CHAPTER VI

A PROTON CHANNEL OF NOVEL POLYAMIDE CONTAINING ADENINE COUPLED WITH N, N'-BIS (2-HYDROXYL-5-ETHYL) CYCLOHEXYLAMINE FOR PEM FUEL CELLS

6.1 Abstract

A novel polymeric material for Polymer Electrolyte Membrane Fuel Cell (PEMFC) with imidazole unit as a proton connection route is prepared. Aza-methylene phenol obtained from the ring opening benzoxazine monomer was applied as a spacer molecule to provide the functionalization with adenine and polyamide. 4-Hydroxybenzoic acid was protected by ester group whereas the tosylation is carried out at hydroxyl group of phenol unit to provide an effective coupling with adenine. Finally, 1, 10-diaminodecane was added to demonstrate the successful polymerization with aza-methylene phenol for polyamide preparation. The preparations were structurally characterized by FTIR, ^{1}H-NMR, MS and EA.

Keywords: Molecular assembly; Aza-methylene phenol compounds; Heterocyclic group; Polymer electrolyte membrane fuel cell (PEMFC)

6.2 Introduction

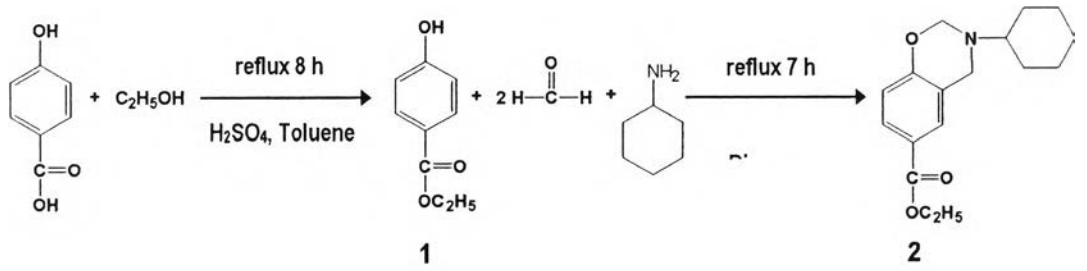
As an environmental friendly and high efficient energy, fuel cells are expected for the several applications such as portable devices, transportation, and stationary power. The polymer electrolyte membrane fuel cell (PEMFC) is one of the successful technologies using a polymer membrane having an effective proton transferring route to the cathode. At present, commercial available membrane such as Nafion® contains hydrated sulfonic acid groups which allow protons migration through the membrane via water molecules. Although, the long-term stability of these polymer membranes have proven to be more than 20,000 h, the high cost (~900 $\$/m^2$) limits the practical uses. High-temperature polymer electrolyte membranes are another point to be considered, due to improving CO tolerance to the impurities in

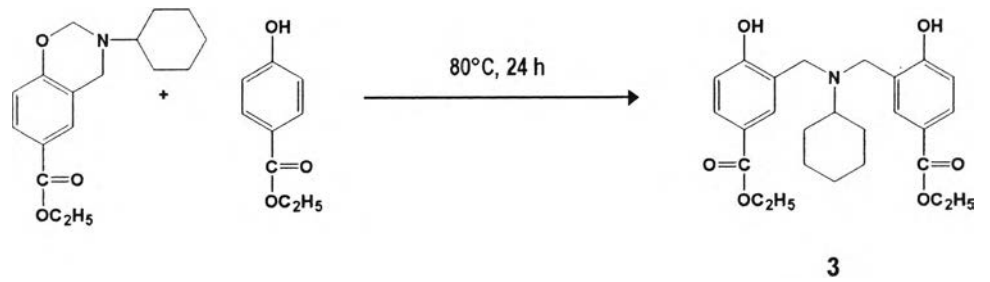
the fuel [1], enhancement of kinetics for both electrode reactions, and ease of water management in the cathode [2].

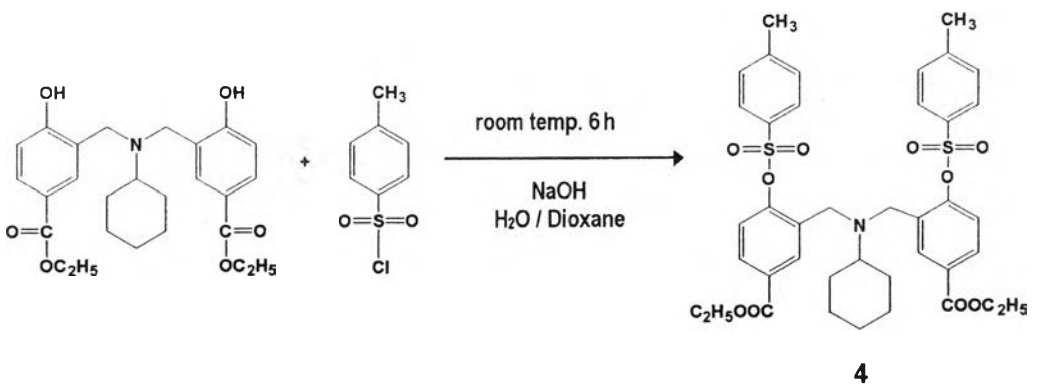
This inspires polymer researchers that the point to develop PEMFC is about on the effective proton connection route through polymer membranes. Recently, there have been many reports about the heterocyclic molecules satisfying the proton donor/acceptor system [3], which may overcome the problems of the traditional PEM. For example, the imidazole is reported [3, 4] that it shows an important feature to contribute to the proton connection route in PEM. The aggregation of imidazoles allows the local dynamics for rapid long range transport of 'excess' protons via structure diffusion, involving proton transfer between heterocyclics [5]. K.D. Kreuer demonstrated the function of heterocyclic in the membranes for fuel cell by the replacement of imidazole with water in sulfonated polyether ketone (SPEK). The proton conductivity results of SPEK/imidazole can be comparable with SPEK/water at higher temperatures [6]. For practical application, however, the protonic conductivity still needs improvement and the imidazole molecules are expected to be immobilized, which is currently attempted by Kreuer and Schuster [7, 8].

