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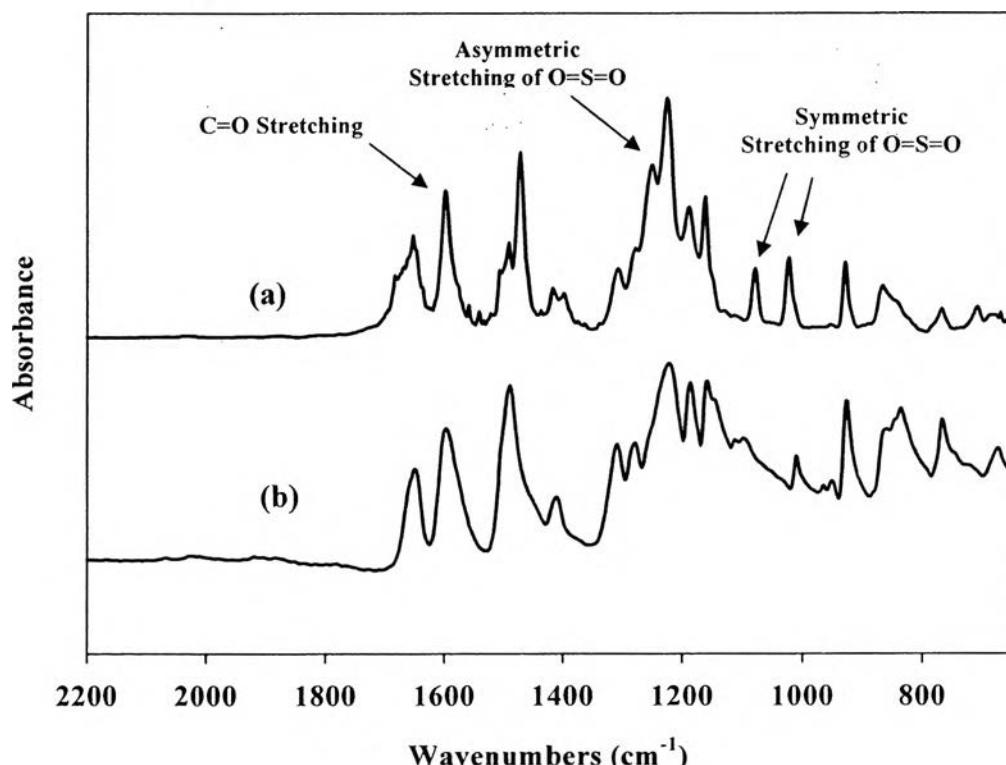
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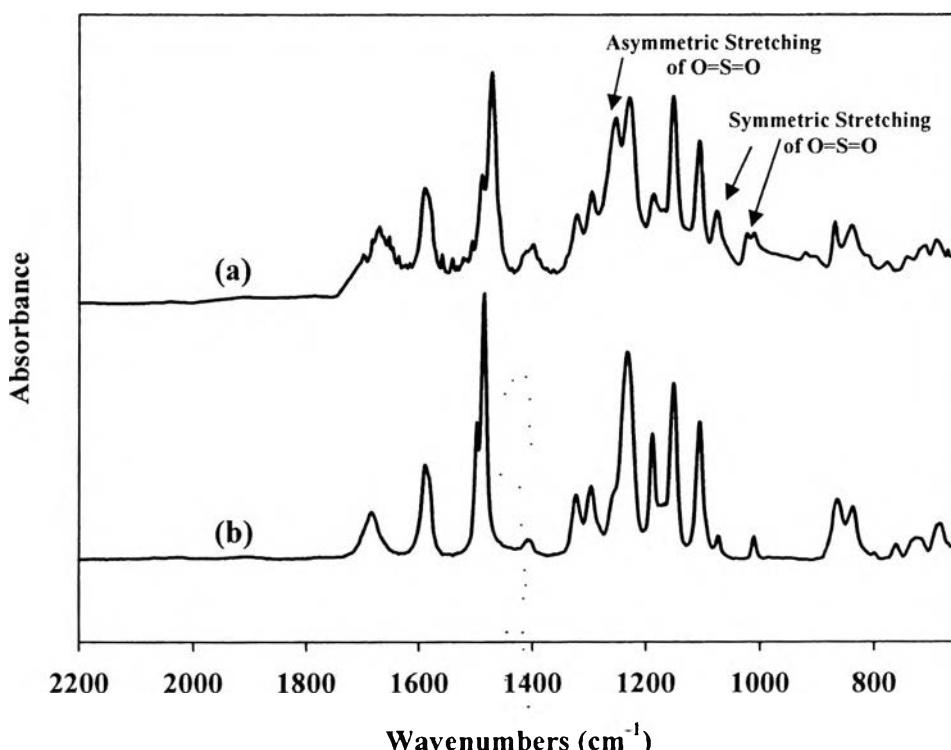
## APPENDICES

### Appendix A Identification of Characteristic Peaks of FT-IR Spectrum of Poly(ether ether ketone), Sulfonated Poly(ether ether ketone), Poly(1,4-phenylene ether ether sulfone) and Sulfonated Poly(1,4-phenylene ether ether sulfone)

The FT-IR spectra of sulfonated and unsulfonated polymers were obtained using a Thermo Nicolet (Nexus 670) spectrometer to identify the presence of sulfonic acid group (-SO<sub>3</sub>H) in polymer samples. The spectrometer was operated in the absorption mode with 64 scans, in the wave numbers range of 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> using a deuterated triglycine sulfate as the detector. KBr and ZnSe disc were used as the background materials. Polymer samples were mixed with a dried KBr. In contrast, each of S-Polymer samples was prepared by casting as thin films of S-Polymer onto the ZnSe disc.



**Figure A1** The FT-IR spectra of: a) sulfonated Poly(ether ether ketone) (S-PEEK) and b) Poly(ether ether ketone) (PEEK).



**Figure A2** The FT-IR spectra of: a) sulfonated Poly(1,4-phenylene ether ether sulfone) (S-PPEES) and b) Poly(1,4-phenylene ether ether sulfone) (PPEES).

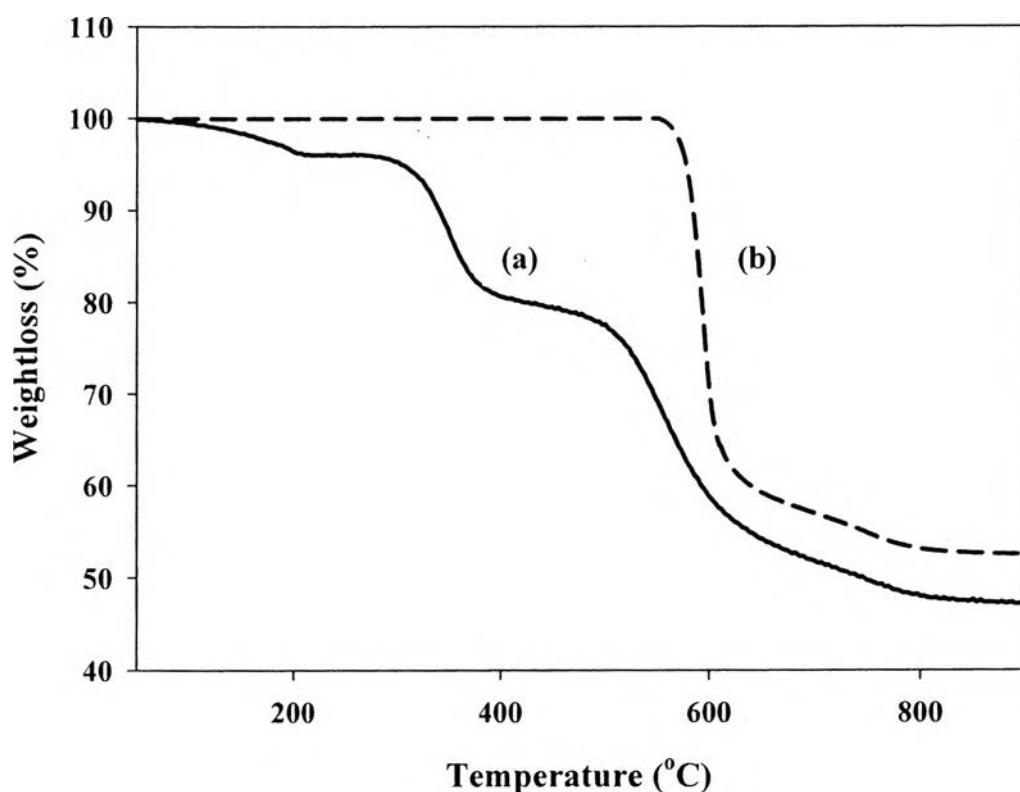
The absorption infrared spectra of PEEK and S-PEEK were shown in comparison in Figure A1 which identifies the sulfonic acid groups. For PEEK the peaks at 1650 and 1222  $\text{cm}^{-1}$  are assigned to C=O and C-O-C stretching of polymer backbone, respectively. For S-PEEK the peak at 708  $\text{cm}^{-1}$  can be assigned to the symmetric S-O stretching vibration. The peak at 1022  $\text{cm}^{-1}$  represents the symmetric S=O stretching. The symmetric and the asymmetric O=S=O stretching vibrations were confirmed by the strong characteristic peaks at 1078 and 1250  $\text{cm}^{-1}$ . Subsequently, PPEES and S-PPEES were shown in Figure A2. The peak at 709  $\text{cm}^{-1}$  can be assigned to the symmetric S-O stretching vibration. The peak at 1022  $\text{cm}^{-1}$  represents the symmetric S=O stretching. Lastly, the peak at 1075 and 1252  $\text{cm}^{-1}$  represent the symmetric and the asymmetric O=S=O stretching vibrations.

**Table A1** The FT-IR absorption spectra of PEEK, S-PEEK, PPEES and S-PPEES.

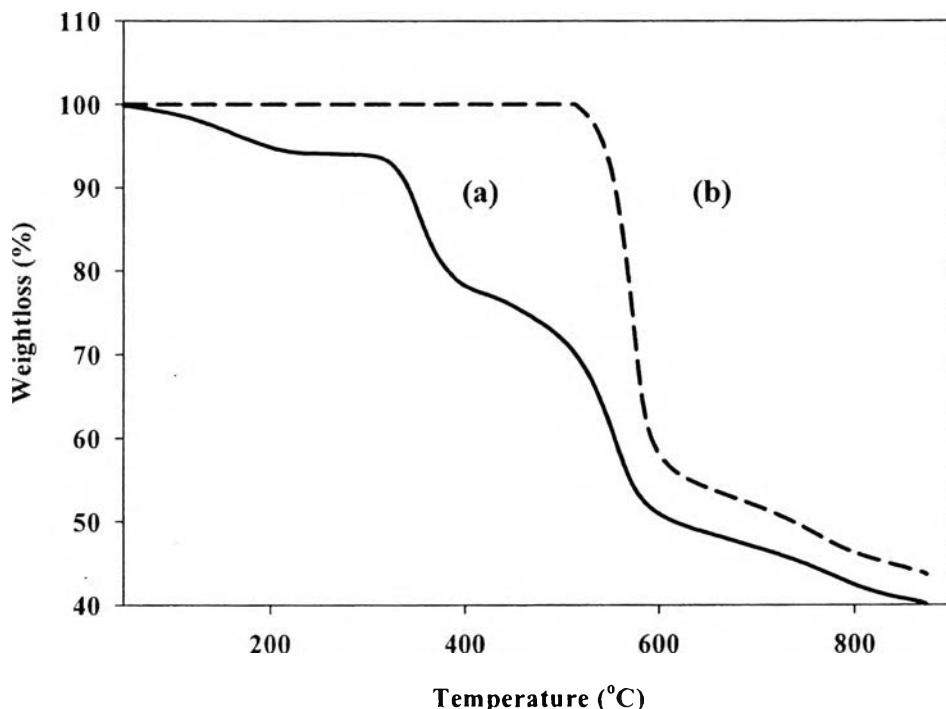
<b>Wavenumbers (cm<sup>-1</sup>)</b>	<b>Assignments</b>	<b>References</b>
709	Symmetric S-O stretching	Zaidi <i>et al.</i> , 2003
1020	Symmetric S=O stretching	Zaidi <i>et al.</i> , 2003
1080	Symmetric O=S=O stretching	Zaidi <i>et al.</i> , 2003
1255	Asymmetric O=S=O stretching	Zaidi <i>et al.</i> , 2003

**Appendix B The TGA Thermogram of Poly(ether ether ketone), sulfonated Poly(ether ether ketone), Poly(1,4-phenylene ether ether sulfone) and sulfonated Poly(1,4-phenylene ether ether sulfone)**

The thermogravimetric analysis (TGA) was used to determine the weight loss and thermal degradation of S-PEEK, and S-PSU from 40 to 850 °C with a scanning rate of 10 °C/min under nitrogen atmosphere by using a thermal analyzer (PerkinElmer, Pyris Diamond TG/DTA). The experiment was carried out by weighting samples of 2-4 mg and placed in alumina pans. The samples were dried at 100 °C for 24 h to remove any moisture.



**Figure B1** TGA thermograms of: (a) S-PEEK; and (b) PEEK.



**Figure B2** TGA thermogram of: (a) S-PPEES; and (b) PPEES.

In Figure B1, the PEEK thermogram exhibits a single step degradation temperature of the polymer chain higher than 580 °C; the S-PEEK thermogram exhibits three steps degradation. Firstly, from 50 to 200 °C in the S-PEEK thermogram is the weight loss of the physically and chemically bound water. Then, the weight loss between 250 to 350 °C is attributed to the decomposition of the sulfonic acid groups. Lastly, the weight loss above 510 °C is the S-PEEK backbone degradation. Figure B2, the degradation of PPEES backbone is shown approximately at 550 °C. The weight loss between 250 to 350 °C is due to the sulfonic acid groups.

### **Appendix C Determination Degree of Sulfonation (DS) by Titration**

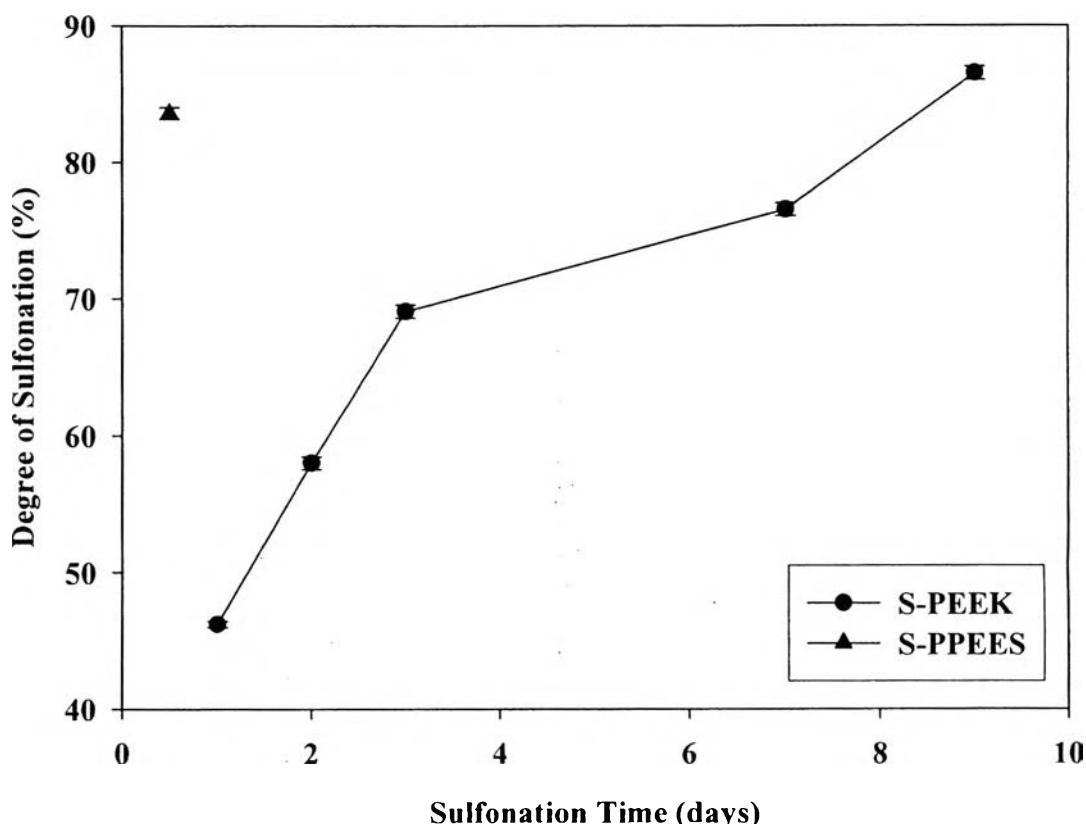
Degree of sulfonation (DS) is defined as the number of sulfonic acid groups per repeating units in the polymer chain. First, the membranes were acidified with an excess 2 M HCl solution at room temperature for 24 h. Subsequently, the membranes in acid form ( $H^+$ ) were dried at 60 °C for 24 h and exchanged to the sodium form by the immersion in a 1 M NaCl solution for 24 h. Then, the solution was titrated with 0.01 M NaOH by using phenolphthalein as an indicator. The titrations were repeated three times and the averaged DS value was obtained.

