Equilibrium Swelling of Poly(p-phenylene sulfide) in Toluene-Ethanol Mixtures

By Yasuhisa FUJII[*]

Equilibrium swelling of poly(p-phenylene sulfide) (PPS) plates was examined in mixtures of toluene and ethanol at 60 °C as a function of the volume fraction u_2 of ethanol in the mixed liquid. The plot of relative increase in weight of swollen PPS plates against u_2 is found to deviate upward from the straight line connecting the two data points at $u_2 = 0$ (pure toluene) and $u_2 = 1$ (pure ethanol), indicating that swelling of PPS plates may be increased by coexistence of ethanol with toluene. Such experimental data are analyzed on the basis of the Flory–Huggins theory, assuming that both toluene and ethanol can interpenetrate only into amorphous regions in PPS plates but not into crystalline regions and also that both the thermodynamic interaction parameters between PPS and toluene and between PPS and ethanol are independent of the volume fraction of PPS molecules in swollen amorphous regions in PPS plates. The experimental values may be quantitatively reproduced by the theoretical ones calculated with the value of the average thickness of amorphous regions in the lamellar stacking structure in a PPS plate determined by small-angle X-ray scattering.

KEY WORDS: Poly(phenylene sulfide) (PPS) / Swelling / Biofuel / Flory–Huggins Theory / Small-angle X-ray Scattering /

Poly(p-phenylene sulfide) [PPS; i.e., poly(thio-1,4-phenylene)] is high-performance semicrystalline thermoplastic having excellent mechanical and thermal properties and strong chemical resistance,[1] and is used all over the world for various purposes, especially for parts in automobile fuel systems and electronic components. Although PPS is durable in touch with a variety of organic solvents, toluene which remains in gasoline has an affinity for PPS and swells solid PPS, because the chemical structure of toluene is similar to that of the repeating unit of PPS. Therefore, swelling of PPS in toluene has been extensively examined in order to confirm its applicability to the fuel systems.

Nowadays, mixtures of gasoline and ethanol, i.e., so-called biofuels, come to be progressively used as engine fuel for environmental reasons. However, effects of coexistence of ethanol with toluene on the swelling of PPS have not yet been well understood. Henceforth, knowledge about the effects is very important for materials design suitable for parts in the fuel systems. In this paper, therefore, we choose miscible mixtures of toluene and ethanol as a simplified fuel, and examine swelling of PPS plates immersed in the mixtures. We also make an analysis of the data so obtained on the basis of the conventional polymer thermodynamic theory, i.e., the Flory–Huggins theory.[2]

EXPERIMENTAL

Materials

Linear PPS was synthesized following the method described elsewhere.[3] Its weight-average molecular weight M_w was 3.6×10^4, and the ratio M_w/M_n of M_w to the number-average molecular weight M_n was 2.0. They were determined by analytical size exclusion chromatography (SEC) by the use of 1-chloronaphthalene at 210 °C as an eluent and of polystyrene as a reference standard. PPS plates of 60 mm × 13 mm with a thickness of 0.8 mm were injection-molded, which were then planed to a thickness of 0.3 mm by a cutter cooled by water. These plates with a thickness of 0.3 mm so prepared were used as test samples. The degree of crystallinity of the sample plates was evaluated to be 29.9% from the value 1.35 g/cm³ of the specific gravity of the plates by the use of the values 1.43 g/cm³ and 1.32 g/cm³ of crystalline and amorphous densities,[4] respectively.

Toluene (> 99.5%) and ethanol (> 99.5%) were from Wako Pure Chemical Industries, Ltd., and were used as received.

Sorption Experiments

The PPS sample plates were immersed in an excess of toluene, ethanol, or their mixtures (ethanol volume fraction: 25, 50, and 75%) at 60 °C. After time t, we took the plate out of the mixed liquid, gave it a quick wipe, measured its weight, and then immersed it again in the mixed liquid for the succeeding measurement. The increase in weight of the sample plates may be considered to be caused by the liquid sorption.