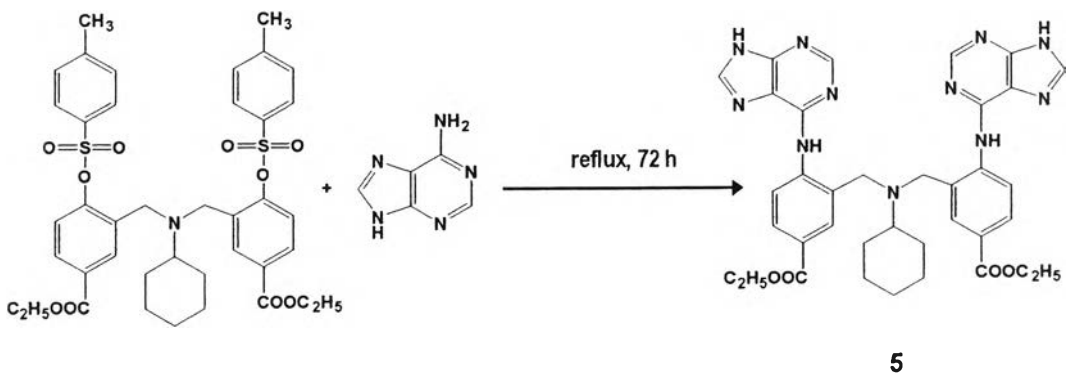
Although heterocyclic molecules such as imidazole group shows an important feature to contribute the proton connection route in PEM membrane without using water as a media, up to now, there is no report about functionalization of polymer chain with the heterocyclics for the objectives of PEM. The present work is, thus, originally proposed the molecular design and synthesis pathway to obtain a controlled structure polymer chain with imidazole unit as shown in Scheme 6.1. It is interesting that, there is aza-methylene phenol molecules related to the structure since it is our own successful result [9] to produce the open-ring structure of benzoxazine monomer at dimerization step. This molecule will be a spacer to conjugate heterocyclic molecules such as adenine group onto polymer backbone. Thereafter, the polyamide will be produced at the aza-methylene phenol molecules by amidation (see Scheme 6.1).

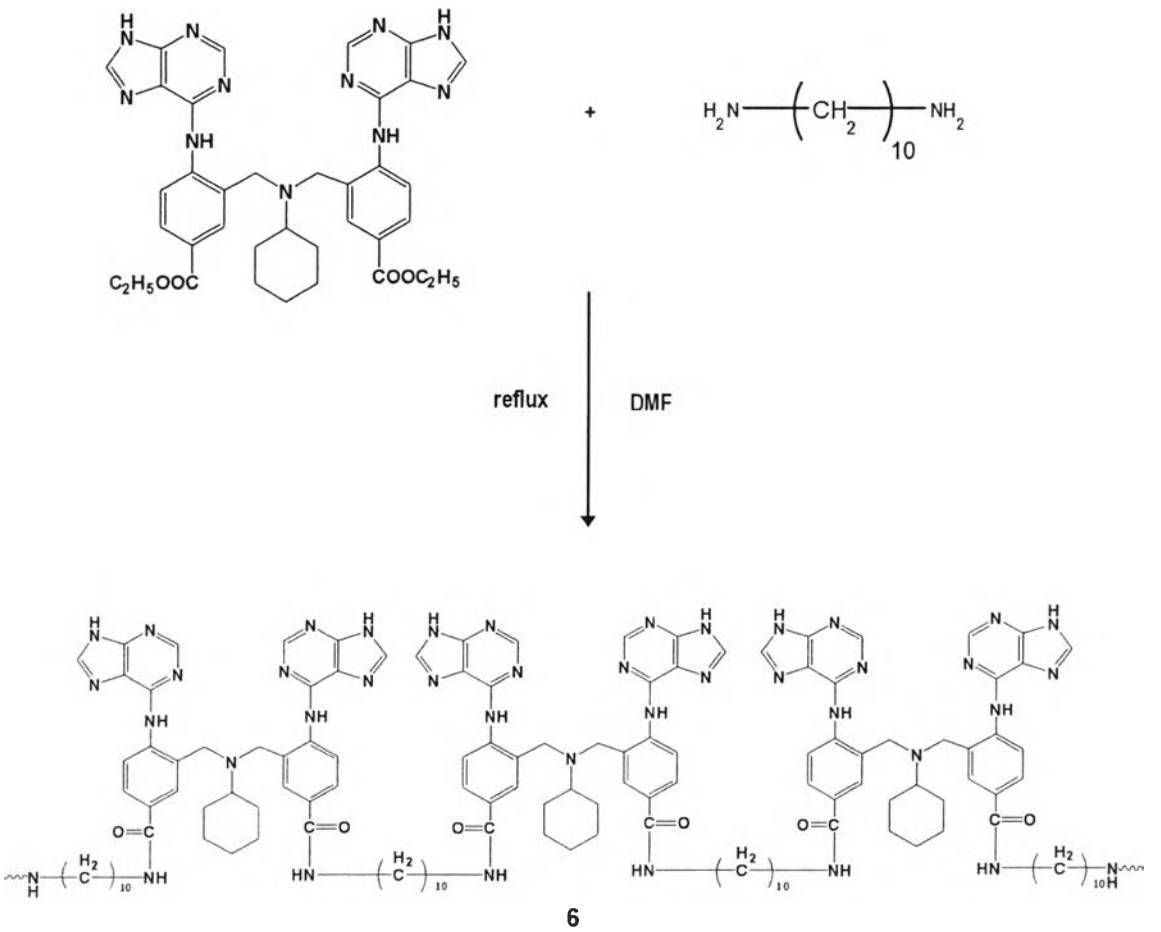
Scheme 6.1 Preparation steps of bis(hydroxybenzyl)amine based proton transfer polyamide











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6.3 Experimental

6.3.1 Materials

4-Hydroxybenzoic acid, adenine, *p*-toluenesulfonyl chloride, benzyl chloride, sodium sulfate anhydrous, and 1, 10-diaminodecane were purchased from Fluka Chemicals (Buchs, Switzerland). Paraformaldehyde, methylamine, potassium carbonate, silica gel and TLC aluminium sheets silica gel 60 were from Merck (Darmstadt, Germany). 1, 4-Dioxane, chloroform, toluene, isopropanol, sulfuric acid and sodium hydroxide were purchased from Lab-Scan (Ireland). Dichloromethane and ethanol were purchased from Carlo Erba (Spain). N, N'-dimethylacetamide was purchased from Acros (USA). Tetrahydrofuran was from J.T. Baker (USA). Deuterated chloroform was from Aldrich (USA). All chemicals were used AR grade and used without further purification.