**Table C1** Degrees of sulfonation of S-PEEK at different sulfonation times

Sulfonation Time (days)	Degree of Sulfonation (%)			Average (%)	STD.
1	46.04	46.47	46.12	46.21	0.2287
2	58.32	58.19	57.45	57.99	0.4693
3	69.43	69.25	68.52	69.07	0.4819
7	76.08	76.39	77.01	76.49	0.4735
9	86.54	86.95	85.97	86.49	0.4932

**Table C2** Degree of sulfonation of S-PPEES

Sulfonation Time (h)	Degree of Sulfonation (%)			Average (%)	STD.
12	83.84	83.80	83.07	83.57	0.4334



**Figure C1** Degree of sulfonation at different sulfonation times of S-PEEK and S-PPEES.

All PPEES were sulfonated at different sulfonation times and temperature which is shown in Table C3. However, PPEES can only be sulfonated at various DS values up to about 80-85%, since the solubility of PPEES is very poor. Due to the short reaction time of PPEES, it cannot be sulfonated to obtain a lower DS value. Then, PPEES was dissolved in n-methyl-2-pyrrolidone (NMP) as a solvent in order to improve the solubility of PPEES. As a result, S-PPEES film cannot be achieved by this method. Furthermore, PPEES was dissolved in NMP and precipitated in ice-cold water to get PPEES powder in order to increase the surface area of PPEES with 98% H<sub>2</sub>SO<sub>4</sub>. Therefore, the solubility of PPEES is faster than the previous methods due to the increase of the surface area of PPEES. However, it cannot be sulfonated to obtain a lower DS value.

**Table C3** Sulfonation of PPEES at different sulfonation times and temperatures

Sample	Solvent	H <sub>2</sub> SO <sub>4</sub> (ml)	Temperature (C°)	Time	Degree of Sulfonation (%)	Remark
S-PPEES	-	40	50	7–12 h	-	Soluble in water
S-PPEES	-	40	50	1–6 h	80 - 85	-
S-PPEES	-	40	50	30 min	-	Cannot be precipitated in ice-cold water
S-PPEES	-	40	25	3–24 h	80 - 85	-
S-PPEES	-	40	25	1–2 h	-	Cannot be precipitated in ice-cold water
S-PPEES	NMP	2	25	7 days	-	Cannot cast a film
S-PPEES	NMP	1	25	24–48 h	-	Cannot cast a film
S-PPEES powder	NMP	40	25	1–24 h	80 - 85	-
PPEES	NMP	-	25	1 h	-	Cannot cast a film

Polysulfone (PSU) was sulfonated by different methods which are shown in Table C4. PSU was dissolved into a solvent in order to improve the solubility of PSU and sulfonated with 98% H<sub>2</sub>SO<sub>4</sub>. As a result, the sulfonation of PSU cannot be achieved by these methods.

**Table C4** Sulfonation of PSU at different sulfonation times and temperatures

Sample	Solvent	H <sub>2</sub> SO <sub>4</sub> (ml)	Temperature (C°)	Time	Degree of Sulfonation (%)	Casting film
S-PSU	dichloromethane	1-7	25	1-6 h	-	-
S-PSU + Polyethylene glycol	dichloromethane	1	25	15-45min	-	-
S-PSU	1,2-dichloroethane	1-4	25	24-72 h	-	-
S-PSU	chloroform	2-4	25	1-2 h	-	-
S-PSU	chloroform	1.5	25	3-10 days	-	-
S-PSU	chloroform	1.5	25	1-2 days	-	OK
S-PSU	chloroform	1	25	1-10 days	-	OK

Poly(1,4-phenylene sulfide) (PPS) was sulfonated at different sulfonation times and temperatures which are shown in Table C5.

**Table C5** Sulfonation of PPS at different sulfonation times and temperatures

Sample	H <sub>2</sub> SO <sub>4</sub> (ml)	Temperature (C°)	Time	Casting film	Remark
S-PPS	60	25	24-72 h	-	Insoluble in H <sub>2</sub> SO <sub>4</sub>
S-PPS	60	50	24-60 h	-	
S-PPS	60	80	72 h	-	

## Appendix D Determination Ion Exchange Capacity (IEC) by Titration

The titration technique was used to determine the IEC of the membranes which indicates number of millie quivalents of ions in 1 g of dry polymer (meq./g). Initially, the membranes were transformed to the sodium form by immersing the membranes in a 1 M NaCl solution for 24 h to exchange the H<sup>+</sup> ions with Na<sup>+</sup> ions. The exchanged H<sup>+</sup> ions within the solutions were titrated with a 0.01 M NaOH solution. Phenolphthalein as the universal indicator was drop to help determine the neutral point. The IEC of the cation exchange membrane was calculated from following equation:

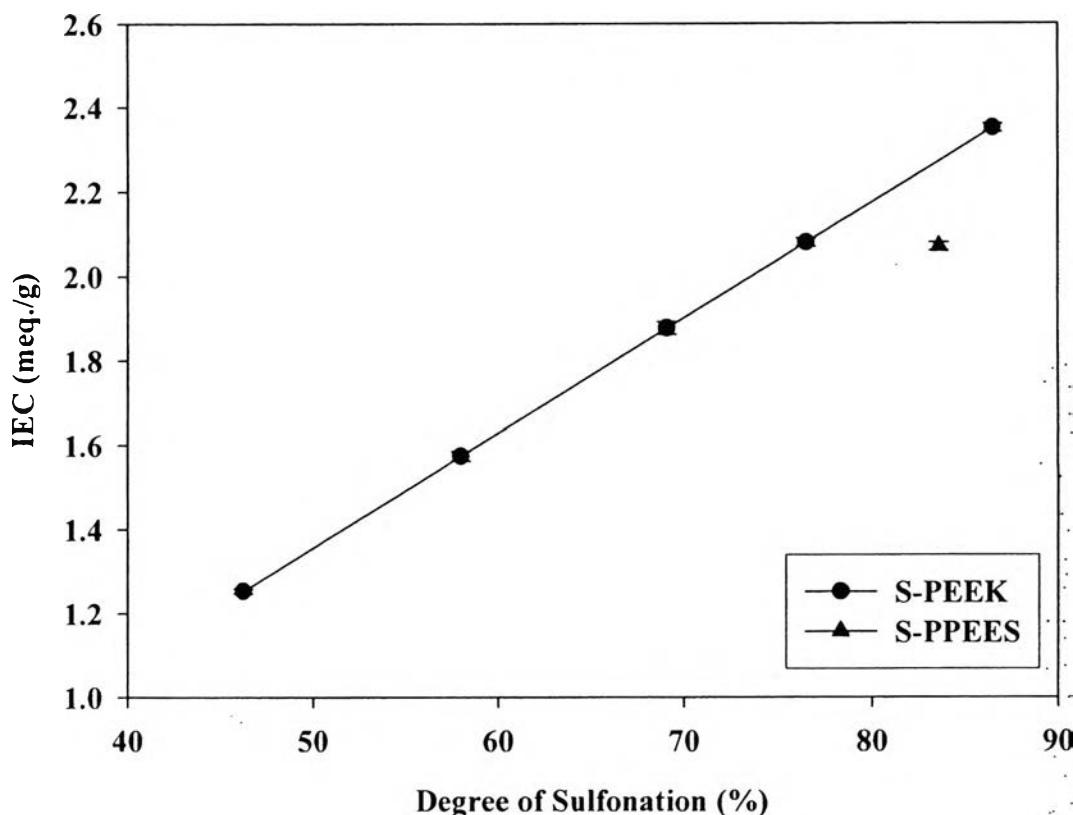
$$IEC \text{ (meq/g)} = \frac{\text{consumed ml NaOH} \times \text{molarity NaOH}}{\text{weight dried membrane}} \quad (\text{D1})$$

**Table D1** Law data of IEC values of S-PEEK

Degree of sulfonation (DS%)	IEC (meq./g)			Average (meq/g)	STD.
46.21	1.25	1.26	1.25	1.25	0.0058
57.99	1.58	1.58	1.56	1.58	0.0128
69.07	1.89	1.88	1.86	1.87	0.0153
76.49	2.07	2.08	2.09	2.08	0.0100
86.49	2.35	2.36	2.34	2.35	0.0120

**Table D2** Law data of IEC values of S-PPEES

Degree of sulfonation (DS%)	IEC (meq./g)			Average (meq/g)	STD.
83.57	2.08	2.07	2.06	2.07	0.0108



**Figure D1** IEC values of S-PEEK and S-PPEES with different degree of sulfonation.

Xue *et al.*, 2006 used a commercial PEEK from victex® for the sulfonation at 38 °C. The DS values of 59, 65, 73, 78, and 93% corresponding to the IEC values were 1.66, 1.76, 2.01, 2.21, and 2.37 meq./g, respectively.

## Appendix E Determination of the Water Uptake

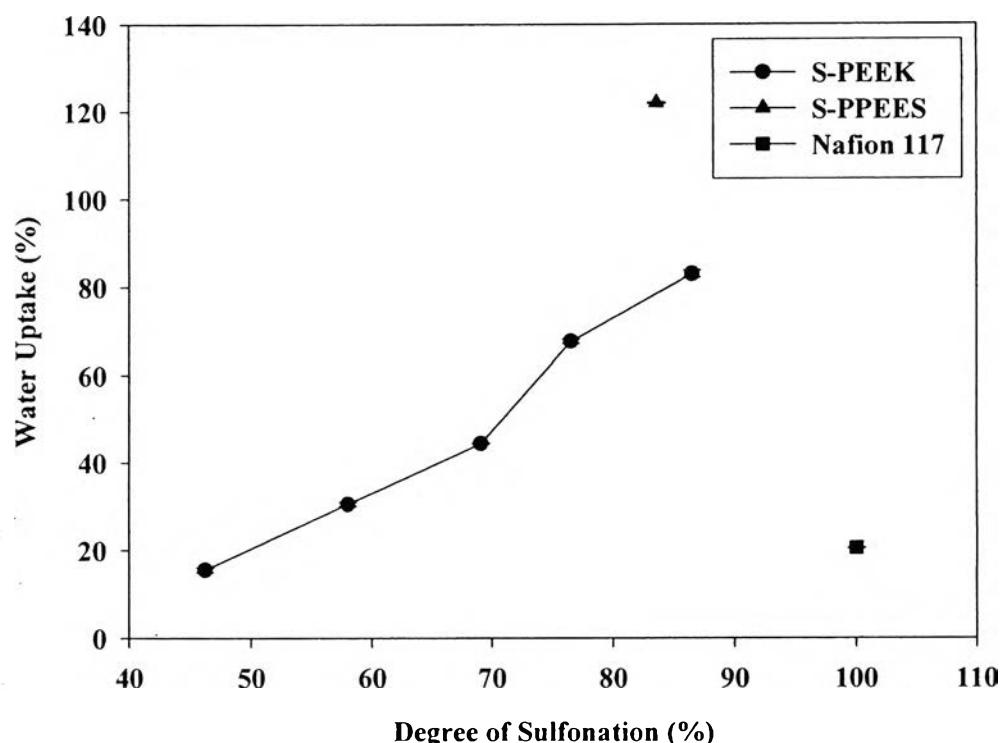
Water uptake is additionally a significant property of any ion exchange membranes. The membranes were dried in an oven at 100 °C for 24 h, weighed, and soaked in de-ionized water overnight at room temperature. After allowing equilibrium for 24 h, each membrane was taken out and the water adhering to the surface was quickly wiped using an absorbent paper. The membrane was weighted again. Thus, the amount of water uptake was calculated from

$$\text{water uptake (\%)} = \left( \frac{G_{\text{wet}} - G_{\text{dry}}}{G_{\text{dry}}} \right) \times 100 \quad (\text{E1})$$

where  $G_{\text{wet}}$  and  $G_{\text{dry}}$  are the weight of the membrane in the wet and the dry states, respectively.

**Table E1** Water uptake of S-PEEK, S-PPEES with various degree of sulfonation and Nafion® 117

Polymer	Water Uptake (%)			Average (%)	STD.
S-PEEK DS 46.21	15.35	16.19	15.09	15.54	0.5749
S-PEEK DS 57.99	30.99	30.03	30.68	30.57	0.4892
S-PEEK DS 69.07	44.40	44.33	44.51	44.41	0.0924
S-PEEK DS 76.49	68.14	67.12	67.68	67.65	0.5108
S-PEEK DS 86.49	82.83	82.30	83.92	83.02	0.8295
S-PPEES DS 83.57	122.05	121.96	121.79	121.93	0.1320
Nafion 117	20.52	20.55	20.50	20.52	0.0276



**Figure E1** Water uptake of S-PEEK, S-PPEES with various degree of sulfonation.

**Table E2** Raw data of water uptake of S-PEEK, S-PPEES at various degrees of sulfonation and of Nafion® 117

<b>Polymer</b>	<b>Wet</b>			<b>Dry</b>		
	<b>1</b>	<b>2</b>	<b>3</b>	<b>1</b>	<b>2</b>	<b>3</b>
S-PEEK DS 46.21	0.0263	0.0287	0.0244	0.0228	0.0247	0.0212
S-PEEK DS 57.99	0.0558	0.0446	0.0477	0.0426	0.0343	0.0365
S-PEEK DS 69.07	0.0696	0.0687	0.0724	0.0482	0.0476	0.0501
S-PEEK DS 76.49	0.0686	0.0610	0.0550	0.0408	0.0365	0.0328
S-PEEK DS 86.49	0.0607	0.0556	0.0572	0.0332	0.0305	0.0311
S-PPEES DS 83.57	0.0735	0.0839	0.0743	0.0331	0.0378	0.0335
Nafion 117	0.0781	0.0786	0.0776	0.0648	0.0652	0.0644

## Appendix F Proton Conductivity

The proton conductivity of the fully hydrated membranes was measured by using an Agilent E4980A LCR impedance analyzer at a potential of 1 V and an alternating frequency range from 20 Hz to 2 MHz. The membranes were cut into 2×2 mm pieces and painted with a silver paint on both sides. The conductivity  $\sigma$  of the fully hydrated membranes was calculated from the impedance data by using the following equation:

$$\sigma = \frac{d}{RS} \quad (\text{F1})$$

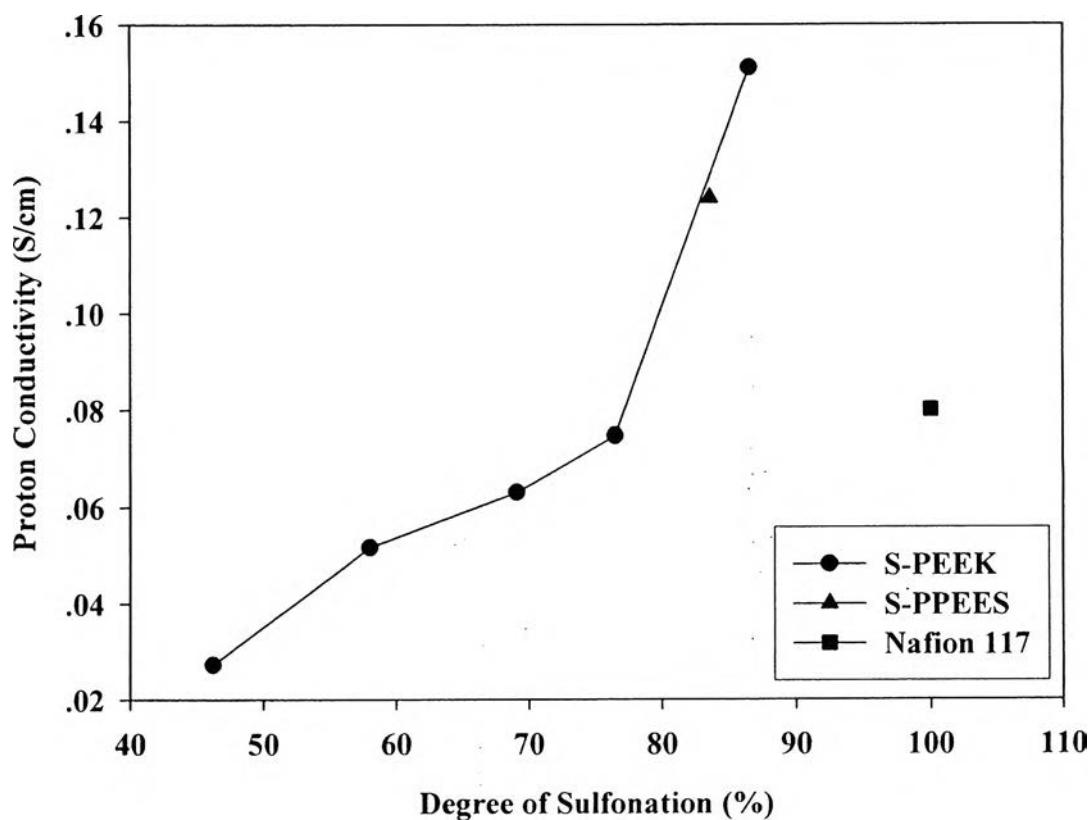
where  $d$  and  $S$  are the thickness and the surface area of the membranes, respectively, and  $R$  is the resistance of the membrane that can be derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the  $\text{Re}(Z)$  axis. The impedance data was corrected for the contribution from the empty and short-circuited cell.

