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Preparation and ionic conductivity of poly(ethylene oxide) oligomers having thiolate groups on the chain ends

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Abstract Poly(ethylene oxide) (PEO) oligomers having alkali metal thiolate groups on the chain ends ($\text{PEO}_m\text{-S}^-\text{M}^+$) were prepared as an ion conductive matrix. The molecular weight of the PEO part (m) and the content of the thiolate groups in the molecule were changed to analyze the effect of carrier ion concentration in the bulk. In a series of potassium salt derivatives, $\text{PEO}_{350}\text{-SK}$ showed the highest ionic conductivity of 6.42×10^{-5} S/cm at 50 °C. In spite of a poor degree of dissociation which was derived from the acidity of the thiolate groups, $\text{PEO}_m\text{-SM}$ showed quite high ionic conductivity among other PEO/salt hybrids. $\text{PEO}_m\text{-SM}$ had glass transition temperatures (T_g) 20 °C lower than other PEO/salt hybrids. Lowering the T_g was concluded to be effective in providing higher ionic conductivity for PEO-based polymer electrolytes.

Key words Poly(ethylene oxide) · Ionic conductivity · Thiolate · Glass transition temperature

Introduction

Fast ion transport in solids, especially in polymers, has been an attractive topic in these past two decades, because such ion conductive polymers (or polymer electrolytes) are expected to be applicable in polymer batteries and other ionic devices in the near future. For effective ion conduction, a matrix is required to have a high concentration of carrier ions and their fast migration. Poly(ethylene oxide) (PEO) has been regarded to be a potential structure since fast ion conduction in PEO was reported by Wright [1]. PEO generally has a low glass transition temperature, far below room temperature, which results in high mobility of ions at room

temperature. A large dipole moment on the ether oxygens [2, 3] with suitable configuration also allows high salt solubility in the bulk even without any solvent. Therefore, most of the studies on ion conductive polymers have employed the PEO structure to design the ion conduction path [4–6]. Initially ion conductive polymers were prepared by a simple mixing of inorganic salts with PEO derivatives. However, neither a large amount of solvating ions in PEO nor their fast transport have been achieved, because pseudo cross-linking between the PEO chains occurs with the cations [7, 8]. When a large amount of salt is dissolved in the matrix, the ionic conductivity is generally decreased because of the steep increase of the glass transition temperature (T_g) which originates from pseudo cross-linking of the PEO. In order to avoid such elevation of T_g , many types of polymeric material have been prepared.

For this purpose, we also prepared several kinds of PEO oligomers having anionic charges on the chain ends [9–13] to realize both high carrier ion concentration and low T_g . These PEO/salt hybrids showed relatively high ionic conductivity, as expected. The PEO oligomers having sulfonate [11], benzenesulfonate [12], and alkyl-sulfonamide groups [13] are able to maintain large numbers of carrier ions because of their high dissociation degree, and thus showed excellent ionic conductivity. Oligomeric PEOs with less massive anionic group such as sulfonate ($-\text{SO}_3^-$) showed relatively higher ionic conductivity than the value expected from the acidity of the terminal group. PEO-sulfonamides ($\text{PEO-N}^-\text{-SO}_2\text{-R}$; $\text{R}=\text{CH}_3$, CF_3 , and C_6H_4) were expected to have higher acidity and lower dissociation energy than PEO-SO_3^- ; however, they showed lower ionic conductivity than $\text{PEO-SO}_3^-\text{M}^+$. This higher ionic conductivity was considered to be brought about by a lower T_g than those for PEOs with other bulky groups. However, the dominant factor to determine the T_g of a matrix is still ambiguous; the size of the charged group may affect the T_g of the hybrid. In order to investigate the size effect on T_g and ionic conductivity, we paid attention to the thiol group as the smallest anionic group. Compared to

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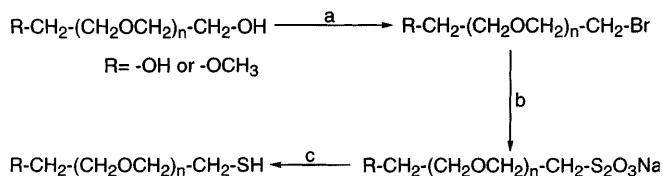
benzenesulfonate or sulfonate groups, the thiol group seemed to be compact enough to suppress the increase of T_g . In addition, the thiolate group is known to have a strong binding force, especially on a gold electrode. This should be useful in modifying the electrode surface with the PEO moiety [14]. An attempt to form monolayers on a gold surface has recently been tried with similar compounds [15]. When such materials are introduced at the interface of the electrode and polymer electrolyte, they might be effective in reducing the interfacial resistance. From these viewpoints, ionic conductivity in PEO-thiolates in the bulk is quite important.

