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Nonaqueous Proton Conduction in Poly(thiophenylenesulfonic acid)/Poly(oxyethylene) Composite

Kenji Miyatake, Kazuaki Fukushima,
Shinji Takeoka, and Eishun Tsuchida*

Department of Polymer Chemistry, Advanced Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555, Japan

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Proton-conducting solid materials have attracted much attention for application as the electrolytes of secondary batteries, fuel cells, electrochromic displays, and electrochemical sensors.[1] One of the current subjects is the development of thermostable polymeric materials with high proton conductivity. The majority of the previous studies has been devoted to aliphatic ionomers such as sulfonated polystyrene[2] and perfluorosulfonated ionomers (Nafion).[3] Particularly, Nafion has been studied most extensively because of its high decomposition temperature above 300 °C, high proton conductivity of more than 10^{-2} S cm^{-1} under moisture, and the high mechanical stability of the flexible thin film. The proton conduction in these polymers is based on the migration of hydronium ions ($(H_2O)_nH^+$) through the hydrophilic clusters of sulfonate aggregates.[4] The conductivity decreases at temperatures above 100 °C due to the evaporation of water and the destruction of the clusters.[5] Some polar polymers such as poly(oxyethylene),[6] poly(iminoethylene),[7] and poly(vinyl alcohol)[8] have been used to replace water as a matrix for sulfonic acid and phosphoric acid. The recent work by K. D. Kreuer et al. shows that imidazole and pyrazole act as a good solvent for sulfonated polymers.[9] The composites show proton conductivity under nonaqueous conditions; however, the conductivity and the stability are still deemed unsatisfactory. The small counteranions as well as protons often migrate thus leading to polarization of the bulk materials.

Although the thermostable polyaromatics are considered to be suitable backbones for the component, aromatic ionomers have rarely been reported because their synthetic procedures are limited. Trials have been done to introduce sulfonic acid or phosphoric acid groups on some polyaromatics, such as poly(1,4-phenylene) (PPP),[10] poly(carbonyl-1,4-phenyleneoxy-1,4-phenyle-

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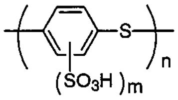
neoxy-1,4-phenylene) (PEEK),[11] and poly(thio-1,4-phenylene) (PPS).[12] Since such polymers are hardly soluble in solvents, the reaction requires severe conditions to cause the unfavorable cross-linking and/or branching. Also, the degree of sulfonation or phosphorination per phenylene unit has been less than 0.5.

We have recently developed a novel and facile synthetic method of highly sulfonated PPS via a poly(arylenesulfonium salt) as a soluble precursor.[13] The degree of sulfonation could be easily controlled and two sulfonic acid groups at maximum are substituted on one phenylene ring without any structural defects. The poly(thiophenylenesulfonic acid) is found to serve as a thermostable proton-conducting polymer with a conductivity greater than 10^{-2} S cm^{-1} under moisture. In this Communication, we report our successful results using the nonaqueous high proton conducting materials composed of poly(thiophenylenesulfonic acid) (**1**) and poly(oxyethylene) (**2**).



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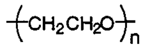

$-\!(CH_2CH_2O)_n\!-$

2

Polymer **1** was prepared by the sulfonation of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) in oleum (10% SO_3/H_2SO_4) followed by the demethylation and the ion exchange procedure.[13b] The degree of sulfonation per phenylene unit (*m*) was determined to be 0.85 by titration. The composite film was prepared by casting from a methanol solution of **1** (10 wt %) and **2** (MW = 600) (10 or 20 wt %). The film of **1** is self-standing but hard and brittle, while the composite forms a flexible and transparent film of a light brown color. The as-prepared composite contains less than 0.5 wt % water, which was determined by the Karl Fischer method. From the DSC measurements, the composite has a single glass transition temperature (T_g) at 20.2 °C for the sample with **1**/**2** = 1/1 (w/w) and 5.0 °C for the sample with **1**/**2** = 1/2 (w/w), indicating a homogeneous mixture. The T_gs of the composite are observed between those of **1** (115 °C) and **2** (−41 °C). In the IR spectrum of the composite, the peak for the asymmetric vibration of the sulfonic acid groups could be observed at 1143 cm^{-1}, a lower wavenumber shift compared to that of **1** (1154 cm^{-1}). Another peak assigned to the sulfonic acid groups appeared at 1183 cm^{-1} for the composite sample. These results indicate the dissociation of sulfonic acid groups of **1** within the poly(oxyethylene) matrix.

