A Study on the Role of -SO₃⁻ Ions in the Dehydration Limit of Poly(styrene-co-styrenesulfonic acid) Membrane

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Abstract: In this work, the effect of low-temperature dehydration of a poly(styrene-*co*-styrenesulfonic acid) (PSSA) membrane was investigated by differential scanning calorimetry, fourier transform infrared spectroscopy (FT-IR), electron magnetic resonancespectroscopy (EMR), and ^{1}H- and ^{13}C solid-state nuclear magnetic resonance spectroscopy. These analyses were performed at room temperature for powdered PSSA specimens with and without dehydration and the following key observations were made. First, FT-IR analysis showed that low-temperature dehydration not only transformed the [SO_3^- ···H$^+$] ionic pair in the non-hydrated PSSA to an SO_3H group, but also induced the formation of -C=C- double bonds in the dehydrated PSSA. Second, the -SO₃· radical was unambiguously identified by EMR spectroscopy. Third, H-abstraction was detected by ^{1}H magic-angle spinning spectroscopy. Finally, an unexpected color shift from white for the non-hydrated PSSA to a yellowish brown for the dehydrated sample was observed. In order to explain these experimental results, it was proposed that the formation of the intermediate hydrogen (H·) or hydroxyl radical (HO·) species was initiated by the dehydration process. The sespecies attacked the SO_3H group and the tertiary proton at the α-carbon, resulting in the formation of -SO· radicals and -C=C- double bonds, which correlated with the color shift in the dehydrated PSSA sample. The semechanisms are useful for understanding the simultaneous loss of an aromatic ring and -SO- groups in the PSSA fuel cell membrane.

Keywords: poly(styrene-co-styrenesulfonic acid), chromatic change, SO_3^- radical, electron magneticresonance

Introduction

Proton conductivity is an essential mechanism of fuel cell.[1] In these case of polymer electrolyte, the proton (H$^+$) exists as [SO_3^-···H$^+$] ionic pairs. Here, the anionic SO_3^- moiety is covalently bonded to a mainchain of polymers, whereas cationic H$^+$ is associated to hydrogen bond networks between H_2O molecules. Therefore, these H$^+$ proton can move via the hydrogen bond networks. This is why the H$^+$ conductivity is very sensitive to a molecular state of SO_3^- ions, as well as to the nature of the hydrogen bond networks. Either Zundel or Eigen cations are representative of the hydrogen bond networks that include H$^+$, and thus a lot of researchers have focused on their investigations into molecular structural behaviors as a function of hydration level.[2-7] However, as a counter anionic partner, there have been few studies on the variation of molecular state of SO_3^- ions. In fact, the role of SO_3^- is expected to critical at very low levels of hydration

because the Zundel or Eigen cations would be broken. Also, [SO_3^-···H$^+$] ionic pairs can experience a reverse dissociation process as the hydration level decrease. Therefore, in order to understand the role of SO_3^- more precisely, it is necessary to extend our study on a variation of molecular state of SO_3^- at the dehydration limit. It is well known that poly(styrene-co-styrenesulfonic acid) (PSSA) had also been used as one of the prototype polymer electrolytes for fuel cell in the early development of spaceship.[8] Here, [SO_3^-···H$^+$] ionic pairs can be controlled by introducing the sulfonic acid groups in the polystyrene skeleton polymers. The H$^+$ ion content and the hydrogen bond networks can be manipulated by adjusting a hydration level. Because of these advantages, we chose PSSA as a model system for exploring a variation of SO_3^- ions at the dehydration limit.

Experimental

1. Sample Preparation

Polystyrene (MW = ca. 580,000, MWD = ca. 1.6) was pre-

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pared via a radical polymerization with benzoyl peroxide as the initiator. For homogeneous sulfonation, the modified method of Makowski et al. was used to produce poly(styrene-co-styrenesulfonic acid) (PSSA) sample.[2] To determine the acid content, the copolymer was dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point; the acid content was 3.2 mol %. The as-prepared PSSA was a white powder in an ambient environment. In order to obtain a PSSA without hydration, we divided the as-prepared PSSA into two portions, one portion was left as-is and the other was thermally treated for dehydration at 60°C in a vacuum oven for 24 h.