Experimental

Materials

PEOs with hydroxyl groups on both chain ends with average molecular weights from 400 to 1000 were purchased from NOF and Kanto Chem. PEO monomethyl ether (PEOME) with MWs of 350, 550, and 750 were purchased from Aldrich. Reagent grade sodium thiosulfate and alkali metal hydroxides (MOH; M=Li, Na, K, Rb, and Cs), were purchased from Kanto Chem. All these salts were used without further purification.

The PEO oligomers with thiolate ends [PEO_m-SH and PEO_m-(SH)₂; here "m" means the average MW of PEO part] were synthesized via Bunte salts (S-alkyl thiosulfates) [16, 17], which were prepared by the reaction of sodium thiosulfate and terminal brominated PEO (PEO_m-Br) as shown in process b in Scheme 1. PEO_m-Br was prepared by the reaction of thionyl bromide with PEO in the presence of triethylamine (process a in Scheme 1; details for the preparation of PEO_m-Br were described in the previous paper [18]). The Bunte salt was prepared by the reaction of equimolar quantities of PEO_m-Br and sodium thiosulfate in 20% ethanol solution. After heating the mixture at 40 °C for 4–6 days, the solvent was removed by evaporation. The viscous residue obtained was dissolved in chloroform and filtered to remove precipitated NaBr. If necessary, this process was repeated several times. The Bunte salt (PEO-SSO₃Na) was hydrolyzed by mixing with 1 N hydrochloric acid for 24 h, when PEO-SH was obtained. Since the thiol group is known to react easily and to form disulfides by exposure it to the air, the hydrolysis of the Bunte salt and all other steps after this were carried out under a nitrogen atmosphere. The structures of the Bunte salt and the thiolate were confirmed by ¹H NMR (DMSO-*d*₆, in ppm): Bunte salt: 2.84, t, -CH₂-S₂O₃Na; 3.18, s, CH₃O-; 3.45, s, -CH₂OCH₂-; 3.58, t, -CH₂CH₂-S₂O₃Na; thiolate: 2.84, t, -CH₂S⁻M⁺; 3.18, s, CH₃O-; 3.45, s, -CH₂OCH₂-; 3.58, t, -CH₂CH₂-S⁻M⁺. The PEO_m-(SH)₂ and PEO_m-SH obtained were neutralized with a series of alkali metal hydroxides in water and the alkali metal salts of PEO-thiolates [PEO_m-(SM)₂ and PEO_m-SM] were obtained.



^a (a) SOBr₂, (CH₃CH₂)₃N; (b) Na₂S₂O₃·5H₂O; (c) H₂O, HCl

Scheme 1

Methods

The bulk ionic conductivity of these salts was measured with an impedance analyzer (Solartron model 1260; Schlumberger). The frequency range was fixed to be from 100 Hz to 1 MHz to draw Cole–Cole plots. When the samples were solid, they were sandwiched with a pair of stainless steel electrodes with a 0.50-mm thickness Teflon spacer. When the samples were viscous liquids, custom-designed liquid cells with stainless steel electrodes were used. The ionic conductivity measurements were carried out from 65 to 10 °C with a scanning rate of 3 °C/min during cooling. The temperature was monitored using a thermocouple (type K) in a sample cell, which was placed within 1 mm of the sample. The sample cell preparation and the measurements were carried out in a glove box filled with dry nitrogen gas.

A differential scanning calorimeter (SEIKO Instruments, DSC-120) was used to measure the glass transition temperature (T_g) of the samples. The temperature range was set from -120 to 150 °C with a scanning rate of 10 °C/min. The sample was quenched by liquid nitrogen from room temperature, and all the data were collected during heating.