The proton conductivity of the composite was measured by the complex impedance method for the film sample sandwiched between gold electrodes, which was set in a closed cell under a dry argon atmosphere (H_2O < 5 ppm). A typical complex plane plot (Cole−Cole plot) for the composite (**1**/**2** = 1/2) is shown in Figure 1. The observed frequency dependence approximating a semicircle indicates an equivalent circuit corresponding to proton-blocking Au electrodes. The proton conductivity (σ) of the composite (**1**/**2** = 1/2) at 30 °C calculated from the radius of the semicircle was found to be 1.2×10^{-5} S cm^{-1}. The conductivity is about 3 orders of magnitude higher than that of **1** without the matrix (poly(oxyethylene)) but containing 3.0 wt % water (5.0×10^{-8} S cm^{-1}). The conductivity of the composite increased with temperature up to 9.6×10^{-4} S cm^{-1} at 150 °C (Figure 2). The composite of poly(perfluorosulfonic acid) (Nafion 1100) and **2** prepared from a DMF solution, a heterogeneous film, also exhibits proton conductivity, however, the values are ~2−3 orders of magnitude lower than those of the composite of **1** and **2** at temperatures from 30 to 150 °C. The higher conductivity of the **1**/**2** composite results from the higher carrier (proton) concentration of **1** (equivalent weight 210) than that of Nafion (equivalent weight 1100) and the incomplete miscibility of Nafion and **2**. The temperature dependence of the proton conductivity of the composite (**1**/**2**) does not follow the Williams−Landel−Ferry (WLF)[14] or

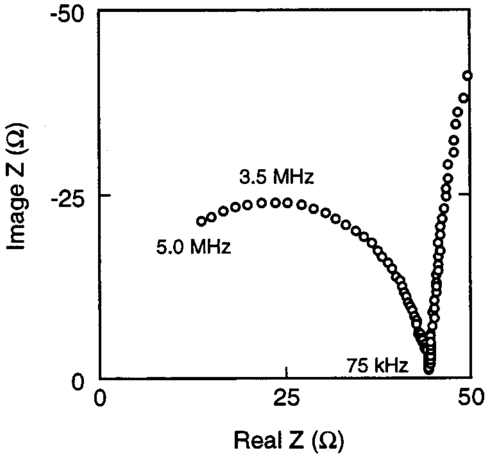

Figure 1. Complex impedance plot for the composite of **1**/**2** (1/2 by weight) at 30 °C with Au electrodes.

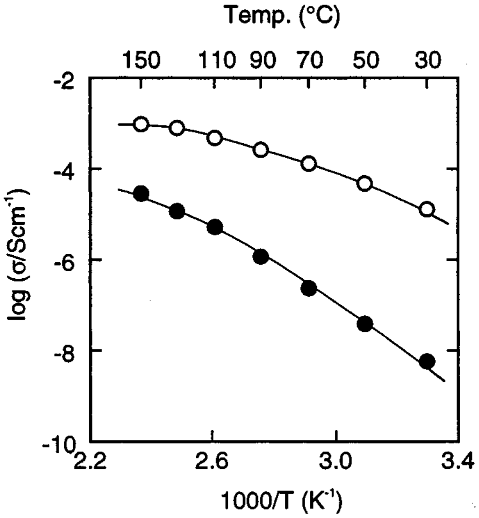

Figure 2. Temperature dependence of the proton conductivity of the composites: **1**/**2** (1/2 by weight) (○) and Nafion/**2** (3/1 by weight) (●).

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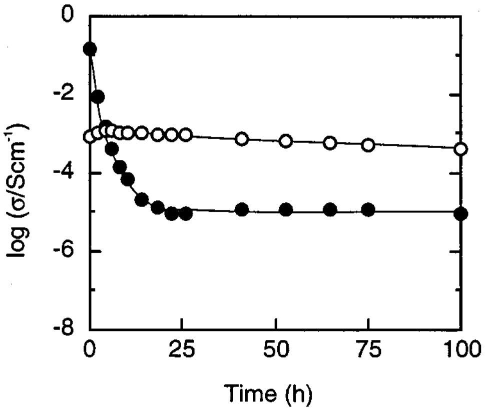

Figure 3. Time course of the proton conductivity at 130 °C: **1**/**2** (1/2 by weight) (○) and hydrated **1** (30 wt % water) (●).

the Vogel−Tamman−Fukher (VTF)[15] equation. These results indicate that the conduction could not be simply explained by the free volume mechanism, where the ion transport depends on the segmental (micro-Brownian) motion of the polymer matrix.

To evaluate the thermal stability of the conductivity, time course measurements were carried out at elevated temperature (Figure 3). In the case of the hydrated sample of **1** (without matrix but containing 30 wt % water), the initial conductivity at 130 °C is 1.5×10^{-1} S cm^{-1}. The conductivity rapidly decreased within 10 h down to the order of 10^{-6} S cm^{-1} since the water evaporates and causes a decrease in the carrier (hydronium ions) concentration and the dissociation of the sulfonic acid groups. The proton conductivity of **1** after 100 h at 130 °C was 9.6×10^{-6} S cm^{-1}. Although the initial conductivity of the composite at 130 °C is 8.0×10^{-4} S cm^{-1} and lower than that of the hydrated **1**, it increases to 1.3×10^{-3} S cm^{-1} within a few hours. There was no decrease in the conductivity after 100 h. It also maintains its proton conductivity at 150 °C. From the thermal gravimetric analysis, no weight loss could be observed for the composite during the treatment.

In conclusion, we have found that the poly(thiophenylenesulfonic acid)/poly(oxyethylene) composite shows a high proton conductivity under nonaqueous conditions. POE plays a role in decreasing the glass transition temperature and in dissociating the sulfonic acid groups. The composite shows a good thermal stability at 130 °C for more than 100 h without decreasing its conductivity ($\sigma = 1.3 \times 10^{-3}$ S cm^{-1}). This nonaqueous proton-conducting polymer might be used as an electrolyte of proton secondary batteries with water-sensitive anodes.

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