) were performed by a Perkin Elmer TGA7 thermogravimetric analyzer under nitrogen atmosphere with a flow rate of 20 ml/min and scanning temperature at 50-900°C with a scanning rate of 10 °C/min. Proton conductivities were analyzed by an AC impedance spectrometer using an IM6 Zahner Elektrik connected to a PC running electrochemical impedance software in the frequency range of $10\text{-}10^6$ Hz at 80-120 °C under the dried condition. In-house stainless steel sealed-off cells connected in series were applied.

4.3.3 Preparation of EDBI and BTBI

In brief, for EDBI, Succinyl chloride (1.30 g, 7.97×10-3 mol) in xylene (150 ml) was added dropwisely into a vigorously stirred solution of 1,2-phenylenediamine (2.66 g, 2.45×10-2 mol) in xylene (50 ml) at 80°C under nitrogen atmosphere. The reaction was proceeded for 24 hours yielding the dark green precipitates. The precipitates were collected and dissolved in methanol prior to reprecipitate by adding 1.0 M NaOH solution to obtain the purple precipitates as the product (Yield 63.6%). For BTBI, 1,3,5-benzenetricarbonyltrichloride (0.2310 g, 8.53×10-4 mol) in xylene (150 ml) was added dropwisely into a vigorously stirred solution of 1,2-phenylenediamine (0.3820 g, 3.51×10-3 mol) in xylene (50 ml) at 70°C under nitrogen atmosphere. The red brownish precipitates were collected after overnight. The precipitates were washed a few times with xylene before neutralizing in methanol with 1.0 M NaOH solution to obtain green yellow solution. The solvent was changed from methanol to ethylene glycol and the solution was refluxed at 150°C under vacuum for 24 h to obtain yellow precipitates as the product (Yield 69%).

4.3.4 Sulfonation of PEEK

In brief, PEEK powder (20 g) was dried in a vacuum oven at 100 °C overnight before dissolving in a liter of concentrated (98%) sulfuric acid (H_2SO_4) at room temperature under strong agitation for 48 h. The solution obtained was gradually reprecipitated in ice-cold water. The suspension was filtered and washed several times with distilled water until neutral pH. The precipitate was dried under vacuum for 12 h at 100 °C to obtain the orange solid.

4.3.5 Preparation of the Membranes

4.3.5.1 Controlled SPEEK membrane

A solution of SPEEK in DMSO (7% (w/v)) was prepared. The solution was poured into a Teflon mold which was kept isothermally at 65 °C in the firm hood for more than 40 h to obtain the membrane. The membrane was removed from the mold and soaked in distilled water for 2 h before drying in vacuum oven at 100 °C overnight.

4.3.5.2 SPEEK-BI membranes

An amount of BI (0.0175) was dissolved into 7% (w/v) of SPEEK solution (5 ml) to obtain SPEEK-BI-5 having 5 phr (part per hundred of SPEEK) of BI in SPEEK. The membrane was casted similar to the SPEEK membrane. Other membranes with 0.035 and 0.0525 g of BI were similarly prepared to obtain SPEEK-BI-10 and SPEEK-BI-15, respectively.

4.3.5.3 SPEEK-EDBI membranes

Since it is only the benzimidazole unit that can be functioned as a proton carrier in the proton transfer mechanism, therefore, in order to compare the proton conductivity of the different model compounds, the use of equivalent amount of benzimidazole unit was considered. Thus, for example, in the case of EDBI, the amount of EDBI was calculated based on equation 4.1 to obtain the equivalent amount of benzimidazole unit as in the case of BI.

$$W_A = (FW_A/n_A)\times(W_{BI}/FW_{BI}) \qquad \text{(eq. 4.1)}$$

Where W_A and W_{BI} are the weight of the compound and BI, FW_A and FW_{BI} are formula weight of the compound and BI, and n_A is number of benzimidazole unit on compound.

Therefore, 0.0195, 0.0390 and 0.0585 g of EDBI were weighed and mixed with 5 ml of 7%(w/v) SPEEK solution to prepare SPEEK-EDBI-5, SPEEK-EDBI-10 and SPEEK-EDBI-15, respectively. Similar membrane casting procedure to that of the SPEEK were carried out.

4.3.5.4 SPEEK-BTBI membranes

Similar to EDBI, the amounts of BTBI were calculated from equation 4.1 to obtain the equivalent amount of benzimidazole unit. Thus, 0.0210, 0.0420 and 0.0630 g of BTBI were added into 5 ml of 7%(w/v) SPEEK solution to prepare SPEEK-EDBI-5, SPEEK-EDBI-10 and SPEEK-EDBI-15, respectively. The membrane casting method was carried out in the same procedure as the previous.

4.3.6 Proton Conductivity Measurements

Prior to the proton conductivity measurement, the membranes were equilibrated in 18% humidity chamber by placing the saturated NaCl solution in a desiccator for overnight. The stack membranes containing 5-6 membranes with a cumulative thickness around 400 μm were assembled in to the impedance test cells which were connected in series by the stainless tubes. Every cells were purged by dry nitrogen for more than 2 h until the impedance value of all samples reached their equilibrium. The measurements were carried out in the frequency range of $10\text{-}10^6$ Hz at 80-120 °C under the continuous dry nitrogen gas flow at 10 ml/min. The proton conductivities were estimated by impedance values at phase angle zero.

4.4 Results and Discussion

4.4.1 Well-packed Structures With Hydrogen Bond Networks Exhibited in Benzimidazole-based Model Compounds

Molecular packing structures and hydrogen bond interactions of the compounds were investigated by WAXD analysis and FTIR spectroscopy, respectively. The results were discussed in detail in our previous work (Chapter III). In brief, all compounds show well packing structures with NH···N intermolecular hydrogen bonds as seen from the sharp peaks in their WAXD patterns (Figure 4.1) and the characteristic bands of N-H···N stretching at 3200-2200 cm^{-1} (Figure 4.2). The schematic of their packing structures were drawn out as shown in Scheme 4.2 indicating the hydrogen bond networks which favor proton hopping between molecules.