The potential window was measured by cyclic voltammetry with a potentiogalvanostat (Nikko Keisoku NPGFZ-251-B) at a sweep rate of 30 mV/s at 30 °C. The temperature of the sample was kept constant by the circulation of thermostated water. The electrochemical cell consisted of three electrodes: PFC (plastic formed carbon), a Pt wire, and an Ag wire were used as the working, counter, and reference electrodes, respectively.

Results and discussion

A series of PEO_m-(SM)₂ and PEO_m-SM (M=Li, Na, K, Rb, and Cs) polymer thiolate salts were found to be liquids at room temperature, except for PEO₇₅₀-(SM)₂ and PEO₁₀₀₀-(SM)₂. The ionic conductivity of the potassium salt of the hybrid (PEO_m-S⁻K⁺), having one CH₃-capped terminal, was analyzed as shown in Fig. 1.

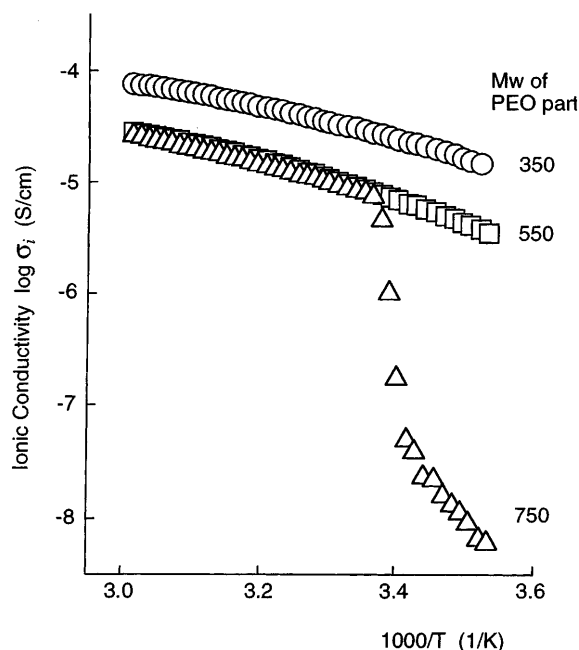


Fig. 1 Temperature dependence of the ionic conductivity for PEO_m-SK; m = ○ 350, □ 550, and △ 750

The ionic conductivity increased with decreasing MW of the PEO part, and PEO₃₅₀-SK showed the highest ionic conductivity of about 6.42×10^{-4} S/cm at 50 °C. It is the highest potassium ionic conductivity in any PEO/salt hybrid which we have ever prepared. Almost the same level of ionic conductivity was observed in PEO₅₅₀-SM and PEO₇₅₀-SM around 60 °C, but a drastic decrease in the ionic conductivity of PEO₇₅₀-SM was found around room temperature. It corresponded to the crystallization of PEO₇₅₀-SM (its melting point was determined to be 31 °C). In polymeric and oligomeric compounds, temperature dependence of the ionic conductivity was depicted as upper convex curve, and this process was proved to be non-Arrhenius behavior. It implies that the ion conduction process in PEO-SM is not simply activated but cooperates with the segmental motion of the polyether, as discussed later.

In order to analyze the factor for the ionic conductivity in these PEO_m-SM and PEO_m-(SM)₂, the effect of T_g should be taken into consideration as a criterion for the matrix mobility. The ionic conductivity and the T_g for PEO_m-(SM)₂ and PEO_m-SM are summarized as a function of the cation concentration in Fig. 2. There was an opposite tendency in the ionic conductivity between mono- and di-charged PEOs, as seen in this figure. In contrast, the ionic conductivity of PEO_m-(SM)₂ (where $m = 400, 600, \text{ and } 1000$, open plots in Fig. 2) increased with increasing the MW of the PEO part. PEO₁₀₀₀-(SM)₂ showed the highest ionic conductivity around 60 °C among these di-charged PEOs. A drastic decrease of ionic conductivity was observed in the Arrhenius plots, which are not shown here, reflecting crystalliza-

