CHAPTER V

SHIFTING FROM HYDROGEN BOND NETWORK TO Π-Π STACKING: A KEY MECHANISM FOR REVERSIBLE THERMOCHROMIC SULFONATED POLY (ETHER ETHER KETONE)

5.1 Abstract

Sulfonated poly (ether ether ketone) (SPEEK) thin film performs reversible thermochromic property by developing the color to be yellowish at the temperature above 190 °C. The detailed analyses based on temperature dependence techniques suggest the thermal treatment inducing the shifting of the hydrogen bond network between the sulfonated group and the hydrated water molecules to the π-π stacking among aromatic rings in SPEEK chains. Although it is general that the polymer chain packing is unfavourable at high temperature, the present work shows a good example that when the polymer chains can form specific molecular interaction, such as π-π stacking, even in harsh thermal treatment, a rearrangement will effectively occur which leads to an external stimuli-responsive property.

5.2 Introduction

Polymer sensors with specific properties or performances under various external stimuli for example, light,[1-3] temperature,[4-6] electricity,[7] etc. are practical for the daily life uses. In the past, many types of polymer sensors, e.g. optical polymer sensors,[2, 3] electronic polymer sensors,[8, 9] thermochromic polymer sensors, etc.[4, 6, 10] were reported. Thermochromic polymer sensors which the signals can be easily recognized with the naked eyes are expected to be applied in smart packagings,[11] temperature indicators, etc.[6]

It should be noted that, in general, the thermochromic can be derived from the specific functional groups, such as conjugated bonds with the excitation of π electrons as seen in the cases of polydiacetylene derivatives,[12, 13] and polythiophene derivatives.[14] In some cases, polymer blends with dyes also show thermochromic property by acid-base equilibrium with temperature.[15-17] In addition, the molecular reorientation, molecular packing, etc. under the secondary forces such as van der Waals, π-π, etc. also play an important role to enhance the performances.

At high temperature, the molecular mobility tends to be significant and those orientation and packing are difficult. The present work, for the first time, shows that the thermochromic effect can be pronounced even in the high temperature if the molecular orientation and packing are favorable by shifting from the structure under hydrogen bond network to the one under π-π stacking.

Sulfonated poly (ether ether ketone) (SPEEK) (Figure 5.1 (a)) can be obtained from sulfonation of poly (ether ether ketone) (PEEK) (Figure 5.1 (b)) and is unique as it consists of the hydrophilic sulfonated group as amorphous soft segment and the hydrophobic aromatic main chain as hard segment.[18-20] SPEEK generally forms the hydrogen bond network between sulfonic acid group and water molecules inside polymer matrix. By simply heating SPEEK to 190 °C, which is closed to glass transition temperature (T_g) of SPEEK,[21] the SPEEK thin film suddenly develops the yellow color suggesting thermochromic property. (Figure 5.1 (c), 5.1 (d), and Video S1). The yellowish film can be recovered to transparent colorless film if it was cooled down to room temperature (Figure 5.1 (e), and Video S2) or put into water or

hot water (Figure 5.1 (f), and Video S3). This highlights the reversible and repeatable thermochromic property.

It comes to the question that how SPEEK thin film performs thermochromic at high temperature and reversible when it is cooled down or treated with water. On this view point, the detailed analyses based on temperature dependence techniques were applied to clarify the change in packing structure of SPEEK thin film related to the development of thermochromic property.
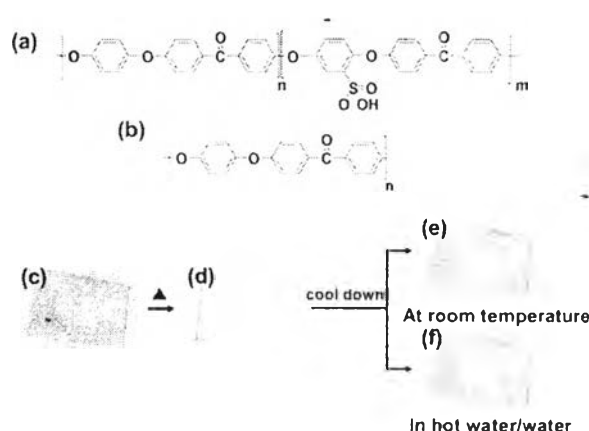

Figure 5.1 Chemical structure of (a) SPEEK, and (b) PEEK, (c) SPEEK thin film at room temperature, (d) at high temperature (above 190°C), (e) after leaving at room temperature, and (f) after putting into water or hot water (80 °C).

