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APPENDICES

Appendix A Structural Characterization of Alkyl Urocanates

All alkyl urocanates (**C1U-C7U**) were successfully prepared as confirmed by FTIR, ^{1}H NMR, and ESI-MS as follows. The compounds obtained showed a significant ester peak at 1710-1720 cm^{-1}. In addition, the imidazole group was confirmed by its characteristic peaks at 3600-2400 cm^{-1} (H---N-H stretching), 1623 cm^{-1} (C-N stretching), 1455 cm^{-1} (C-C stretching), and 1272 cm^{-1} (C-N stretching).The imidazole protons and the hydrocarbon were confirmed at 12.45-6.40 ppm and proton at 5.05-0.85 ppm, respectively. ESI-MS further confirmed the molecular weight with the m/z to be 153.07, 167.08, 195.12, 181.10, 209.13, 223.14, and 237.16, for **C1U-C7U**, respectively.

^{1}H NMR of **C1U** (DMSO-d6) δ: 12.48 (1H, s, N-H), 7.78(1H, s, CH imidazole ring), 7.56 (1H, s, CH imidazole ring), 7.54 (1H, d, CH=CH), 6.34 (1H, d, CH=CH), and 3.68 (3H, t, CH_3).

^{1}H NMR of **C2U** (DMSO-d6) δ: 12.48 (1H, s, N-H), 7.78 (1H, s, CH imidazole ring), 7.54 (1H, s, CH imidazole ring), 7.51 (1H, d, CH=CH), 6.34 (1H, d, CH=CH), 4.15 (2H, m, CH_2), and 1.23 (3H, t, CH_3).

^{1}H NMR of **C3U** (DMSO-d6) δ: 12.50 (1H, s, N-H), 7.78 (1H, s, CH imidazole ring), 7.55 (1H, s, CH imidazole ring), 7.51 (1H, d, CH=CH), 6.36 (1H, d, CH=CH), 4.06 (2H, m, CH_2), 1.65 (2H, m, CH_2), and 0.92 (3H, t, CH_3).

^{1}H NMR of **C4U** (DMSO-d6) δ: 12.38 (1H, s, N-H), 7.75 (1H, s, CH imidazole ring), 7.59 (1H, s, CH imidazole ring), 7.54 (1H, d, CH=CH), 6.35 (1H, d, CH=CH), 4.11 (2H, t, CH_2), 1.61 (2H, m, CH_2), 1.37 (2H, m, CH_2) and 0.92 (3H, t, CH_3).

^{1}H NMR of **C5U** (DMSO-d6) δ: 12.41 (1H, s, N-H), 7.78 (1H, s, CH imidazole ring), 7.60 (1H, s, CH imidazole ring), 7.54 (1H, d, CH=CH), 6.35 (1H, d, CH=CH), 4.08 (2H, t, CH_2), 1.62 (2H, m, CH_2), 1.32 (2H, m, CH_2) and 0.88 (3H, t, CH_3).

^{1}H NMR of **C6U** (DMSO-d6) δ: 12.49 (1H, s, N-H), 7.77 (1H, s, CH imidazole ring), 7.53 (1H, s, CH imidazole ring), 7.50 (1H, d, CH=CH), 6.35 (1H, d, CH=CH), 4.09 (2H, t, CH_2), 1.62 (2H, m, CH_2), 1.32 (2H, m, CH_2) and 0.87 (3H, t, CH_3).

^{1}H NMR of **C7U** (DMSO-d6) δ: 12.37 (1H, s, N-H), 7.76(1H, s, CH imidazole ring), 7.54(1H, s, CH imidazole ring), 7.51 (1H, d, CH=CH), 6.33 (1H, d, CH=CH), 4.10 (2H, t, CH_2), 1.62 (2H, m, CH_2), 1.32 (2H, m, CH_2) and 0.87 (3H, t, CH_3).

Table A1 Single crystal parameter of urocanic acid, **C0**

Compound	**C0**
Empirical formula	$C_6H_6N_2O_2$
Formula weight	138.13
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	6.70(3)
b (Å)	9.50(3)
c (Å)	12.80(8)
V (Å^3)	815(6)
Z	4
Goodness-of-fit on F^2	1.082

Appendix B Proton Conductivity of C1U, C2U, C3U, C5U, and C7U by VTF Equation

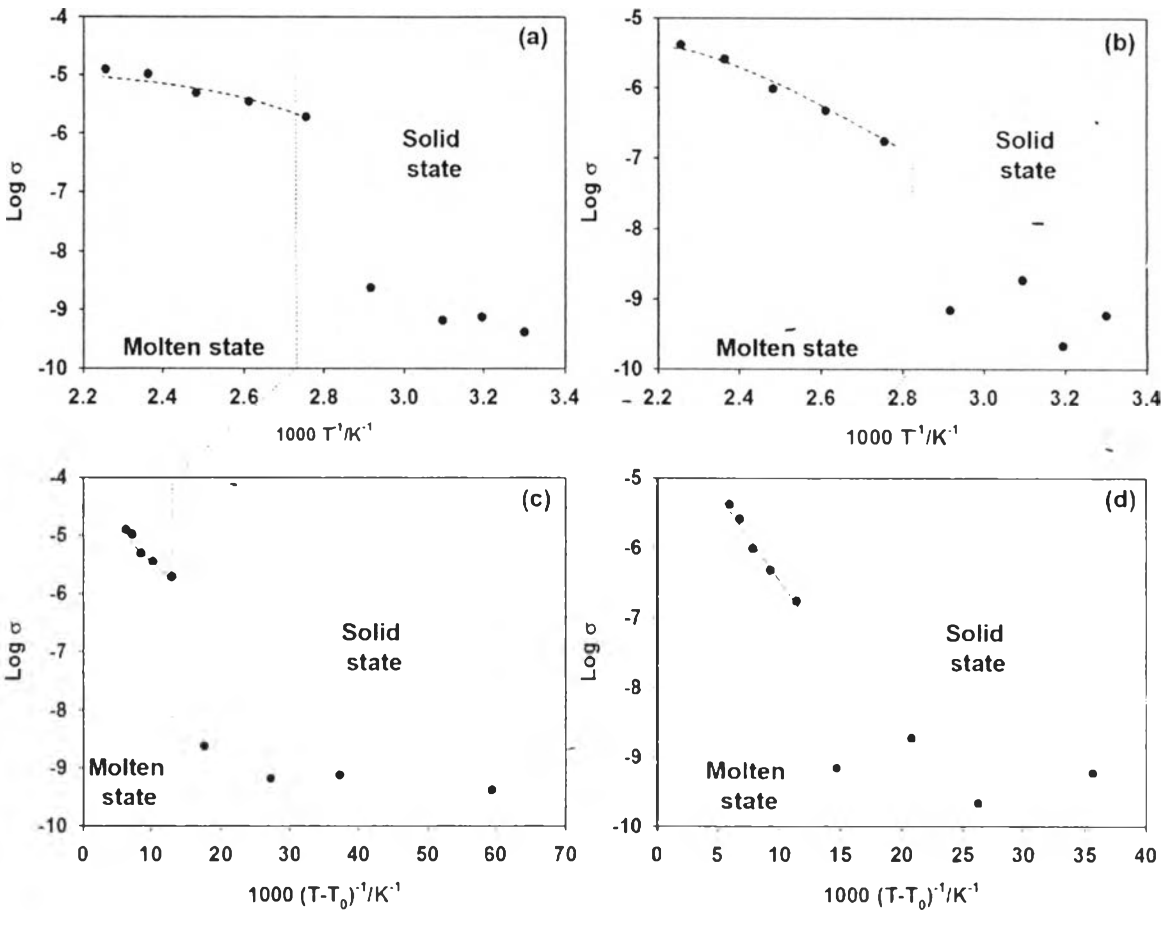

Figure B1 Proton conductivity of **C1U** (a) evaluated by Arrhenius equation and (b) evaluated by VTF equation, and **C2U** (c) evaluated by Arrhenius equation and (d) evaluated by VTF equation with a dot line referring to T_m.