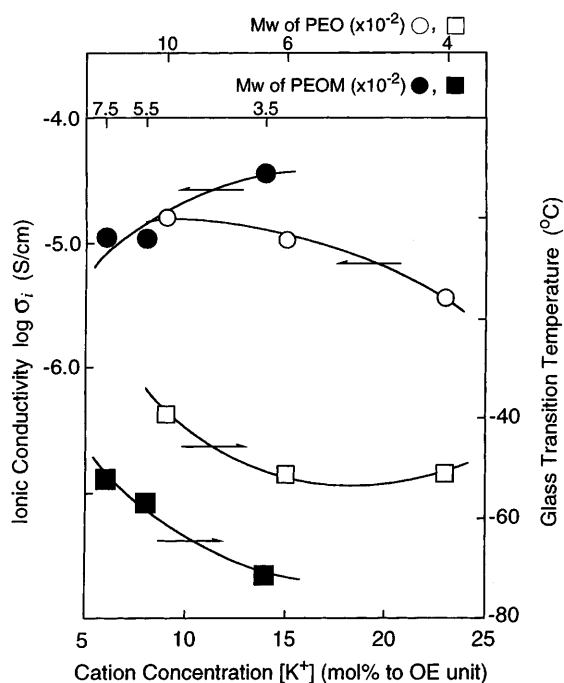


Fig. 2 Effect of cation concentration on the ionic conductivity (at 30 °C) and T_g for PEO_m-SM (closed plots) and PEO_m-(SM)₂ (open plots)

tion at a lower temperature. Such a different tendency of the effect of molecular weight of the PEO part on the ionic conductivity is explained by the mobility of the matrix. Assuming the ion mobility is related to the matrix mobility, a lower T_g suggests a higher mobility of the carrier ions. A certain correlation is apparently shown in Fig. 2, i.e., the PEO-thiolates with lower T_g showed high ionic conductivity. This correlation is also observed in mono- and di-charged PEOs. Mono-charged PEOs (closed plots), which showed higher ionic conductivity, had a relatively lower T_g than di-charged ones. Among these PEOs, PEO₃₅₀-SM showed the highest ionic conductivity because of the lowest T_g of about -70 °C. It is a common tendency that di-charged PEOs had higher T_g values than mono-charged ones even in the same cation concentration as other PEO/hybrids with different end groups [12]. This increase of T_g in di-charged PEOs would be attributed to the formation of pseudo-high-molecular-weight compounds through the electrostatic interaction between the terminal groups and dissociated ions. It should not be attributed to the formation of disulfide compounds, because the decrease of ionic conductivity in di-charged PEO has generally been observed in other PEO/salt hybrid systems, which never form covalent-bond dimers at the terminal.

One of the distinctive features of these PEO-thiolates was the compactness of the charged group, which was suggested to provide a lower T_g . Since a relatively lower T_g and higher ionic conductivity was observed in PEO-thiolates, the ionic conductivity of PEO_m-SM was compared with other PEO/salt hybrids, as shown in Fig. 3. At room temperature, PEO-thiolates (PEO₃₅₀-SK in Fig. 3) had a higher fluidity, than other hybrids such as PEO-benzensulfonates (PEO₃₅₀-BsK) and PEO-sulfonates (PEO₃₅₀-SO₃ K). All the temperature dependences

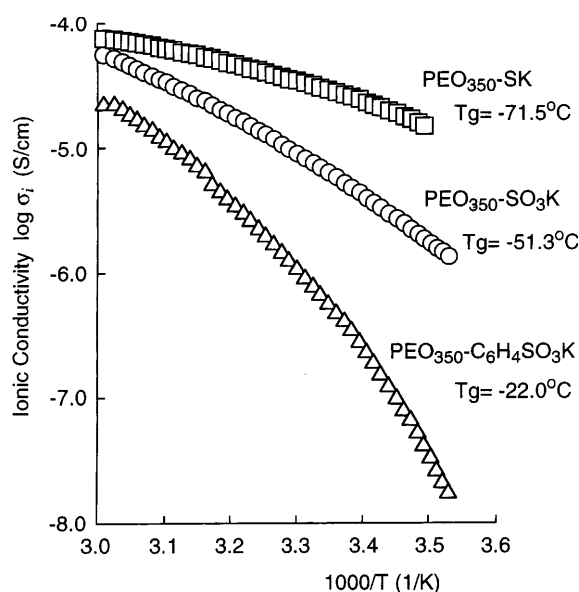


Fig. 3 Arrhenius plots of the ionic conductivity for PEO/potassium salt hybrids. The molecular weight of the PEO part was fixed at 350

