

Single-Ion Conducting Polymeric Electrolytes Based on Sulfonated Poly(phenylene oxide)

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SYNOPSIS

In the present paper, the ionic conducting properties of sulfonated poly(phenylene oxide) (PPO) and its alkali-metal salts were investigated in detail. It was found that the material had moderate conductivity, which could reach as high as 10^{-6} S/cm at room temperature. Its conductivity dependence on temperature conformed to the Arrhenius equation in a temperature range of 20–90°C. The cation's transference number determined by polarizing reversion was approximately unity. Differential scanning calorimeter, X-ray diffraction, and transmission electron microscope were used to analyze the condensed state structure of the material. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

As a kind of novel functional materials, polymeric solid electrolytes have attracted extensive interest worldwide owing to their practical and theoretical significance.¹ Much research effort has been applied on the systems of poly(oxyethylene)/Li salt hybrid and polymer matrix/Li salt additives, where ionic conductivity as high as 10^{-5} S/cm has been established. However, as the conductive properties of these materials are bi-ionic in character, one of their major shortcomings is the low conducting stability under long-term subjection to direct current, even when nonblocking electrodes are employed.²

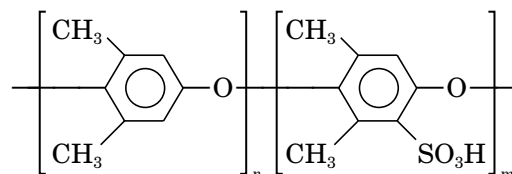
To avoid the drawbacks mentioned above, single-ion conducting materials have been devised in which the anions are attached to a polymer chain.^{3–6} As the anions are covalently bound, their transference number will be zero, and only the cations will contribute to a permanent flow of charge. To make the dissociation of ion easy, salts of anionic polymers derived from strong acidic polymers were generally employed.

The present investigation is concerned with the

conducting properties of sulfonated poly(phenylene oxide) (SPPO) and its alkali-metal salts. Results from the studies of their condensed state structure are also presented.

EXPERIMENTAL

Sulfonated poly(phenylene oxide) (SPPO) with various sulfonation degrees, defined as the percentage of sulfonated structural units, were prepared by the reaction of poly(phenylene oxide) (PPO) and fuming sulfuric acid in the media of chloroform. The details of the preparation of SPPO are the subject of a separate publication.⁷ The structure of SPPO is as follows:



In the methanol solution, SPPO was neutralized into SPPOM ($M = \text{Li, Na, K}$) by LiOH, NaOH, and KOH, respectively. After stirring for 10 h, the solution was cast into a flat glass dish. Films ~ 0.1 – 0.3 mm thickness were typically used. The X-ray diffraction patterns of the films were measured by an X-ray diffractometer (Rigaku Model D/MAX-1200) with Cu $K\alpha$ irradiation.

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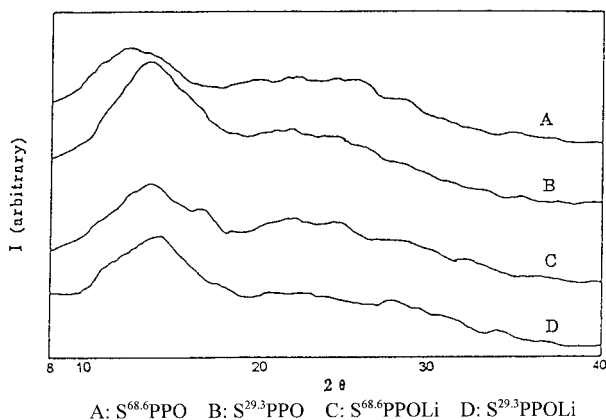


Figure 1 WAXD of SPPO and its lithium salts.

tion. Transmission electron microscopy was performed on a JEOL TEM100CXII. Thermograms of the films were obtained with a Perkin-Elmer differential scanning calorimeter (Model DSC-2) under a dry nitrogen atmosphere. The conductivity was determined in a cell under a constant temperature. With a frequency range from 12 Hz to 100 kHz, the testing instrument was a ZL-5 LCR meter coupled to an IBM microcomputer. A disk sample with a diameter of 10 mm was sandwiched between two stainless steel blocking electrodes. The alternating current ionic conductivity could be calculated from the complex impedance plots by computer curve fitting. The temperature dependence of conductivity was determined with a temperature-controlled apparatus at 20–90°C. To determine the ion transference number, the method of instant voltage reversion after dc polarizing was used: the samples were polarized under dc for an hour, the voltage reversed instantly, recording the current dependence on time. The ion transference number could

be calculated according to the time when the two current peaks appeared. All measurements were conducted under dry nitrogen atmosphere.