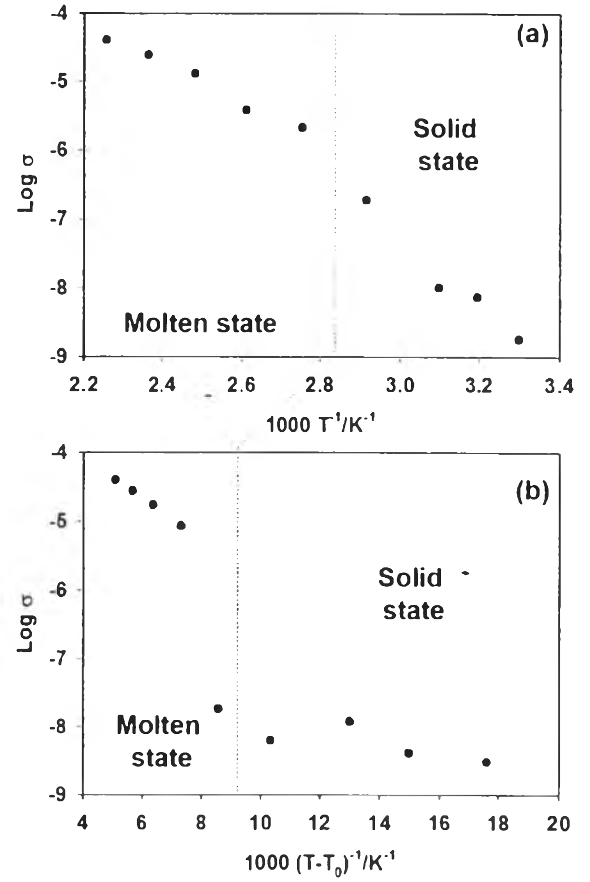

Figure B2 Proton conductivity of **C3U** (a) evaluated by Arrhenius equation and (b) evaluated by VTF equation with a dot line referring to T_m.

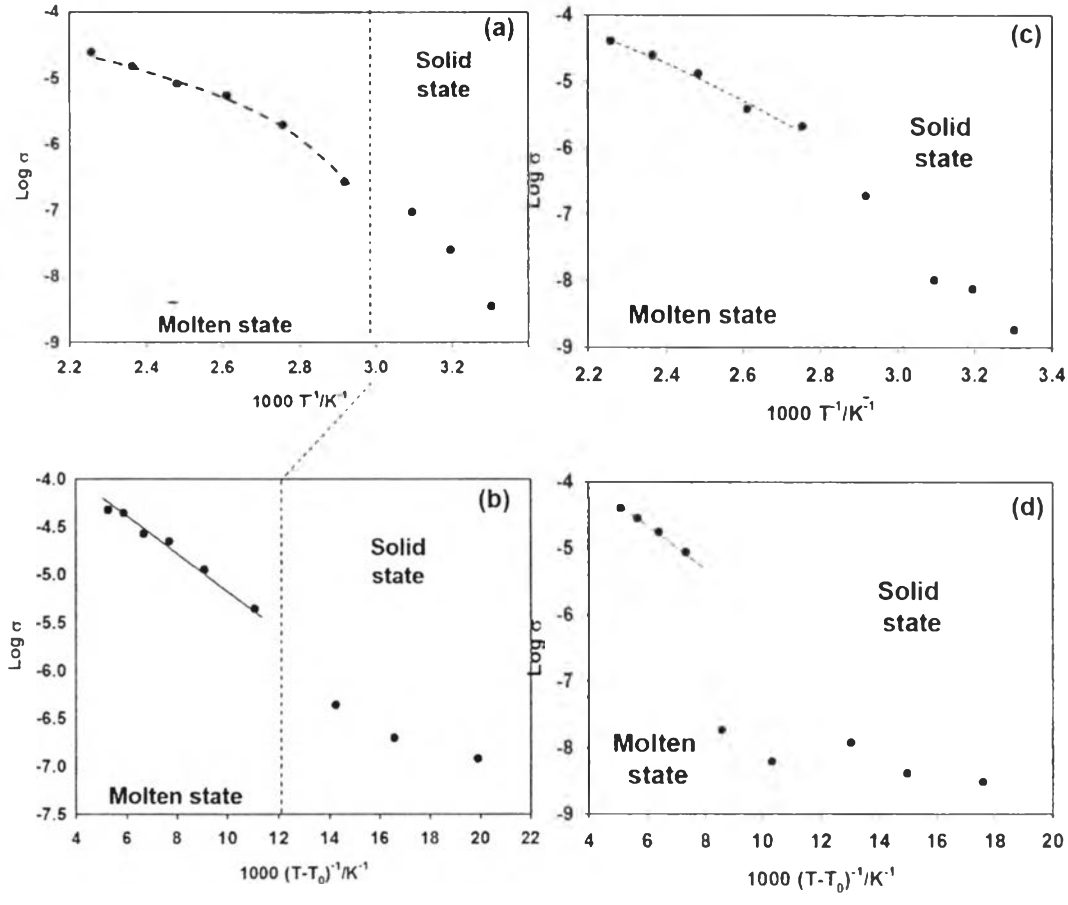

Figure B3 Proton conductivity of **C5U** (a) evaluated by Arrhenius equation and (b) evaluated by VTF equation, and **C7U** (c) evaluated by Arrhenius equation and (d) evaluated by VTF equation with a dot line referring to T_m.

Appendix C Glass Transition Temperature of Alkyl Urocanates

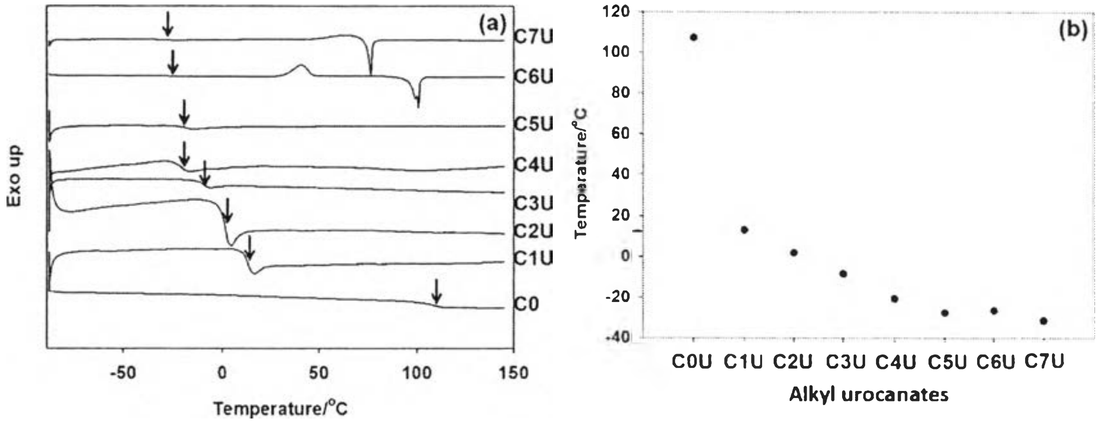

Figure C1 Glass transition temperature (T_g) of alkyl urocanates (a) 2nd heating profile from DSC and (b) T_g in each derivative.

Appendix D Determination of Ion Exchange Capacity (IEC) and Degree of Sulfonation (DS)

The ion exchange capacity (IEC) of SPEEK was estimated by titration. Before titration, the membrane was acidified by soaking in HCl solution (1 mol L^{-1}) for 6 hours at 80 °C. Next, the membrane was dried in a hot air oven for 1 day. A standard aqueous NaOH (1 mol L^{-1}) was used for titration. The protonated membranes (0.5–1.0 g) were immersed in NaCl solution (1 mol L^{-1}) more than 18 hours. The solutions obtained were then titrated with NaOH (0.1 mol L^{-1}) to determine the sulfonation degree based on the IEC value using the following equations [1,2]. The molar quantity of the sulfonic acid group in the SPEEK membrane was calculated by:

$$N_{H^+} = (MV)_{NaOH}/V_{NaCl} \qquad (1)$$

where M_{NaOH} is the molar concentration of NaOH, V_{NaOH} is volume of NaOH solution, and V_{NaCl} is volume of NaCl solution. IEC can be calculated by:

$$IEC = [N_{H^+}/W_{Sample}] \text{ (mol (l.g)}^{-1}) \qquad (2)$$

where N_{H^+} is the molar concentration of protons obtained from the sulfonic acid group and W_{Sample} is the weight of the SPEEK membrane that was used for titration. The IEC of our SPEEK is 1.654 mol $(l\cdot g)^{-1}$.

The sulfonation degree (DS) of SPEEK can also be evaluated by ^1H NMR [3,4] as Eq. 3.

$$n/12\text{-}2n = I_{H13} / [I_{H1\text{-}H12} + I_{H14\text{-}H15}] \qquad (3)$$

$$DS = n \times 100 \qquad (4)$$

where n is the number of I_{H13} per repeat unit, I_{H13} refers to integration value of particular proton next to sulfonic acid group, $I_{H1\text{-}H12}$, and $I_{H14\text{-}H15}$ refers to integration of aromatic ring which no substitution of sulfonic acid group.