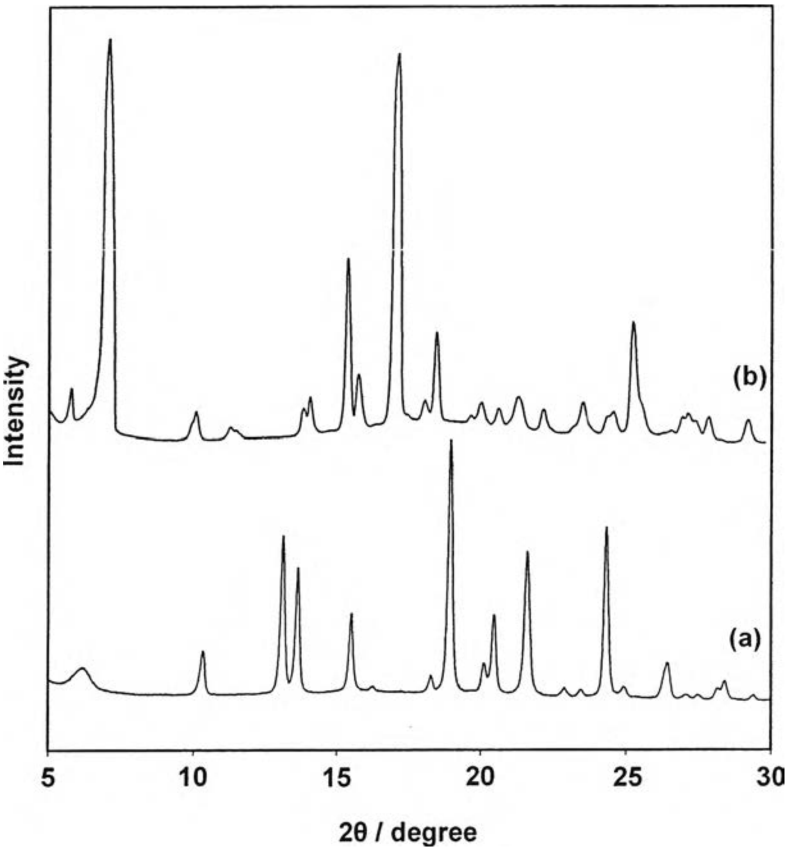


Figure 4.1 WAXD patterns of EDBI (a), and BTBI (b).

Temperature dependencies studies on hydrogen bond interactions revealed that by modifying the molecular structure from BI to EDBI and finally to BTBI, we could enhance the intermolecular interaction of the compounds, consequently, the thermal vibrational resistance of the packing structures was improved as observed in temperature dependent FTIR results (Figure 4.3).

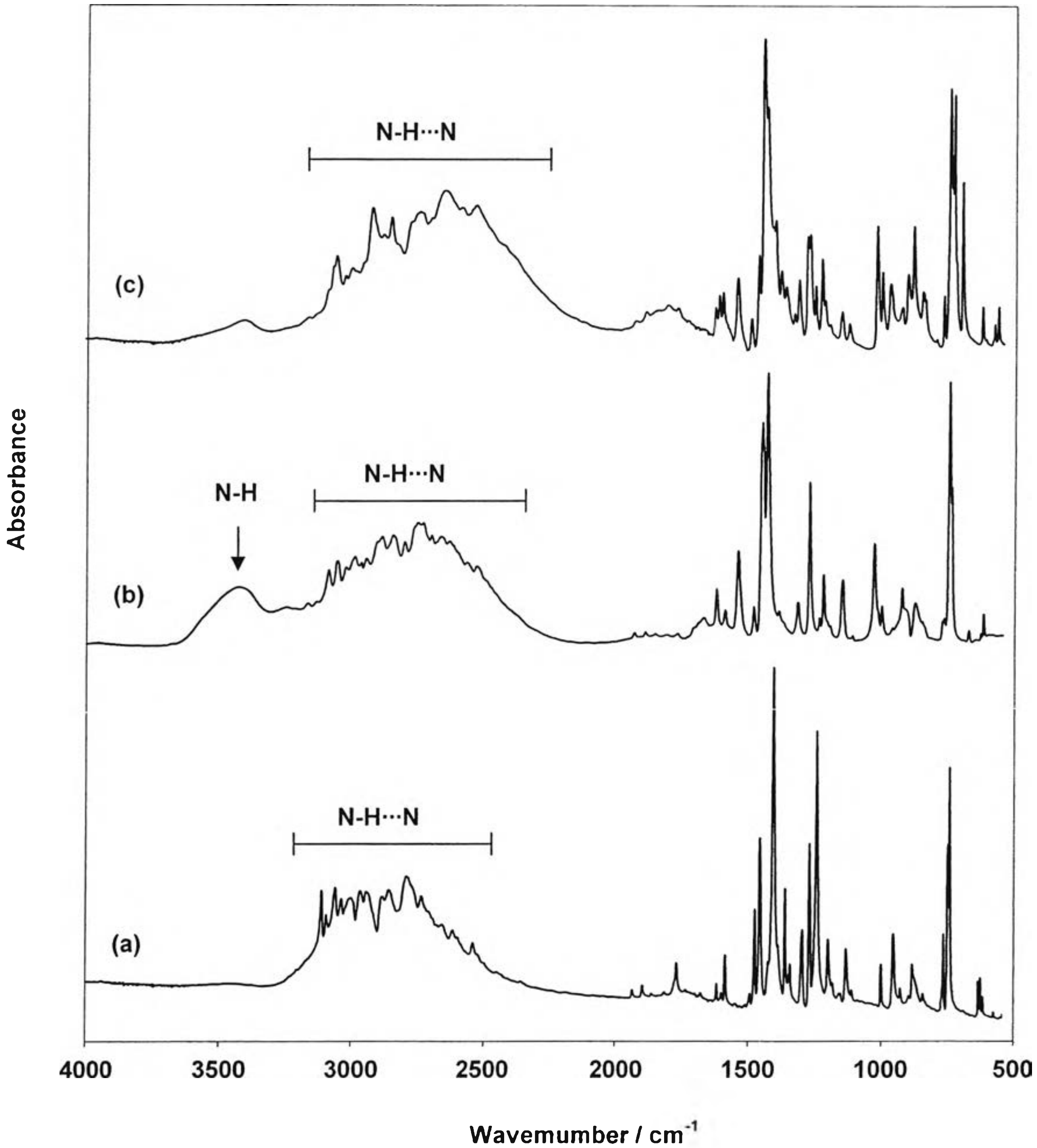
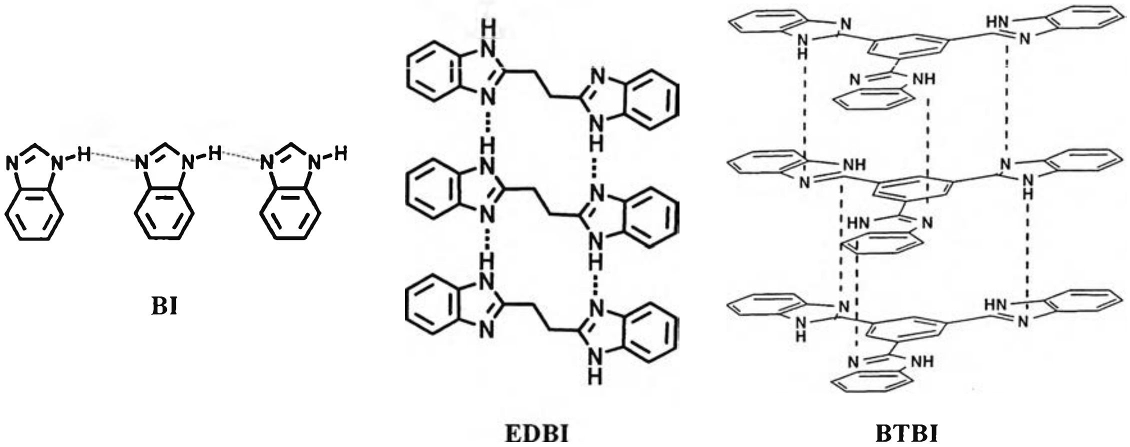