5.3 Experimental

5.3.1 Materials

All chemicals were reagent grade and used without further purification. Poly ether ether ketone (PEEK) was a gift from JJ Degussa Chemical (Thailand) Ltd., Thailand. Sulfuric acid (H$_2$SO$_4$) and dimethyl sulfoxide (DMSO) were purchased from Lab scan, Ireland. Deuterated-dimethylsulfoxide (DMSO-d_6) was purchased from Aldrich, Germany. Potassium bromide, KBr powder was bought form Merck, Germany.

5.3.2 Synthesis of SPEEK

Synthesis of SPEEK was carried out as reported by Vetter et. *al.*, 2005.[20] In brief, PEEK (4.0 g) was dried in hot air oven for 2 days and treated with concentrated sulfuric acid (400 ml) at room temperature for 6 hours. The brown solution obtained was precipitated in iced-water (4 L). The white precipitate was filtrated and washed several times by de-ionized water until neutral pH. The white precipitate obtained was dried in vacuo at 60 °C for a day to obtain SPEEK (Figure 5.1(a)).

5.3.3 Preparation of SPEEK Thin Film

The SPEEK (0.05 g) was dissolved in DMSO (5 mL) to achieve 1 % (wt/v) before casting on the glass plate. The 0.5 mL of 1 % (wt/v) of SPEEK solution was completely dried at 80 °C for 30 minutes to obtain the thin film with the thickness of 30 μm (Figure 5.1(a)). The structural characterization of SPEEK and the thermochromic performance of the film were carried out as reported in Appendices.

5.4 Results and Discussions

The sulfonation of SPEEK was about 57 % as quantitatively analyzed by ^{1}H NMR and titration method (Appendix D). This sulfonation degree is the optimal condition at which SPEEK becomes soluble in DMSO and is good for casting the film (Appendix L, and Table S1).

The fact that the SPEEK thin film was obtained from only sulfonation of PEEK without any additional conjugating with other functional groups or blending with dyes. The thermochromic performance as shown in Figure 5.1, therefore, has to come from the structure of SPEEK itself, such as sulfonic acid pendants and/or the aromatic ring in the main chain.

In order to confirm the thermochromic phenomenon, the UV-Vis spectra as a function of temperatures were traced. Since the sample is a thin film, the peak saturation is difficult to avoid (Figure M4). After applying heat, there is a change of shoulder peak around 300 - 400 nm (Figure 5.2 (a)). To clarify the π-π stacking of aromatic ring on SPEEK polymer backbone, the relationship between optical

absorption coefficient (α) and photon energy to represent energy band gap under heat treatment was evaluated (Appendix M).[22] The direct optical band gap, α^2, was plotted as a function of photon energy (hν) (Figure M5). The optical energy band gap, E_g, calculated from the intersection of the extrapolated line at zero photon energy (α^2). It is clear that the optical energy band gap decreases (from 3.94 to 3.88 eV) with an increase of temperature (Figure 5.2 (b)). This implies that the electrons on valence band were excited to the conduction band.[22] Moreover, the π-π stacking of aromatic ring can be explained by the clusters of aromatic carbons (N) which can be determined by the modified Tauc's equation (Appendix M).[23] Figure 5.2 (c) shows the number of aromatic carbon in cluster determined by E_g at each temperature. The higher temperature, the more cluster of aromatic carbon. The results exhibit that at the high temperature, the aromatic rings on polymer backbone are easily form clusters than at the low temperature. This leads to an answer that the π-π stacking plays the role on inducing the yellow color at its T_g (190 °C).
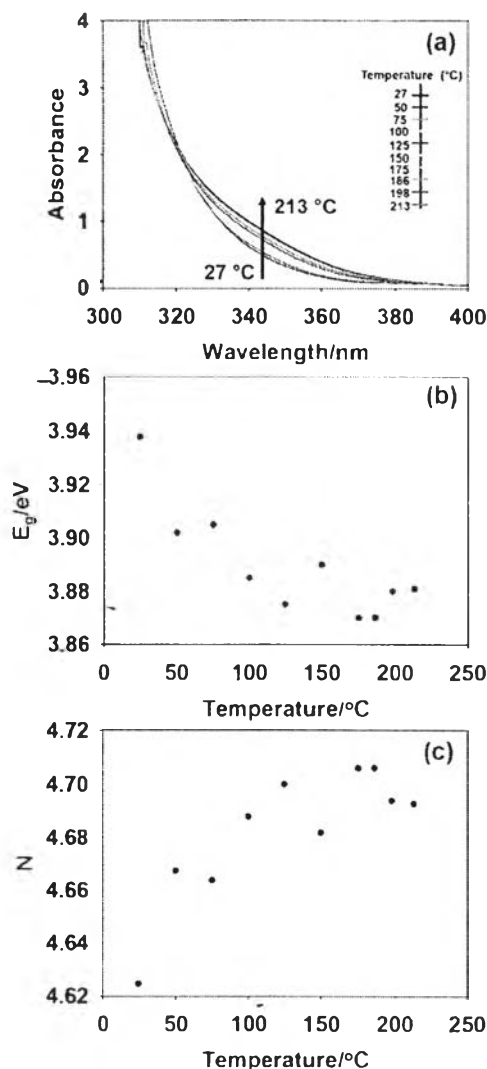
Figure 5.2 (a) Temperature dependence UV-Vis spectra of SPEEK thin film at various temperatures, (b) optical energy band gap, and (c) number of aromatic carbon in cluster as a function of temperatures.