6.3.2 Measurements

Fourier transform infrared (FTIR) spectra were taken at a resolution 4 cm^{-1} by using a Bruker Equinox55/S spectrophotometer equipped with deuterated triglycine (DTGS) detector. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained from a Varian Mercury-400BB. The ^{1}H-NMR chemical shifts (δ) are expressed in parts per million (ppm) relative to the proton form of the solvent used. Mass spectra were obtained using a VG Autospec model 7070R from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment (FAB(+)MS) mode using glycerol as a matrix. Cesium gun was used as an initiator and cesium iodide (CsI) was used as a reference. Elemental analysis (EA) was performed by using a Perkin-Elmer 2400 Series II CHNS/O analyzer with the combustion temperature of 975 °C and reduction temperature of 500 °C.

6.3.3 Procedures

6.3.3.1 Preparation of Ethyl-4-hydroxybenzoate, ***1***

4-Hydroxybenzoic acid (20.71 g, 150.00 mmol) was dissolved in toluene (500 mL). Ethanol (30 mL) was added with a catalytic amount of concentrated sulfuric acid (1 mL). The mixture was stirred and refluxed for 8 h. The progress of reaction was monitored by TLC. The solvent was removed to obtain the white powder. The product was recrystallized from tetrahydrofuran (THF) to give **1** in 85 % yield.

R_f = 0.57 (60% ethyl acetate in $CHCl_3$); FTIR (KBr, cm^{-1}): 3220 (ν_{O-H}), 1674 ($\nu_{C=O}$); ^{1}H-NMR (400MHz, $CDCl_3$, ppm): 8.00 (d, 2H, *J* = 6.8, 1.8 Hz, Ar-*H*), 6.91 (d, 2H, *J* = 6.4, 2.4 Hz, Ar-*H*), 4.39 (q, 2H, *J* = 7.1 Hz, O-C*H*$_2$-CH$_3$), 1.42 (t, 3H, *J* = 7.2 Hz, O-CH$_2$-C*H*$_3$); FAB(+)MS, *m/z* 167 (M^+); Anal. Calcd. for $C_9H_{10}O_3$: C, 65.06; H, 6.02. Found: C, 63.89; H, 6.50.

6.3.3.2 3-Cyclohexyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, ***2***

1 (3.32 g, 20.00 mmol), cyclohexylamine (2.30 mL, 20.00 mmol) and paraformaldehyde (1.20 g, 40.00 mmol) were dissolved in 1, 4-dioxane (100 mL).

The solution was stirred and refluxed for 7 h to obtain a clear yellowish solution. The progress of reaction was monitored by TLC. After the solvent was removed, the yellowish viscous solution was obtained. The solution was dissolved in chloroform (50 mL) and washed with 3N sodium hydroxide aqueous solution. Sodium sulfate anhydrous was added and left overnight. The solvent was removed to obtain the crude yellowish product. The product was further purified by vacuum distillation to give the viscous product **2** in 85% yield.

R_f = 0.71 (5% methanol in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1712 ($\nu_{C=O}$), 1497 (δ_{C-N}); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 7.83 (d, 2H, *J* = 8.4, 2 Hz, Ar-*H*), 7.72 (d, 1H, *J* = 1.2, Ar-*H*), 6.78 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 5.70 (s, 2H, O-C*H*$_2$-N), 4.36 (q, 2H, *J* = 7.2 Hz, O-C*H*$_2$-CH_3), 4.14 (s, 2H, Ar-C*H*$_2$-N), 2.67-2.73 (m, 1H, N-C*H*$_{cyclohexyl}$), 1.40 (t, 3H, *J* = 7.0 Hz, O-CH_2-C*H*$_3$), 2.02-1.14 (m, 10H, C-*H*$_{cyclohexyl}$); FAB(+)MS, *m/z* 289 (M^+); Anal. Calcd. for $C_{17}H_{23}O_3N$: C, 70.59; H, 7.96; N, 4.84. Found: C, 70.57; H, 8.16; N, 5.16.

6.3.3.3 N,N'-bis(5-ethylformyl-2-hydroxyl)cyclohexylamine, 3

1 (2.75 g, 16.56 mmol) was added in portion to **2** (4.35 g, 15.00 mmol). The mixture was stirred and heated at 80 °C for 24 h. The crude product was precipitated by diethyl ether to obtain white powder. The product was recrystallized from isopropanol to obtain **3** in 80% yield.

R_f = 0.54 (10% acetone in CH_2Cl_2); FT-IR (KBr, cm^{-1}): 3408 (ν_{O-H}), 1713 ($\nu_{C=O}$), 1686 ($\nu_{C=O}$), 1448 (δ_{C-N}); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 7.87 (d, 2H, *J* = 8.4, 2 Hz, Ar-*H*), 7.81 (d, 2H, *J* = 2 Hz, Ar-*H*), 6.87 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 4.35 (q, 4H, *J* = 7.2 Hz, O-C*H*$_2$-CH_3), 4.09 (s, 4H, Ar-C*H*$_2$-N), 3.09 (t, 1H, *J* = 11.8 Hz, N-C*H*$_{cyclohexyl}$), 1.40 (t, 6H, *J* = 7.2 Hz, O-CH_2-C*H*$_3$), 2.15-1.16 (m, 10H, C-*H*$_{cyclohexyl}$); FAB(+)MS, *m/z* 456 (M^+); Anal. Calcd. for $C_{26}H_{33}O_6N$: C, 68.57; H, 7.25; N, 3.08. Found: C, 68.58; H, 7.39; N, 3.04.

6.3.3.4 Tosylation of N,N'-bis(5-ehtylformyl-2-hydroxyl)cyclohexylamine, ***4***

3 (2.77 g, 6.10 mmol) was dissolved in dioxane (30 mL) and added with the solution of sodium hydroxide (0.68 g, 12.20 mmol) in distilled water (10 mL). The solution of *p*-toluenesulfonyl chloride (2.56 g, 13.42 mmol) in dioxane (30 mL) was slowly added to the mixture. After the addition, the mixture was stirred at room temperature for 8 h. The solvent was evaporated to obtain the crude product. It was dissolved in dichloromethane (30 mL), washed with water, and dried over sodium sulfate anhydrous. The solvent was removed to obtain **4** in 93% yield.