**Table F1** The proton conductivity of S-PEEK and S-PPEES membranes

<b>Polymer</b>	<b>Proton Conductivity (<math>\text{S.cm}^{-1}</math>)</b>		
	<b>No. 1</b>	<b>No. 2</b>	<b>Average</b>
S-PEEK DS 46.21	$2.71 \times 10^{-2}$	$2.73 \times 10^{-2}$	$2.72 \times 10^{-2}$
S-PEEK DS 57.99	$5.30 \times 10^{-2}$	$5.03 \times 10^{-2}$	$5.17 \times 10^{-2}$
S-PEEK DS 69.07	$6.27 \times 10^{-2}$	$6.35 \times 10^{-2}$	$6.31 \times 10^{-2}$
S-PEEK DS 76.49	$7.51 \times 10^{-2}$	$7.43 \times 10^{-2}$	$7.47 \times 10^{-2}$
S-PEEK DS 86.49	$1.60 \times 10^{-1}$	$1.43 \times 10^{-1}$	$1.51 \times 10^{-1}$
S-PPEES DS 83.57	$1.23 \times 10^{-1}$	$1.25 \times 10^{-1}$	$1.24 \times 10^{-1}$
Nafion 117 <sup>a</sup>		$8.00 \times 10^{-2}$	

<sup>a</sup> Ref. Zhao *et al.*, 2006

Li *et al.*, 2009 sulfonated PEEK membranes exhibit conductivities at 0.02, 0.06, 0.08, 0.12, 0.15, and 0.16 S/cm corresponding to the DS values of 46, 54, 58, 62, 73, and 79%, respectively.



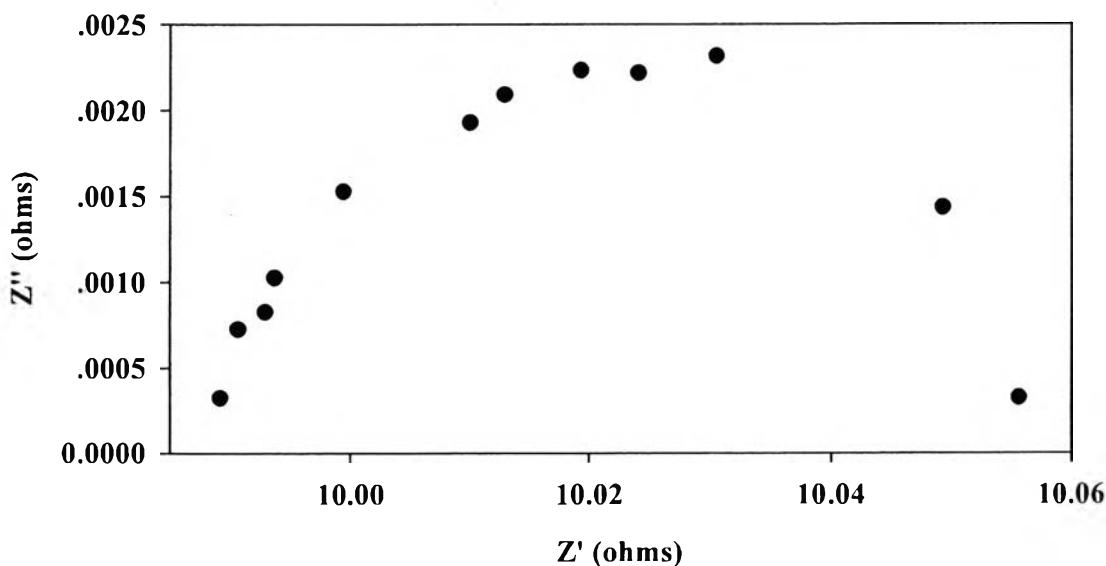
**Figure F1** The proton conductivity of S-PEEK, S-PPEES, and Nafion® 117 membranes at various degrees of sulfonation.

**Table F2** Raw data of proton conductivity calculations

Polymer	Thickness (cm)	Area (cm <sup>2</sup> )	R (ohms)	Conduct (S.cm <sup>-1</sup> )
S-PEEK DS 46.21	0.019267	0.070714286	10.056	$2.7094533 \times 10^{-2}$
	0.019633	0.070714286	10.175	$2.7286328 \times 10^{-2}$
S-PEEK DS 57.99	0.020400	0.070714286	5.440	$5.3030302 \times 10^{-2}$
	0.019300	0.070714286	5.424	$5.0318822 \times 10^{-2}$
S-PEEK DS 69.07	0.018167	0.070714286	4.095	$6.2736769 \times 10^{-2}$
	0.018567	0.070714286	4.135	$6.3497856 \times 10^{-2}$
S-PEEK DS 76.49	0.016767	0.070714286	3.156	$7.5129623 \times 10^{-2}$
	0.016333	0.070714286	3.110	$7.4267433 \times 10^{-2}$
S-PEEK DS 86.49	0.019500	0.070714286	1.017	$1.5990782 \times 10^{-1}$
	0.020467	0.070714286	1.107	$1.4307483 \times 10^{-1}$
S-PPEES DS 83.57	0.023700	0.070714286	2.721	$1.2317218 \times 10^{-1}$
	0.024833	0.070714286	2.802	$1.2532967 \times 10^{-1}$

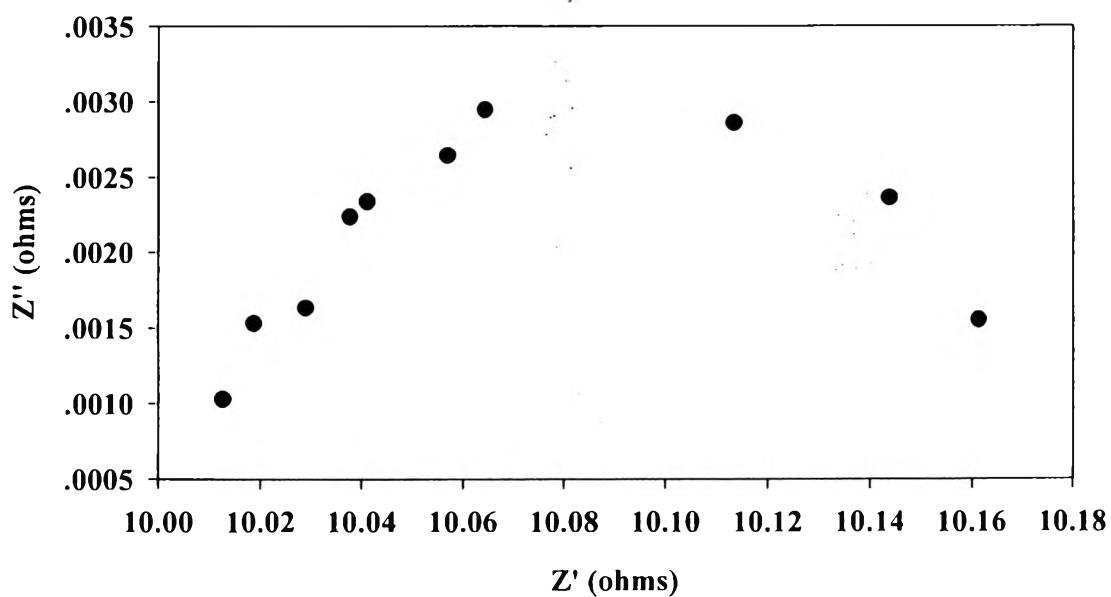
**Table F3** Proton conductivity raw data of S-PEEK DS 46.21 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	10.5396	0.000413	10.5396	0.004349
40	10.1558	0.000233	10.1558	0.002363
50	10.1244	0.000173	10.1244	0.001748
60	10.1196	0.000233	10.1196	0.002354
70	10.0993	0.000203	10.0993	0.002047
80	10.8280	0.000163	10.828	0.001761
100	10.0659	0.000103	10.0659	0.001033
120	10.0489	8.27E-05	10.0489	0.000831
130	10.0556	3.27E-05	10.0556	0.000328
140	10.0493	0.000143	10.0493	0.001434
150	10.0306	0.000231	10.0306	0.002314
180	10.0241	0.000221	10.0241	0.002216
200	10.0193	0.000223	10.0193	0.002231
250	10.0129	0.000209	10.0129	0.002089
300	10.0100	0.000193	10.0100	0.001928
400	9.99940	0.000153	9.99940	0.001526
500	9.99365	0.000103	9.99365	0.001026
600	9.99286	8.27E-05	9.99286	0.000826
700	9.99066	7.27E-05	9.99066	0.000726
800	9.98918	3.27E-05	9.98918	0.000326

**Figure F2** Nyquist plot of the S-PEEK DS 46.21 membrane.

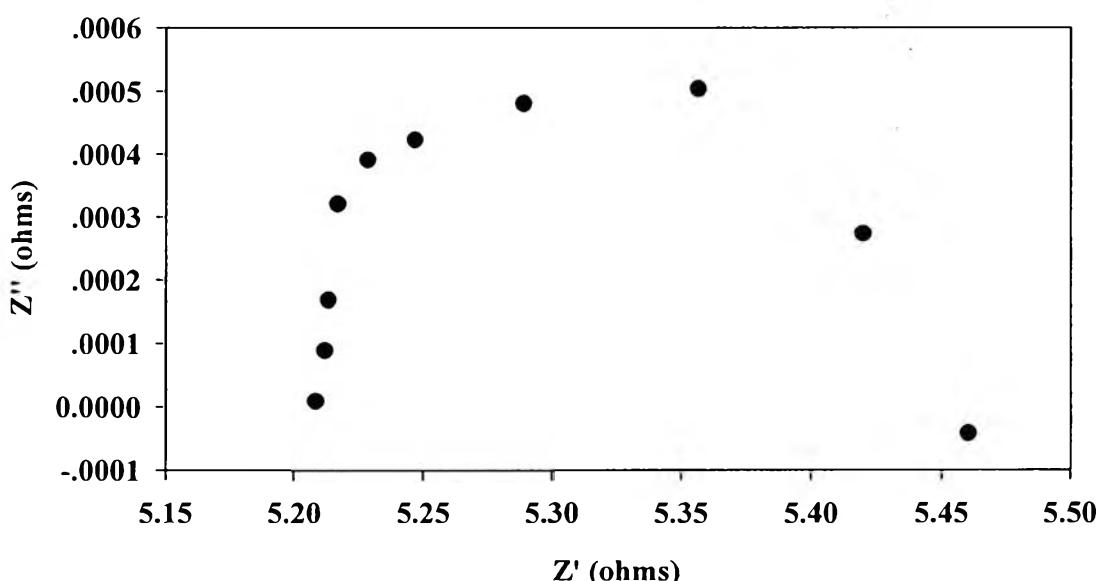
**Table F4** Proton conductivity raw data of S-PEEK DS 46.21 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	10.5684	0.000383	10.5684	0.004044
40	10.1863	0.000233	10.1863	0.00237
50	10.1613	0.000153	10.1613	0.001551
60	10.1438	0.000233	10.1438	0.00236
70	10.1134	0.000283	10.1134	0.002859
150	10.06430	0.000293	10.0643	0.002945
170	10.05690	0.000263	10.0569	0.002641
190	10.0411	0.000233	10.0411	0.002336
200	10.0377	0.000223	10.0377	0.002235
300	10.029	0.000163	10.029	0.001631
400	10.0187	0.000153	10.0187	0.001529
500	10.0126	0.000103	10.0126	0.001028
600	9.99719	8.27E-05	9.99719	0.000826

**Figure F3** Nyquist plot of the S-PEEK DS 46.21 membrane.

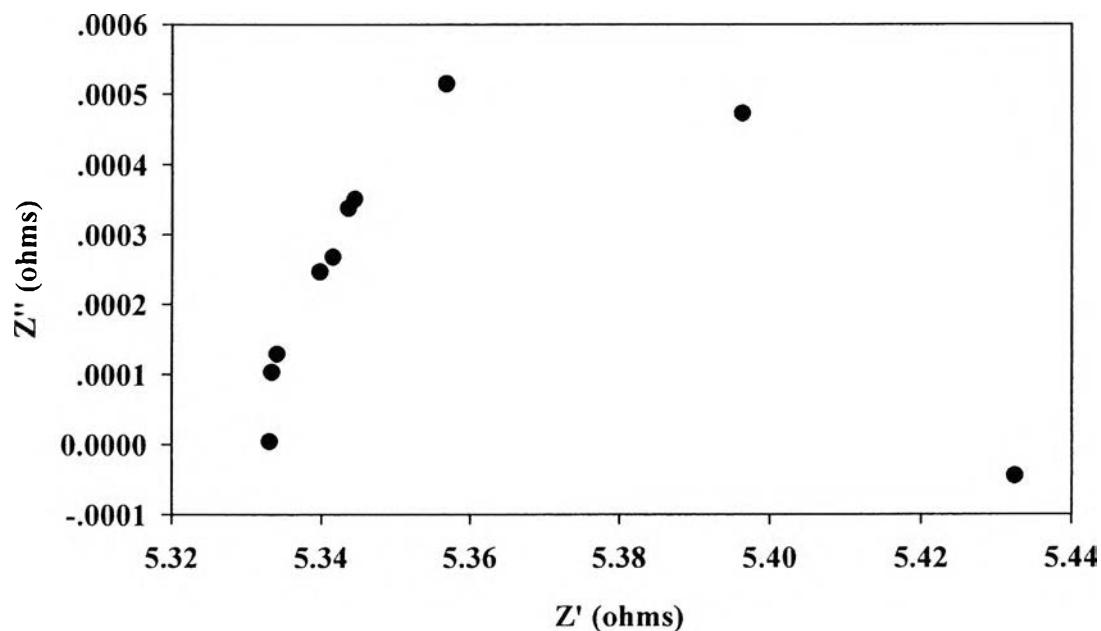
**Table F5** Proton conductivity raw data of S-PEEK DS 57.99 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	5.43778	218.708	5.43777987	0.00118929
40	5.44732	99.979	5.44731997	0.00054462
60	5.57187	42.799	5.57186999	0.00023847
80	5.73333	-7.66303	5.73333	-4.3935E-05
100	5.72032	-1.65201	5.72032	-9.45E-06
110	5.71769	-3.50261	5.71769	-2.0027E-05
120	5.46013	-7.73611	5.46013	-4.224E-05
130	5.41981	50.4532	5.41980999	0.00027345
140	5.35629	93.9818	5.35628998	0.00050339
150	5.28895	90.6794	5.28894998	0.0004796
160	5.24665	80.4779	5.24664998	0.00042224
170	5.2285	74.6561	5.22849999	0.00039034
180	5.21705	61.4919	5.21704999	0.00032081
200	5.21344	32.286	5.21344	0.00016832
250	5.21207	17.044	5.21207	8.8835E-05
300	5.20863	1.71898	5.20863	8.9535E-06