2. Differential Scanning calorimetry (DSC)

Thermal analysis of the polymer samples was carried out using a differential scanning calorimetry (DSC) (TA Instrument, USA) technique. Before being measured the polymer samples, the DSC was calibrated with indium. Each sample (1-10 mg) was firstly loaded into an aluminum pan, heated to 300°C and then immediately cooled to 10°C at a heating rate of 10°C /min during a purge of dry nitrogen. These thermal cycles were used to check whether or not there was thermal hysteresis.

3. Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was performed over a frequency range of 4000-600 cm^{-1} using NICOLET 6700 FT-IR spectrometer (Thermo Scientific, USA). Every IR signal was drawn from the average of 64 scans. To prepare thin film specimens for FT-IR spectroscopy, each DMF solution containing as-prepared sample (10 mg/mL) with/without thermal treatment was cast onto a polytetrafluoroethylene (PTFE) mold and dried in an ambient condition for 24 h and dried further in a vacuum oven at room temperature for 24 h.

4. Solid State Nuclear Magnetic Resonance Spectroscopy

^{13}C cross-polarized magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR) were carried out for each sample at room temperature using Unity Inova 500 NMR (Bruker Co., Germany). For the ^{13}C CP-MAS NMR, 4 µs and 5 µs of π/2 pulses were used for ^{13}C and ^{1}H nuclei,

respectively, at spinning rate of 15 kHz. The contact time of 1 ms was used for cross polarization between the ^{13}C and ^{1}H nuclei. For the ^{1}H MAS NMR, a π/2 pulse of 5 µs was used at a spinning rate of 50 kHz. Every spectrum was obtained from the average of fast Fourier transforming of free induction decay of 50 scans.

5. Electron Magnetic Resonance Spectroscopy

The X-band electron magnetic resonance spectra were recorded at room temperature by using a JES-FA200 spectrometer (Jeol, Japan). The static magnetic field was swept from 3150 G to 3350 G. The amplitude of AC magnetic modulation was 5 G at 100 kHz. The microwave power was 1 mW and the amplifier gain was 5×10^2. Each sample was sealed in a quartz tube (diameter = 3 mm) under a pressure of 5×10^{-5} torr.

Results and Discussion

Figure 1 presents DSC thermograms obtained from the as-prepared poly(styrene-co-styrenesulfonic acid) copolymers (as-PSSA) and the dehydrated-poly(styrene-co-styrenesulfonic acid) copolymers (dhyd-PSSA), respectively.

For the case of as-PSSA, the first heating run shows two thermal transitions; one is the broad concave endothermic peak in the temperature range from 25°C to 100°C centered around 80°C, the other is a stepwise transition at 115°C. Interestingly, this combination of thermal transitions is only
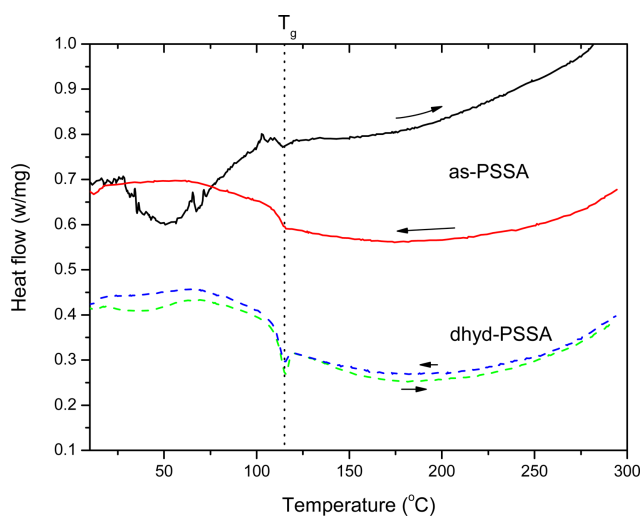