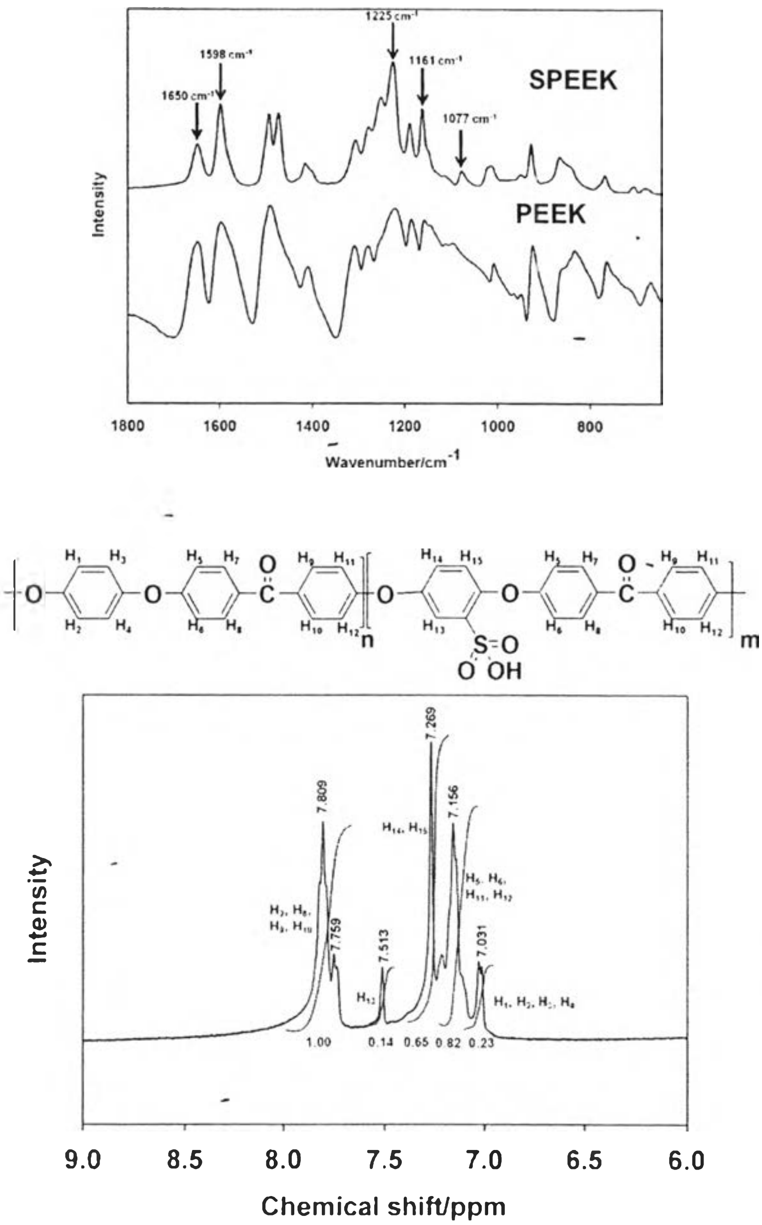

Figure D1 FTIR spectra of PEEK powder, SPEEK precipitate and ^{1}H NMR of SPEEK.

Appendix E: Characterization of SPEEK-CxU by FTIR

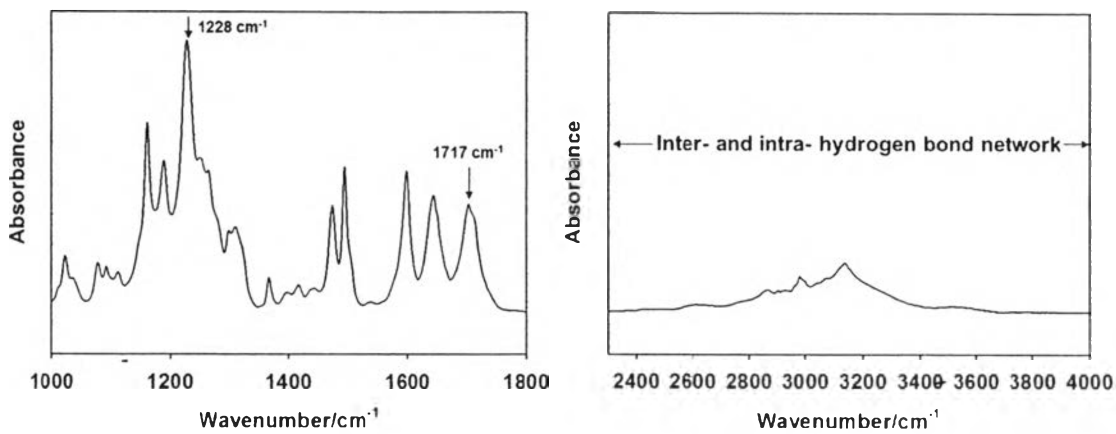

Figure E1 FTIR spectra of **SPEEK-C1U**.

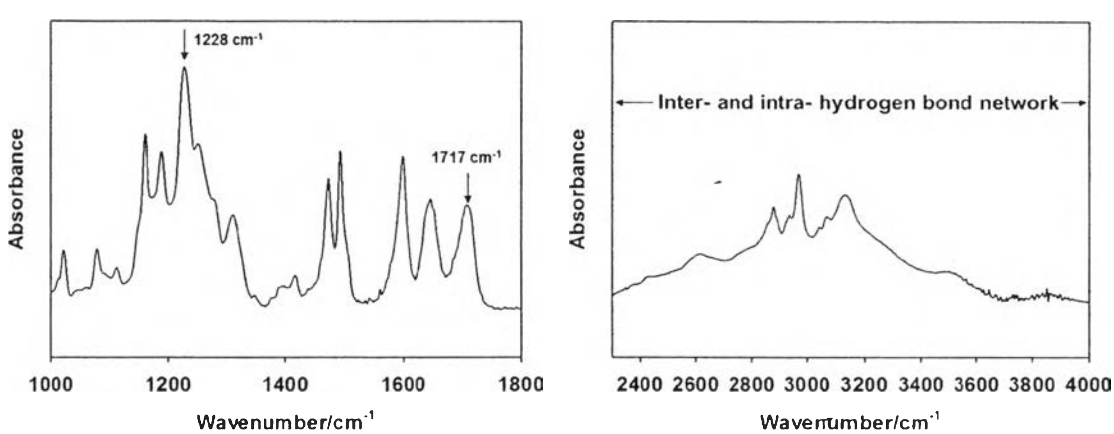

Figure E2 FTIR spectra of **SPEEK-C2U**.

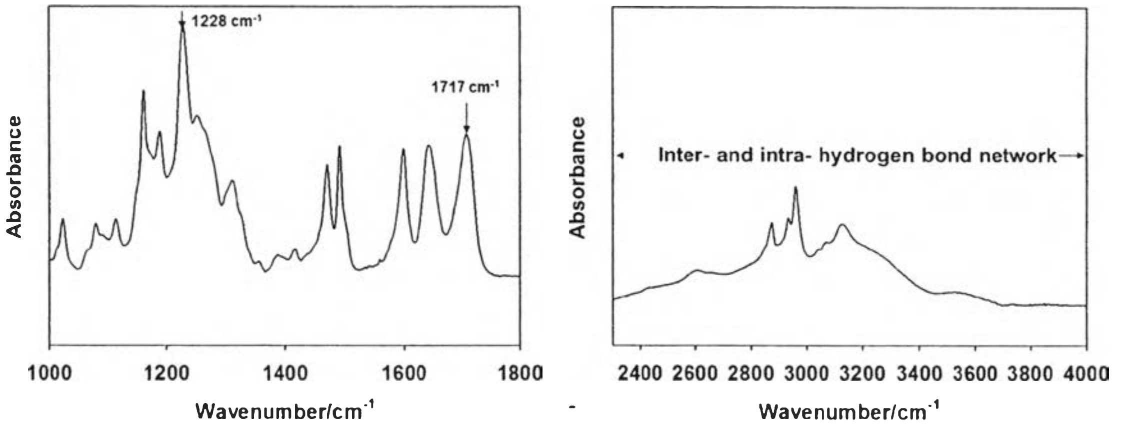

Figure E3 FTIR spectra of **SPEEK-C3U**.

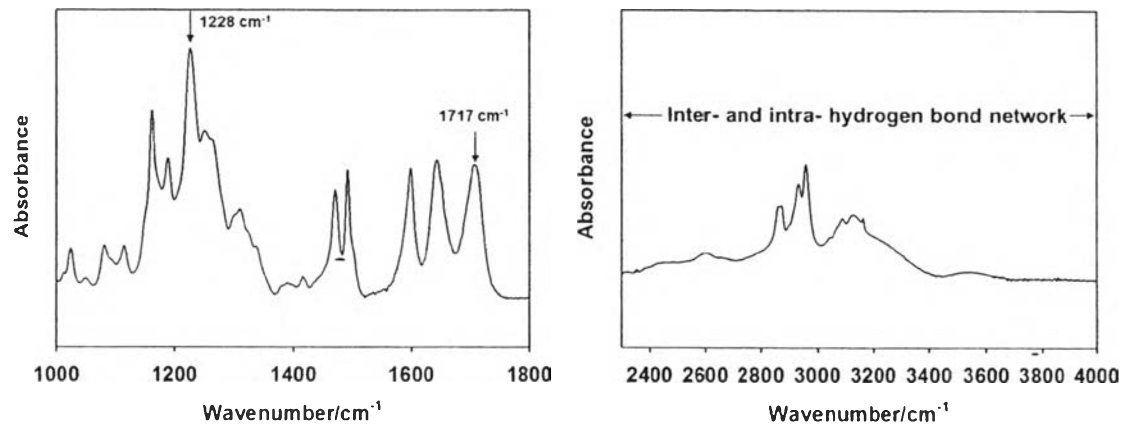

Figure E4 FTIR spectra of **SPEEK-C4U**.