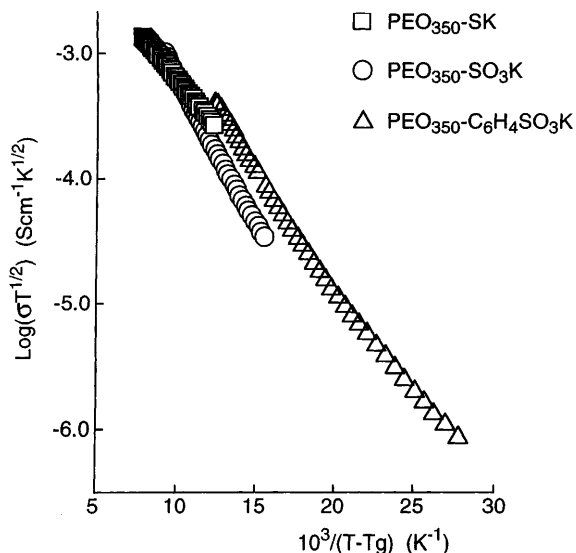


Fig. 4 Vogel-Tamman-Fulcher plots for PEO/salt hybrids

of the ionic conductivity for PEO/salt hybrids showed upper convex curves with different slopes (Fig. 3).

To clarify the reason why PEO_m-SM showed the highest ionic conductivity in these hybrids, the Vogel-Tamman-Fulcher (VTF) equation was applied as shown in Fig. 4. The ionic conductivity of these hybrids showed nearly identical lines under the normalized temperature, $T-T_g$. This is part of the evidence that the ion conduction is explained by the configuration entropy model and coupled with the relaxation time of the polymer matrix. The values in the Y-axis should show the ionic conductivity of every system at the normalized T_g . These conductivity values are comparable with each other under the same mobility. Figure 4 indicates that the concentration of cations in each matrix was almost the same, and the most effective factor for high ionic conductivity is T_g .

In order to apply these PEO/salt hybrids in a battery or other electrochemical devices, not only the lithium ionic conductivity but also their electrochemical stability should be analyzed. Ionic conductivity for PEO₃₅₀-SM and PEO₄₀₀-(SM)₂ increased with increasing the cation radius, as shown in Fig. 5. The reason why a larger cation provided higher ionic conductivity is understood by the following two explanations. One is the difference in the strength of interaction between the cation and the ether oxygens, i.e., a smaller cation interacted stronger to reduce the mobility of the ions because of its higher surface charge density [19, 20]. The other is the difference in the dissociation degree of the salt, which would be also affected by the difference of the surface charge density. Generally, different salts had different dissociation constants, depending on the cation species, and a smaller cation such as lithium would give a lower dissociation constant than larger ones. Since the salt with the higher dissociation constant was expected to provide the higher carrier ion concentration in the matrix, higher

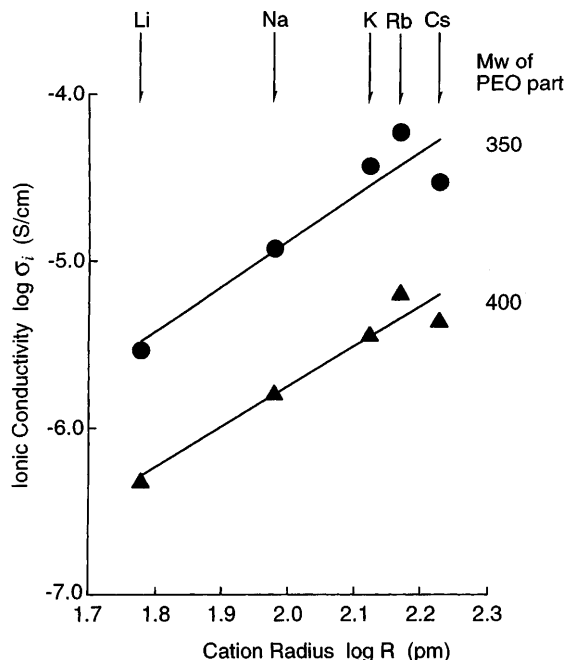


Fig. 5 Effect of cation radius on the ionic conductivity (at 30 °C) for PEO₃₅₀-SM and PEO₄₀₀-(SM)₂