Figure 1. DSC thermograms obtained for the as- and dhyd-PSSA. The dashed-vertical line indicates the glass transition temperature (T_g).

observed at the first heating run for the as-PSSA. In the successive cooling run, the as-PSSA shows the stepwise glass transition alone at 115°C with no trace of a thermal transition at 80°C, which means that the thermal transition of the as-PSSA copolymer is irreversible for thermal cyclization. Therefore, the former can be identified to be due to a dehydration of water molecules involved in the as-PSSA, and the latter stepwise transition to a glass transition. On the contrary, the dhyd-PSSA exhibits only a glass transition for thermal cyclization, indicating that the dehydration mechanism is efficiently terminated even at 60°C.

Except for these differences in the DSC thermograms during thermal cyclization, there was unexpected but clear shift of color from white for the as-PSSA to yellowish brown for the dhyd-PSSA, as shown in Figure 2. Physically, such a color shift could be cause by selective absorption of blue, which is the complementary color of the yellowish brown, from visible light. In the current case, the molecular group capable of absorbing blue is the benzene ring. However, either carbon-carbon (C=C) or carbon-oxygen double bonds (C=O) are possible if they can be formed during low-temperature dehydration. Finally, there are $SO_3^•$ radical, which have been known to absorb specific wavelengths of light.[10] Thus, we examined radical species using EMR.

Figure 3 shows EMR results at room temperature. The as-PSSA copolymer is EMR silent; however, the dhyd-PSSA copolymer has an EMR peak of $g = 2.0031$, where g is a spectroscopic splitting factor and equals to $h\nu/\mu_B H_{res}$ (h: Planck constant, ν: microwave frequency, μ_B: Bohr magneton, H_{res}: resonant magnetic field). As pointed out in our previous study, the peak is attributed to the presence of $-SO_3^•$ radical.[11] Because double integration of EMR spectrum has been known to be proportional to the spin number, one can quantify the absolute spin number under a spectrum by obtaining an additional EMR signal from a standard sample
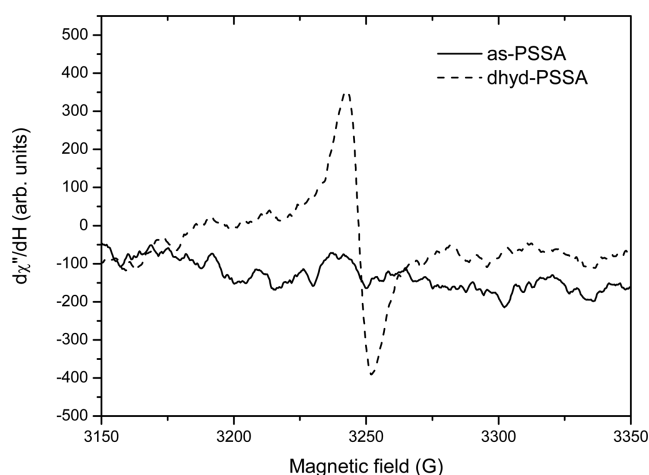

Figure 3. Electron magnetic resonance signals obtained for the as- and dhyd-PSSA copolymers.

with a known absolute spin number under same conditions. For our case, double integration of EMR spectrum for dhyd-PSSA (13 mg) gave 1.64×10^{11} spins when 210 μg (5.24×10^{17} spins) of $CuSO_4 \cdot 5H_2O$ was used as the standard sample. This means that the sub-ppm $SO_3^•$ radical are generated by the low-temperature dehydration because 2.35×10^{18} units of sulfonic acid are calculated to be included in 13 mg of dhyd-PSSA (3.2 mol%). When referring to Nafion membranes, this type of $SO_3^•$ radical can be generated by an attack of intermediate hydrogen ($H^•$) or hydroxyl radical ($OH^•$) to SO_3H.