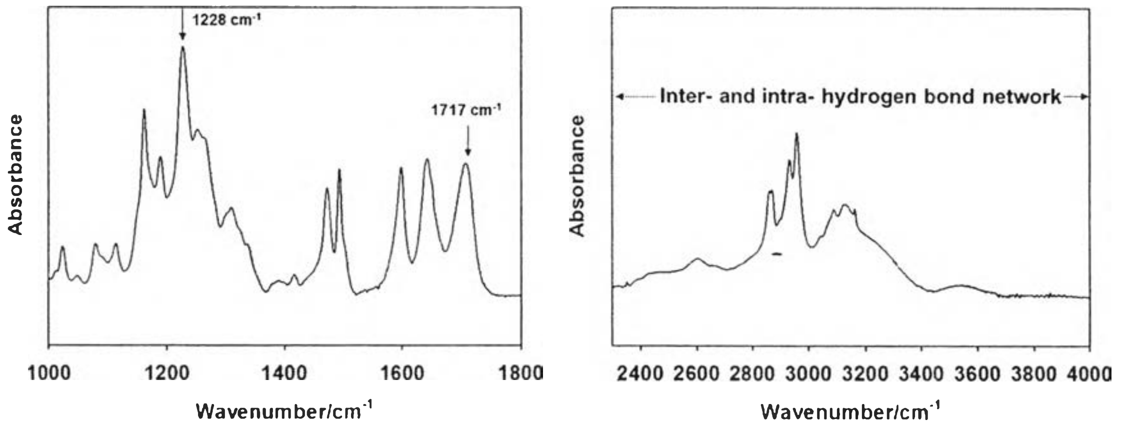

Figure E5 FTIR spectra of **SPEEK-C5U**.

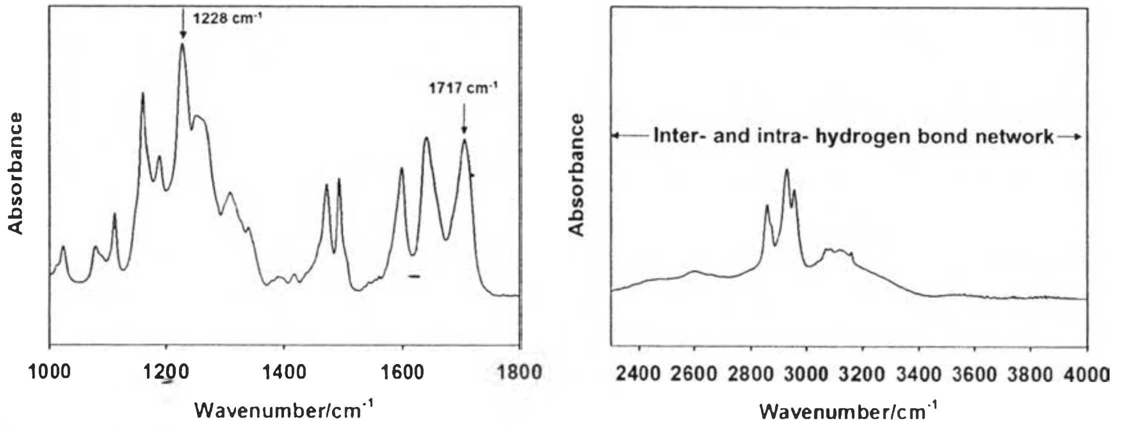

Figure E6 FTIR spectra of **SPEEK-C6U**.

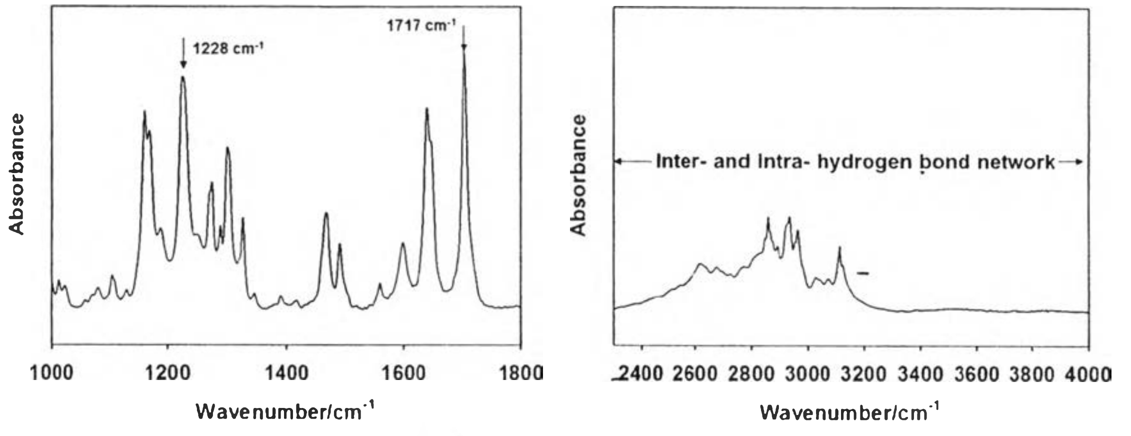

Figure E7 FTIR spectra of **SPEEK-C7U**.

Appendix F Degradation Temperatures of SPEEK-CxU

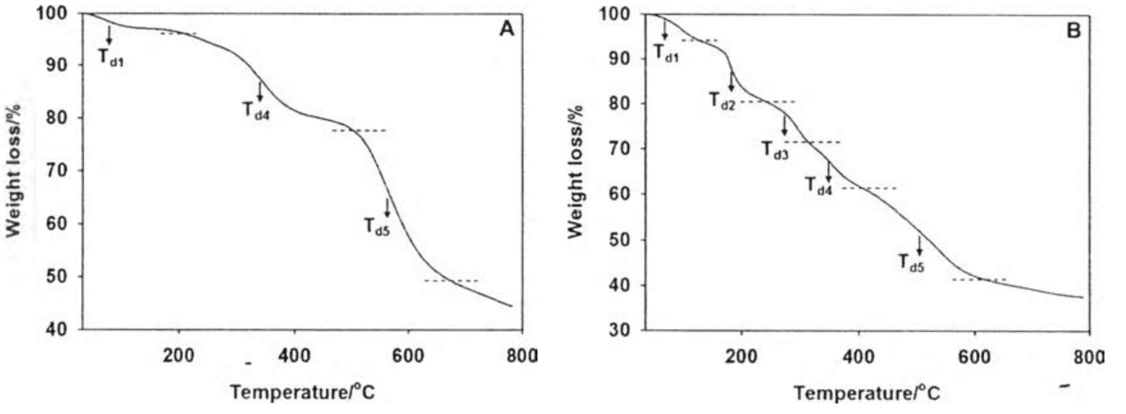

Figure F1 Degradation temperature of (a) SPEEK, and (b) **SPEEK-C1U**.

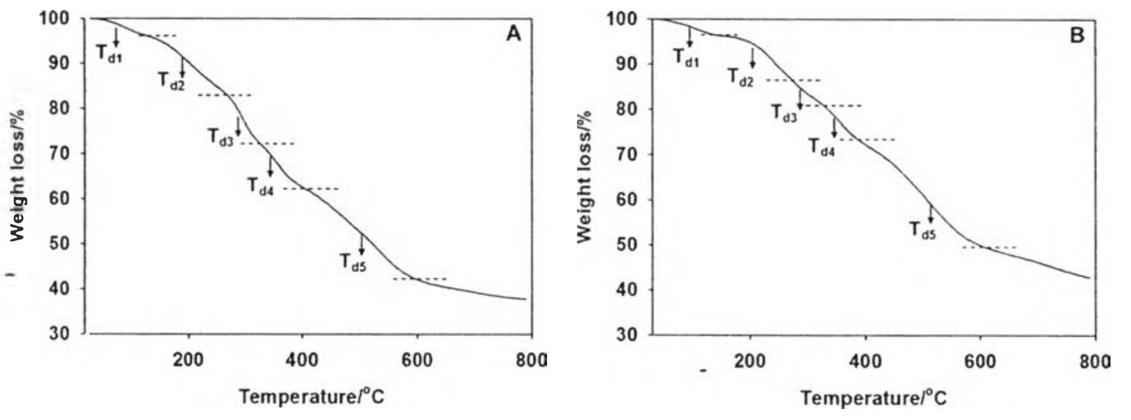

Figure F2 Degradation temperature of (a) **SPEEK-C2U**, and (b) **SPEEK-C3U**.