**Figure F4** Nyquist plot of the S-PEEK DS 57.99 membrane.

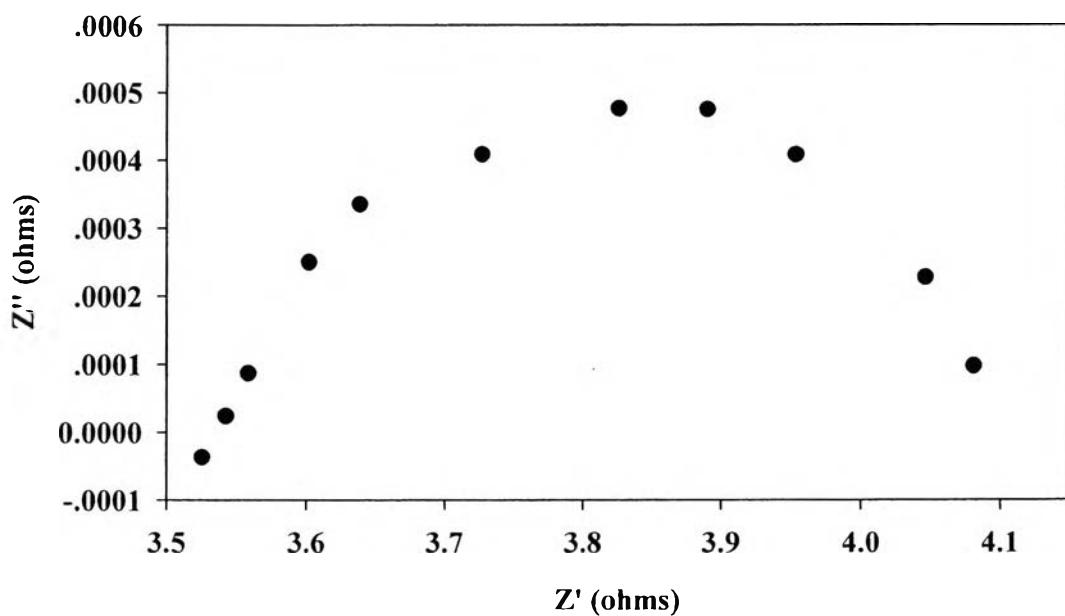
**Table F6** Proton conductivity raw data of S-PEEK DS 57.99 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	5.5571	145.847	5.55709994	0.00081049
40	5.5332	75.5476	5.53319998	0.00041802
60	5.5159	30.2652	5.5159	0.00016694
80	5.50727	12.3684	5.50727	6.8116E-05
100	5.5006	-20.6982	5.5006	-0.00011385
110	5.49507	-25.5137	5.49507	-0.0001402
120	5.43242	-8.2961	5.43242	-4.5068E-05
130	5.39633	87.5347	5.39632998	0.00047237
140	5.35678	96.0215	5.35677998	0.00051437
150	5.34361	63.2076	5.34360999	0.00033776
160	5.34445	65.56	5.34444999	0.00035038
170	5.34154	50.1466	5.34153999	0.00026786
180	5.33978	46.166	5.33977999	0.00024652
200	5.3341	24.211	5.3341	0.00012914
210	5.33343	19.2863	5.33343	0.00010286
250	5.3331	0.723891	5.3331	3.8606E-06
300	5.33016	4.29898	5.33016	2.2914E-05

**Figure F5** Nyquist plot of the S-PEEK DS 57.99 membrane.

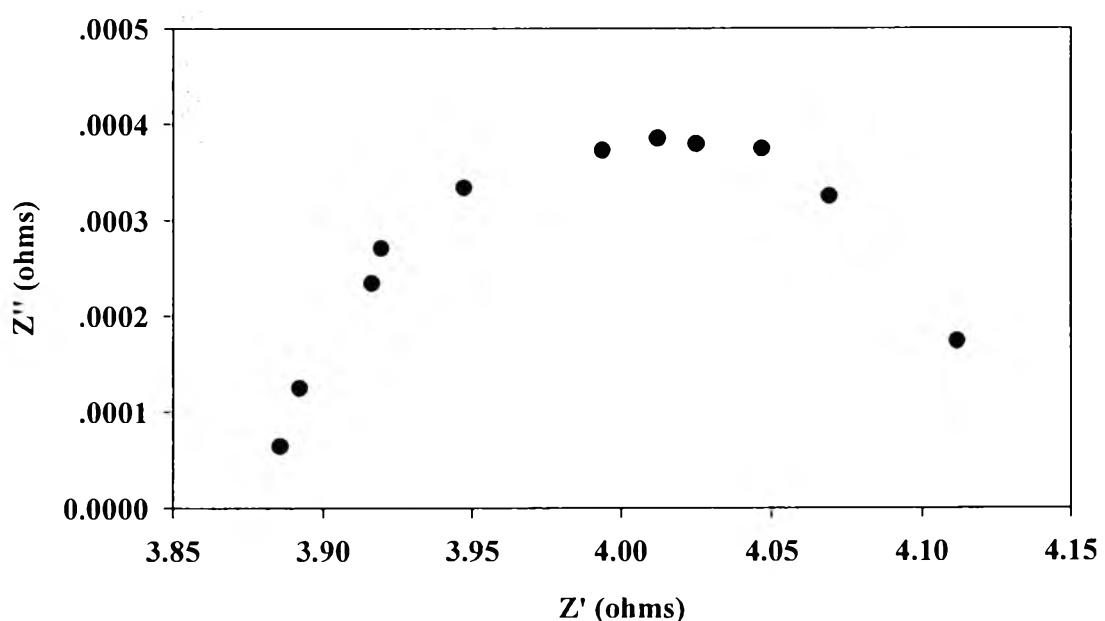
**Table F7** Proton conductivity raw data of S-PEEK DS 69.07 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	4.37899	176.919	4.37899	0.000775
40	4.28241	104.236	4.28241	0.000446
60	4.22297	69.4237	4.22297	0.000293
80	4.14391	67.4134	4.14391	0.000279
100	4.08085	23.8727	4.08085	9.74E-05
120	4.04631	56.0658	4.04631	0.000227
130	3.95337	103.189	3.95337	0.000408
140	3.8902	122.137	3.8902	0.000475
150	3.82586	124.4928	3.82586	0.000476
170	3.72732	109.5823	3.72732	0.000408
200	3.63873	92.0016	3.63873	0.000335
250	3.60181	69.30498	3.60181	0.00025
300	3.55796	24.4447	3.55796	8.7E-05
400	3.5422	6.75303	3.5422	2.39E-05
500	3.5254	-10.483	3.5254	-3.70E-05
600	3.49224	-19.2141	3.49224	-6.71E-05
800	3.46631	-31.2091	3.46631	-0.00011

**Figure F6** Nyquist plot of the S-PEEK DS 69.07 membrane.

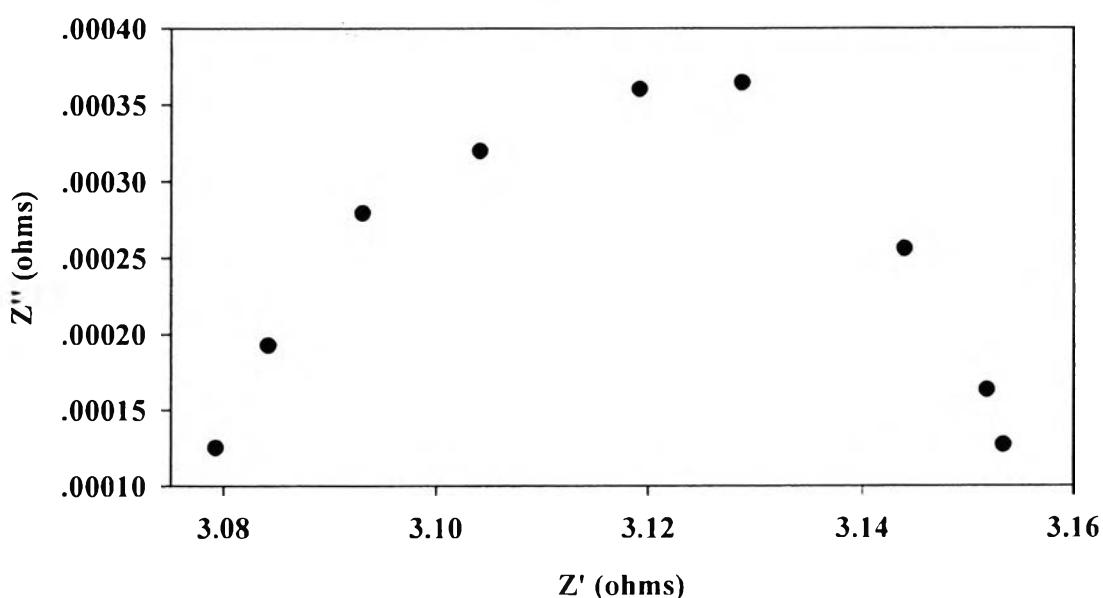
**Table F8** Proton conductivity raw data of S-PEEK DS 69.07 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	4.23331	222.185	4.23331	0.000941
40	4.21582	117.639	4.21582	0.000496
60	4.18592	98.2547	4.18592	0.000411
80	4.11169	42.0794	4.11169	0.000173
100	4.06906	79.7555	4.06906	0.000325
120	4.04662	92.4677	4.04662	0.000374
130	4.02483	94.188	4.02483	0.000379
150	4.01203	95.9399	4.01203	0.000385
170	3.99356	93.221	3.99356	0.000372
200	3.94703	84.4597	3.94703	0.000333
220	3.9193	69.1201	3.9193	0.000271
250	3.91609	59.7592	3.91609	0.000234
300	3.89209	31.9517	3.89209	0.000124
400	3.88562	16.4551	3.88562	6.39E-05
500	3.82709	20.2923	3.82709	7.77E-05
600	3.81747	17.6774	3.81747	6.75E-05

**Figure F7** Nyquist plot of the S-PEEK DS 69.07 membrane.

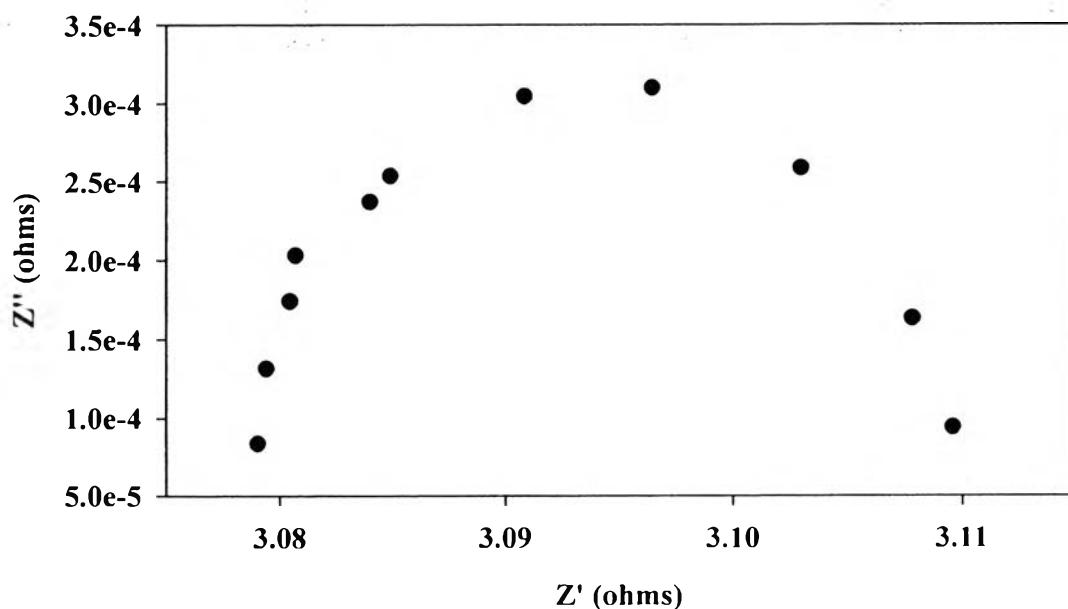
**Table F9** Proton conductivity raw data of S-PEEK DS 76.49 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	3.18565	179.285	3.185649949	0.0005711
40	3.17528	111.367	3.17527998	0.0003536
60	3.16873	93.6897	3.168729986	0.0002969
80	3.15331	40.2849	3.153309997	0.000127
100	3.15174	51.7463	3.151739996	0.0001631
120	3.14402	81.4323	3.14401999	0.000256
130	3.12882	116.473	3.128819979	0.0003644
150	3.11921	115.507	3.119209979	0.0003603
200	3.10411	102.9743	3.104109984	0.0003196
220	3.0931	90.2513	3.093099987	0.0002792
250	3.08415	62.4677	3.084149994	0.0001927
270	3.07922	40.6546	3.079219997	0.0001252
300	3.04845	39.8977	3.048449998	0.0001216
350	3.04288	52.3839	3.042879996	0.0001594
400	3.02767	37.1335	3.027669998	1.12E-04
500	3.02187	33.3595	3.021869998	1.01E-04
700	3.01549	16.7446	3.01549	5.049E-05
900	3.00276	74.9815	3.002759992	2.25E-04
1200	3.00261	-103.274	3.002609984	-3.10E-04

**Figure F8** Nyquist plot of the S-PEEK DS 76.49 membrane.

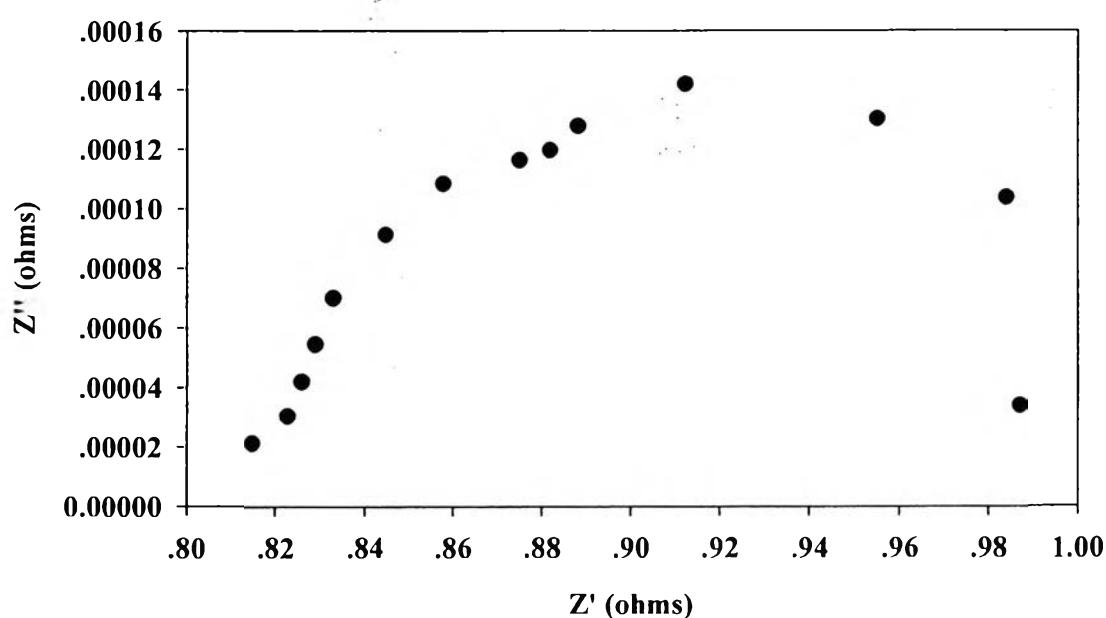
**Table F10** Proton conductivity raw data of S-PEEK DS 76.49 membrane

<b>Frequency, Hz</b>	<b>Z, Ohm</b>	<b>r, Radius</b>	<b>Z'=Zcosr</b>	<b>Z''=Zsinr</b>
20	3.1215	214.224	3.121499928	0.0006687
40	3.11464	127.107	3.114639975	0.0003959
60	3.11425	88.9842	3.114249988	0.0002771
80	3.10994	50.9628	3.109939996	0.0001585
100	3.10957	30.2576	3.109569999	9.409E-05
120	3.10781	52.4746	3.107809996	0.0001631
130	3.10293	83.271	3.102929989	0.0002584
150	3.09644	100.049	3.096439985	0.0003098
170	3.09083	98.5164	3.090829985	0.0003045
200	3.08486	82.1595	3.08485999	0.0002535
220	3.08397	76.8301	3.083969991	0.0002369
250	3.08069	65.901	3.080689993	0.000203
300	3.08044	56.4999	3.080439995	0.000174
400	3.07939	42.7078	3.079389997	0.0001315
500	3.07902	27.2387	3.079019999	8.39E-05
600	3.07728	22.8719	3.077279999	7.04E-05
700	3.06909	22.5656	3.069089999	6.926E-05
900	3.0677	65.7404	3.067699993	2.02E-04
1200	3.06474	-95.132	3.064739986	-2.92E-04