R_f = 0.30 (10% hexane in CH_2Cl_2); FTIR (KBr, cm^{-1}): 1720 ($\nu_{C=O}$), 1485 (δ_{C-N}), 1379 ($\nu as_{S=O}$), 1161 ($\nu s_{S=O}$), 816 (ν_{S-O}); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 8.15 (d, 2H, *J* = 1.6 Hz O-Ar-*H*), 7.79 (dd, 2H, *J* = 8.4, 1.6 Hz, O-Ar-*H*), 7.68 (d, 4H, *J* = 8.4 Hz, SO_3-Ar-*H*), 7.30 (d, 4H, *J* = 8.0 Hz, SO_3-Ar-*H*), 7.07 (d, 2H, *J* = 8.4 Hz, O-Ar-*H*), 4.31 (q, 4H, *J* = 7.2 Hz, O-CH_2-CH_3), 3.28 (s, 4H, Ar-CH_2-N), 2.42 (s, 6H, SO_3-Ar-CH_3), 2.22 (t, 1H, *J* = 10.6 Hz, N-C$H_{cyclohexyl}$), 1.32 (t, 6H, *J* = 7.2 Hz, O-CH_2-CH_3), 1.74-0.99 (m, 10H, C-$H_{cyclohexyl}$); Anal. Calcd. for $C_{40}H_{45}O_{10}NS_2$: C, 62.91; H, 5.90; N, 1.84. Found: C, 62.97; H, 5.69; N, 1.84.

6.3.3.5 Adenine coupled with N,N'-bis(2-hydroxyl-5-ethyl)cyclohexylamine, ***5***

A solution of **4** (0.38g, 0.50 mmol) in 60 mL of N,N'-dimethylacetamide (DMAc) was added into a solution of adenine (0.15 g., 1.10 mmol) in DMAc (50 mL). Potassium carbonate (1.38 g., 10.00 mmol) was then added in portion. After the addition, the mixture was stirred and refluxed for 24 hours. The solvent was removed and chloroform (50 mL) was added and washed with water. The organic phase was collected and evaporated to give the crude product. The residue was chromatographed on a silica gel with 50% ethyl acetate in hexane as an eluent to give **5** in 21% yield.

R_f = 0.33 (50% ethyl acetate in hexane); IR (KBr, cm^{-1}): 3287 (ν_{N-H}), 1711 ($\nu_{C=O}$), 1609 ($\nu_{C=N}$), 1462 (δ_{C-N}); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 12.62 (s(br), 2H, N-$H_{adenine}$), 8.54 (s(br), 2H, C-N*H*-C), 8.01 (s, 2H, N-C*H*-N), 7.95 (s, 2H, NH-C*H*-N), 7.837 (d, 2H, J = 0.8 Hz, NH-Ar-*H*), 7.81 (d, 2H, J = 8.8 Hz, NH-Ar-*H*), 6.87 (d, 2H, J = 8.0 Hz, NH-Ar-*H*), 4.37-4.31 (m, 4H, O-CH_2-CH_3), 3.96 (s, 4H, Ar-CH_2-N), 3.75-3.63 (m, 1H, N-C$H_{cyclohexyl}$), 1.91-1.16 (m, 10H, C-$H_{cyclohexyl}$).

6.3.3.6 Polymerization of aza-methylene derivative with difunctionalamine, 6

5 (0.6 g, 0.87 mmol) in N,N'-dimethylformamide (10 mL) was dissolved in 1,10-diaminodecane (0.15 g, 0.87 mmol in DMF 10 mL). This solution was gradually added with trimethylamine (0.12 mL, 0.87 mmol) and refluxed for 24 h. The solvent was removed and dried in the vacuum oven at 70 °C for 48 h to obtain **6** in 9% yield.

FT-IR (ZnSe, cm^{-1}): 3292 cm^{-1} (ν_{N-H}), 1668 cm^{-1} ($\nu_{C=O}$, amide I), 1606 cm^{-1} (ν_{N-H}, amide II); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 7.95 ppm (1H, s, purine N-CH-N), 7.92 ppm (1H, s, purine N-CH-CH), 5.85 ppm (1H, br, NH), 1.1-1.8 ppm (2H, m, CH_2).

6.4 Results and Discussion

6.4.1 Protection of 4-hydroxybenzoic acid

Our preliminary studies pointed out that the Mannich reaction of 4-hydroxybenzoic acid initiates the side reaction due to the carboxylic acid group and obstructed the oxazine ring formations [9]. Here, 4-hydroxybenzoic acid was esterified by using ethanol to avoid the side reaction. Compound **1** gives the C=O peak at 1674 cm^{-1} referred to the carbonyl moiety of ester group (see Figure 6.1). Comparing to 4-hydroxybenzoic acid, the broad band of hydroxyl group at 3000–2400 cm^{-1} was disappeared implying the complete substitution of carboxylic acid

group to ester one, while the hydroxyl group of phenol is confirmed at 3220 cm^{-1}. ^{1}H-NMR clarifies the ethyl ester group by the peaks at 1.43 and 4.39 ppm belonging to methyl and methylene protons of ethyl group, respectively (see Figure 6.2). Thus, it can be concluded that compound **1** was successfully prepared.

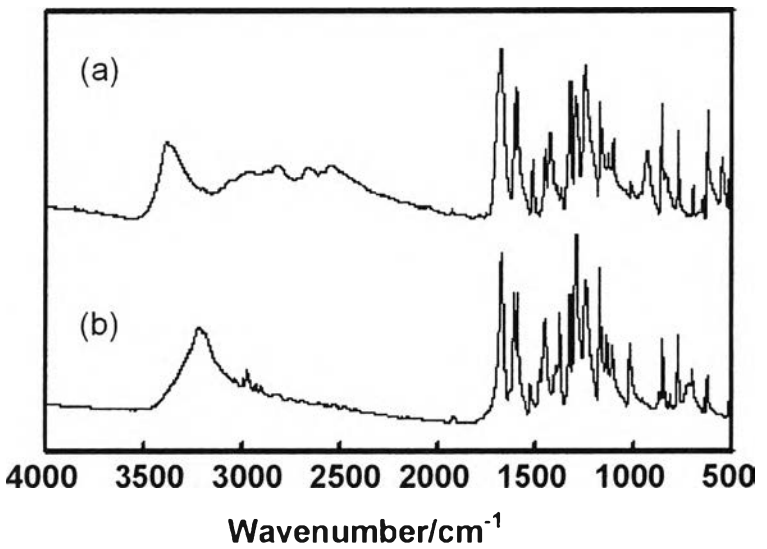

Figure 6.1 FTIR spectra of: (a) 4-hydroxybenzoic acid, and (b) **1**.