RESULTS AND DISCUSSION

Analysis of the Condensed-State Structure for the SPPO

The results of X-ray diffraction showed that the regularity of the condensed-state structure was deteriorated after a high polar sulfonation group, $-\text{SO}_3\text{H}$, was attached covalently to the phenylene ring, that is, when PPO was sulfonated, and the higher the sulfonation degree, the lower the regularity. Here, the sulfonated PPO was denoted as S^xPPO , where x meant the sulfonation degree of the polymer chain, while salified SPPO was denoted as S^xPPOM^y ($\text{M}=\text{Li}, \text{Na}, \text{or K}$). The superscript y , salification degree, meant the percentage of the neutralized sulfonation groups. Figure 1 illustrates the X-ray diffraction results of the $\text{S}^{68.6}\text{PPO}$, $\text{S}^{29.3}\text{PPO}$, and their lithium salts. The broad diffraction peaks responsible for the 2θ between 10° and 20° of $\text{S}^{68.6}\text{PPO}$ was much weaker than that of $\text{S}^{29.3}\text{PPO}$. This indicated that the structure of partially crystallizing PPO⁸ was destroyed to form an amorphous structure by the increase of sulfonation groups covalently attached to PPO chains. Moreover, the salification of $\text{S}^{68.6}\text{PPO}$ could somewhat raise its diffraction intensity (comparing curve A with curve C in Fig. 1), which implied that the regularity of the chains was somewhat improved. However, SPPO with a low sulfonation degree, such as $\text{S}^{29.3}\text{PPO}$, has somewhat further decreased regularity after salification. These morphology changes may be attrib-

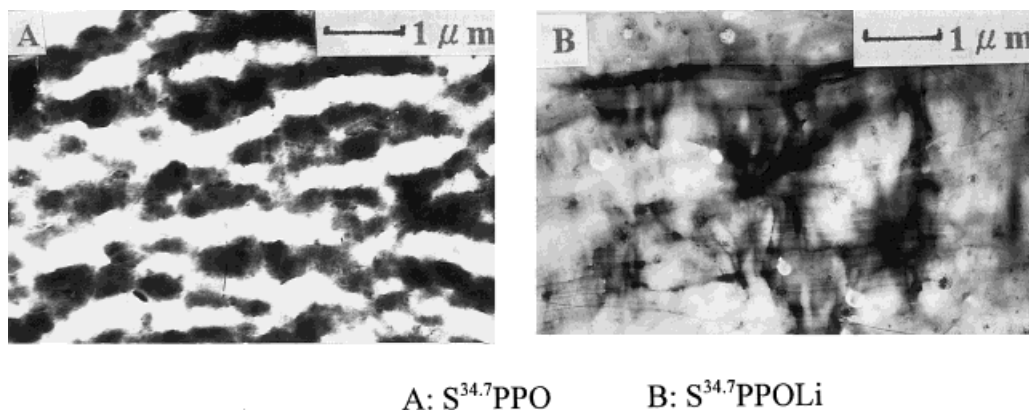


Figure 2 TEM photographs of SPPO and its lithium salt.

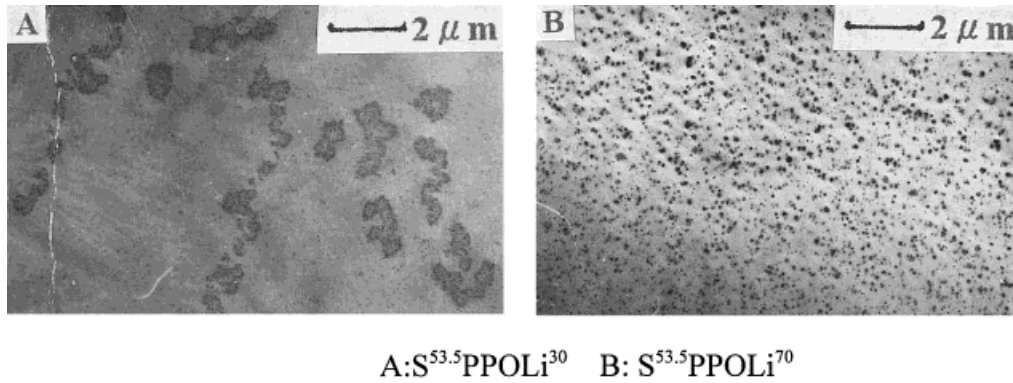


Figure 3 TEM photographs of $S^{53.5}PPOLi^y$.

uted to the high contents of sulfonyl groups on PPO chains; which caused steric hindrance and therefore led to destruction of the crystallizing structure of PPO chains; meanwhile, the substituent polarity was strong enough to establish the ionic interaction between polymer chains, so the sulfonated PPO studied here was an amorphous polymer and with some regular morphology. This would be confirmed by TEM measurement. In a word, the amorphous structure of SPPO was favorable to ion moving, making the conducting property better.