**Figure F9** Nyquist plot of the S-PEEK DS 76.49 membrane.

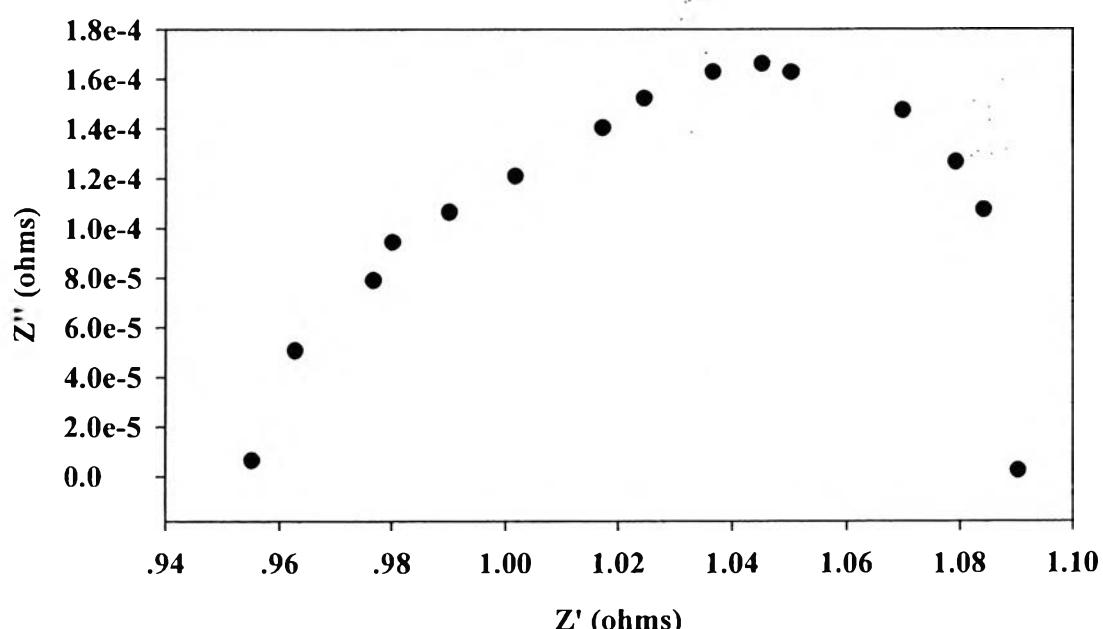
**Table F11** Proton conductivity raw data of S-PEEK DS 86.49 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
100	0.987157	34.1841	0.987157	3.37E-05
110	0.984043	105.08	0.984043	0.000103
120	0.955027	135.9845	0.955027	0.00013
130	0.912307	155.18	0.912307	0.000142
140	0.888121	143.475	0.888121	0.000127
150	0.88185	135.395	0.88185	0.000119
160	0.875048	132.648	0.875048	0.000116
170	0.857802	125.97	0.857802	0.000108
180	0.84473	107.845	0.84473	9.11E-05
200	0.832959	83.8994	0.832959	6.99E-05
250	0.828997	65.7106	0.828997	5.45E-05
300	0.825969	50.6677	0.825969	4.18E-05
400	0.822784	36.8893	0.822784	3.04E-05
500	0.814868	26.0417	0.814868	2.12E-05
700	0.805784	36.1616	0.805784	2.91E-05
800	0.813654	22.5836	0.813654	1.84E-05

**Figure F10** Nyquist plot of the S-PEEK DS 86.49 membrane.

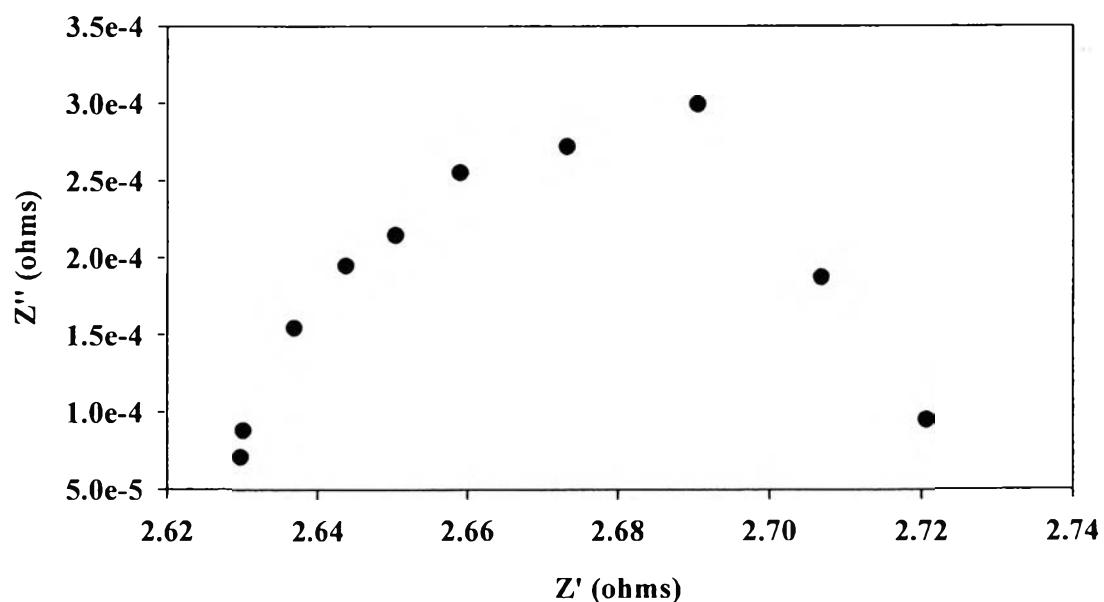
**Table F12** Proton conductivity raw data of S-PEEK DS 86.49 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
100	1.09023	2.16425	1.09023	2.36E-06
110	1.08417	98.945	1.08417	0.000107
120	1.07925	117.222	1.07925	0.000127
130	1.06987	137.577	1.06987	0.000147
140	1.05026	154.846	1.05026	0.000163
150	1.04523	158.787	1.04523	0.000166
160	1.03662	156.947	1.03662	0.000163
170	1.02456	148.426	1.02456	0.000152
180	1.0173	137.978	1.0173	0.00014
200	1.00179	120.689	1.00179	0.000121
250	0.99015	107.515	0.99015	0.000106
300	0.98013	96.2035	0.98013	9.43E-05
400	0.97668	80.8144	0.97668	7.89E-05
500	0.96279	52.5848	0.96279	5.06E-05
600	0.95517	6.82125	0.95517	6.52E-06
700	0.944941	5.91028	0.944941	5.58E-06

**Figure F11** Nyquist plot of the S-PEEK DS 86.49 membrane.

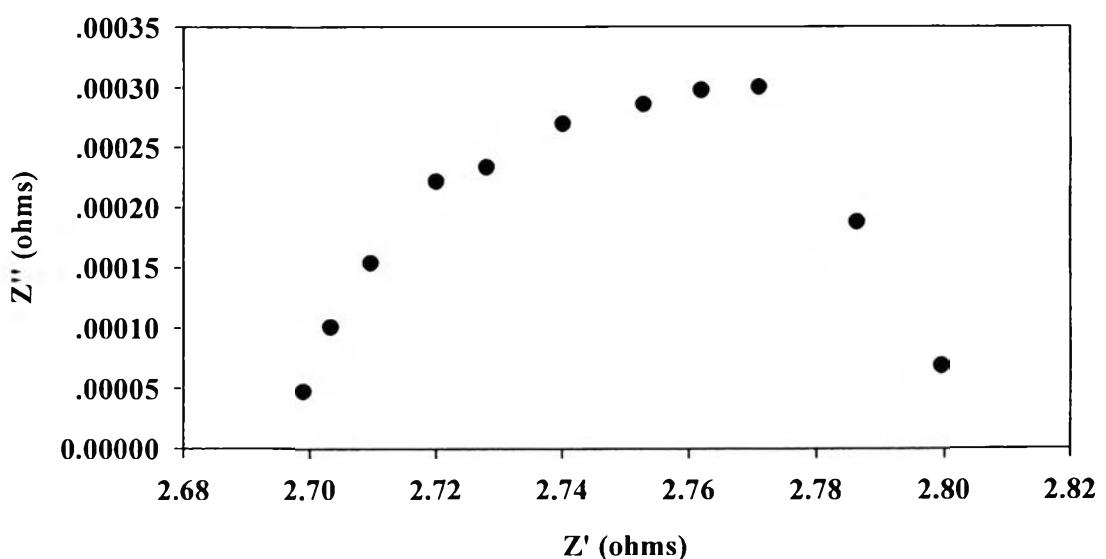
**Table F13** Proton conductivity raw data of S-PPEES DS 83.57 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	2.79173	199.8	2.79173	0.000558
40	2.78001	93.9291	2.78001	0.000261
60	2.77654	91.3895	2.77654	0.000254
80	2.76306	62.3775	2.76306	0.000172
100	2.72061	34.9222	2.72061	9.5E-05
120	2.70674	69.1168	2.70674	0.000187
130	2.69056	111.151	2.69056	0.000299
140	2.67326	101.647	2.67326	0.000272
150	2.65902	95.8517	2.65902	0.000255
170	2.65045	80.8254	2.65045	0.000214
200	2.6438	73.6111	2.6438	0.000195
250	2.63682	58.5953	2.63682	0.000155
300	2.63008	33.5436	2.63008	8.82E-05
400	2.629737	27.0282	2.629737	7.11E-05
500	2.60848	31.2206	2.60848	8.14E-05
600	2.59302	50.5721	2.59302	0.000131
800	2.58294	16.2968	2.58294	4.21E-05
1000	2.58005	-80.1644	2.58005	-0.00021

**Figure F12** Nyquist plot of the S-PPEES DS 83.57 membrane.

**Table F14** Proton conductivity raw data of S-PPEES DS 83.57 membrane

Frequency, Hz	Z, Ohm	r, Radius	Z'=Zcosr	Z''=Zsinr
20	2.83294	239.908	2.83294	0.00068
40	2.82553	104.109	2.82553	0.000294
60	2.81673	100.225	2.81673	0.000282
80	2.80753	46.7366	2.80753	0.000131
100	2.80467	59.8715	2.80467	0.000168
110	2.79953	24.5285	2.79953	6.87E-05
120	2.78632	67.2456	2.78632	0.000187
130	2.77103	108.19	2.77103	0.0003
140	2.76188	107.596	2.76188	0.000297
150	2.75295	103.68	2.75295	0.000285
170	2.74013	98.2107	2.74013	0.000269
200	2.72806	85.3872	2.72806	0.000233
250	2.72001	81.326	2.72001	0.000221
300	2.70959	56.5422	2.70959	0.000153
400	2.70332	37.2922	2.70332	0.000101
500	2.69903	17.6211	2.69903	4.76E-05
600	2.6701	48.4851	2.6701	0.000129
800	2.65412	12.0049	2.65412	3.19E-05

**Figure F13** Nyquist plot of the S-PPEES DS 83.57 membrane.

## Appendix G Determination Vanadium Permeability

The vanadium permeability of the membranes was determined by using the two reservoirs. The left reservoir was filled with 50 ml of 1 M VOSO<sub>4</sub> in 2 M H<sub>2</sub>SO<sub>4</sub>, and the right reservoir was filled with 50 ml of 1 M MgSO<sub>4</sub> in 2 M H<sub>2</sub>SO<sub>4</sub>. The two reservoirs were separated by the membrane samples. MgSO<sub>4</sub> was used to equalize the osmotic pressure. The two solutions were continuously stirred at room temperatures ( $25 \pm 2$  °C). Samples of the MgSO<sub>4</sub> solution were taken at a regular time interval in order to investigate the vanadium ions concentration by using an UV-VIS spectrometer at 760 nm. Therefore, the vanadium ion concentration in the right reservoir as a function of time was calculated from following equation:

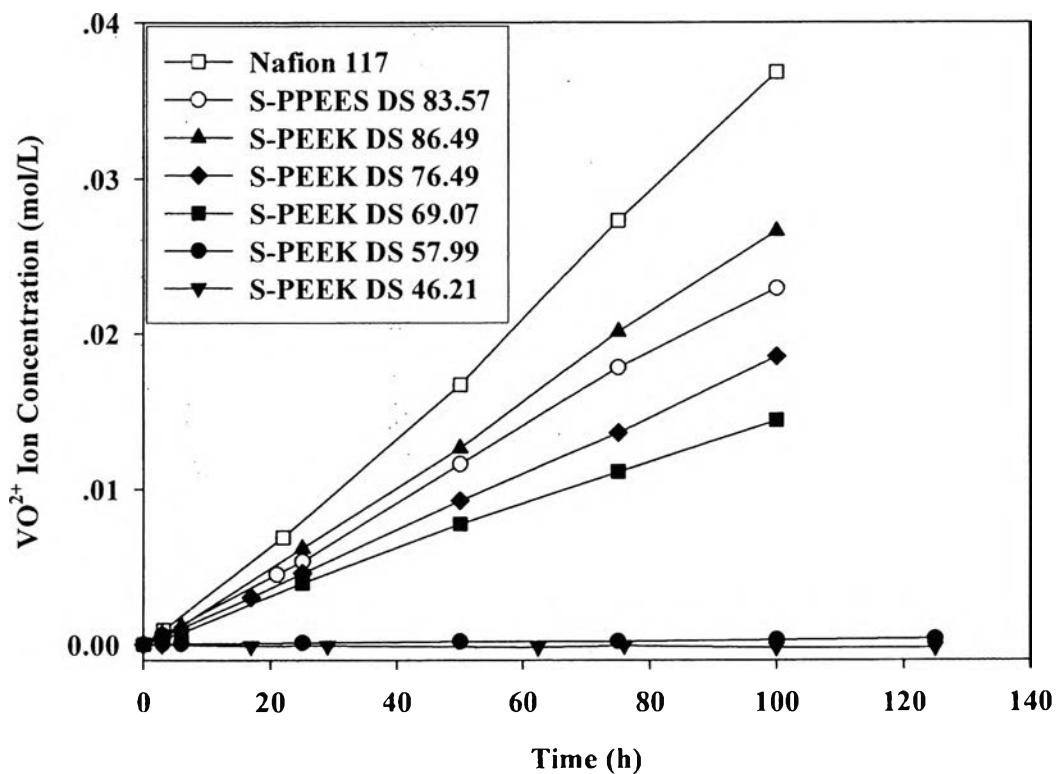
$$V_B \frac{dc_B(t)}{dt} = A \frac{P}{L} (C_A - C_B(t)) \quad (G1)$$

where V<sub>B</sub> represents the volume of the right reservoir. C<sub>A</sub> is the vanadium ion concentration in the left reservoir, and C<sub>B</sub>(t) is the vanadium ion concentration in the right reservoir as a function of time. P represents the permeability of vanadium ions. A is the area (1.767 cm<sup>2</sup>) and L is the thickness of the membrane.

The calibration curve is taken by plotting the area peak of absorbance versus the vanadium concentrations (mol/L) (Figure G1). The straight line from the calibration data was used to determine the vanadium concentration in the diffusion samples by substituting the ratios of the vanadium to the standard peak area.