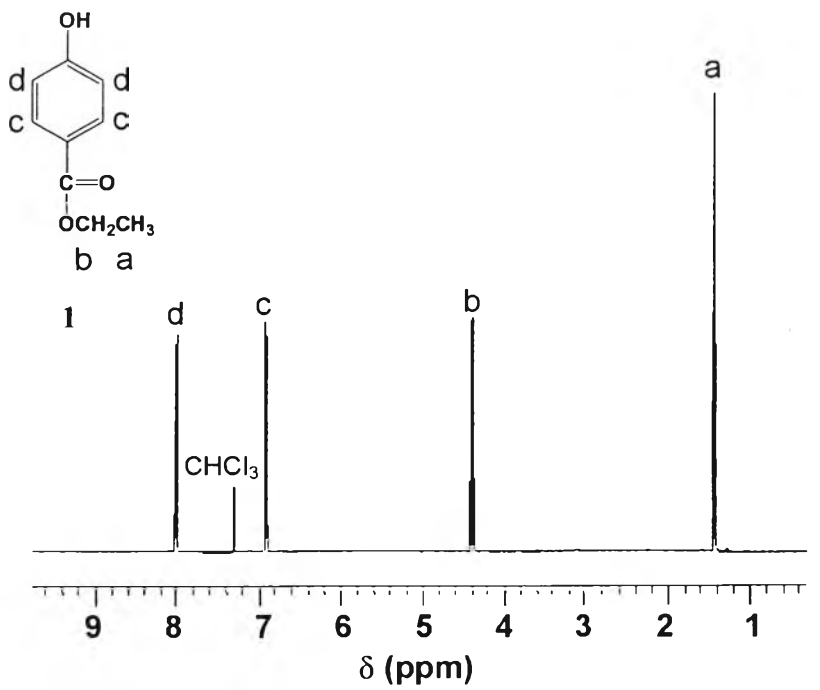

Figure 6.2 ^{1}H-NMR spectrum of **1**.

6.4.2 Oxazine Ring Formation of 1

The Mannich reaction of **1** gave the product with the oxazine ring as demonstrated by FTIR spectrum of the peak at 1497 cm^{-1} (see Figure 6.3). ^{1}H-NMR shows two singlet peaks at 4.14 and 5.70 ppm referring to methylene protons on the oxazine ring (see Figure 6.4). The results suggest that **2** was successfully prepared. Two doublet peaks at 6.84 and 7.89 ppm refer to protons of **3** which can occur in this step.

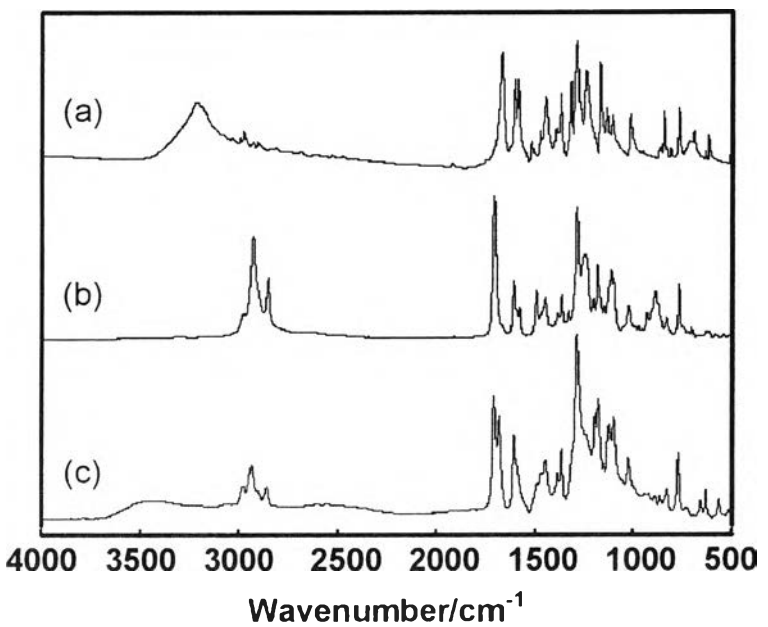

Figure 6.3 FTIR spectra of: (a) **1**, (b) **2**, and (c) **3**.

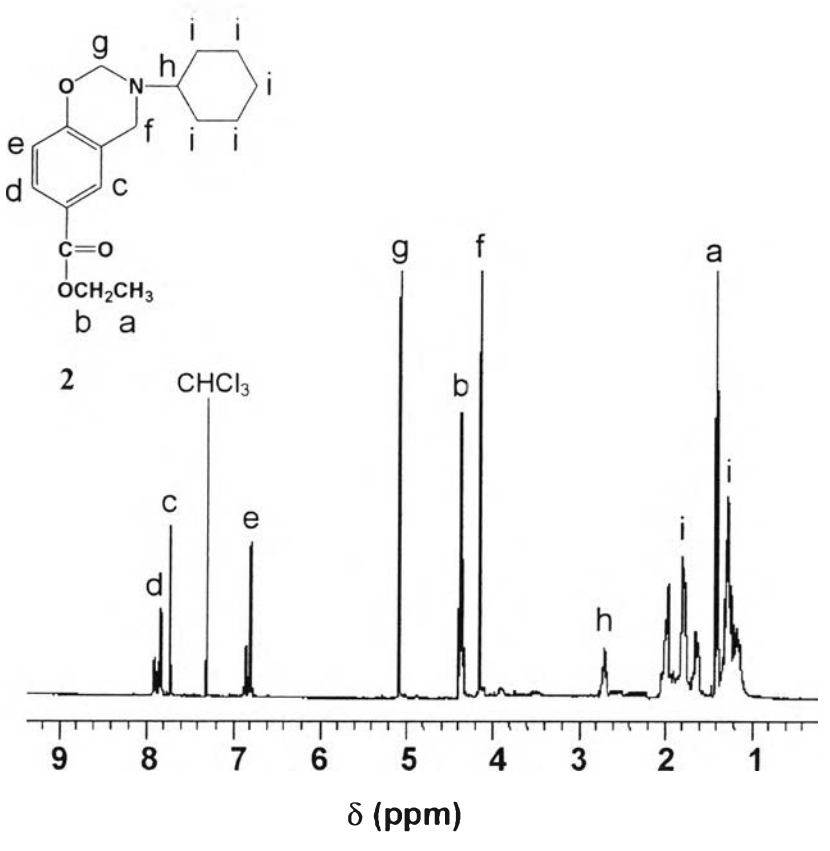

Figure 6.4 ^{1}H-NMR spectrum of **2**.