The hydrogen bond network between sulfonic acid groups and water molecules are also evaluated by using the temperature dependence FTIR technique.[24] The symmetric $O=S=O$ peak at 1228 cm^{-1} was focused. In general, the shift of the peak position under heat treatment gives isosbestic point. Here, it was found at 1221 cm^{-1}. At the isosbestic point, it can-be assumed that the hydrogen bonds are in equilibrium (Figure 5.3 (a)). At that time, the sulfonic acid groups of SPEEK thin film might form the hydrogen bond with water molecules. It is clear that

the O=S=O peak is shifted to 1224 cm^{-1} under heat treatment which means that the vibration of this bond requires more energy when the temperature increased (Figure 5.3 (b). This suggests the aromatic ring on polymer backbone might form π-π stacking. The result is relevant to that obtained from UV spectra.

The plots of full width half maximum, FWHM, of symmetric O=S=O peak represents the changes of secondary interactions[25] which are the combination between the hydrogen bond network and π-π stacking. There are two significant changes of FWHM at 100 °C and 190 °C (Figure 5.3 (c)). The first one from room temperature to 100 °C reflects the hydrogen bond of symmetric O=S=O with water molecules. This suggests a weakening of hydrogen bonds between water molecules and sulfonic acid groups as the temperature increased. It is possible that the weakening of hydrogen bond occurs during the SPEEK polymer chains were rearranged. This can be confirmed by the second step from 120 °C to 190 °C. The rearrangement might be under π-π stacking conformation as evidenced from the yellow color developed at 190 °C. Therefore, the aromatic rings and sulfonic acid groups on SPEEK polymer chain play an important role to control thermochromic property. After cooling down to room temperature, the sulfonic acid groups might reform the hydrogen bond with the water molecules absorbed from the surrounding. At that time, the yellow color was completely disappeared.

There might be a question whether the color was from the trace amount of DMSO solvent used in casting the film. If that is the case, DMSO should give brownish color and the film may not be able to show reversible yellowish color.

One may wonder the performance of PEEK (without any sulfonation) thin film, especially, the thermochromic phenomenon. Generally, PEEK is not soluble in most organic solvents. Here, PEEK was compressed to prepare thin film (thickness ~ 0.1 mm). It was found that PEEK did not show any color during heating (to 190 °C) and cooling (to room temperature) (Appendix N). In addition, the temperature dependence FTIR of PEEK thin film did not show any isosbestic point (Appendix O).

In order to clarify the shifting of hydrogen bond network between sulfonic acid group and water molecules related to π-π stacking among aromatic rings in SPEEK, the humidity of the system was varied. It is expected that by decreasing the