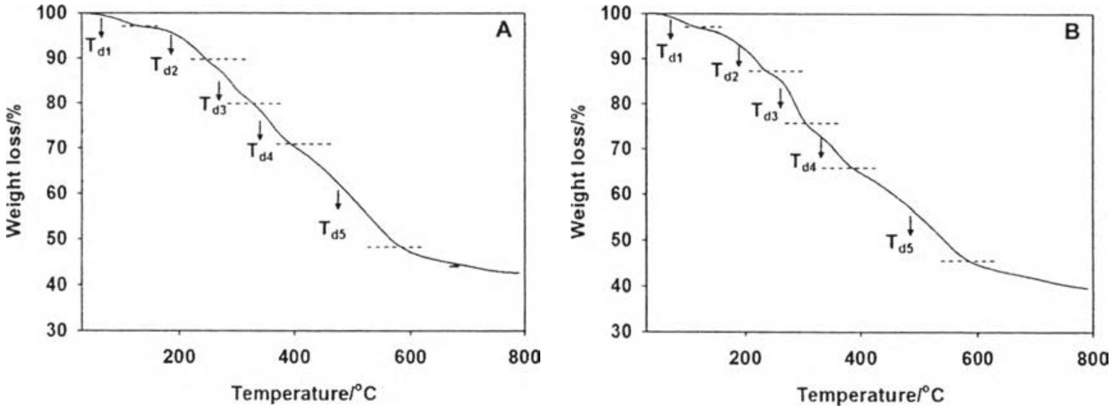

Figure F3 Degradation temperature of (a) **SPEEK-C5U**, and (b) **SPEEK-C7U**.

Table F1 Degradation and melting temperatures of SPEEK and **SPEEK-CxU**

Sample name	Degradation temperature (°C)						Melting temperature (°C)
	T_{d1}	T_{d2}	T_{d3}	T_{d4}	T_{d5}	Water content (%)	T_m
SPEEK	.			317.5	514.6	2.98	90
SPEEK-C1U	93.71	179.26	295.48	356.01	538.41	6.51	150.7
SPEEK-C2U	91.26	201.5	295.48	357.63	532.77	3.76	140
SPEEK-C3U	107.43	243.02	279.34	357.63	502.1	3.66	149.4
SPEEK-C4U	94.5	233.34	295.48	356.82	534.38	3.47	157.7
SPEEK-C5U	102.59	235.76	290.64	360.86	530.34	3.16	137.4
SPEEK-C6U	77.57	184.9	293.87	359.24	541.64	2.35	158.3
SPEEK-C7U	95.33	221.23	284.17	360.05	539.22	3.61	153

Appendix G Proton Conductivity of SPEEK-CxU by VTF Equation

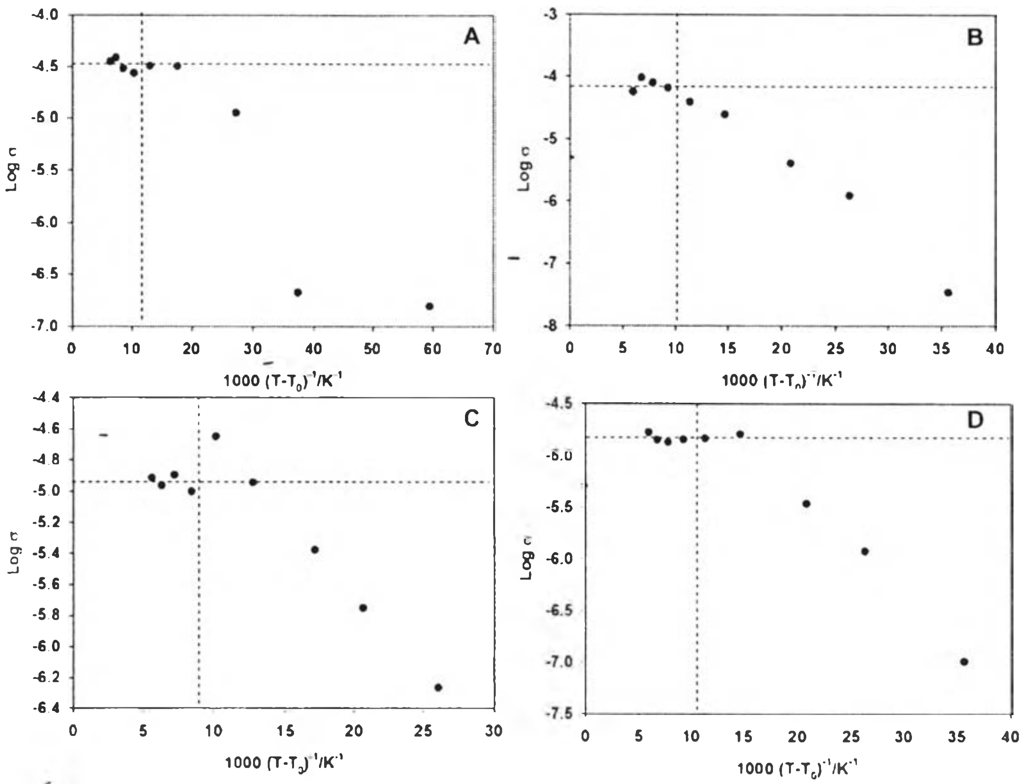

Figure G1 Proton conductivity of (a) **SPEEK-C1U**, (b) **SPEEK-C2U**, (c) **SPEEK-C3U**, and (d) **SPEEK-C5U** by VTF equation.

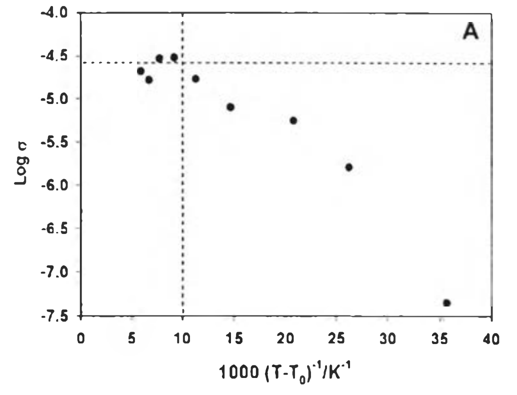

Figure G2 Proton conductivity of (a) **SPEEK-C7U** by VTF equation.

Appendix H Isosbestic Point of SPEEK-CxU

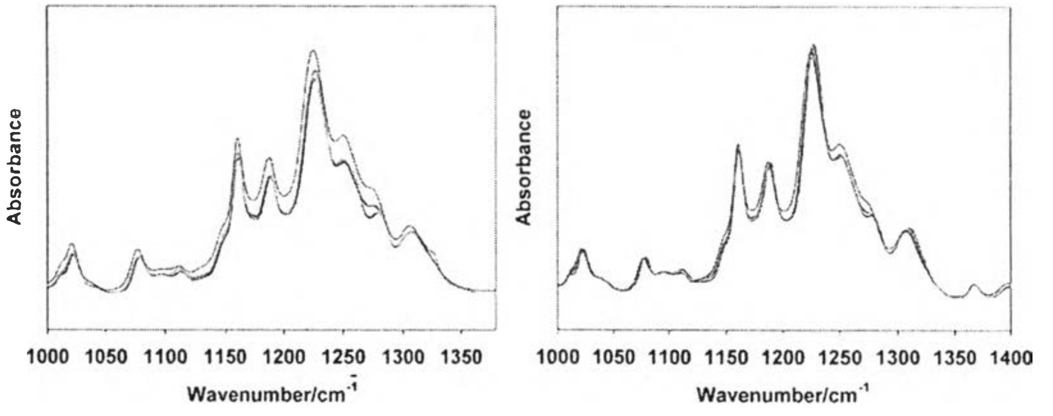

Figure H1 Temperature dependence FTIR spectra of (a) **SPEEK-C1U**, and (b) **SPEEK-C2U** at wavenumber 1000-1400 cm^{-1}.

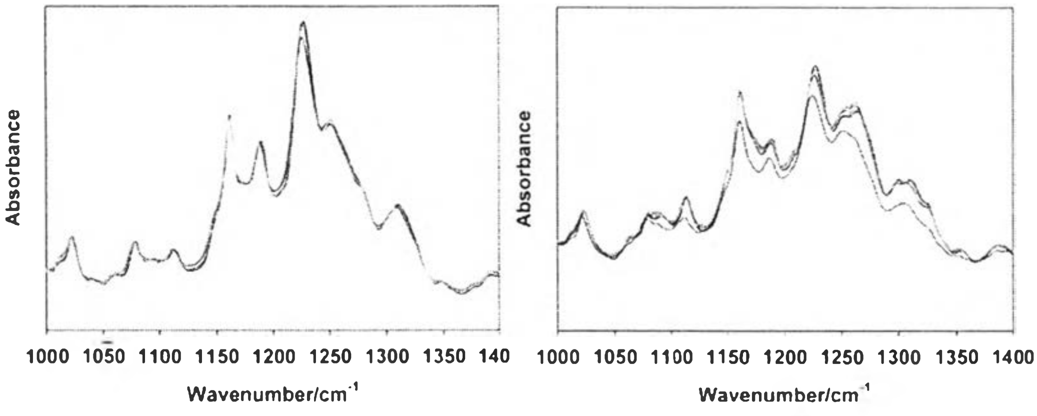

Figure H2 Temperature dependence FTIR spectra of (a) **SPEEK-C3U**, and (b) **SPEEK-C5U** at wavenumber 1000-1400 cm^{-1}.