Small-angle X-ray Scattering

A small-angle X-ray scattering (SAXS) measurement was carried out for a sample plate before the immersion by a Rigaku RINT 2500 at 25 °C in order to obtain the average thickness of amorphous regions in the lamellar stacking structure. The X-ray source is an 18 kW rotating-anode X-ray generator with a Cu target, the incident X-ray beam from it being passed through an Osmic collimating multilayer optics. The incident X-ray point beam was normal to the sample plate.

Technical Solution Center, Polyplastics Co., Ltd., Miyajima 973, Fuji 416-8533, Japan
*To whom correspondence should be addressed (Tel: +81-545-61-5995, Fax: +81-545-61-4195, E-mail: yasuhisa.fujii@polyplastics.com).
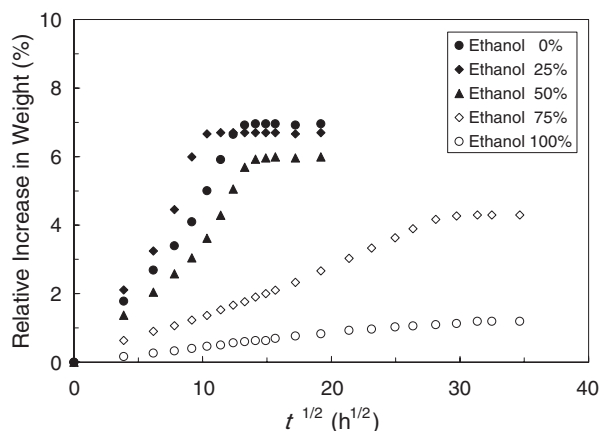
Figure 1. Plots of relative increase in weight of the sample plates, defined by the increase divided by its original weight before the immersion, against the square root $t^{1/2}$ of immersion time t at 60 °C for toluene, ethanol, and their mixtures.

Figure 2. The values of relative increase in weight at the equilibrium swelling are plotted against the volume fraction u_2 of ethanol in the mixed liquid where the sample plate was immersed. The plot deviates upward from the straight line (dashed one) connecting the two data points at $u_2 = 0$ (pure toluene) and $u_2 = 1$ (pure ethanol).

The intensity of the scattered X-ray was detected by a flat imaging plate system.

RESULTS AND DISCUSSION

Sorption Experiments

Figure 1 shows plots of relative increase in weight of the sample plates, defined by the increase divided by its original weight before the immersion, against the square root $t^{1/2}$ of immersion time t at 60 °C for toluene, ethanol, and their mixtures. Non-Fickian diffusion behavior was observed for all the mixtures including pure toluene and ethanol. Each of the plots initially shows an almost linear increase (Fickian diffusion) up to *ca.* 50% of the equilibrium swelling, then turns up, and finally tends to level off. It is 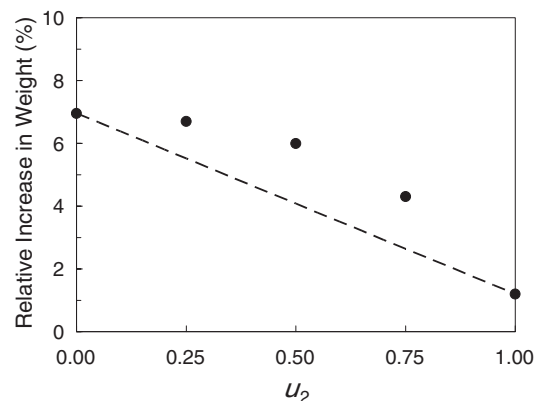noted that the sorption rate is highest in the ethanol 25% mixture. The values of relative increase in weight at the equilibrium swelling are plotted against the volume fraction u_2 of ethanol in the mixed liquid where the sample plate was immersed, in Figure 2. The plot deviates upward from the straight line connecting the two data points at $u_2 = 0$ (pure toluene) and $u_2 = 1$ (pure ethanol).

We cannot characterize PPS in solutions by standard analytical methods, for example, nuclear magnetic resonance (NMR), because PPS is insoluble in all known liquids below 200 °C. Hence, the swollen PPS plates were analyzed by gas-chromatograph-mass-spectrometer (GC-MS) to determine the weight fraction of ethanol to the absorbed liquid. Unfortunately, however, reliable data could not be obtained.