6.4.3 Stoichiometry of Ring Opening Reaction of 2

Recently, Laobuthee *et al.* reported that the ring opening reaction of *p*-substituted benzoxazine terminated at dimer level [10]. Here, **3** was prepared from stoichiometric reaction of **2** and **1**. FTIR spectrum (see Figure 6.3) confirms the success of the reaction to give **3** by C-N deformation at 1448 cm^{-1} and OH stretching vibration peak at 3300–3410 cm^{-1}. ^{1}H-NMR clarifies the existence of aza-methylene linkage by the singlet at 4.09 ppm (see Figure 6.5).

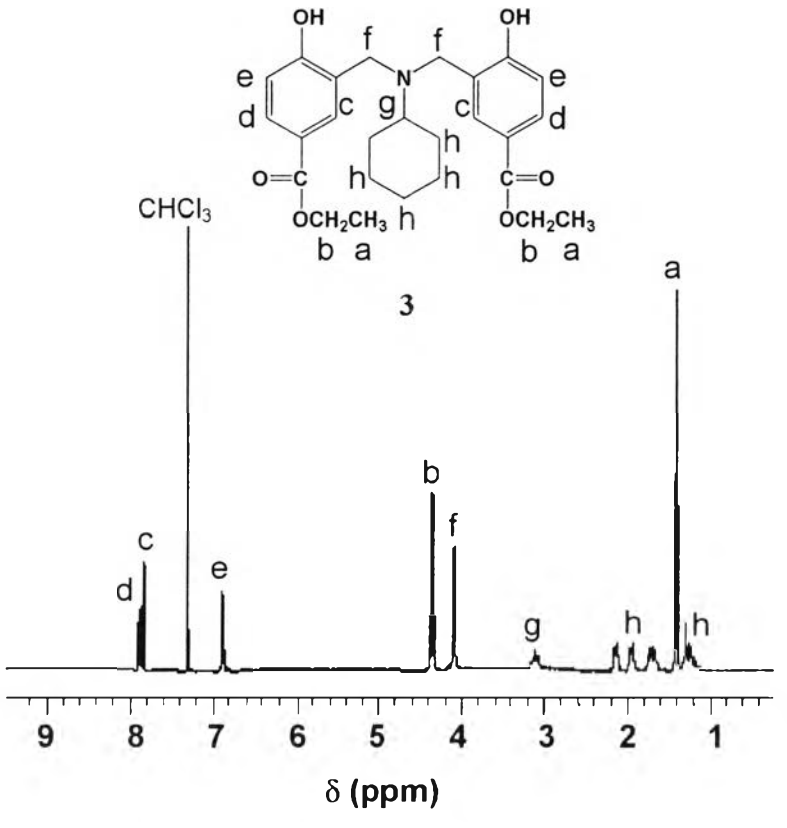

Figure 6.5 ^{1}H-NMR spectrum of **3**.

6.4.4 Introduction of Adenine onto 3 via Tosyl Group

Adenine was used because it has imidazole unit to expect for transferring proton. Adenine has amino group to be bound to aza-methylene phenol unit. In order to achieve the reaction as designed the conjugation with adenine was attempted (see Scheme 6.1). Due to the direct reaction between hydroxyl group of aza-methylene phenol and amine group of adenine is difficult, then, tosylation of aza-methylene phenol was carried out to prepare the reactive ester species. Basic catalyst was added to deprotonate hydroxyl group of aza-methylene phenol. It can be expected that electron withdrawing group stabilizes phenoxide ions, and as a result, tosylation occured quantitatively. The FTIR spectrum of compound **4** (see Figure 6.6) shows the asymmetric and symmetric stretching vibration of sulfonyl groups at 1379 and 1161 cm^{-1}. The existence of 1720 cm^{-1} insists the remaining of ethyl carboxylate group at each C-4 position in the phenol ring. The completion of the reaction was

confirmed from the disappearance of hydroxyl signal belonging to the aza-methylene phenol at 3300–3410 cm^{-1}. ^{1}H-NMR spectrum (see Figure 6.7) clarifies the protons in benzene ring at 7.30 and 7.68 ppm referring to the tosyl group.

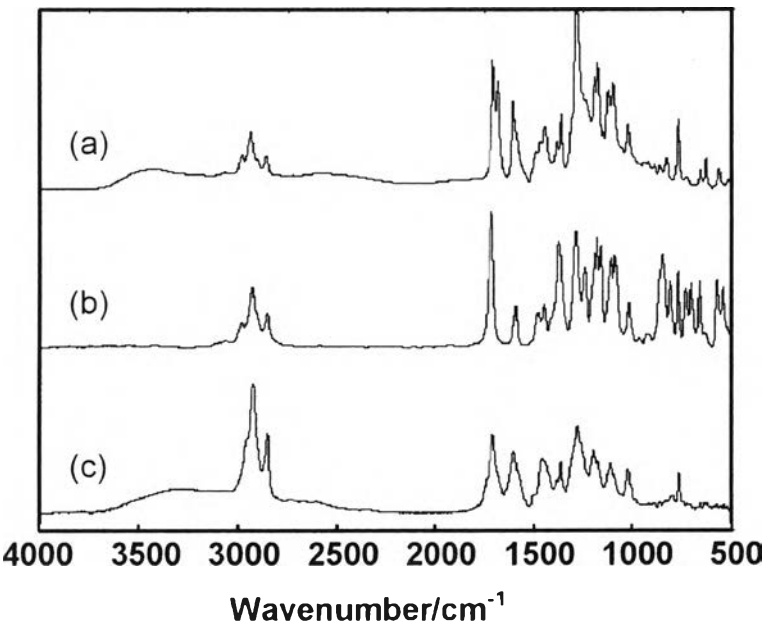

Figure 6.6 FTIR spectra of: (a) **3**, (b) **4**, and (c) **5**.