ionic conductivity was observed in systems containing larger cation salts. Regarding the slope of the ionic conductivity versus the cation radius in Fig. 5, this gave a relatively steeper slope than other PEO/salt hybrids. According to our previous studies on PEO/salt hybrids, the slope of ionic conductivity for a cation species is almost proportional to the acidity of the terminal group, empirically [12, 13]. For example, PEO-benzenesulfonates showed larger slopes than PEO-sulfonates [12]. PEO-thiolates also seemed to obey this tendency, and the slope for PEO-thiolates is larger than for PEO-benzenesulfonates. This order was the same as that of the pK_a of model compounds in acid form (pK_a values in water at 25 °C of methanesulfonic acid, benzenesulfonic acid, and methanethiol are -1.86, 2.55, and 10.70, respectively) [21, 22]. Therefore, this larger slope indicated a lower dissociation degree of the thiolate groups on the chain ends. Estimation of the lattice energy with Reichard dye, which was recently confirmed in our group [23], suggested that the energy for the cesium salt of PEO-thiolate, -benzenesulfonate, and -sulfonate [PEO₄₀₀-(SCs)₂, PEO₄₀₀-(BSCs)₂, and PEO₄₀₀-(SO₃Cs)₂, respectively] was found to be 810, 325, and 315 (kJ/mol), respectively. Since the dissociation degree of the thiolate salts was not so high, the higher ionic conductivity was concluded to be attributed to a very low T_g of the matrix. In other words, the reduction in volume of the charged terminal group was also effective in realizing the higher ionic conductivity as well as in introducing the highly dissociable groups onto the terminal of the PEOs.

Potential windows of the bulk PEO_m-SM were also measured with cyclic voltammetry for the purpose not only of applying this to batteries but also to confirm the

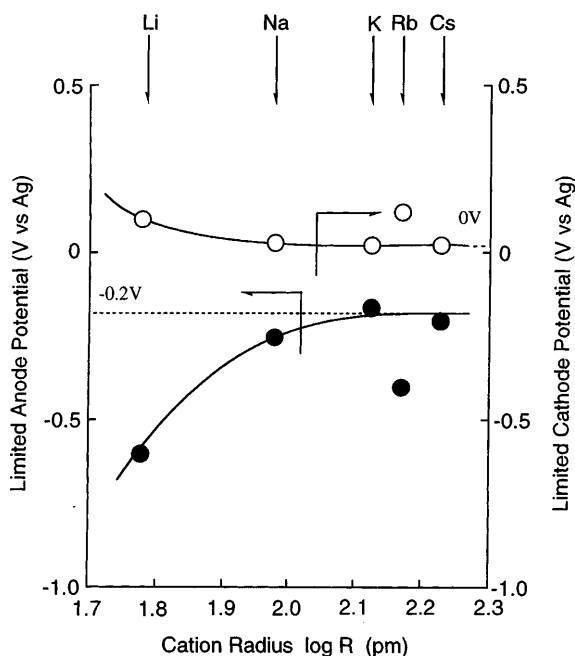


Fig. 6 Effect of cation radius on the potential window of PEO₅₅₀-SM

electrochemical reactivity of this for electrode modification. PEO_m-SM can form dimers, and these have only a narrow potential window. The potential window of the lithium salt was relatively wide, but the potassium and cesium salts were revealed to have rather narrow ones, as shown in Fig. 6. The potential window was narrow compared to other PEO derivatives or organic solvents, which may be the major drawback when they are applied to lithium batteries; however, such electrochemical reactivity indicated the possibility that PEO-thiolates could be used for modification of the electrodes. Detailed discussion on these topics will be published elsewhere.

Conclusion

The thiolate group was introduced onto the terminal of PEO oligomers and the alkali metal salts of the PEO-thiolates obtained were evaluated as an ion conductive

matrix. Among the PEO-thiolates, PEO₃₅₀-SM showed the highest ionic conductivity of about 6.42×10^{-5} S/cm at 50 °C, because of the lowest T_g of about -70 °C. The ionic conductivity of PEO_m-SM depended on the molecular weight of the PEO part. Since the thiolate group was not bulky enough to increase the T_g of the matrix, PEO_m-SM showed a high ionic conductivity compared to other PEO/salt hybrids.

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