Figure 4.2 FTIR spectra of BI (a), EDBI (b), and BTBI (c).

By heating the compounds from room temperature to 250 °C, the packing structures will either expanded or vibrated as shown in Scheme 4.3 which will weaken the hydrogen bond interactions held between molecules. Thus, during heating, the FTIR spectra representing strong N-H···N hydrogen bond are decrease, whereas the other ones belonging to the weak N-H···N hydrogen bond are increase as observed in Figure 4.3. The critical wavenumbers where peak intensity change from decrease to increase under heating, i.e., 3030, 2930 and 2810 cm^{-1} for BI, EDBI and BTBI, respectively, were considered as a position to distinguish the hydrogen bond interactions between the strong ones and the weak ones. The peaks below this wavenumber were assigned to the strong hydrogen bond, while the peaks above this wavenumber were identified as the weak one. Therefore, as the molecule was developed from BI to EDBI and to BTBI, the critical wavenumber was shifted from 3030, 2930 and 2810 cm^{-1} indicating the higher capability of the packing structure to retain the strong hydrogen bond interaction from the transition to the weak one under thermal treatment. This implies the stronger intermolecular interaction of the compound achieved by increasing number of benzimidazole unit on the molecule.

Scheme 4.2 Speculated packing structures of BI, EDBI, and BTBI.



BI

EDBI

BTBI

4.4.2 Sulfonation of PEEK

Figure 4.4 shows ^{1}H NMR spectrum of SPEEK. The result indicates the success of sulfonation as seen from the peak at 7.48 ppm represents the proton at the adjacent position to the sulfonic acid (H_{13}), and the signal at 7.22 ppm implies the