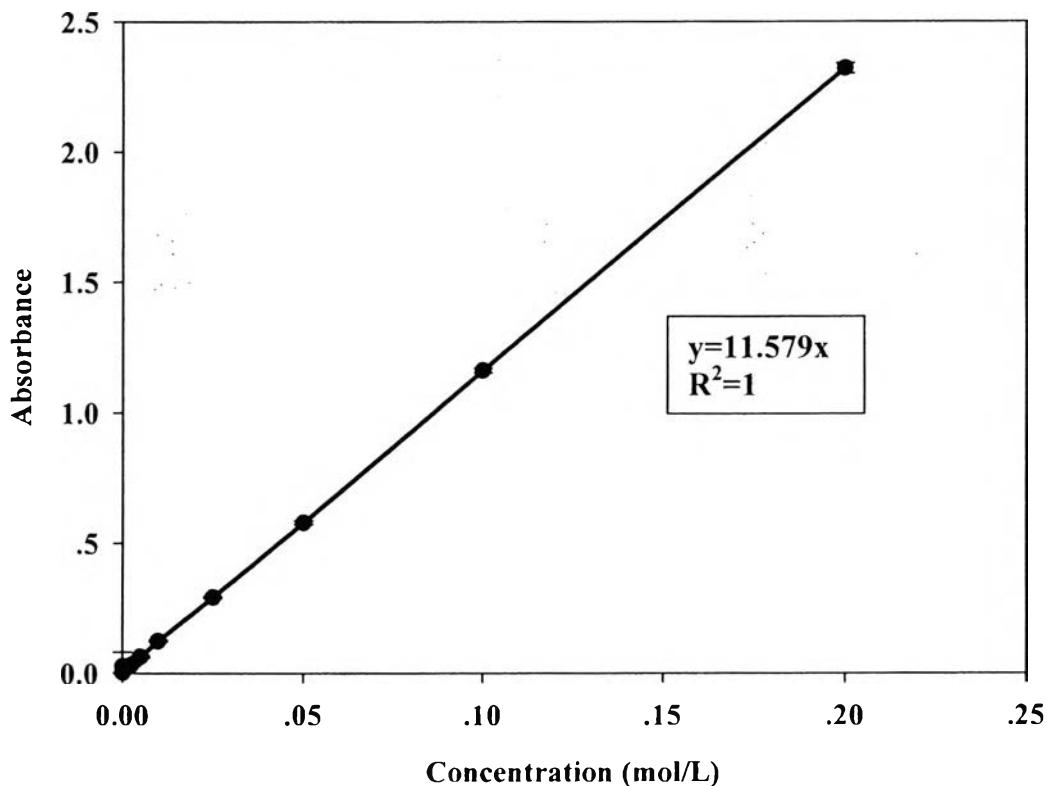
**Table G1** Calculation of vanadium permeability

Polymer	Thickness, $L$ (cm)	Slope, $\frac{dC_E(t)}{dt}$ (mol/L.min)	Vanadium permeability, $P$ (cm <sup>2</sup> /min)
S-PEEK DS 46.21	0.0150	0	0
S-PEEK DS 57.99	0.0181	$4.7212 \times 10^{-8}$	$24.18 \times 10^{-9}$
S-PEEK DS 69.07	0.0179	$2.4829 \times 10^{-6}$	$12.58 \times 10^{-7}$
S-PEEK DS 76.49	0.0160	$3.1206 \times 10^{-6}$	$14.13 \times 10^{-7}$
S-PEEK DS 86.49	0.0182	$4.4319 \times 10^{-6}$	$22.82 \times 10^{-7}$
S-PPEES DS 83.57	0.0226	$3.9017 \times 10^{-6}$	$24.95 \times 10^{-7}$
Nafion 117	0.0180	$6.0541 \times 10^{-6}$	$30.84 \times 10^{-7}$

**Figure G1** The vanadium ions permeability across S-PEEK, S-PPEES, and Nafion® 117.

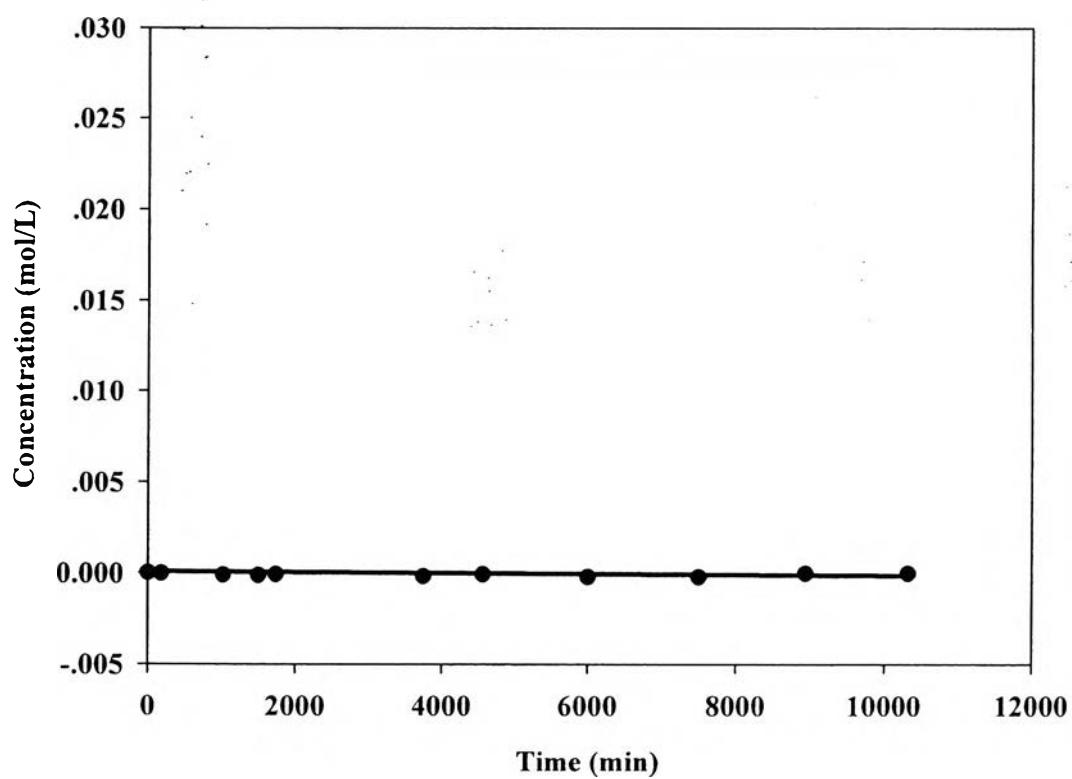
**Table G2** Raw data of internal standard curve of vanadium concentration

Vanadium Concentration (mol/L)	Absorbance				
	1	2	3	4	5
0	0	0	0	0	0
0.0001	0.00049	0.00089	0.00570	0.00199	0.00120
0.001	0.01160	0.04089	0.01369	0.02040	0.02000
0.0025	0.03559	0.03530	0.03060	0.02899	0.02949
0.005	0.06149	0.06199	0.06989	0.05880	0.06019
0.01	0.11900	0.12739	0.12270	0.12579	0.12180
0.025	0.28739	0.28860	0.29580	0.29119	0.29070
0.05	0.56839	0.58150	0.57999	0.58660	0.57949
0.1	1.14789	1.16310	1.17320	1.16390	1.16049
0.2	2.31819	2.31929	2.29390	2.32220	2.31669

**Figure G2** Calibration curve of vanadium concentration.

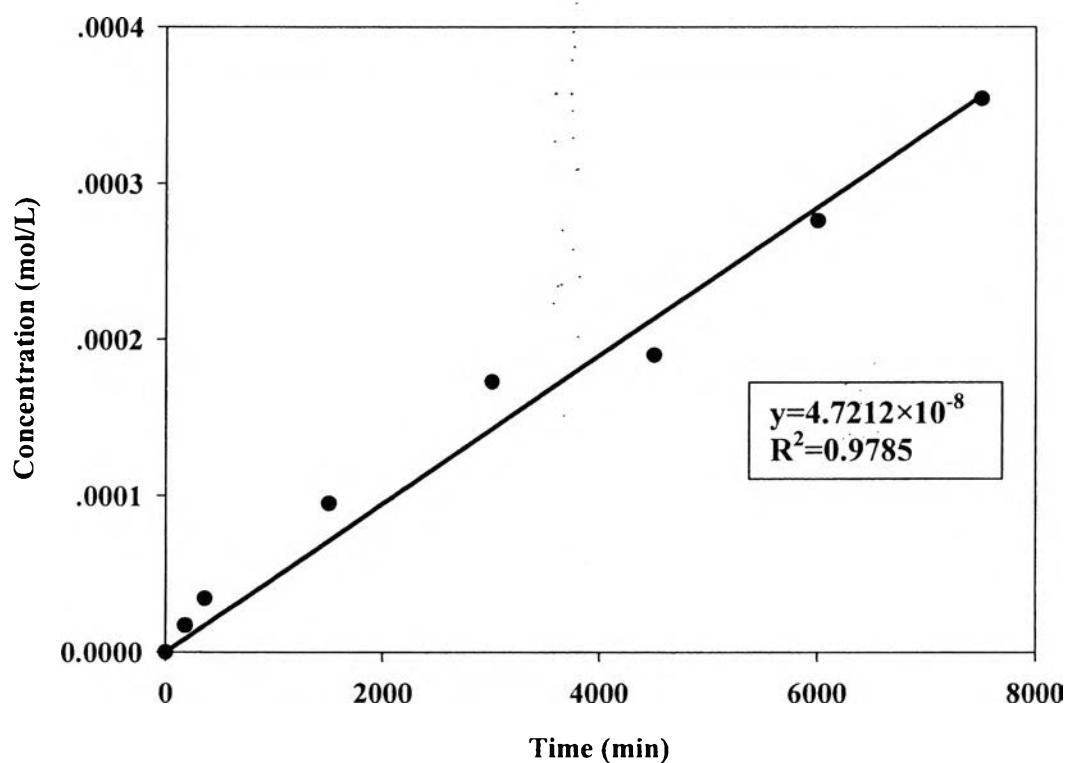
**Table G3** Raw data of vanadium permeability of S-PEEK DS 46.21 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
180	-0.0004	-3.5E-05
1020	-0.0013	-0.00011
1500	-0.0017	-0.00015
1740	-0.001	-8.6E-05
3750	-0.0023	-0.0002
4560	-0.001	-8.6E-05
6000	-0.0026	-0.00022
7500	-0.0026	-0.00022
8940	-0.0003	-2.6E-05
10320	-0.0003	-2.6E-05

**Figure G3** The vanadium permeability vs. time of S-PEEK DS 46.21 membrane.

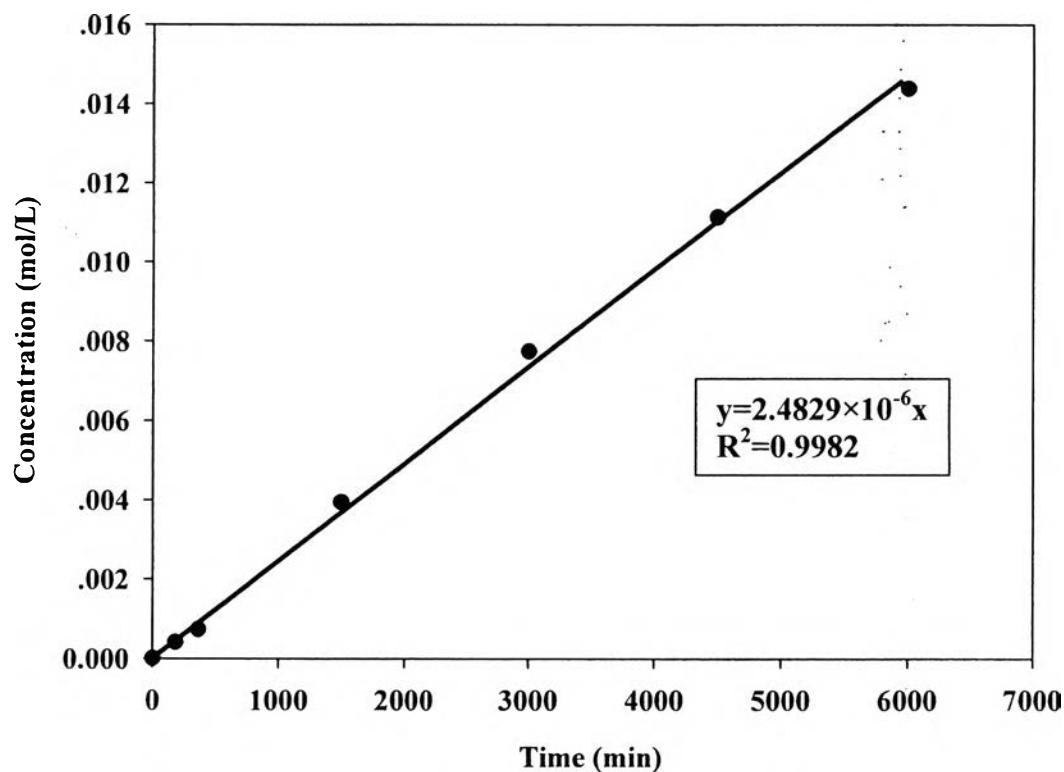
**Table G4** Raw data of vanadium permeability of S-PEEK DS 57.99 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
180	0.0002	1.72726E-05
360	0.0004	3.45453E-05
1500	0.0011	9.49996E-05
3000	0.002	0.000172726
4500	0.0022	0.000189999
6000	0.0032	0.000276362
7500	0.0041	0.000354089

**Figure G4** The vanadium permeability vs. time of S-PEEK DS 57.99 membrane.

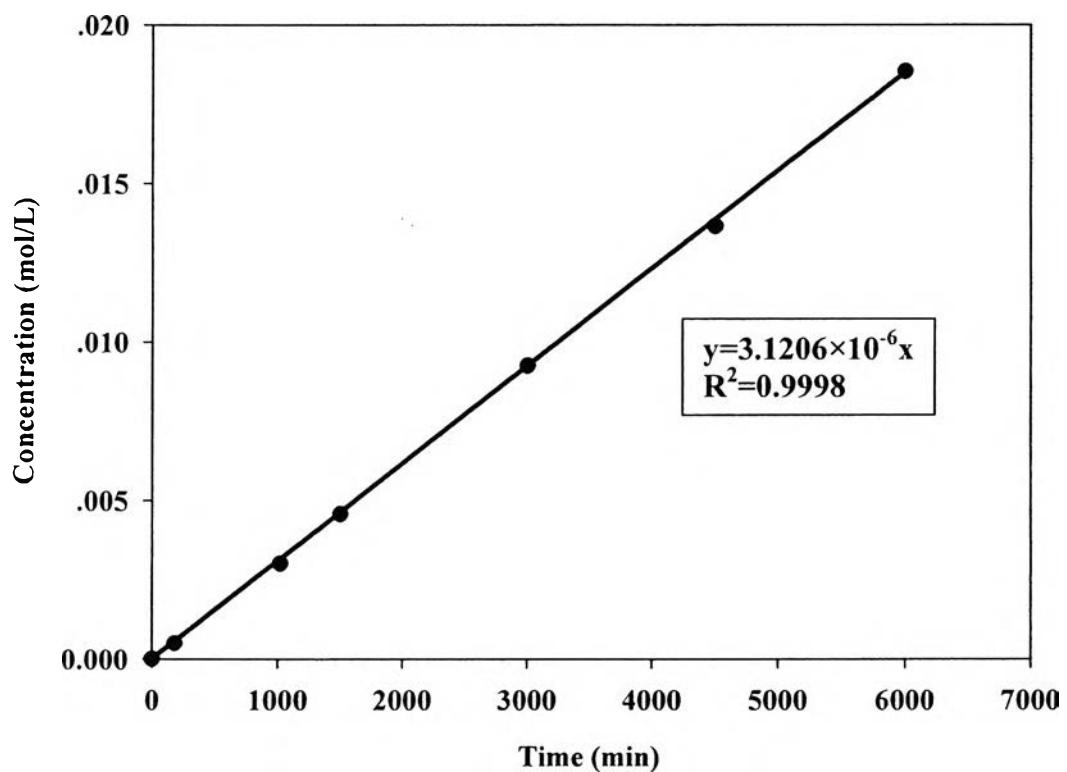
**Table G5** Raw data of vanadium permeability of S-PEEK DS 69.07 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
180	0.0047	0.000406
360	0.0084	0.000725
1500	0.0456	0.003938
3000	0.0896	0.007738
4500	0.1289	0.011132
6000	0.1666	0.014388

**Figure G5** The vanadium permeability vs. time of S-PEEK DS 69.07 membrane.

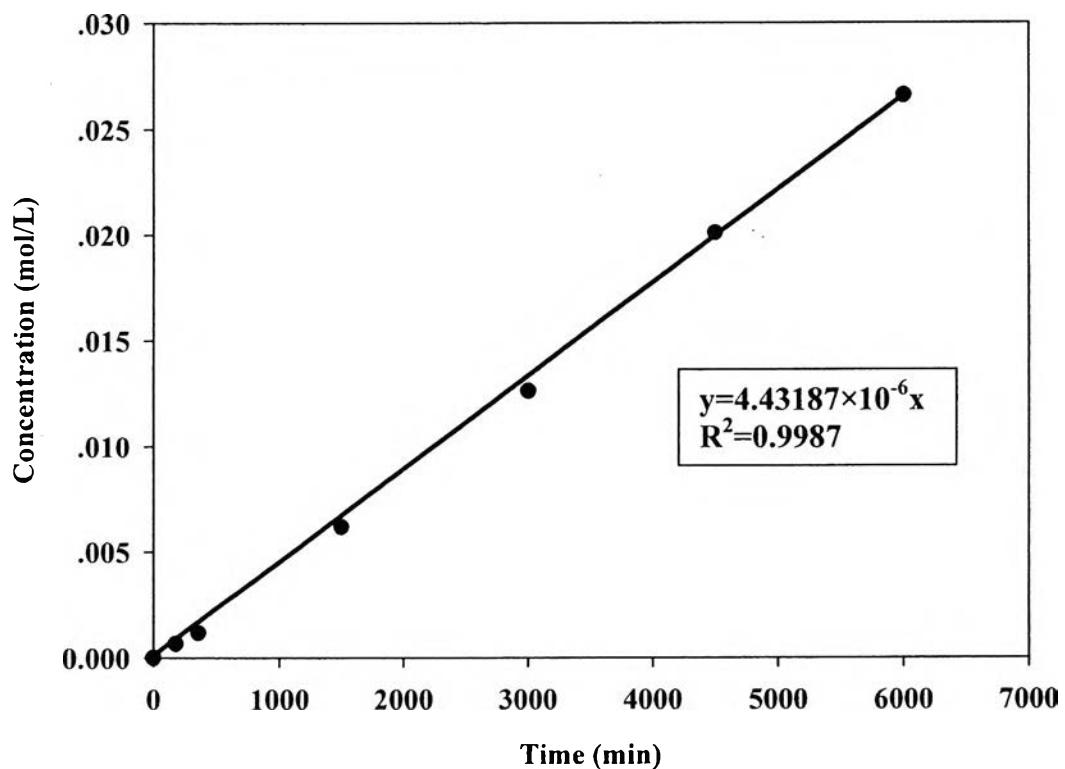
**Table G6** Raw data of vanadium permeability of S-PEEK DS 76.49 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
180	0.0057	0.000492
1020	0.0349	0.003014
1500	0.0529	0.004569
3000	0.1071	0.009250
4500	0.1580	0.013645
6000	0.2145	0.018525