humidity, the color recovery time of SPEEK would be longer. Figure 5.3 (d) shows that when the humidity of the system was 80 %, the thermochromic recovery time is 14 seconds. The yellowish film was put into an extremely dry condition, i.e. the close chamber with calcium chloride dehydrated to find that the color was lasting without change. (Video S4, and Appendix P). The yellowish film became transparent immediately (about 6 seconds) when it was immersed in water or hot water (Video S3). In fact, the treatment with hot water was for an objective to show that the thermochromic effect was depending on the water (hydrogen bond effect with water) not on the temperature (the cooling down effect). In addition, this thermochromic can be repeated in many cycles (around 10 cycles) as seen in Video S5. This supports the mechanism that the SPEEK under π-π stacking was suddenly changed to SPEEK under hydrogen bond if it was accelerated with water molecules from the surroundings.
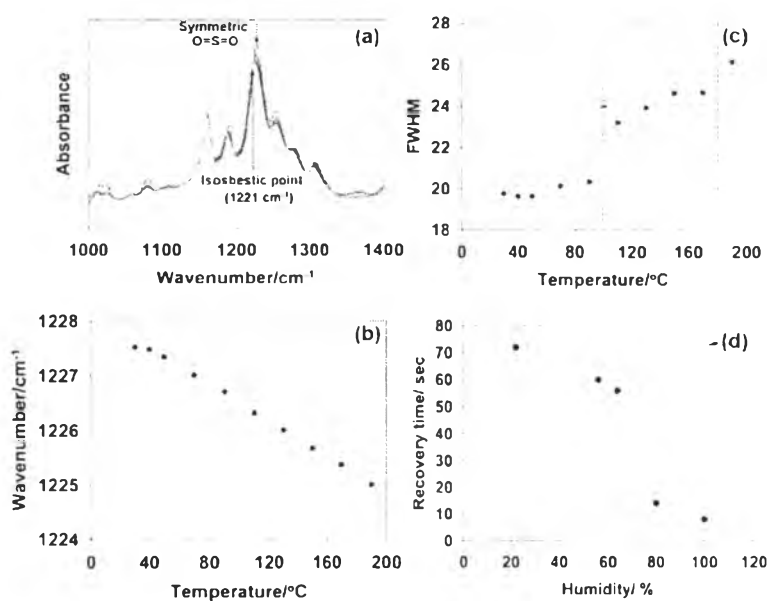

Figure 5.3 (a) Temperature dependence FTIR spectra of SPEEK thin film, (b) symmetric peak position of O=S=O, and (c) FWHM of O=S=O as a function of temperatures, and (d) thermochromic recovery time under variation of humidity.

Scheme 5.1 represents the possible reversible thermochromic SPEEK thin film at molecular level. At room temperature, the SPEEK film is packed randomly as stage I by the hydrogen bond among sulfonic acid groups with water molecules. By heating the film to T_g, the molecular motion leads to the loss of hydrogen bond and the dehydration of water (stage II). Consequently, the phenyl ring forms π-π stacking among each other bringing in the color (stage III). At that time, if the film is treated with water, the hydration will be recovered to generate the hydrogen bond between sulfonic acid groups and water molecules (stage IV). As a result, the color will be disappeared.

Scheme 5.1 Possible reversible thermochromic SPEEK thin film at molecular level.
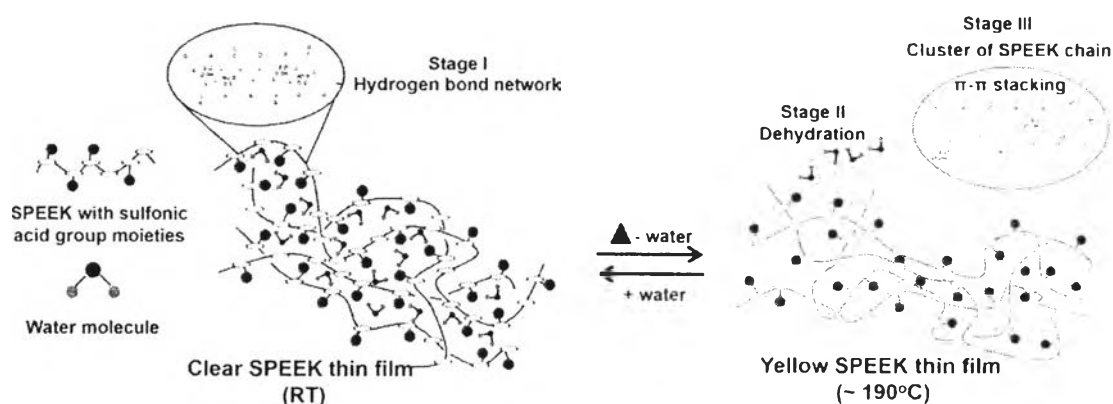
5.5 Conclusions

The present work shows the thermochromic effect of SPEEK thin film at its T_g. Although it is natural that the packing of polymer chains becomes random after thermal treatment, in the case of SPEEK, it is totally different. That is to say, an increase of temperature leads to the change from the hydrogen bonded packing to the π-π stacking packing structure. This stacking conformation leads to the thermochromic effect. Although this is the first report about the thermochromic generated from the shifting from hydrogen bond packing structure to π-π stacking

one in SPEEK, we believe that other sulfonated aromatic polymers also perform similarly and those are now under our investigations. It is expected that the thermochromic responsive temperature can be easily varied by simply fine-tuning the T_g of the materials.