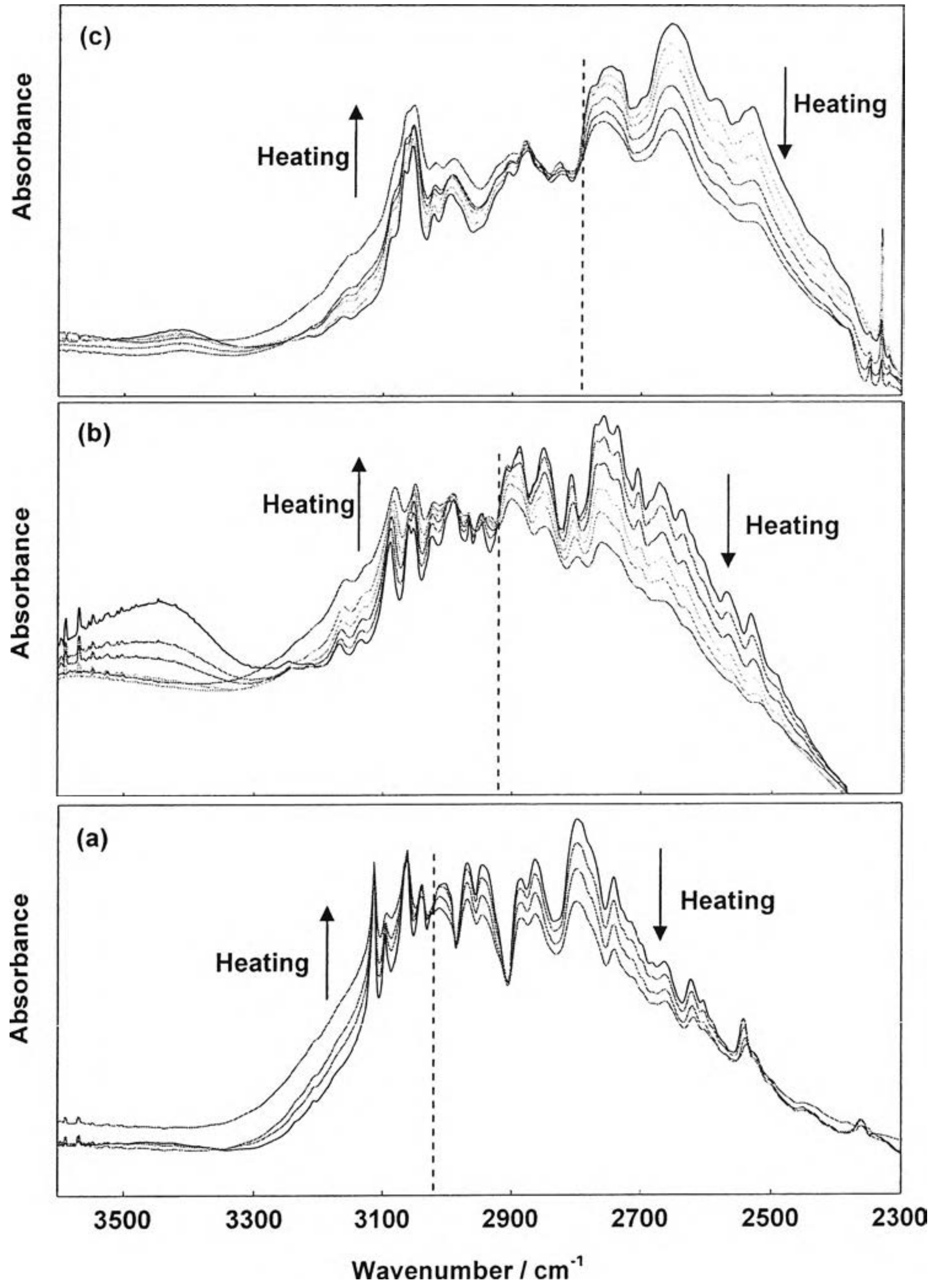


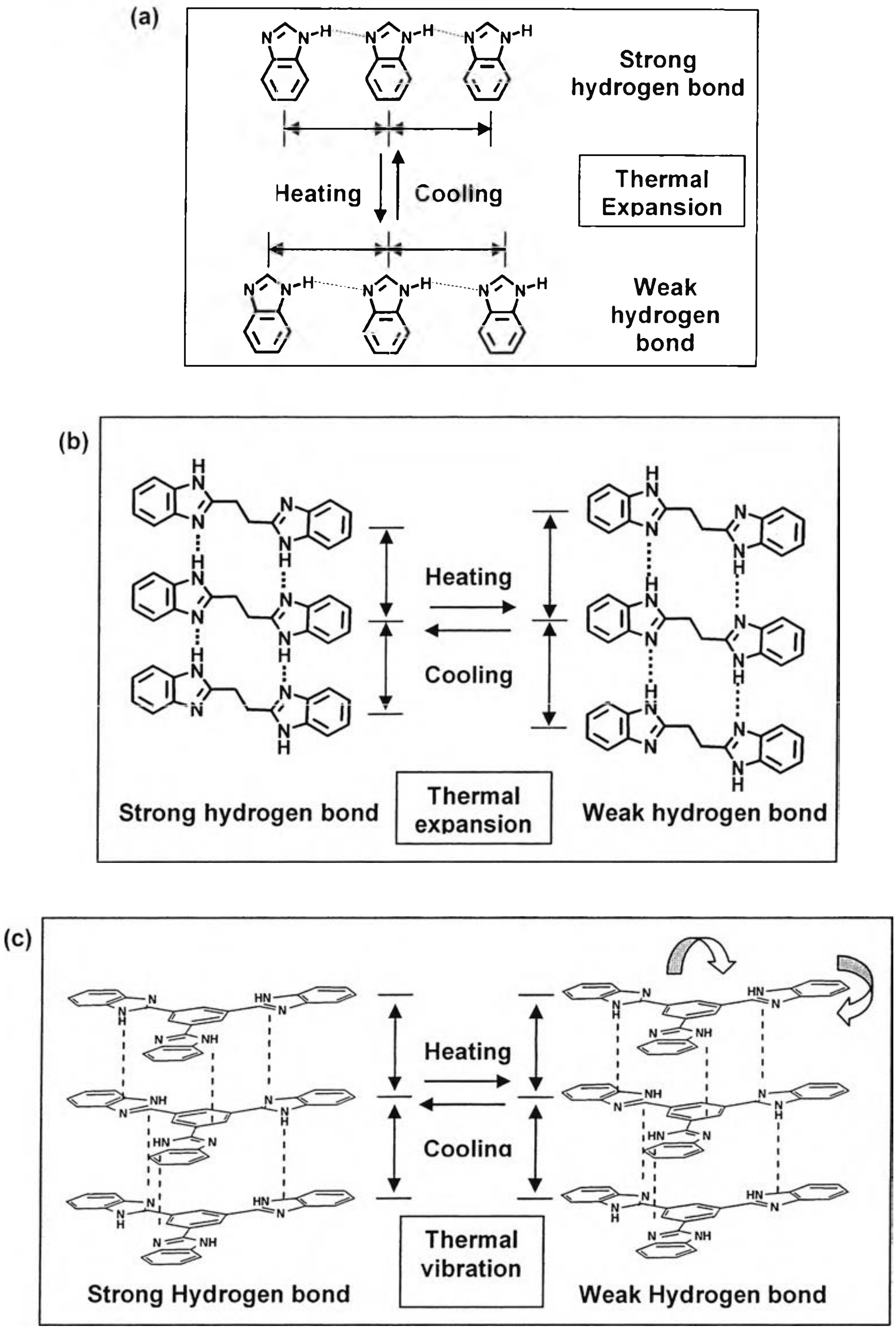
Figure 4.3 Temperature dependent FTIR spectra of BI (a), EDBI (b), and BTBI (c).

protons at H_{14}, H_{15}. The degree of sulfonation (DS) can be calculated from the peak area regarding to equation 4.2. The calculation reveals the DS of 65%.

$$DS\,(\%) = 100 \times A_{7.48} / [(A_{7.84\text{-}7.68} / 2) + A_{7.48} + (A_{7.0} / 4)] \quad \text{(eq. 4.2)}$$

Where $A_{7.84-7.68}$, $A_{7.48}$ and $A_{7.0}$ are the peak areas at 7.84-7.68, 7.48 and 7.0 ppm, respectively.

Scheme 4.3 Temperature effect on molecular packing structures: BI (a), EDBI (b), and BTBI (c).



4.4.3 Thermal Degradation Properties of Benzimidazole-based Compounds

TGA results of the model compounds were illustrated in Figure 4.5. It is important to note that while BI shows a single degradation temperature (T_d) at 275 °C, EDBI, which is the structure of two BIs linked by ethylene unit, exhibits much higher T_d, 460 °C. This reflects the stronger hydrogen bond in EDBI than that of BI. In the case of BTBI, the compound shows a T_d as high as 531 °C with about 60 % weight loss. This also implies the effect of strong molecular packing structure governed by both hydrogen bonds and π-π interaction.