**Figure G6** The vanadium permeability vs. time of S-PEEK DS 76.49 membrane.

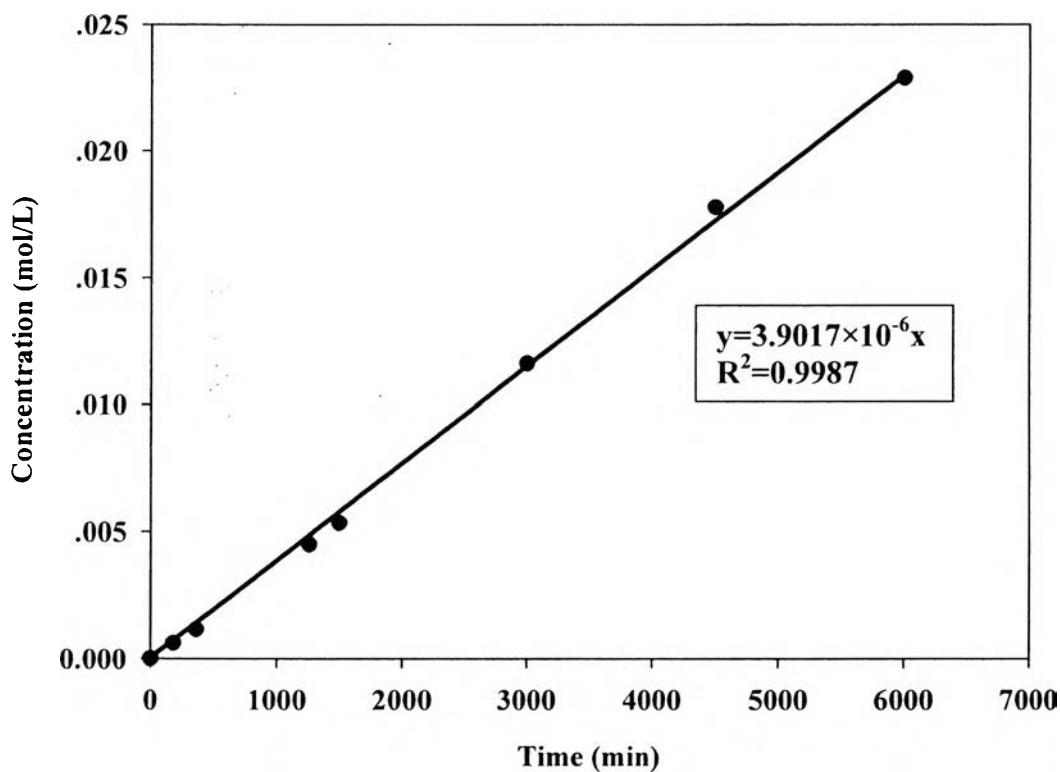
**Table G7** Raw data of vanadium permeability of S-PEEK DS 86.49 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
180	0.0076	0.000656
360	0.0135	0.001166
1500	0.0714	0.006166
3000	0.1461	0.012618
4500	0.2327	0.020097
6000	0.3079	0.026591

**Figure G7** The vanadium permeability vs. time of S-PEEK DS 86.49 membrane.

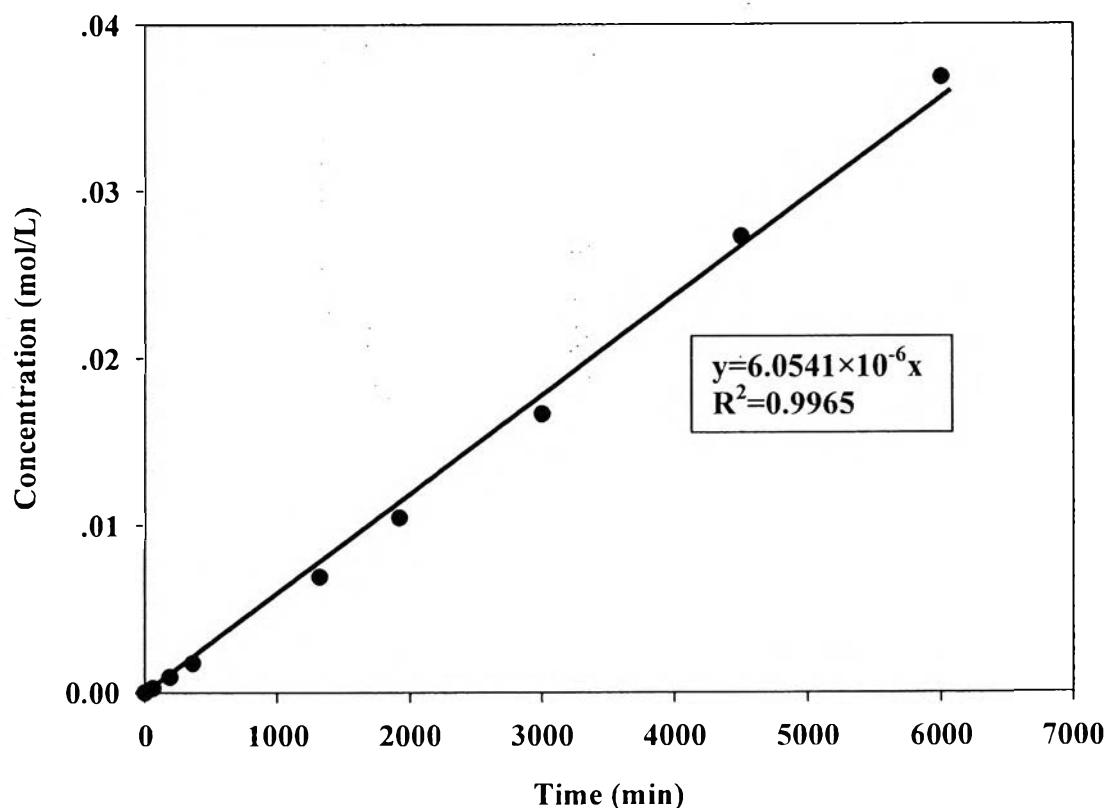
**Table G8** Raw data of vanadium permeability of S-PPEES DS 83.57 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
180	0.0070	0.000605
360	0.0133	0.001149
1260	0.0520	0.004491
1500	0.0617	0.005329
3000	0.1344	0.011607
4500	0.2058	0.017774
6000	0.2649	0.022878

**Figure G8** The vanadium permeability vs. time of S-PPEES DS 83.57 membrane.

**Table G9** Raw data of vanadium permeability of Nafion<sup>®</sup> 117 membrane

Time (min)	Absorbance	Concentration (mol/L)
0	0	0
60	0.003	0.000259
190	0.0106	0.000915
360	0.0202	0.001745
1320	0.0798	0.006892
1920	0.1211	0.010459
3000	0.1931	0.016677
4500	0.3158	0.027274
6000	0.4265	0.036834

**Figure G9** The vanadium permeability vs. time of Nafion<sup>®</sup> 117 membrane.

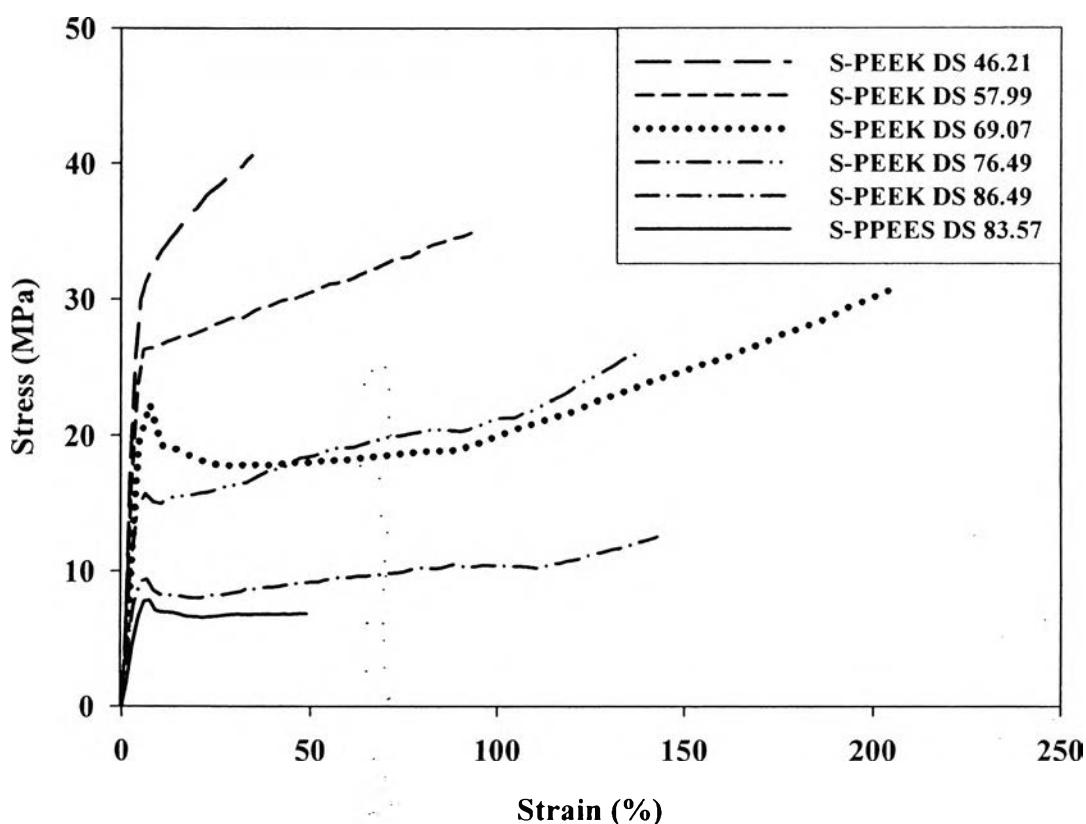
## **Appendix H Determination Mechanical Properties of Sulfonated Poly(ether ether ketone) and Sulfonated Poly(1,4-phenylene ether ether sulfone)**

The tensile strength of the membranes was measured by using Universal Testing Machine (Lloyd, model SMT2-500N) for characterization of the mechanical properties of the membrane at the thickness between 110-280  $\mu\text{m}$  and the size of 1cm  $\times$  5cm. The membranes were immersed in de-ionized water for 24 h before testing and measured by using at gauge length 30.0 mm and speed of 10mm/min at room temperature. For each testing reported, at least five samples were measured and average value was calculated.

**Table H1** The mechanical property of membranes

Polymer	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PEEK DS 46.21	40.85	1136.60	33.82
S-PEEK DS 57.99	34.56	881.68	99.08
S-PEEK DS 69.07	31.66	654.52	204.05
S-PEEK DS 76.49	25.58	512.90	134.44
S-PEEK DS 86.49	12.57	339.76	137.29
S-PPEES DS 83.57	8.16	194.27	53.03
Nafion 117 <sup>a</sup>	28.40	1000.00	329.20

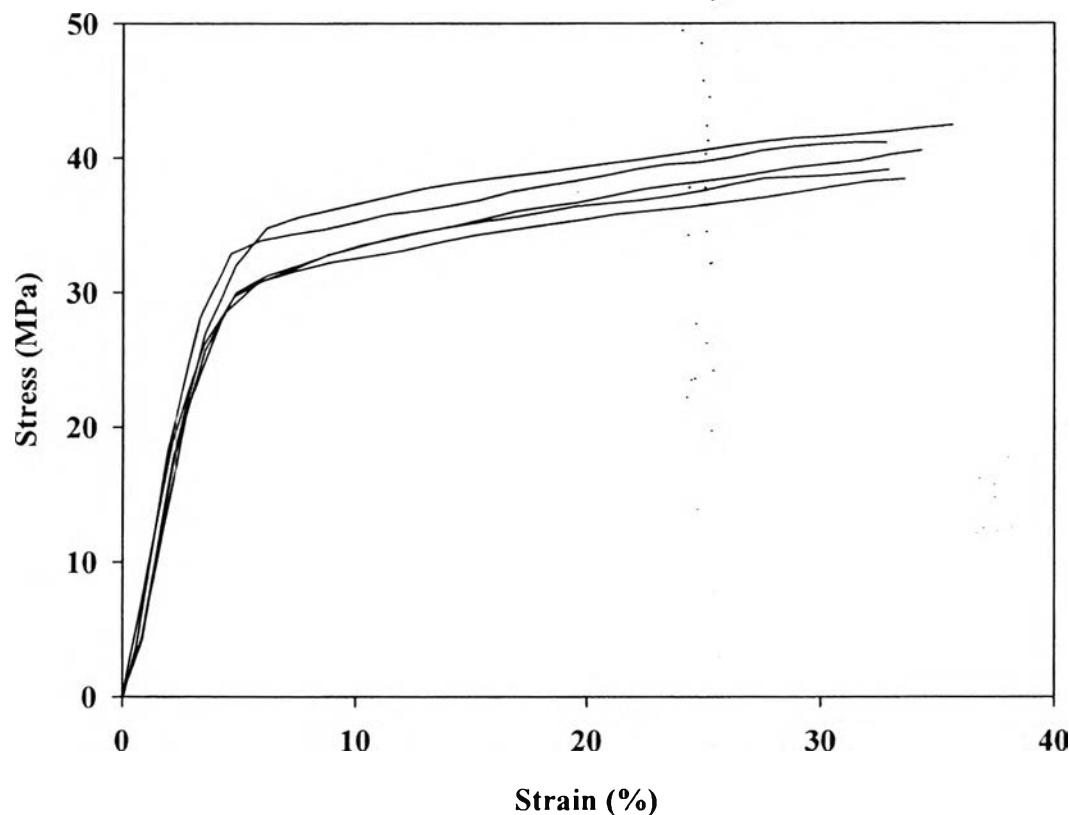
<sup>a</sup> Ref. Liu *et al.*, 2007



**Figure H1** Stress-strain behaviors of S-PEEK and S-PPEES membranes with different degree of sulfonation.

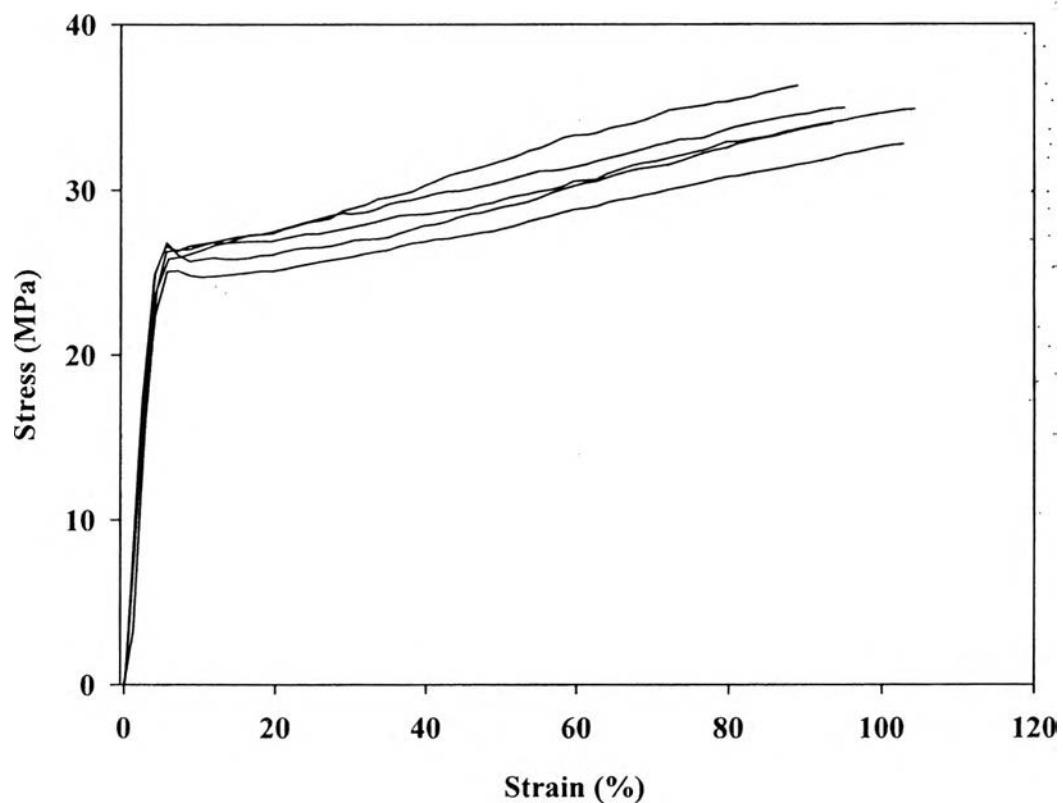
**Table H2** Tensile test results of S-PEEK DS 46.21 membranes