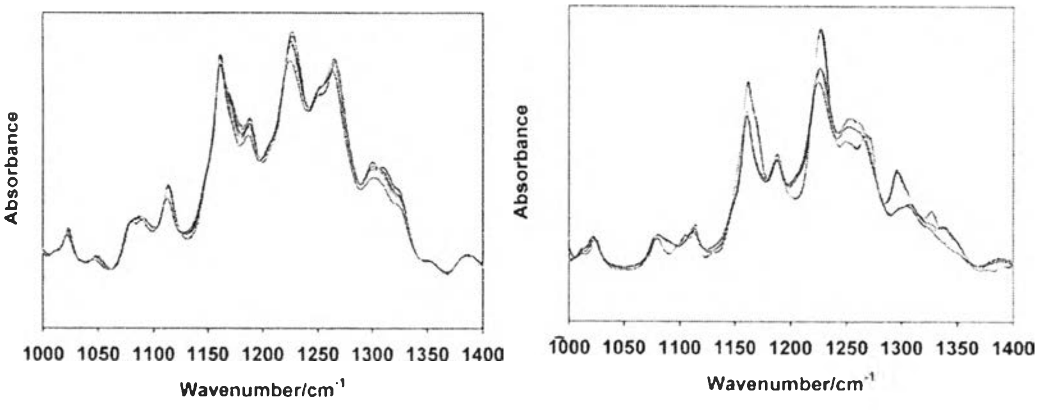

Figure H3 Temperature dependence FTIR spectra of (a) **SPEEK-C6U**, and (b) **SPEEK-C7U** at wavenumber 1000-1400 cm^{-1}.

Appendix I Full Width Haft Maximum of Symmetric Sulfonic Acid Peak of SPEEK-CxU as a Function of Temperatures

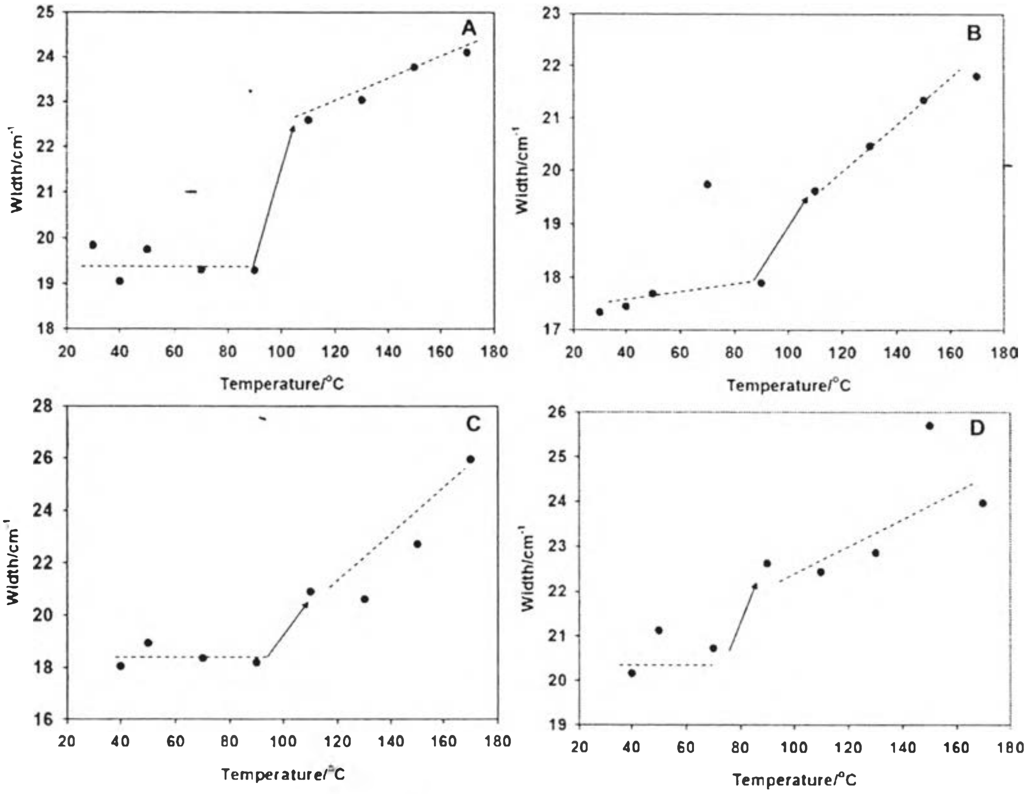

Figure I1 Full width half maximum of sulfonic acid group as a function of temperatures of (a) **SPEEK-C1U**, (b) **SPEEK-C2U**, (c) **SPEEK-C3U**, and (d) **SPEEK-C5U** using the OPUS 5.5 program.

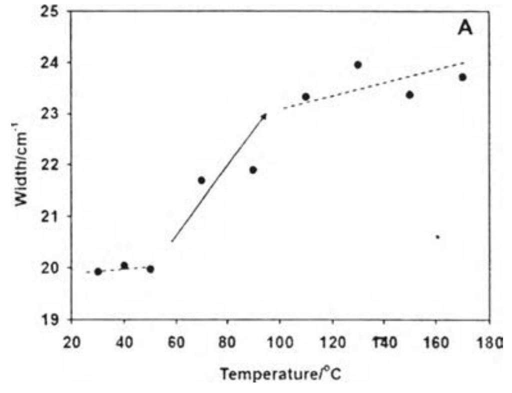

Figure I2 Full width half maximum of sulfonic acid group as a function of temperatures of (a) **SPEEK-C7U** using the OPUS 5.5 program.

Appendix J Temperature Dependence FTIR of Inter- and Intra- Hydrogen Bond Networks

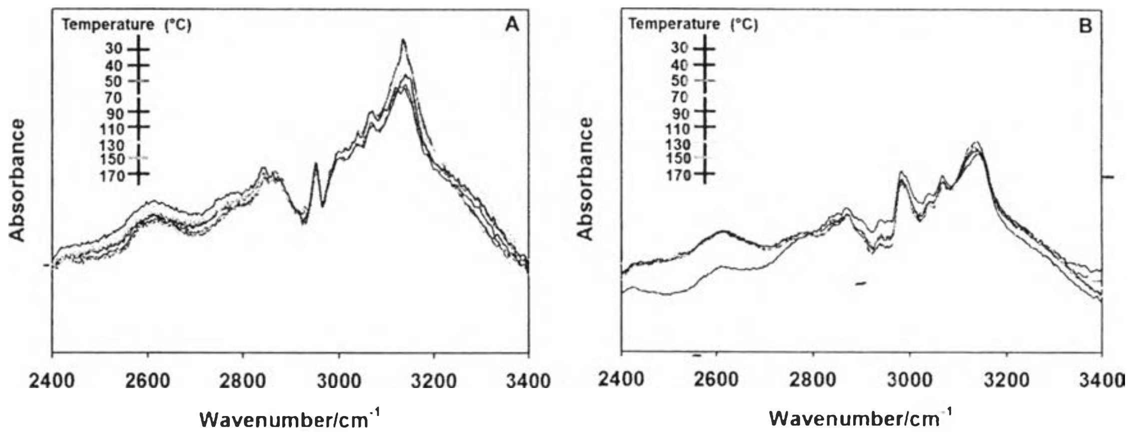

Figure J1 Temperature dependence FTIR spectra of (a) SPEEK-C1U, and (b) SPEEK-C2U in range of 2400 cm^{-1} – 3400 cm^{-1}.