Flory-Huggins Theory

Consider an equilibrium swollen polymeric network in an excess of mixture of liquid 1 and liquid 2 with the volume fraction $u_1{:}u_2$ ($u_2 = 1 - u_1$). Further assume that the molecular size of the liquids is similar to the size of the repeating unit of the polymer and that all of the chains in the polymeric network are elastically active, as assumed by Schlick *et al.*[5] based on the theory by Flory and Rehner[2] and on its expansion by Iwatsubo

et al.[6] Then the equilibrium volume fractions v_1, v_2, and v_3 of Component 1 (liquid 1), Component 2 (liquid 2), and Component 3 (polymer), respectively, in the swollen polymeric network (polymer-occupied region) may be calculated from the following simultaneous equations

$$v_1 + v_2 + v_3 = 1 \tag{1}$$

$$\ln v_1 + v_3 + (1 - v_1)(\chi_{12}v_2 + \chi_{13}v_3)$$
$$- \chi_{23}v_2v_3 + \frac{1}{n}\left(v_3^{1/3} - \frac{v_3}{2}\right) = \ln u_1 + \chi_{12}(1 - u_1)^2 \tag{2}$$

$$\ln v_2 + v_3 + (1 - v_2)(\chi_{12}v_1 + \chi_{23}v_3)$$
$$- \chi_{13}v_1v_3 + \frac{1}{n}\left(v_3^{1/3} - \frac{v_3}{2}\right) = \ln(1 - u_1) + \chi_{12}u_1^2 \tag{3}$$

where n is the number of units between cross-links in the network, and χ_{ij} is the thermodynamic interaction parameter between components i and j ($i \neq j$). We note that n may be set equal to the number of repeating units because of the above first assumption. We also note that the equations (2) and (3) are derived from the assumption that the absolute value of the decrease in free energy by mixing is equal to that of the increase in the elastic free energy consequent on the entropy change associated with the expansion of the polymeric network.

The affinity of component i for component j is represented by the thermodynamic interaction parameter χ_{ij} in the Flory-Huggins theory.[2] χ_{13} and χ_{23} are considered to be dependent on the volume fraction of Component 3 (polymer), because the mixing entropy of polymers with small molecules is not accurately estimated in the Flory-Huggins theory.[7,8] Here, however, χ_{13} and χ_{23} are assumed to be constant.

The simultaneous equations (1), (2), and (3) were applied to PPS in toluene-ethanol mixtures by regarding the crystalline regions as cross-links, and the tie molecules as chains between the cross-links, as shown schematically in Figure 3. The calculations of the equilibrium swelling were carried out for the amorphous regions, because the diffusion of liquids in the crystalline regions is negligible.[9,10]
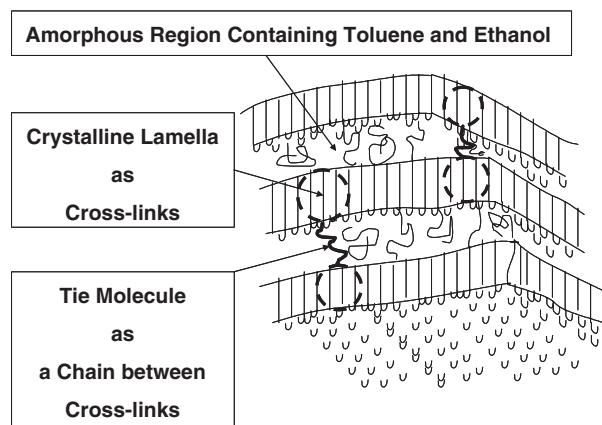
Figure 3. Schematic representation of the lamellar stacking structure. The amorphous regions contain toluene and ethanol. The crystalline regions may be regarded as cross-links, and the tie molecules as chains between the cross-links.

Figure 5. One-dimensional correlation function calculated from the circular-averaged q profile of the SAXS pattern in Figure 4.