Accordingly, we carefully performed FT-IR spectroscopy to demonstrate the existence of $-SO_3H$. The experimental results are shown in Figure 4, and the main assignments for the as- and dhyd-PSSAs are listed in Table 1.[4,12-14] The dhyd-PSSA clearly shows various bands for SO_3H; 1172 cm^{-1} (symmetric stretching vibration of S=O), 1101 cm^{-1} (in-plane skeleton vibration of benzene ring with $-SO_3H$ substitutes), and 891 cm^{-1} (S-O stretching vibration of $-SO_3H$). On the other hand, as-PSSA does not show any FT-IR bands described
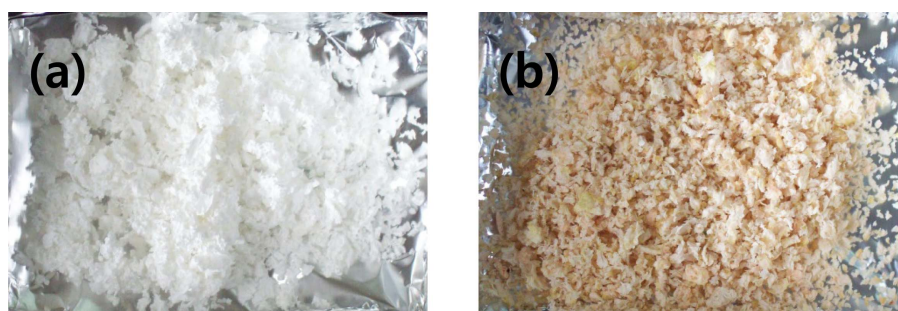

Figure 2. Color shift from white for the (a) as-PSSA to yellowish brown for the (b) dhyd-PSSA.
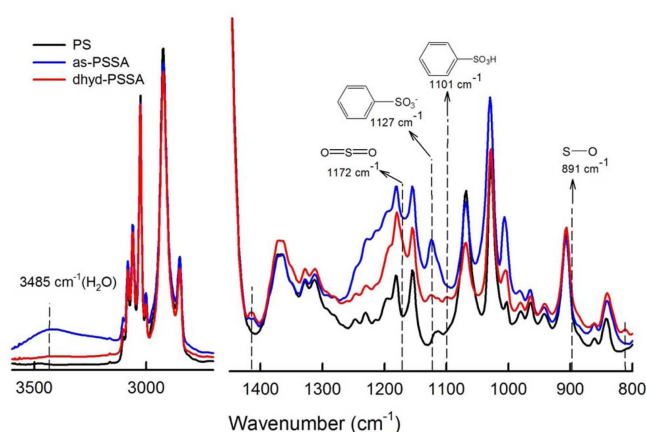
Figure 4. Room-temperature FT-IR spectra of as- and dhyd-PSSA. Note that the FT-IR spectrum of polystyrene is displayed, together with those of as- and dhyd-PSSA, in order to visualize the vibration bands from the polystyrene skeleton.

above. Instead, as-PSSA reveals FT-IR characteristics caused by the presence of H_2O, and SO_3^-; 3485 cm^{-1} (OH stretching vibration of hydrated H_2O), 1248 cm^{-1} (antisymmetric stretching vibration of -SO_3^-), 1127 cm^{-1} (in-plane skeleton vibration of benzene ring with SO_3^- substitutes), and 1004 cm^{-1} (in-plane C-H bending of benzene ring with -SO_3^- substitutes). These results mean that the SO_3H group appears in the dhyd-PSSA after disappearance of the [-SO_3^-…H^+] ionic pair.

Therefore, one can say that the presence of $SO_3^{\cdot}$ radicals is caused by an attack of intermediate $H^{\cdot}$ or $OH^{\cdot}$ on the SO_3H groups; at the same time, the possibility that such interme-

diate radicals are capable of attacking another chemical group in PSSA cannot be excluded. For this, the most plausible scenario is that either $H^{\cdot}$ or $HO^{\cdot}$ attack the tertiary hydrogen at the α-carbon of PSSA and thus induce a proton abstraction reaction, leading to a C=C bond. Interestingly, close inspection of the FT-IR spectrum of dhyd-PSSA shows an additional band at 811 cm^{-1}, which is known to be one of the FT-IR bands from a substituted C=C group. Furthermore, the proton abstraction was detected as a lacking ^1H nuclei in ^1H nuclear magnetic resonance (NMR) spectroscopy, as described below.