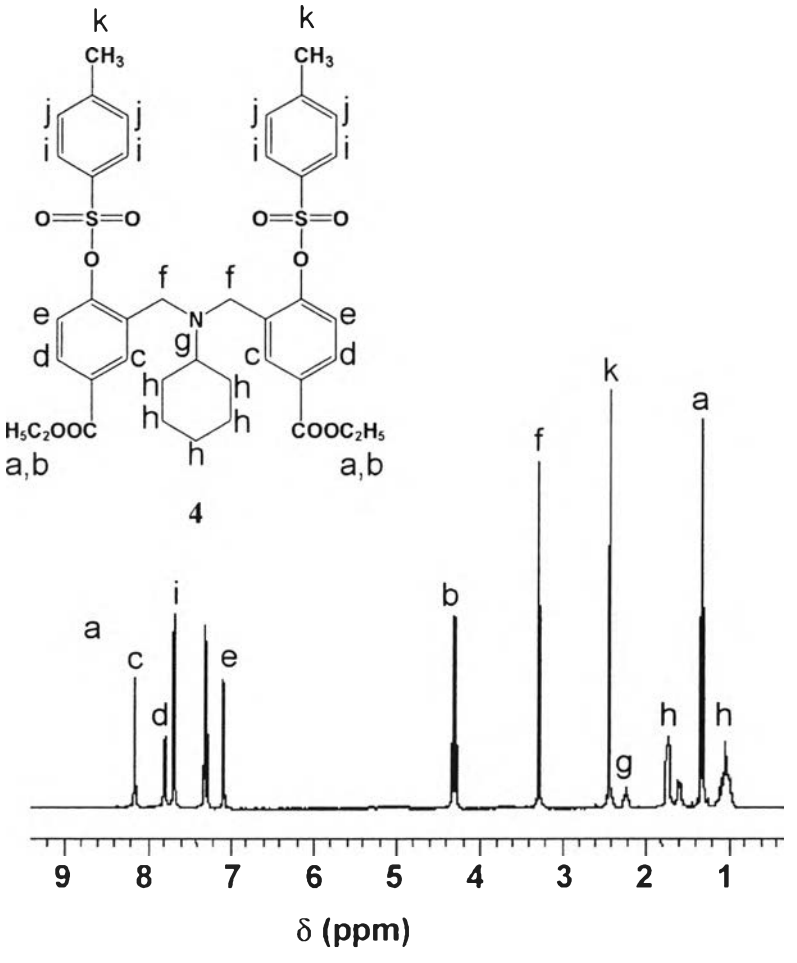

Figure 6.7 ^{1}H-NMR spectrum of **4**.

Taking advantage of the best leaving group of tosyl group, compound **3** was coupled with adenine by basic catalyst. The coupling reaction of adenine with **4** was confirmed from N-H broad peak at 3287 cm^{-1} and C=N peak at 1609 cm^{-1}. ^{1}H NMR gives the peaks at 7.95 ppm and small broad peak around 12.62 ppm referring to protons on adenine group. In addition, ^{1}H-NMR clarifies the N-H bond of adenine bound to aza-methylene phenol from the small broad peak at 8.54 ppm (see Figure 6.8). The results suggest the structure of **5**.

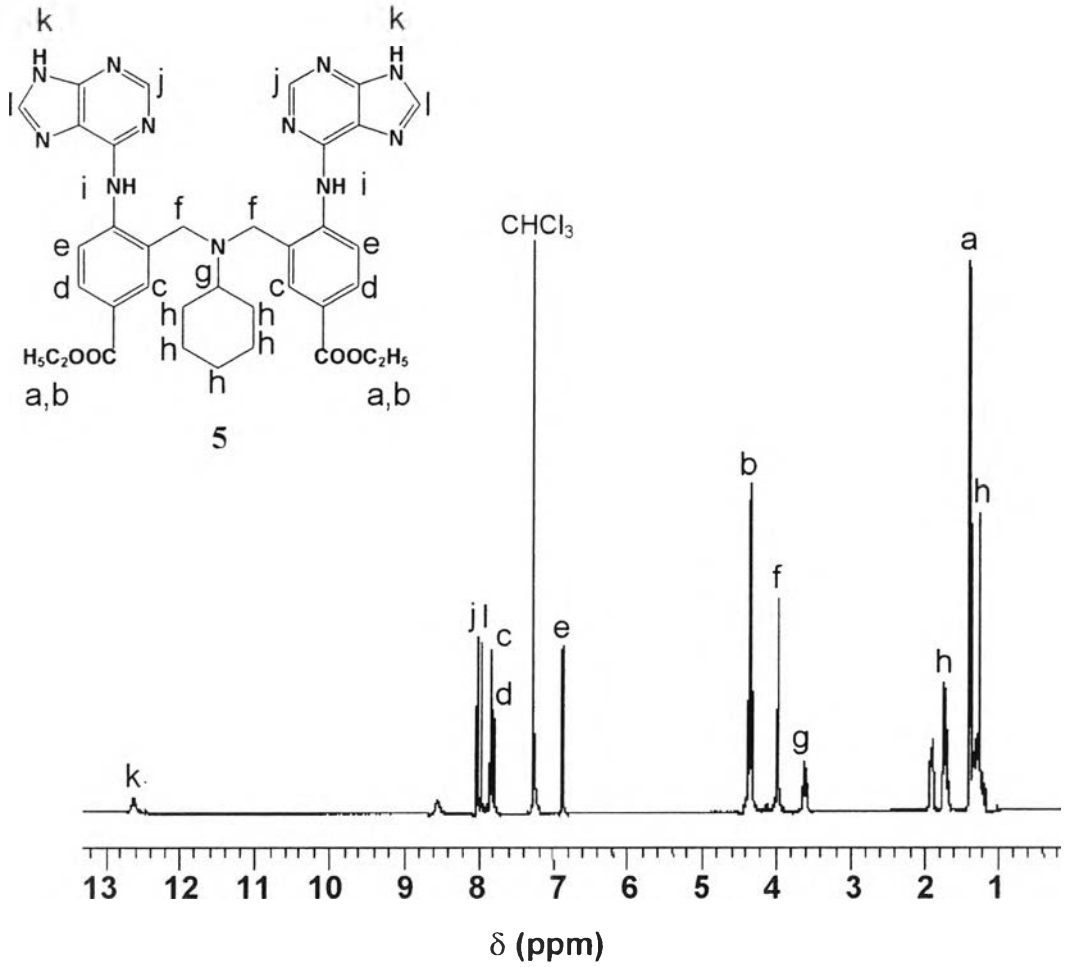

Figure 6.8 ^{1}H-NMR spectrum of **5**.

6.4.5 Polymerization of aza-methylene derivative with difunctionalamine

With a simple structure of diamine, 1, 10-diaminodecane was used to prove the possibility to synthesize the polyamide with **5**. The reaction between ester group of **5** and amine group of 1, 10-diaminodecane was done via esteraminolysis Alkyl groups of 1, 10-diaminodecane reduces the steric effect of adenine compound in compound **5**. After functionalization, N-H stretching bands are found at 3292–3063 cm^{-1} with amide I (C=O) 1668 cm^{-1} and amide II (N-H bending) 1606 cm^{-1}, respectively (see Figure 6.9).