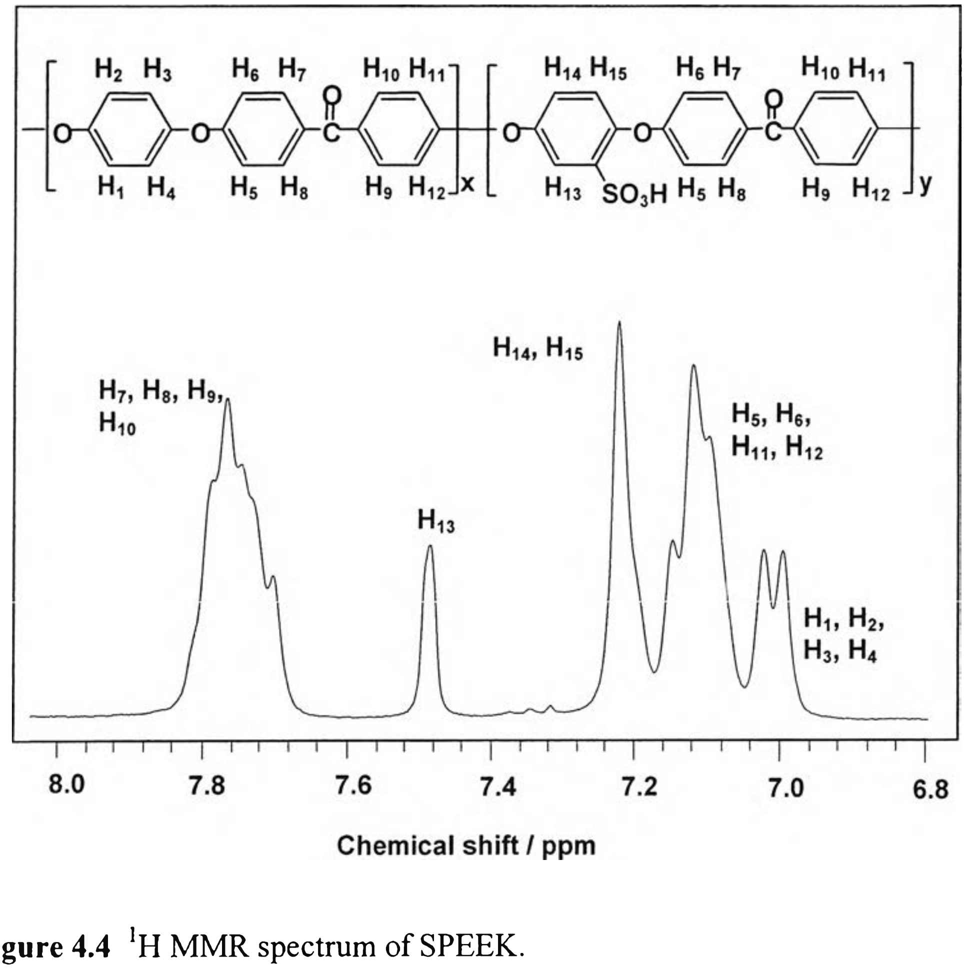


Figure 4.4 ^{1}H MMR spectrum of SPEEK.

4.4.4 Thermal Degradation of SPEEK Affected by Benzimidazole-based Compounds

Investigation of thermal properties of the SPEEK membranes as a consequence of adding benzimidazole model compounds leaded us to confirm the

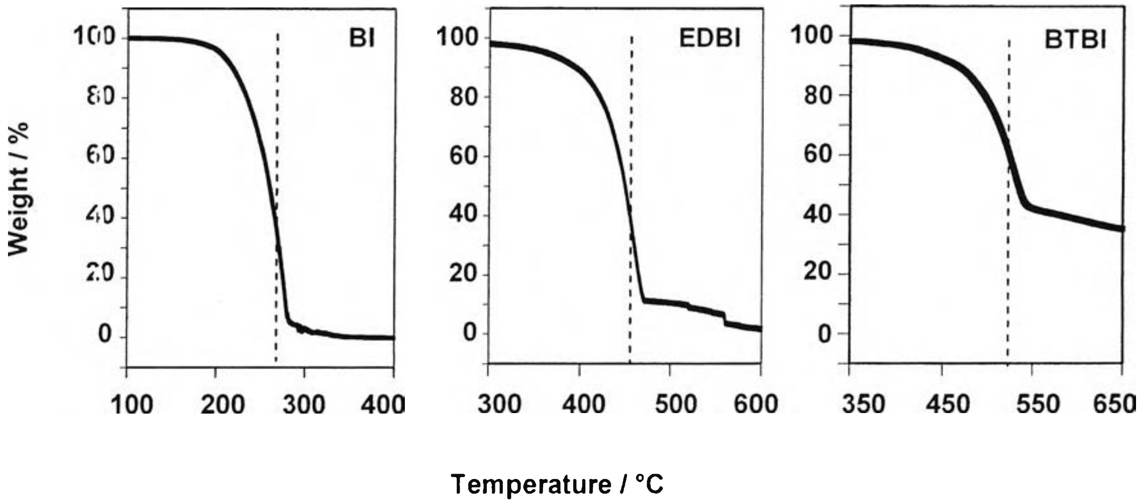


Figure 4.5 Thermal degradation of BI (a), EDBI (b), and BTBI (c).