Polymer	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PEEK DS 46.21	120	38.423	1120.2	33.573
	110	41.151	1186.0	32.760
	120	40.551	1150.5	34.279
	120	42.004	1117.2	35.621
	130	39.121	1109.2	32.882
Average	<b>120±7.07</b>	<b>40.85±2.56</b>	<b>1136.6±31.74</b>	<b>33.823±1.17</b>

**Figure H2** Stress-strain behavior of S-PEEK DS 46.21 membranes.

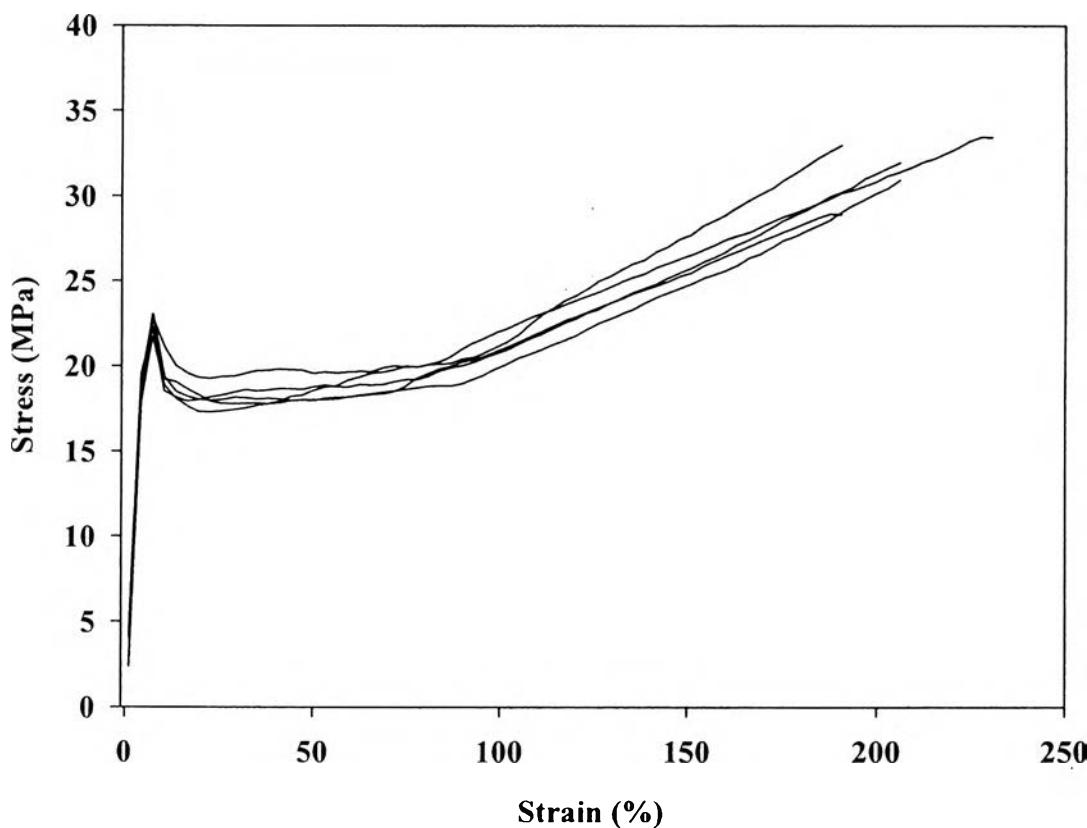
**Table H3** Tensile test results of S-PEEK DS 57.99 membranes

Polymer	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PEEK DS 46.21	156	34.869	913.62	105.81
	151	34.935	860.55	99.70
	160	32.743	829.49	104.32
	155	34.007	873.21	95.068
	156	36.269	931.51	90.506
Average	<b>156±3.21</b>	<b>34.56±1.30</b>	<b>881.68±41.06</b>	<b>99.08±6.38</b>

**Figure H3** Stress-strain behavior of S-PEEK DS 57.99 membranes.

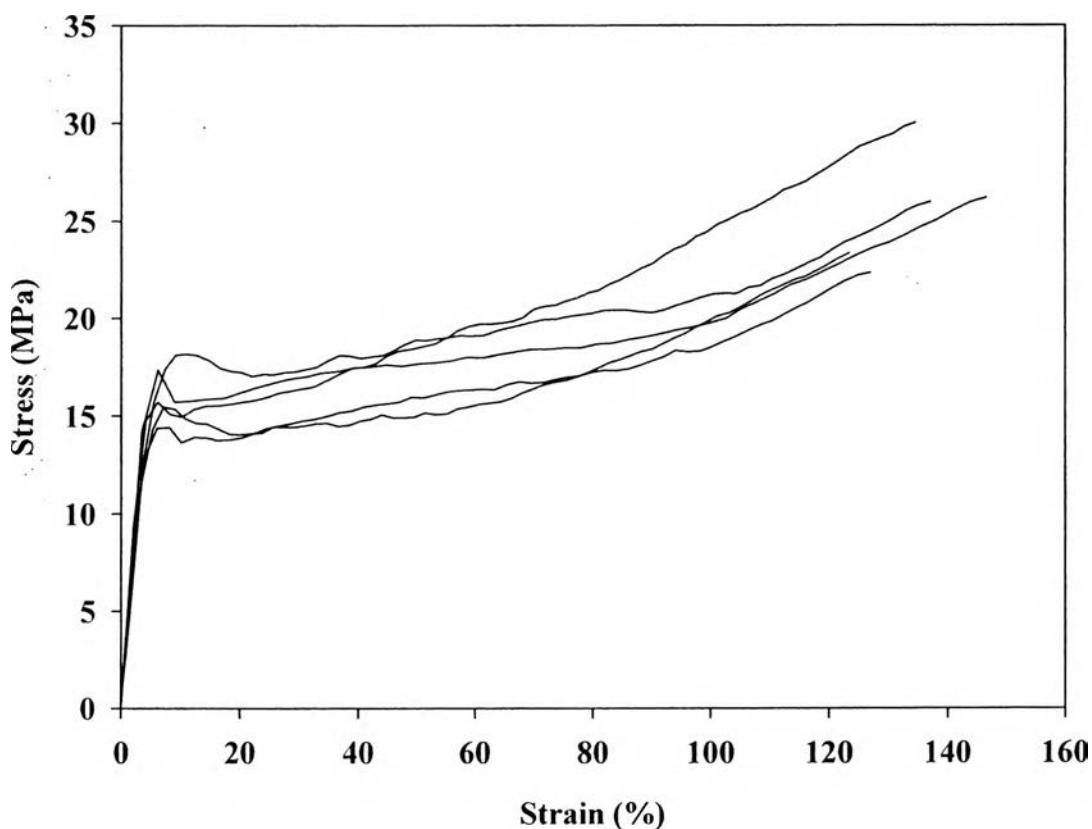
**Table H4** Tensile test results of S-PEEK DS 69.07 membranes

Polymer	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PEEK DS 69.07	185	31.956	661.00	205.91
	201	28.956	646.02	190.60
	220	33.472	641.78	227.26
	165	32.980	639.93	190.59
	225	30.936	683.90	205.91
Average	<b>199±24.86</b>	<b>31.66±1.80</b>	<b>654.52±18.39</b>	<b>204.05±15.06</b>

**Figure H4** Stress-strain behavior of S-PEEK DS 69.07 membranes.

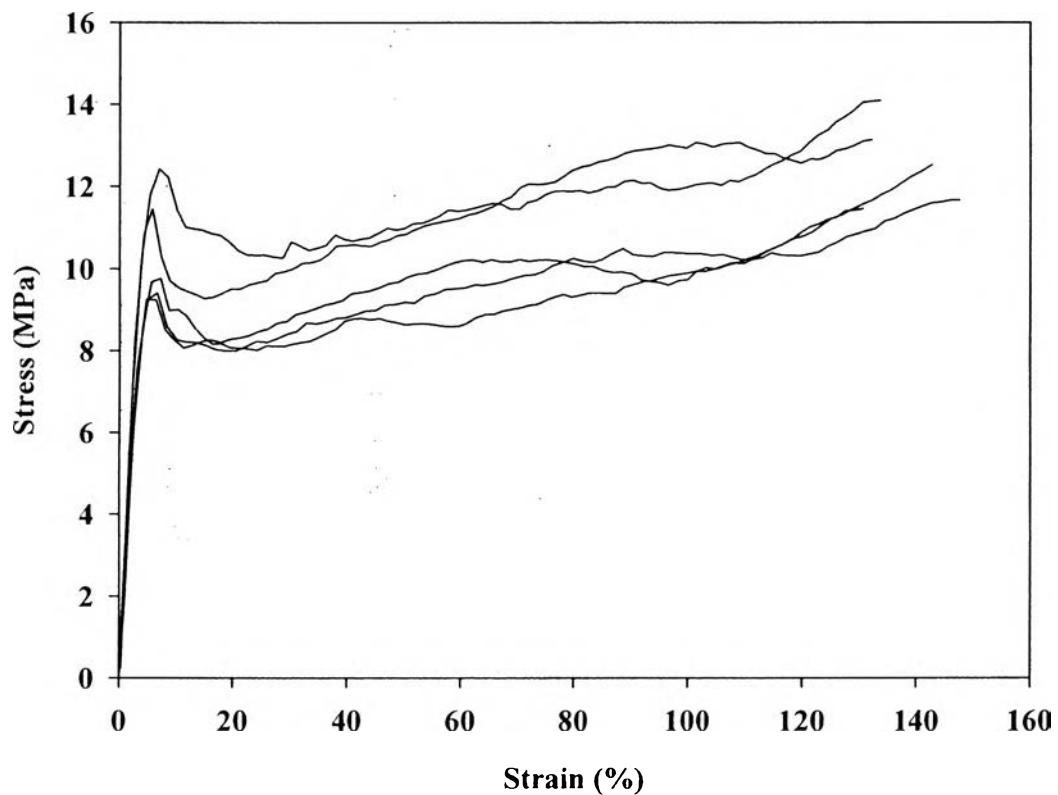
**Table H5** Tensile test results of S-PEEK DS 76.49 membranes

Polymer	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PEEK DS 76.49	130	22.346	548.12	126.87
	130	25.967	535.27	137.11
	130	26.196	545.73	146.64
	110	30.017	467.77	136.35
	120	23.353	467.60	125.24
Average	<b>124±8.94</b>	<b>25.576±2.98</b>	<b>512.9±41.46</b>	<b>134.442±8.68</b>

**Figure H5** Stress-strain behavior of S-PEEK DS 76.49 membranes.

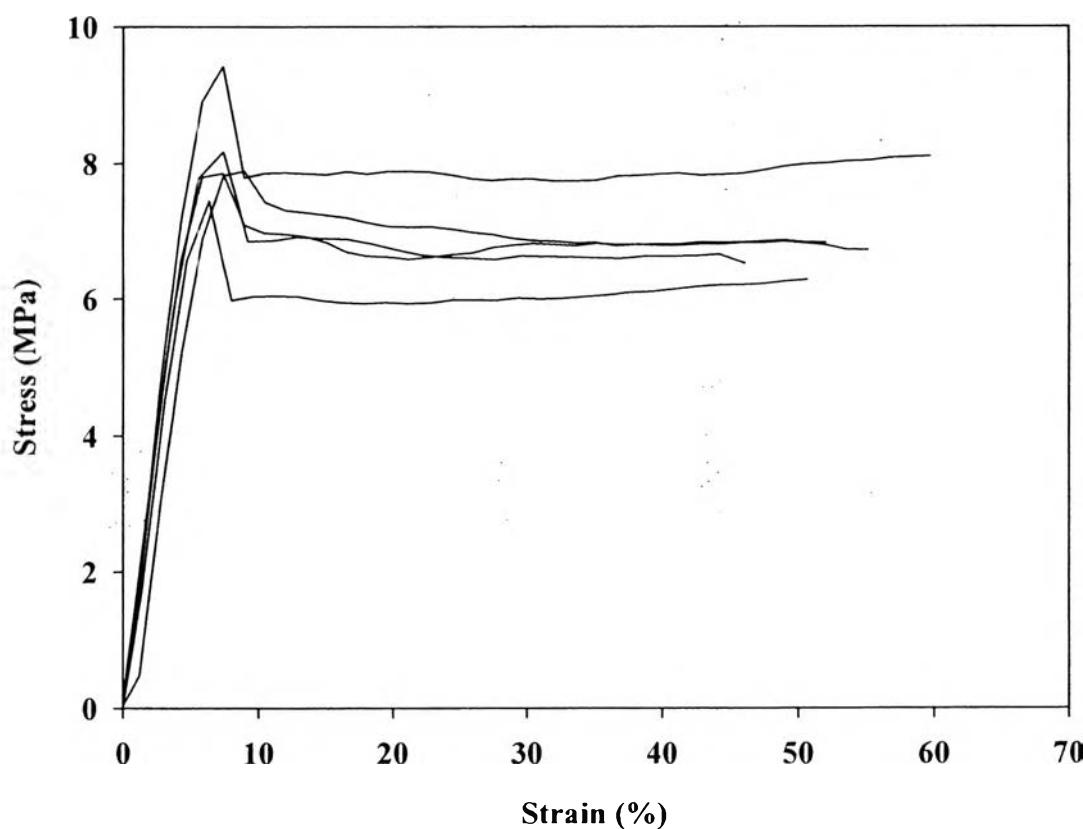
**Table H6** Tensile test results of S-PEEK DS 86.49 membranes

Polymer	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PEEK DS 86.49	165	14.090	373.20	133.59
	170	13.136	380.01	132.10
	176	11.458	298.61	130.55
	174	11.665	314.92	147.54
	169	12.525	332.04	142.68
Average	<b>171±4.32</b>	<b>12.575±1.08</b>	<b>339.76±35.74</b>	<b>137.292±7.42</b>

**Figure H6** Stress-strain behavior of S-PEEK DS 86.49 membranes.

**Table H7** Tensile test results of S-PPEES DS 83.57 membranes

Polymer	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
S-PPEES DS 83.57	280	7.8575	194.40	53.567
	260	9.4148	215.52	59.706
	270	7.8894	187.13	55.122
	280	8.1696	189.84	46.049
	270	7.4470	184.48	50.645
Average	272±8.37	8.156±0.75	194.27±12.43	53.028±5.09

**Figure H7** Stress-strain behavior of S-PPEES DS 83.57 membranes.

## CURRICULUM VITAE

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**Proceeding:**

1. Macksasitorn, S.; Sirivat, A.; and Siemanond, K. (2011, April 26). Sulfonated Poly(ether ether ketone) and Sulfonated Poly(1,4-phenylene ether ether sulfone) Membranes for Vanadium Redox Flow Battery. Proceedings of The 2<sup>nd</sup> Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17<sup>th</sup> PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

**Presentation:**

1. Macksasitorn, S.; Sirivat, A.; and Siemanond, K. (2011, April 26). Sulfonated Poly(ether ether ketone) and Sulfonated Poly(1,4-phenylene ether ether sulfone) Membranes for Vanadium Redox Flow Battery. Paper presented at The 2<sup>nd</sup> Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17<sup>th</sup> PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