^1H NMR MAS spectra obtained for as- and dhyd-PSSA at a spinning rate of 50 kHz. As a whole, three different ^1H MAS peaks were obtained at chemical shifts of 1.4, 3.6, and 6.5 ppm, respectively. Since CH_2, CH, phenyl rings, and hydrated water molecules are major ^1H sources from the PSSA copolymer, 1.4, 3.6, and 6.5 ppm can be assigned to CH_2, CH, and phenyl rings, respectively. It should be noted here that the NMR peaks from [$H^+(H_2O)_m$], where m is the number of water molecules in hydrogen-bonded networks,[16-20] are considered to overlap with the peak at $\delta = 6.5$ ppm.[15,16] One can immediately know that the ^1H intensity at 6.5 ppm is drastically diminished at dhyd-PSSA when the absorption maxima of $\delta = 1.4$ ppm are kept at the same amplitude, indicatingthe disappearance of [$H^+(H_2O)_m$] protons for dhyd-PSSA.[18] Simultaneously, the decrease at $\delta = 3.6$ ppm for the CH group is manifested as well. The Lorentzian function fitting to $\delta = 3.6$ ppm reveals that the ^1H MAS intensity for

Table 1. Vibrational Band Assignments for as- and Dhyd-PSSA.

Vibrational assignments and mode descriptions	as-PSSA (cm^{-1})	dhyd-PSSA (cm^{-1})
OH stretching vibration of hydrated H_2O	3485[a]	-
CH_2 stretching	2900-2950	2900-2950
Polystyrene stretching bands	2800-3100	2800-3100
C-C in-plane stretching of ring	1600	1600
S-O_2 stretching in SO_3H	1415[b]	1415[c]
SO_3^- stretching vibration, antisymmetric	1248	-
S=O stretching vibration, symmetric	-	1172
In-plane skeleton vibration of benzene ring with SO_3^- substituents	1127	-
In-plane skeleton vibration of benzene ring with SO_3H substituents	-	1101
In-plane C-H bending of benzene ring with SO_3^- substituents	1004[d]	-
S-O stretching vibration	891[e]	891[e]
C-H out-of-plane vibration for para position	834	834
=CH_2 bending vibration	-	811
C-H out-of-plane bending	756	756
Phenyl out-of-plane bending	697	697

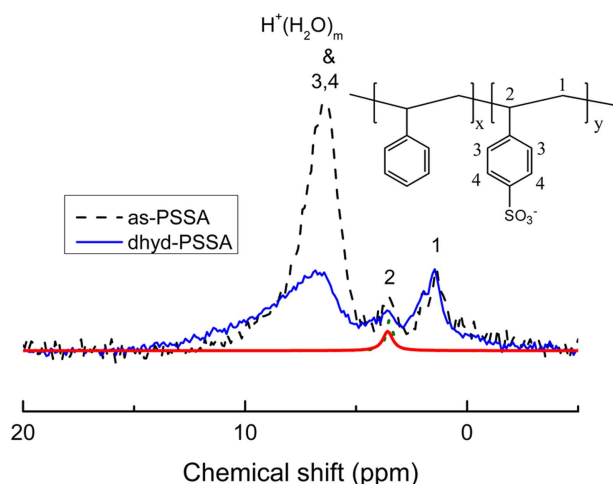[a]broad, [b]strong, [c]weak, [d]very weak, [e]shoulder

Figure 5. Solid-state ^1H MAS nuclear magnetic resonance signals obtained for as- and dhyd-PSSA. The chemical structure at right-up side is the molecular structure of PSSA. The Arabic numerals on both the molecular structure and the NMR spectra represent the ^1H MAS chemical shifts expected for different chemical sites in PSSA. The olive dotted line and the red solid line indicate Lorentzian functions fitted to δ = 3.6 ppm signals from as- and dhyd-PSSA, respectively.