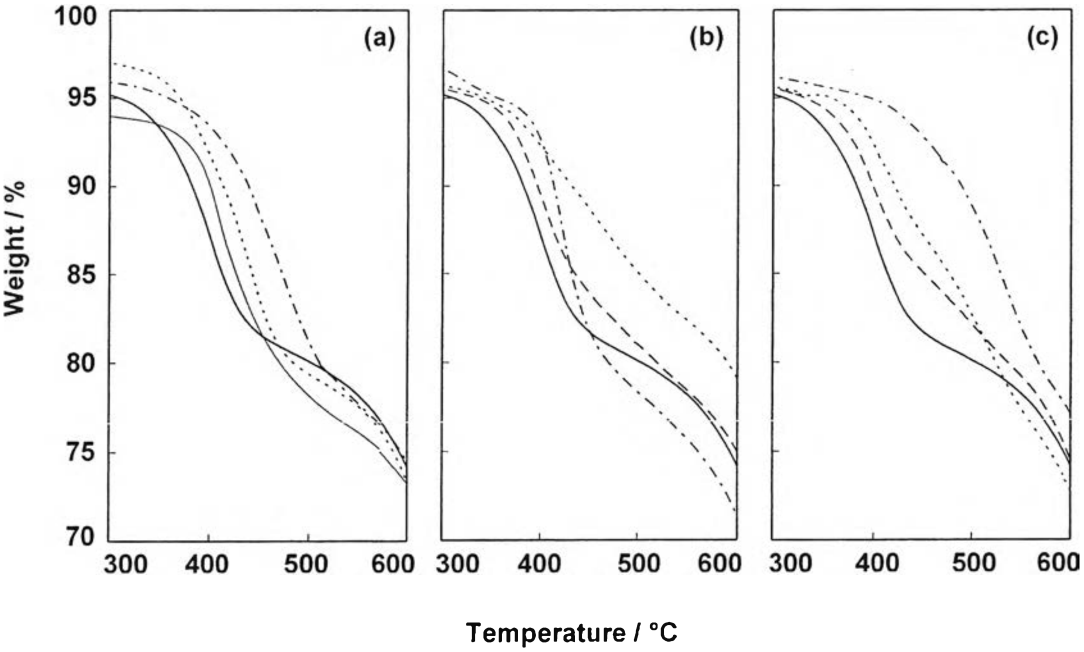


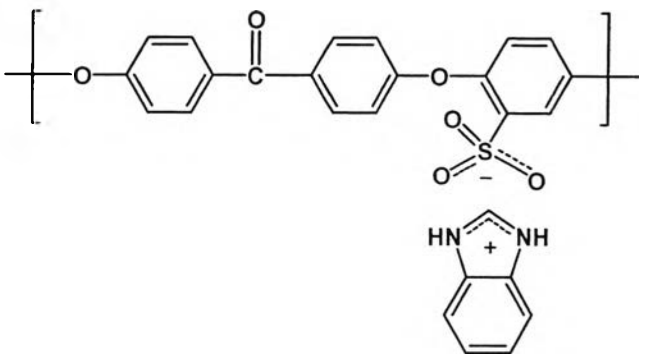
Figure 4.6 Thermal degradation of SPEEK-BI (a), SPEEK-EDBI (b), and SPEEK-BTBI (c): 0 phr (——), 5 phr (– – –), 10 phr (-----), and 15 phr (–·–··).

possibility of using the membranes at the high temperature. Here, TGA was applied to study the degradation behavior of the blend membranes. Figure 4.6 are the TGA results of SPEEK-BI, SPEEK-EDBI and SPEEK-BTBI membranes with different content of benzimidazole compounds, i.e., 0, 5, 10 and 15 phr.The controlled SPEEK membrane (0 phr) shows two degradation steps under the temperature ranging from

50 to 900 °C. The first step is observed at around 400 °C with the weight loss about 15%, corresponds to the elimination of the sulfonic acid side groups as the result shows good agreement with the calculated content of sulfonic acid group (15.3 % (w/w)) in 65% DS SPEEK. The second degradation step occurs around 650 °C which may belong to the degradation of the main chain of the polymer. For the SPEEK-BI membranes (Figure 4.6 (a)), unexpectedly, the blending of BI in SPEEK found to shift the first degradation step of SPEEK to higher temperature without any significant degradation observed at T_d of BI (275 °C). Moreover, we also found that the higher BI content leads to the higher first step degradation temperature, while gives no significant change in the second degradation temperature. Focusing on this point, similar result was reported by Yamada M. *et. al.* in 2003.[19] There, they showed that the thermal degradation of mono-dodecylphophate is decreased by mixing it with benzimidazole, and the explanation they proposed are due to the acid-base complexation between mono-dodecylphosphate (acid) and benzimidazole (base). Taking this into our consideration, our results can be explained by the similar acid-base complexation between sulfonic acid side group of SPEEK and BI as shown in Scheme 4.4. The strong binding force between BI and sulfonic acid might prevents the degradation of BI at temperature higher than 275 °C and also improve the degradation of sulfonic acid to a little higher temperature. As a result, we can not observe the degradation of BI before the elimination of sulfonic acid side group. At the same time, the interaction might induce system to require higher energy to remove the bounded sulfonic acid group than that of the free one. These results also imply that BI molecules are well distributed in SPEEK matrix.

The similar evidences of enhancing the first step degradation temperatures by incorporating the model compounds are also observed in case of SPEEK-EDBI (Figure 4.6 (b)) and SPEEK-BTBI membranes (Figure 4.6 (c)). However, for the SPEEK-EDBI ones, we found that the addition of EDBI at the content of 10 phr can prolong the first step degradation of the membrane to be slower than that of the 15 phr one, although, shows the lower onset temperature of the degradation.

Scheme 4.4 Acid-base complexation of SPEEK and BI.



In the case of SPEEK-BTBI membranes, since BTBI degrades at the temperature as high as 531 °C, therefore, the incorporation of this compound can improve the thermal stability of SPEEK membrane more than the others. For example, when the content of BTBI is at 15 phr we can obtain more than 100 °C higher in the first degradation step than that of the pristine SPEEK membrane. All the TGA results suggest us that the interaction between the benzimidazole compounds and sulfonic acid group of SPEEK not only provide good distribution of the compounds in polymer matrix but also improve the thermal stability of the SPEEK membranes.

4.4.5 Proton Conductivity of SPEEK Membranes Affected by Benzimidazole-based Compounds

In order to investigate the structural effect of the model compounds on the proton conductivity, the interference of proton transfer based on water molecule must be avoided. Thus, all measurements had to be performed in dry condition. To achieve such condition, prior to the proton conductivity measurement, the membranes were kept in a desiccators filled with saturated NaCl solution, which offers the 18% humidity atmosphere, overnight. In this step, the moisture levels in the membranes were equilibrated with the moisture of the chamber resulting in the 18% humidifying condition of the membranes. Thereafter, the samples in the same series, i.e., SPEEK-BI-5, SPEEK-BI-10 and SPEEK-BI-15, were assembled into the test cells, which were connected together by stainless steel tubes. The cells were put in the oven set at 80 °C and purged thoroughly with dry nitrogen gas to ensure the