Hereafter, u_1 is the volume fraction of toluene and u_2 ($u_2 = 1 - u_1$) is the one of ethanol in the liquid mixture. v_1, v_2, and v_3 are the equilibrium volume fractions of toluene, ethanol, and PPS molecules, respectively, in amorphous regions in a sample plate. n is the number of repeating units between cross-links, which was estimated by dividing the average thickness of amorphous regions by the length of c-axis (fiber axis) in the PPS crystal unit cell per repeating unit. χ_{12}, χ_{13}, and χ_{23} are the thermodynamic interaction parameters between toluene and ethanol, between toluene and PPS, and between ethanol and PPS, respectively.

Average Thickness of Amorphous Regions

Figure 4 shows the two-dimensional SAXS pattern for a sample plate before the immersion. As seen from the figure, the direction of the stacking lamella is random. Figure 5 shows the one-dimensional correlation function $G(r)$, with the correlation distance r, which was calculated from the circular-averaged q (the magnitude of scattering vector) profile of the SAXS pattern in Figure 4. As shown in Figure 5, the average long period L was determined from the r-axis value of the first maximum ($r > 0$), and the average thickness l_c of the crystalline lamella was determined from the r-axis value of
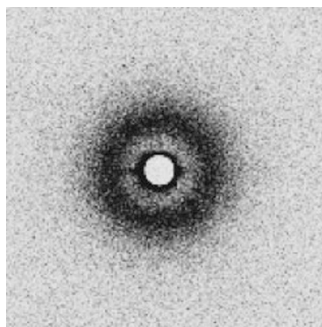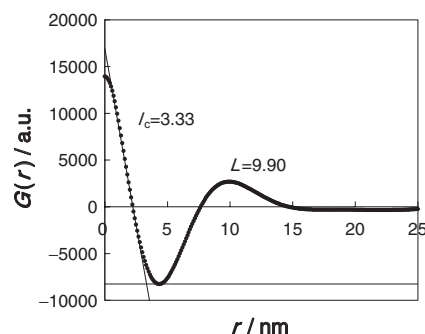
the intersection of the tangential line at $G(r) = 0$ before the first minimum and the one at the first minimum. The average long period L was 9.90 nm, and the average thickness l_c of the crystalline lamella was 3.33 nm. Therefore, the thickness l_a of the amorphous region was 6.57 nm.

Comparison between Theory and Experiment

The unit cell of PPS has an orthorhombic crystal structure with $a = 0.867$ nm, $b = 0.561$ nm, and c (fiber axis) $= 1.026$ nm, and the c-axis is composed of two repeating units.[4] The length of c-axis per repeating unit is 0.513 nm. The average thickness l_a of amorphous regions was 6.57 nm (See above). We roughly assume that the tie molecules stand perpendicularly to the crystalline lamellae, and that the conformation of the tie molecules is the same as that in the crystalline lamellae. Then, $n = 12.8$ was obtained by dividing l_a by the length of c-axis per repeating unit.

The thermodynamic interaction parameter, $\chi_{13} = 1.49$ (toluene–PPS) was calculated from the simultaneous equations (1), (2), and (3), with $v_2 = 0$ and the relative increase in weight of 6.95 wt % at the equilibrium swelling for toluene. In the calculation, the fraction of amorphous regions in the sample plates was assumed to be 0.701 from the crystallinity of 29.9%, and the specific gravity of toluene at 15 °C, $d^{15} = 0.87160$,[11] was used as its density. $\chi_{23} = 2.73$ (ethanol–PPS) was also calculated with the relative increase in weight of 1.19 wt % at the equilibrium swelling for ethanol and the specific gravity of ethanol at 20 °C, $d^{20} = 0.7893$.[11] We note that the volume fraction and the weight one may be converted to each other on the assumption that the partial molar volumes of toluene, ethanol, and amorphous PPS are equal to the ones of pure toluene, pure ethanol, and pure amorphous PPS, respectively, independently of the volume fraction.