DSC analysis shows that SPPO glass transition temperature increased with the increased degree of sulfonation because high polarity sulfonyl groups in polymer chains could form interchain linking points and reduce the overall segmental mobility, for example, the T_g of $S^{53.5}PPO$ was about 15°C higher than that of PPO.

Figure 2 shows the microphotographs of $S^{34.7}PPO$ and its lithium salt, in which the phase separation morphology was obvious because of the aggregations of polar substituent groups. Figure 3 shows the effects of the salification degree on the morphology of $S^{53.5}PPO$ lithium salts. It is obvious that the ionic aggregation phase of low salification degree was collapsed by further salification and resulted in the more homodispersion of ion-aggregated domains. This is very different from those of ionomers where the ionic clusters increase with increasing degree of salification.

Conducting Property of PPO Sulfonate

Impedance Spectroscopy of PPO Sulfonate

Figure 4 shows the complex impedance which was obtained under alternating current with a frequency ranging from 12 Hz to 100 KHz. For the

restriction of the frequency, the plots with the overall impedance (including bulk impedance, charge transference impedance, and diffusion impedance), response couldn't be obtained. However, the bulk impedance of the electrolytes could be got from the plot (as the point A in the figure).

Influence of Degree of Sulfonation on the Conducting Property

Figure 5 shows the conductivity dependence of SPPOM ($M=\text{H, Li, Na, K}$) on the sulfonation degree. It shows that the conductivity sequence was $\sigma_{SPPOLi} > \sigma_{SPPONa} > \sigma_{SPPOK} > \sigma_{SPPOH}$, and the difference between the conductivity of SPPOH and that of SPPOM ($M=\text{Li, Na, K}$) was obvious. This was mainly for the reason that the covalent bond percentage of $\text{O}-\text{H}$ in SPPOH was rather high, which was difficult to dissociate, while the other three kinds of salt were all mainly connected with ionic bonds, which were easier to dissociate

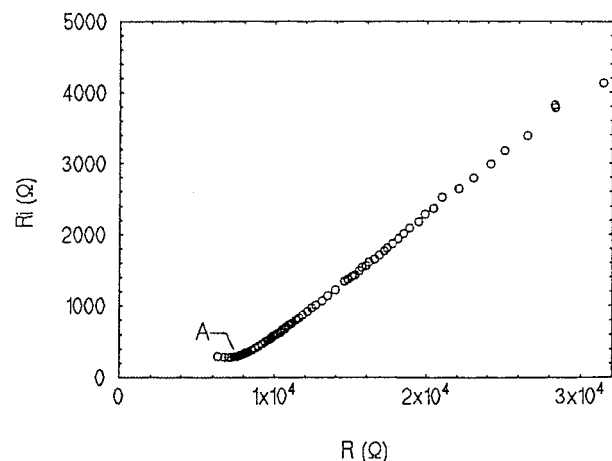


Figure 4 Impedance spectrum of SPPOLi.

under the polarization of electric field. Furthermore, the self-congregation was much stronger for SPPO before salification. It would block the ion transporting path. Meanwhile, as the resistance to the ion transportation increased with cation radii, all these factors brought about the conductivity sequence mentioned above.

Figure 5 also showed that the conductivity of SPPO increased with the sulfonation degree, especially for the samples with a lower sulfonation degree. A rise of sulfonation degree generally increased the concentration of charge carrier. However, the microviscosity of the conducting column was also increased, causing a drop of the ion mobility. This made it difficult to have a further progress of conductivity for the samples with high sulfonation degrees.

Conductivity Dependence on Degree of Salification

Figure 6 shows the influence of degree of salification on conductivity. It demonstrated that the conductivity rose with the salification degree, and reached maximum at a salification degree of 70–80%, and had no significant increase anymore. This may be due to that at the beginning of salification degree increasing, the increasing of concentration for charge carriers brought an increase in conductivity. And when the salt concentration reached a rather high level, the microviscosity of the ion environment began to weaken the capacity for the charge carrier; obviously, then, the conductivity reached the upper limit. The conductivity dependence on salification degree shows clearly

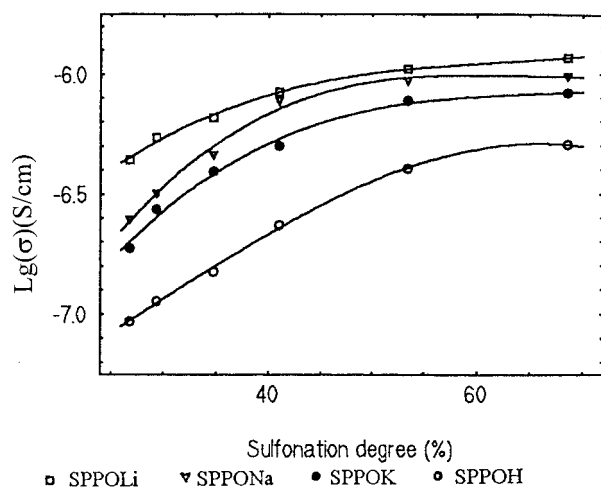


Figure 5 Conductivity dependence on sulfonation degree.