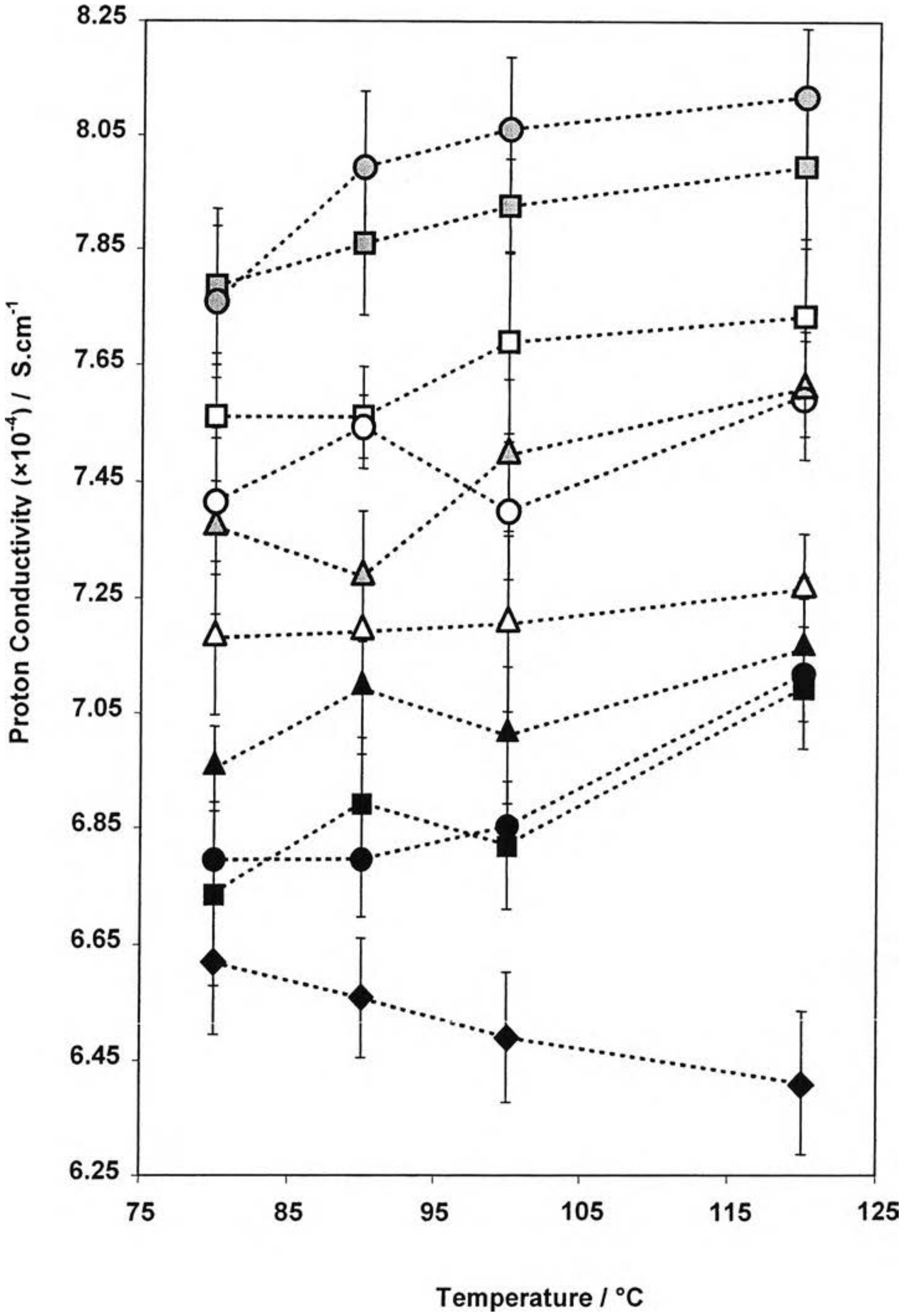


Figure 4.7 Proton conductivity of the membrane under dry condition: SPEEK (◆); SPEEK-BI-5 (▲),SPEEK-BI-10 (△), SPEEK-BI-15 (▲); SPEEK-EDBI-5 (■), SPEEK-EDBI-10 (□), SPEEK-EDBI-15 (▨); SPEEK-BTBI-5 (●), SPEEK-BTBI-10 (○), and SPEEK-BTBI-15 (●).

dry and similar conditions in all samples. The samples were kept in this condition until the monitoring impedance values of all cells reached equilibrium value, indicating the lowest humidification of the membranes was obtained. The flow of nitrogen gas was continued at 10 ml/min along the measurement. The temperature was varied from 80-120 °C. The proton conductivity was estimated by impedance values at phase angle zero. The results of proton conductivities were illustrated in Figure 4.7. For the controlled SPEEK membrane, the increasing temperature results in the decrease of proton conductivity which might be due to the reduction of membrane humidity under higher temperature (> 80 °C). In contrast, the membranes mixed with the model compounds show the increase in proton conductivities when the samples were heated. This implies that the heteroaromatic compounds, i.e., BI, EDBI and BTBI, can be functioned as proton carriers in SPEEK under water-free condition. Furthermore, we found that the more content of the compounds lead to the higher proton conductivities. Comparing between all the heteroaromatic compounds, BI provided the highest conductivity at low content (5 phr). At higher content (10 phr), the highest conductivity was achieved from EDBI compound. And after the additive content reached the highest amount (15 phr), BTBI turned to be the compound giving the highest conductivity.

4.4.6 Role of Molecular Packing Structures of the Benzimidazole Compounds on Proton Conduction

Figure 4.8 is the plot between the proton conductivity at 120 °C and the content of benzimidazole compounds comparing between all blend membranes. The plot indicates that the more number of benzimidazole functional group on the molecule the higher efficiency in proton conductivity is obtained. However, the higher benzimidazole functional molecule requires higher blending content to take its function. This evidence may be explained by the stronger molecular packing structure when the compounds are developed from mono- to di- and to trifunctional benzimidazole compounds as reported in our previous work (Chapter III). Hence, the structural effect of the model compounds on the proton transfer properties might be clarified by Scheme 4.5.

As the measurements were carried out under dry condition, proton conduction of the membranes have to be relied on proton hopping between the heteroaromatic compounds distributed throughout the SPEEK matrix. Therefore, proton transfer properties depend on both the characteristic of the packing structures and the distribution of the molecules in the matrix. Taking this into our consideration, the smaller molecule of BI than EDBI and BTBI results in the better distribution of BI in the membrane than the others at low blending content (5 phr). At the same time, the stronger intermolecular interaction of EDBI and BTBI than that of BI causes the molecules held in the packing structure leading to the poor distribution of the compounds at low blending content. Thus, the conductivity of SPEEK-BI membrane shows highest conductivity at low mixing content.