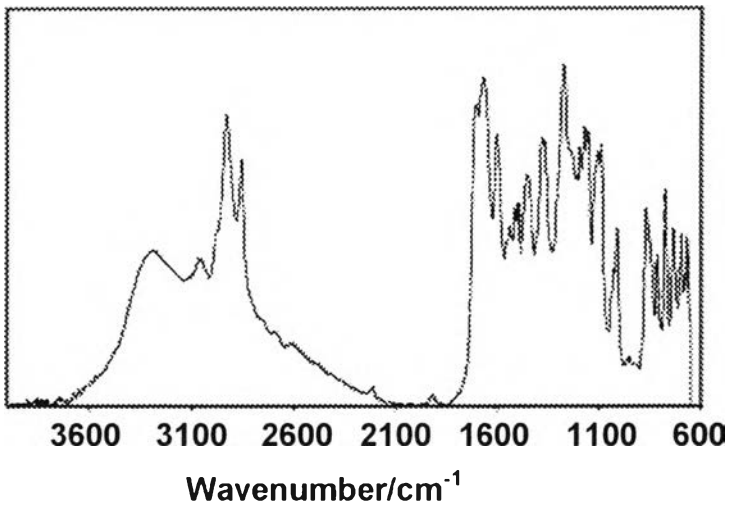

Figure 6.9 FTIR spectra of **6**.

^{1}H-NMR of **6** was shown in Figure 6.10. Amide protons with alkyl proton coupled with CH_2-N were identified at 5.85 ppm (1H, br, NH), and 3.2–3.4 ppm (CH_2-N), respectively. The methylene protons of polyamide main chain were appeared at 1.1–1.8 ppm (2H, m, CH_2). The characteristic chemical shifts of adenine groups were determined as follows, 4.25 ppm (1H, s, NH), 7.95 ppm (1H, s, purine N-CH-N), and 7.92 ppm (1H, s, purine N-CH-NH).

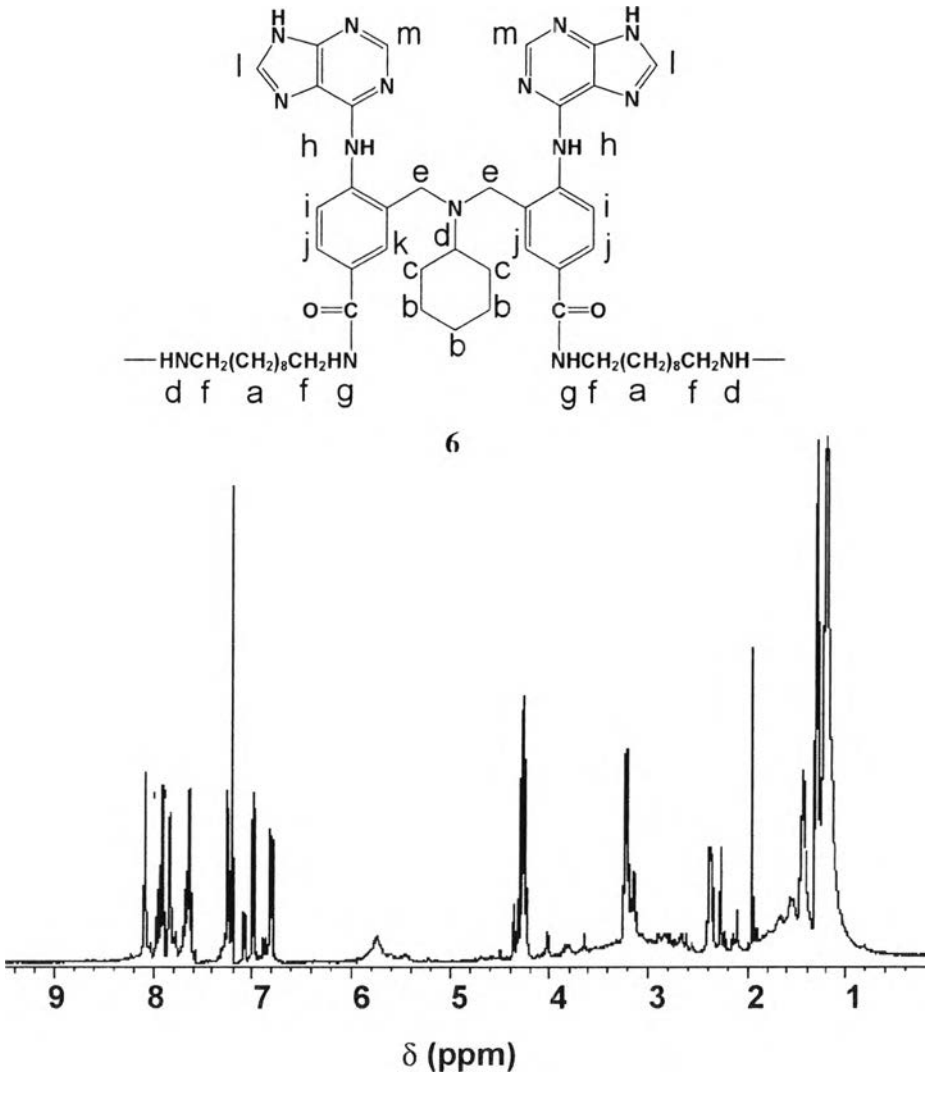

Figure 6.10 ^{1}H-NMR spectrum of **6**.

6.5 Conclusions

Heterocyclic derivative of polyamide chain was prepared by using aza-methylene phenol as a spacer and adenine as a proton transferring part. The present work demonstrates the molecular design and synthesis of polymer chain with functionalized heterocyclic molecules as a proton transferring group. Aza-methylene phenol derivatives were an appropriate spacer to be successfully coupled with adenine via tosylation. The polyamide was obtained from the polymerization of aza-methylene phenol with 1, 10-diaminodecane. The membrane preparation and proton conductivity of polyamide are under investigation.

6.6 Acknowledgements

The author would like to thank Asst. Prof. Sanong Ekgasit and Asst. Prof. Buncha Pulpoka (Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand) for FTIR and ^{1}H NMR measurement. I also gratefully thank Asst. Prof. Vanida Bhavakul (Department of Chemistry, Faculty of Science, King Mongkut's University of Technology, Thonburi, Thailand) for her valuable comments and discussions. We gratefully acknowledge the research fund from Joint Research Program between the National Research Council of Thailand and Japan Society for the Promotion of Science (NRCT-JSPS). We would like to thank National Metal and Materials Center-Chiang Mai University (MTEC-CMU) for the scholarship, and Fuel Cell Research Unit, Chulalongkorn University for the support.

6.7 References and Notes

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