The equilibrium volume fractions, v_1, v_2, and v_3, of toluene, ethanol, and PPS molecules, respectively, in amorphous regions in the sample plate were calculated from the simultaneous equations (1), (2), and (3) for a given volume fraction u_1 of toluene in the liquid mixture, using the above values of n, χ_{13}, and χ_{23} with a hypothetical value of χ_{12} (toluene–ethanol). The simultaneous equations were solved numerically by using the mathematical software of Maple™ 11. Figure 6 shows a

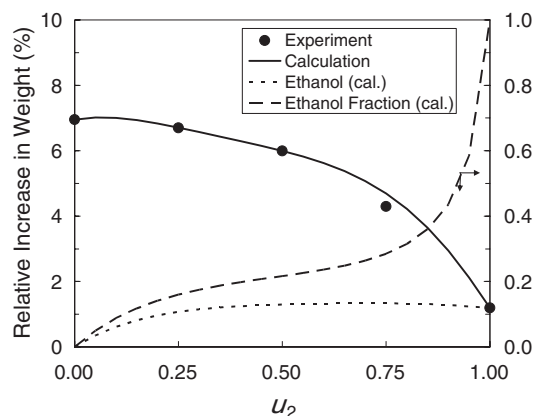Figure 4. Two-dimensional SAXS pattern for a sample plate before the immersion.

Figure 6. Comparison between the theoretical curve (solid curve) and the experimental data (circles) as to relative increase in weight at the equilibrium swelling. The dotted curve shows the theoretical values of relative increase in weight by ethanol, and the dashed one represents the theoretical weight fraction of ethanol to the absorbed liquid.

comparison between the theoretical curve and the experimental data as to relative increase in weight at the equilibrium swelling. The experimental values may be quantitatively reproduced by the theoretical ones calculated with the value of $\chi_{12} = 1.49$, which coincides with that in the literature, $1.5 \leq \chi_{12} \leq 2.0$ at $60\,^\circ\text{C}$.[12] Figure 6 shows also the theoretical weight fraction of ethanol to the absorbed liquid in the sample plate, which could not be determined in our experiment.

CONCLUSION

Equilibrium swelling of PPS plates has been examined in mixtures of toluene and ethanol at $60\,^\circ\text{C}$ as a function of the volume fraction u_2 of ethanol in the mixed liquid. It has then been shown that the plot of relative increase in weight of swollen PPS plates against u_2 deviates upward from the straight line connecting the two data points at $u_2 = 0$ (pure toluene) and $u_2 = 1$ (pure ethanol). Such behavior may be quantitatively explained by the Flory–Huggins theory with the assumptions that both toluene and ethanol can interpenetrate only into amorphous regions in PPS plates but not into crystalline regions and also that both the thermodynamic interaction parameters between PPS and toluene and between PPS and ethanol are independent of the volume fraction of PPS molecules in swollen PPS plates.

REFERENCES

1. L. C. Lopez and G. L. Wilkes, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C29**, 83 (1989).
2. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, NY, 1953.
3. Y. Iizuka, T. Iwasaki, T. Katto, and Z. Shiiki, U.S. Patent 4 645 826 (1987).
4. B. J. Tabor, E. P. Magré, and J. Boon, *Eur. Polym. J.*, **7**, 1127 (1971).
5. S. Schlick, Z. Gao, S. Matsukawa, I. Ando, E. Fead, and G. Rossi, *Macromolecules*, **31**, 8124 (1998).
6. T. Iwatsubo, K. Ogasawara, A. Yamasaki, T. Masuoka, and K. Mizoguchi, *Macromolecules*, **28**, 6579 (1995).
7. M. Kurata, "Thermodynamics of Polymer Solutions," Harwood Academic Publishers, New York, 1982.
8. R. Koningsveld, W. H. Stockmayer, and E. Nies, "Polymer Phase Diagrams: A Textbook," Oxford University Press, Clarendon, Oxford, 2001.
9. S. Manabe, in "Diffusion in Polymers," P. Neogi, Ed., Marcel Dekker, New York, 1996, chap. 5, p 211.
10. Y. Fujii and H. Shen, *J. Polym. Sci., Polym. Phys. Ed.*, **45**, 1234 (2007).
11. "Rikagaku-jiten," 5th ed., S. Nagakura, H. Iguchi, H. Esawa, S. Iwamura, F. Sato, and R. Kubo, Ed., Iwanami, Tokyo, 1998.
12. C. Gagnard, Y. Germain, P. Keraudren, and B. Barrière, *J. Appl. Polym. Sci.*, **90**, 2727 (2003).