dhyd-PSSA (olive dotted line in Figure 5) is 5% less than that foras-PSSA (red solid line in Figure 5). This suggests the possibility that 5% of the proton atoms can be abstracted at the CH group (α-carbon) of dhyd-PSSA by attacking intermediate H$^\bullet$ or HO$^\bullet$ radical species, as mentioned the above. In contrast, the ^{13}C CP-MAS NMR spectrum of as-PSSA (not shown here) is exactly the same as that of dhyd-PSSA when each spectrum is normalized by the mass.[21] The ^{13}C CP-MAS NMR spectrum showed no change in the carbon skeletons after dehydration of the as-PSSA copolymer. The SSNMR studies thus show a disappearance of $[H^+(H_2O)_m]$, as well as partial abstraction of the tertiary H at the α-carbon in dhyd-PSSA.

Conclusions

To conclude, to explain the presence of SO$_3^\bullet$ radicals and C=C bonds within dhyd-PSSA, one should consider that intermediate H$^\bullet$ or HO$^\bullet$ radical species can be generated in the process of low-temperature dehydration of as-PSSA. Such intermediate H$^\bullet$ or HO$^\bullet$ radicals can attack the SO$_3$H moiety as well as the tertiary proton at the α-carbon of PSSA, as shown in Figure 6. As is well known, SO$_3^\bullet$ radicals can absorb light in the wavelength range from 210 nm to 320 nm.[10] The substituted C=C bond can also absorb light with a 200 nm wavelength to obtain the excited state of the π_z - orbital (π-π∗ transition). Here, it is worth recalling that poly(p-phenylenevinylene) (PPV) with light absorption in a similar wavelength range was yellowish brown.[22-24] Thus, it is thought that light absorption by the SO$_3^\bullet$ radical and the substituted C=C bond induce a color shift in the present system.

PSSA has been widely used as a proton exchange membrane material for fuel cells, and its thermal degradation is a hot issue. According to previously reported results, the degradation can be caused by either very high temperatures or radicals.[25] With very high temperatures, fuel cells based on PSSA membranes cannot be operated above 60°C. With radicals, two different degradation mechanisms have been suggested so far; one is the degradation of hydrogen at the α-carbon of PSSA[26] and the other is oxidative decomposition due to oxidative radicals in the cathode reaction.[27,28] More recently, the simultaneous loss of an aromatic ring and SO$_3^-$ groups has also been suggested as a degradation mechanism of PSSA membranes.[29] In any case, the formation of intermediate and reactive radicals plays a major role in the degradation of the polymers. However, our experimental results show that all degradation mechanisms mentioned above can
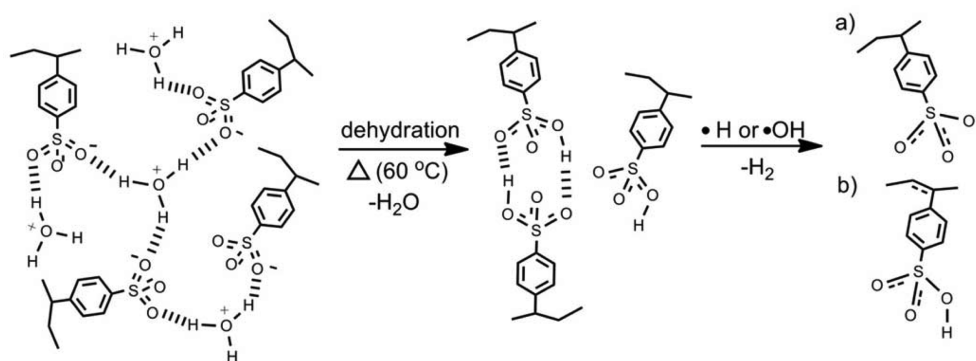

Figure 6. Schematic of the varying molecular structure of PSSA by low-temperature dehydration.

be triggered by dehydration, even below 60ºC. In a further study, we plan to study the low-temperature dehydration effect of Nafion membranes as well.

Acknowledgments

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