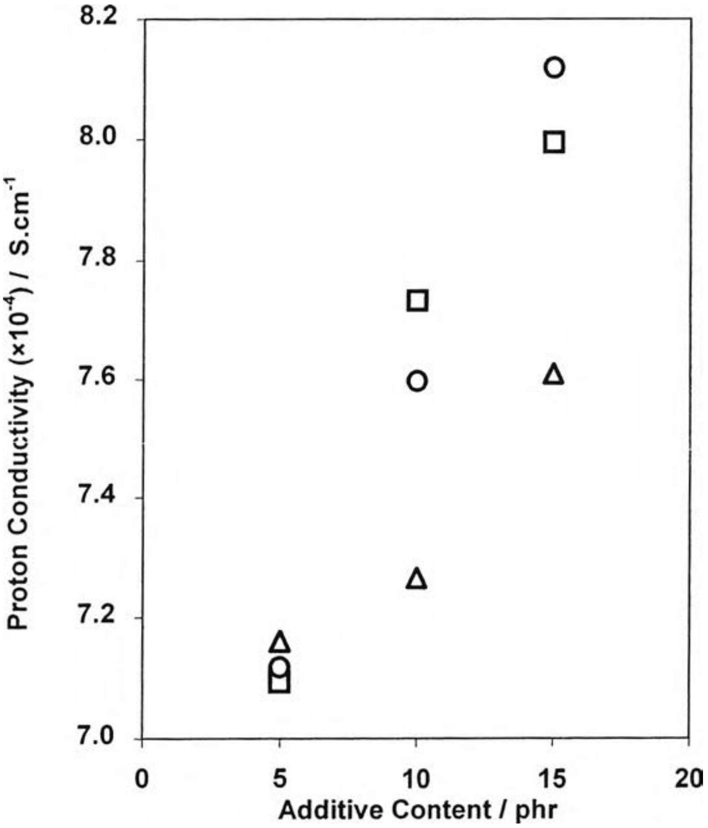
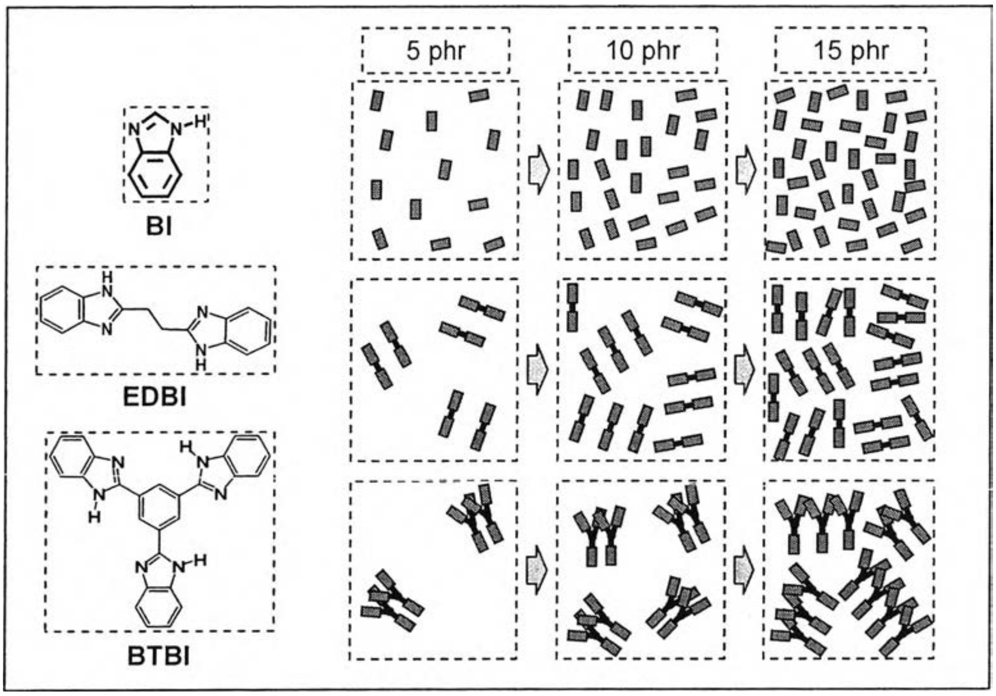


Figure 4.8 Proton conductivity of the blend membrane at 120 °C: SPEEK-BI (△), SPEEK-EDBI (□), and SPEEK-BTBI-15 (○).

After the blending content increases to 10 phr, the distribution of EDBI in the matrix might be comparable with that of the BI system, so the stronger intermolecular interaction of EDBI than that of BI provides the easier proton hopping in EDBI than BI system. At this stage, the distribution of BTBI in the matrix may not comparable with the other two systems, so the conductivity of SPEEK-BTBI is lower that the one obtained from SPEEK-EDBI. When the additive content reaches 15 phr, the amounts of the compounds are high enough to obtain good distribution in all blending systems. Thus, the strong intermolecular interaction of BTBI functions effectively and results in the highest proton conductivity of SPEEK-BTBI membrane than the other systems.

Scheme 4.5 Effect of packing structures on proton transfer properties.



In this way, the results suggest us the role of molecular packing structure induced proton transfer properties of heteroaromatic compounds. The enhancement of intermolecular interaction of the heterocycles is a new aspect to develop the proton exchange membrane for fuel cells.

4.5 Conclusion

Benzimidazole-based model compounds, i.e., BI, EDBI and BTBI, were developed to provide the well-packed structures with hydrogen bond networked. The higher number of benzimidazole unit on molecule offered the stronger packing structure. Incorporation of all benzimidazole compounds in SPEEK was found to improve thermal stability of the polymer matrix. Among the model compounds, BTBI was found to be the most effective molecule to improve thermal degradation property of SPEEK with as high as 130 °C higher than that of the pure polymer at the blending content of 15 phr. For proton conduction study, addition of the model compounds offered the water-independent proton transfer property to the SPEEK membrane. Consequently, proton conductivity of the membrane could be enhanced under increasing temperature even in dry condition. In addition, the work revealed that the stronger intermolecular interaction of the heteroaromatic compound leads to the better proton transfer property.

4.6 Acknowledgement

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