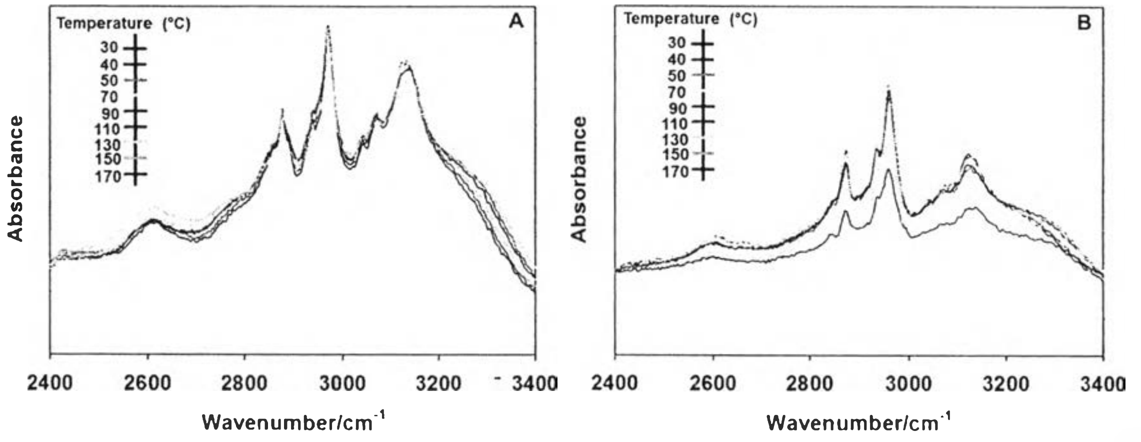

Figure J2 Temperature dependence FTIR spectra of (a) SPEEK-C3U, and (b) SPEEK-C4U in range of 2400 cm^{-1} – 3400 cm^{-1}.

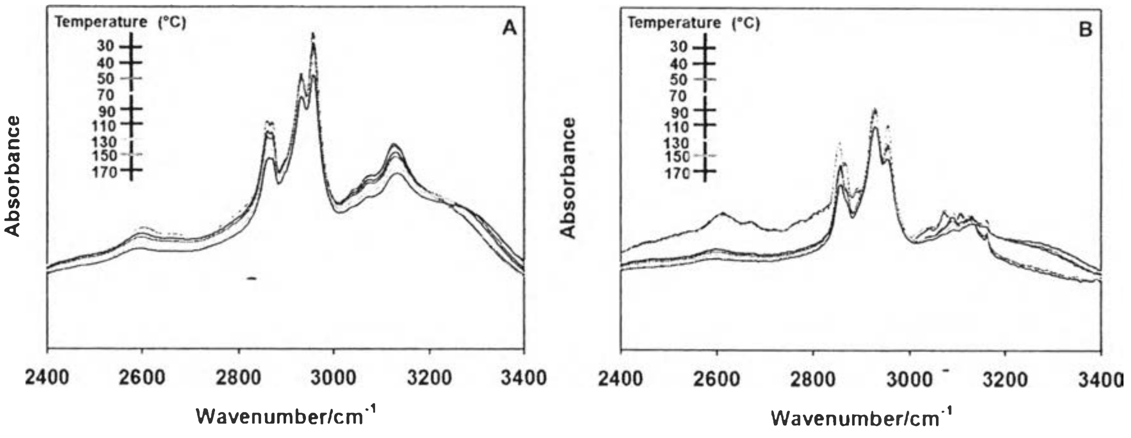

Figure J3 Temperature dependence FTIR spectra of (a) SPEEK-C5U, and (b) SPEEK-C6U in range of 2400 cm^{-1} – 3400 cm^{-1}.

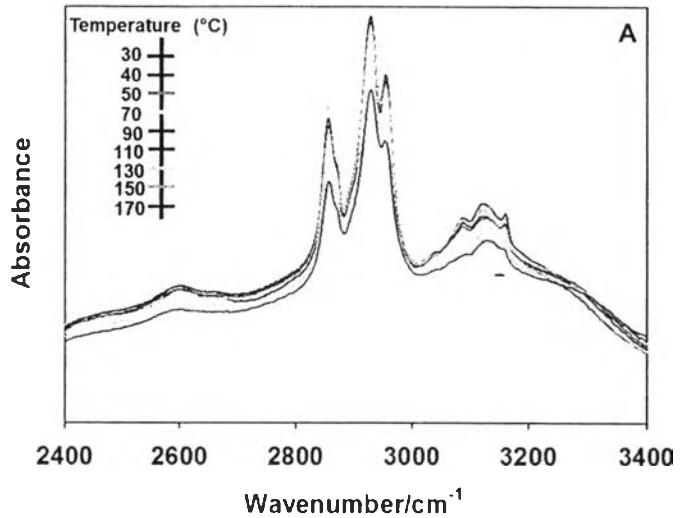

Figure J4 Temperature dependence FTIR spectra of (a) SPEEK-C7U in range of 2400 cm^{-1} – 3400 cm^{-1}.

Appendix K Comparison of Proton Conductivity between SPEEK-C4U and SPEEK-C6U

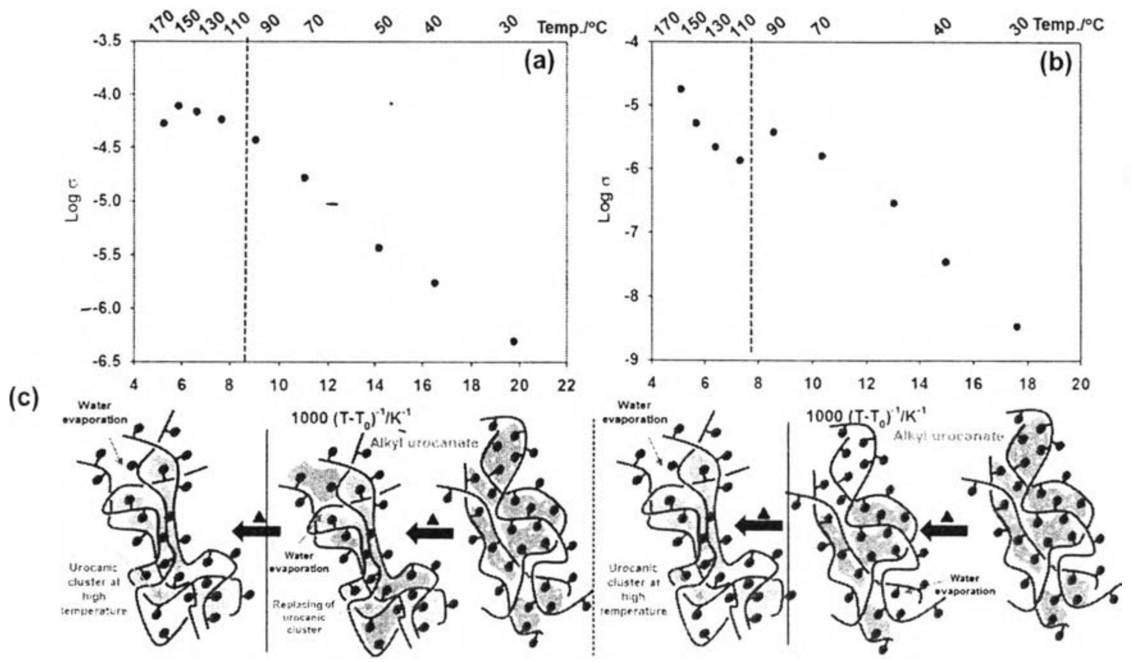

Figure K1 Proton conductivity of (a) **SPEEK-C4U**, (b) **SPEEK-C6U** as a function of temperatures based on VTF equation, and (c) schematic draw of proton channel in polymer matrix related to temperature.

Appendix L Solubility of SPEEK

Table L1 Degree of sulfonation and solubility in DMSO of SPEEK under variation of reaction time

Reaction time (hours)	DS (%)*	Solubility in DMSO
2	21	×
3	43	▲
4	47	▲
6	57	○

Note: × = insoluble, ▲ = partially soluble, and ○ = soluble

*DS is calculated from titration method.

Appendix M Calculation of Energy Band Gap (E_g) and Aromatic Carbon in Cluster (N)

The relationship between optical absorption coefficient (α) and photon energy is used to explain about energy band gap under heat treatment which might be attributed to thermochromic property of polymer as described by using Eq. 1.[5] In addition, The optical absorption coefficient can be calculated by Eq. 2 derived from Urbach rule.[6]

$$\alpha = A(h\nu - E_g)^n \quad (1)$$

$$\alpha = 1/L \ln (I_0/I_t) \quad (2)$$

Where A is the constant, h is the Plank's constant (6.626×10^{-34} Joules sec), ν is the frequency of the radiation, and E_g is the optical energy band gap. The type of transition is responsible for the absorption depending on the value of n, where n refers to an index that can take any of the values 1/2, 3/2, 2, or 3. In our case, n = 1/2, which means an allowed direct transition. In the allowed direct transition, simply electron is transferred vertically from the top of valence band to bottom of the conduction band, whereas the non-vertical transitions are normally forbidden.[5,7] I_o and I_t are the intensities of incident and transmitted light, respectively, L is the thickness of the sample (cm).

The number of aromatic carbon (N) in a cluster is correlated to E_g determined by using modified Tauc's equation.[6]

$$N = 2\beta\pi / Eg \quad (3)$$

Where 2β is the band structure energy of a pair of adjacent π sites and β is taken to be 2.9 eV associated with $\pi \rightarrow \pi^*$ optical transition in –C=C– structure of aromatic ring.