5.6 Acknowledgements

5.7 References

[1] X. Y. Zhao, M. Z. Wang, *eXPRESS Polymer Letters* **2007**, *1*, 450.

[2] P. Kar, N. C. Pradhan, B. Adhikari, *Sensors Actuators B: Chem.* **2009**, *140*, 525.

[3] S. A. Wilson, R. P. J. Jourdain, Q. Zhang, R. A. Dorey, C. R. Bowen, M. Willander, Q. U. Wahab, S. M. Al-hilli, O. Nur, E. Quandt, C. Johansson, E. Pagounis, M. Kohl, J. Matovic, B. Samel, W. van der Wijngaart, E. W. H. Jager, D. Carlsson, Z. Djinovic, M. Wegener, C. Moldovan, R. Iosub, E. Abad, M. Wendlandt, C. Rusu, K. Persson, *Materials Science and Engineering: R: Reports* **2007**, *56*, 1.

[4] J. S. Moore, S. I. Stupp, *Macromolecules* **1986**, *19*, 1815.

[5] D. Q. Feng, A. N. Caruso, D. L. Schulz, Y. B..Losovyj, P. A. Dowben, *The Journal of Physical Chemistry B* **2005**, *109*, 16382.

[6] D. J. Ahn, S. Lee, J.-M. Kim, *Adv. Funct. Mater.* **2009**, *19*, 1483.

[7] Y. S. Chiam, K. S. Lim, S. W. Harun, S. N. Gan, S. W. Phang, *Sensors and Actuators A: Physical* **2014**, *205*, 58.

[8] M. A. Druy, R. J. Seymour, "Poly (2,2'-bithiophene): an Electrochromic Conducting Polymer", Journal De Physique, 1983, p. 48/561.

[9] A. Rembaum, A. Eisenberg, R. Haack, R. F. Landel, *J. Am. Chem. Soc.* **1967**, *89*, 1062.

[10] S. Bao, B. Fei, J. Li, X. Yao, X. Lu, J. H. Xin, *Dyes and Pigments* **2013**, *99*, 99.

[11] M. G. Baron, M. Elie, *Sensors Actuators B: Chem.* **2003**, *90*, 271.

[12] J. P. Huo, G. H. Deng, W. Wu, J. F. Xiong, M. L. Zhong, Z. Y. Wang, *Macromol. Rapid Commun.* **2013**, *34*, 1779.

[13] J. Yoon, K. A. B. Azizan, H. O. Yoo, S. Okada, J.-M. Kim, *Macromol. Rapid Commun.* **2009**, *30*, 981.

[14] M. J. Cho, J. Seo, K. H. Kim, D. H. Choi, P. N. Prasad, *Macromol. Rapid Commun.* **2012**, *33*, 146.

[15] A. Seeboth, R. Ruhmann, O. Mühling, *Materials* **2010**, *3*, 5143.

[16] G. N. Patel, R. R. Chance, J. D. Witt, *The Journal of Chemical Physics* **1979**, *70*, 4387.

[17] G. Wenz, M. A. Mueller, M. Schmidt, G. Wegner, *Macromolecules* **1984**, *17*, 837.

[18] M. I. Ahmad, S. M. J. Zaidi, S. U. Rahman, *Desalination* **2006**, *193*, 387.

[19] X. Li, C. Zhao, H. Lu, Z. Wang, H. Na, *Polymer* **2005**, *46*, 5820.

[20] S. Vetter, B. Ruffmann, I. Buder, S. P. Nunes, *J. Membr. Sci.* **2005**, *260*, 181.

[21] S. Swier, Y. S. Chun, J. Gasa, M. T. Shaw, R. A. Weiss, *Polymer Engineering & Science* **2005**, *45*, 1081.

[22] A. M. Abdul-Kader, *Appl. Surf. Sci.* **2009**, *255*, 5016.

[23] L. Singh, R. Singh, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2004**, *225*, 478.

[24] A. Pangon, P. Totsatitpaisan, P. Eiamlamai, K. Hasegawa, M. Yamasaki, K. Tashiro, S. Chirachanchai, *J. Power Sources* **2011**, *196*, 6144.

[25] Y. Mikhaylova, G. Adam, L. Häussler, K. J. Eichhorn, B. Voit, *J. Mol. Struct.* **2006**, *788*, 80.