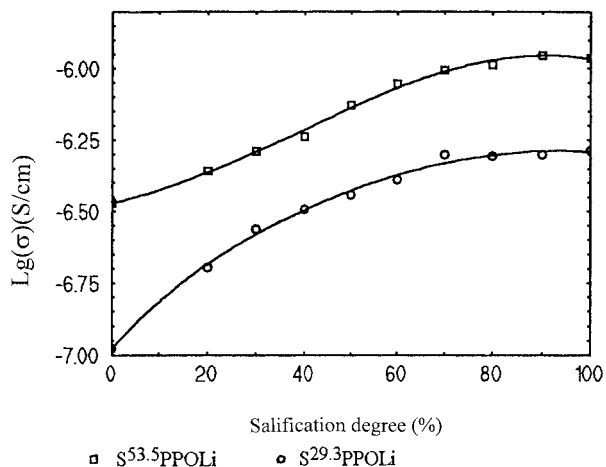


Figure 6 Conductivity dependence on salification degree.

that the increasing pace of conductivity caused by the increasing of salification degrees for $S^{29.3}PPOLi^y$ is much more comparatively than that of $S^{53.5}PPOLi^y$. This may be caused by the fact that the electrostatic restraining power would increase the microviscosity and therefore affect the ion moving. In the $S^{29.3}PPOLi^y$, the microviscosity of the ion environment was much lower than that of $S^{53.5}PPOLi^y$, so it has a higher potential to be increased in conductivity.

Conductivity Dependence on the Temperature

Temperature was an important exotic factor influencing the conducting properties of polymeric solid electrolytes. When temperature was high, ions were activated, and the interaction between the polymer chains and the salt ion relaxed. The number of dissociated ions went up, thus the ions could also move more freely. These factors were favorable to the ionic moving.

Figure 7 is a plot of the logarithm of the conductivity versus reciprocal temperature for the $S^{29.3}PPOLi^y$. The conductivity of SPPOLi in the temperature range basically conformed to the Arrhenius equation. The apparent activating energy for ion transportation of this system was about 40 KJ/mol, which was calculated by linear regression. All the results suggested that in the system of alkali-metal salts of SPPO, the ion transportation energy was rather high, and the motivation for the ion transportation was not from the segmental motion of the polymer chain, but under the help of the polarization by a neighboring group with high polarity.

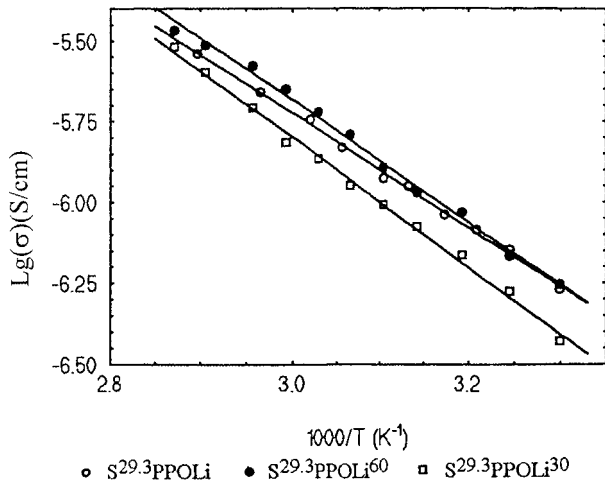


Figure 7 Conductivity dependence on temperature of SPPOLi.

Ion Transference Number of SPPO

After polarization for 1 h with a constant voltage to the blocking electrode sandwiched with the tested sample, a space charge layer would form on the interface between the sample and the electrode. After reversing the voltage instantly, the current would reach a peak when the ion from one interface charge layer reached the other electrode. The time when the current peak appeared was the ion transport span τ , while $\mu_i = d^2/(V \cdot \tau_i)$, where μ_i was the ion fluidity, d was the thickness of sample, V was the polarizing voltage.⁹ As t_i was assigned to the ion transference number, then $t_i = \mu_i / \sum \mu_i$. The testing result for the S^{68.6}PPOLi is as follows: $\mu^+ = 2.3$ min, $\mu^- = 202$ min, so

$t^+ = 0.99$ and $t^- = 0.01$ could be obtained. This indicated that the conductivity in this system was mainly due to the devotion of cation, and the system belonged to single-ion conducting solid electrolytes.

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