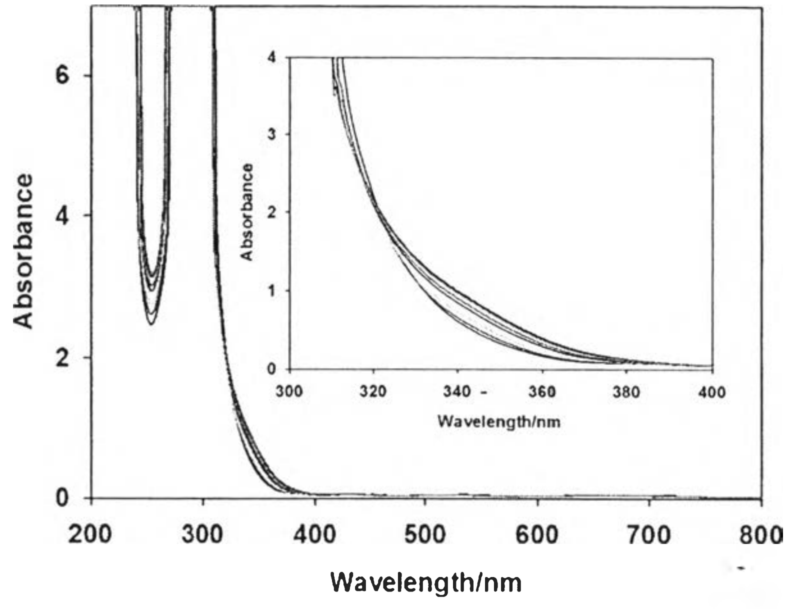

Figure M1. Temperature dependence UV-Vis spectra of SPEEK thin film in range of 200-800 nm and temperature dependence UV-Vis spectra in range of 300-400 nm (inserted figure): 27 °C (——), 50 °C (——), 75 °C (——), 100 °C ( ), 125 °C (——), 150 °C (——), 175 °C (——), 186 °C (——), 198 °C (——), and 213 °C (——).

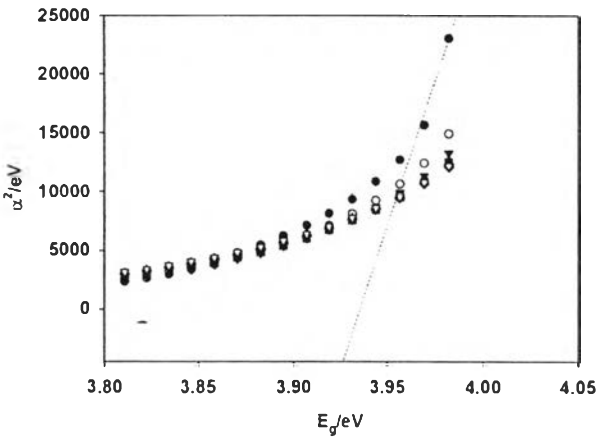

Figure M2. Relationship of optical absorption coefficient (direct optical band gap, α^2) and photon energy of SPEEK thin film as a function of temperatures: 25 °C (●), 50 °C (○), 75 °C (▼), 100 °C (Δ), 125 °C (■), 150 °C (□), 175 °C (♦), 186 °C (◊), 198 °C (▲), and 213 °C (∇). Broken line refers to 25 °C.

Appendix N Thermochromic Property of PEEK Thin Film

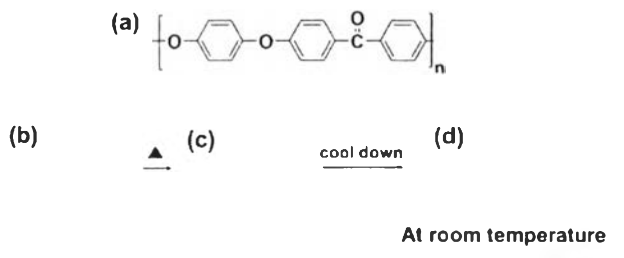

Figure N1 (a) Chemical structure of PEEK, (b) SPEEK thin film at room temperature, (c) at high temperature (above 190°C), and (d) leaving at room temperatures.

Appendix O Temperature Dependence FTIR of PEEK Thin Film

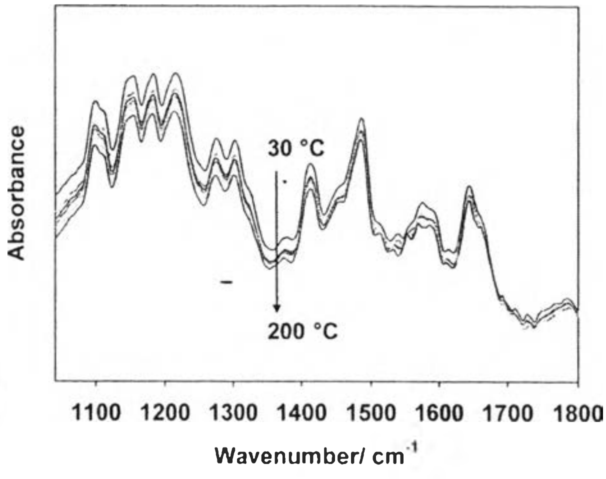

Figure O1 Temperature dependence FTIR spectra of PEEK thin film as a function of temperatures.

Appendix P SPEEK Thin Film in Dry System

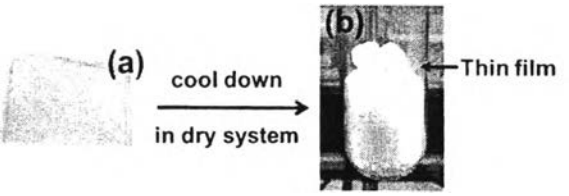

Figure P1 (a) SPEEK thin film at 190 °C (yellow film), and (b) SPEEK thin film at dry system for an hour in tube containing calcium chloride dehydrated (yellow film).

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(7) Pejova, B.; Tanuševski, A.; Grozdanov, I. *J. Solid State Chem.* **2004**, *177*, 4785.

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Publications:

1. Jarumaneeroj, C.; Tashiro K; and Chirachanchai, S. (2014) Molecular Mobility of Imidazoles in Molten State as a Key Factor to Enhance Proton Conductivity Journal of Power Sources, 249, 185-192.
2. Jarumaneeroj, C.; and Chirachanchai, S. Alkyl Urocanates as Proton Transfer Species in Molten State: An Access to Proton Conductivity in the Long Range of Operating Temperature (Submitted to Macromolecules).
3. Jarumaneeroj, C.; Tashiro, K.; and Chirachanchai, S. (2014) Shifting from Hydrogen Bond Network to π-π Stacking: A Key Mechanism for Reversible Thermochromic Sulfonated Poly (Ether Ether Ketone) Macromolecular Rapid Communications (accepted).

Proceedings:

1. Jarumaneeroj, C.; Pangon, A.; and Chirachanchai, S. (2010, October 8) Effect of Hydrogen Bond Network and Chain Mobility on Proton Conductivity in Heterocyclic System for Polymer Electrolyte Membrane Fuel Cell (PEMFC). The 1st Polymer Conference of Thailand, Bangkok, Thailand (Oral presentation).

Presentations:

1. Jarumaneeroj, C.; Pangon, A.; and Chirachanchai, S. (2010, July 9-10) Systematic Molecular Design of Heterocyclic to Improve Proton Conductivity. Paper presented at The Joint Symposium on Advanced Polymer Science and Nanomaterials by Chulalongkorn University – Inha University, Bangkok, Thailand (Poster presentation).
2. Jarumaneeroj, C.; Pangon, A.; and Chirachanchai, S. (2010, October 8) Effect of Hydrogen Bond Network and Chain Mobility on Proton Conductivity in Heterocyclic System for Polymer Electrolyte Membrane Fuel Cell (PEMFC). Paper presented at The 1st Polymer Conference of Thailand, Bangkok, Thailand (Oral presentation)
3. Jarumaneeroj, C.; and Chirachanchai, S. (2011, June 25-July 1) Synergistic Effect of H-bond and Chain Mobility in Enhancing Proton Transfer: A Study Case in Urocanic acid system. Paper presented at European Polymer Congress, Granada, Spain (Oral presentation).
4. Jarumaneeroj, C.; Tashiro, K.; and Chirachanchai, S., (2013, April 6) Imidazole Derivatives with Various Chain Lengths as a Proton Conductive Species for Systematic Studies on the Balance of Chain Mobility and Hydrogen Bond in Enhancing Proton Conductivity, Paper presented at RGJ-Ph. D. Congress XIV, Chonburi, Thailand (Oral presentation, Outstanding presentation awards).
5. Jarumaneeroj, C.; Tashiro, K.; and Chirachanchai, S., (2014, March, 27-28) Role of Hydrogen Bond Network and Chain Mobility of Alkyl Urocanates to Improve Proton Conductivity, Paper presented at The 4th Polymer Conference of Thailand, Bangkok, Thailand (Poster presentation).