

# Study of Hyperbranched Poly(glycidol) Sulfate Electrolyte

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**ABSTRACT:** Hyperbranched poly(glycidol) alkali sulfate (SHPG-M) was prepared based on hyperbranched poly(glycidol). Polyurethane–hyperbranched poly(glycidol) (PU–SHPG-M) sulfate electrolyte is a kind of single ionic or cationic conducting polymer electrolyte. Such a single ionic polymer electrolyte can obviously reduce the polarization and has little decay of direct current (DC) conductivity. SHPG-M was characterized by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), atomic force microscopy (AFM) and impedance analysis. The optimum conductivity is  $\sim 3 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ , with 30–40% SHPG-M in the polymer elec-

trolyte at room temperature. The species of cation greatly effects the ionic conductivity of the polymer electrolyte; that is,  $\sigma_{\text{SHPG-Li}} > \sigma_{\text{SHPG-Na}} > \sigma_{\text{SHPG-K}}$ , with same SHPG-M content in the polymer electrolyte. The ionic conductivity increases with an increase of temperature, and the dependence of ionic conductivity on temperature fits the Arrhenius equation well. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1185–1190, 2003

**Key words:** hyperbranched; polyelectrolytes; polyurethanes; conducting polymers

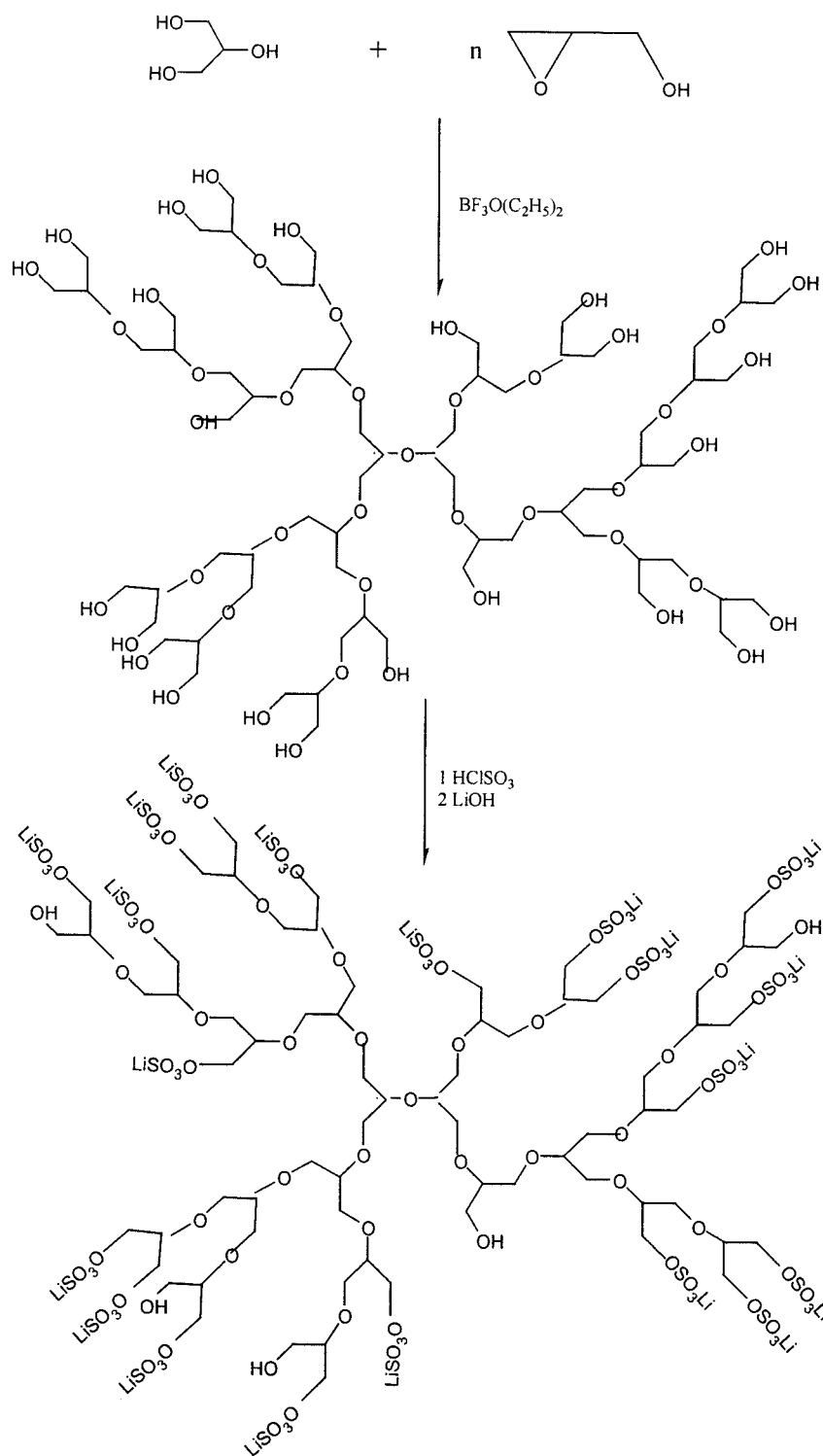
## INTRODUCTION

Since Wright first reported that the ionic conductivity of poly(ethylene oxide)–KSCN is  $\sim 10^{-5} \text{ S}\cdot\text{cm}^{-1}$  at room temperature, various polymers used as electrolytes have been extensively studied.<sup>1</sup> Most reports have focused on poly(ethylene oxide) (PEO) or its derivative blends with various salts. However, these polymer electrolytes have limitations that hinder their application; for examples, poor mechanical properties, lower ionic conductivity, and obvious polarization. To get a polymer electrolyte that could be applied commercially, new molecular structure polymers and their blends have been studied. As a novel kind of polymer electrolyte, hyperbranched polymer has great potential because of its lower degree of chain entanglement, lower glass transition temperature ( $T_g$ ), and larger number of cavities than that of linear polymers.<sup>2–6</sup> Generally the mechanical properties or dimensional stability of hyperbranched polymers are very poor and hinder their use as polymer electrolytes. Polyurethane has often been blended with hyperbranched polymer to achieve good polymer electrolytes because of the excellent mechanical properties of polyurethane. In previous reports, hyperbranched poly(glycidol) polymers were synthesized, blended with polyurethane, and doped with salt to prepare a polyurethane–hyperbranched poly(glycidol)&–salt (PU–HPG–

salt) polymer electrolyte.<sup>7</sup> Hyperbranched polymer electrolytes show excellent capability to solvate salt and higher ionic conductivity but poor dimensional stability. On the other hand, PU–HPG–salt is referred to as a “bi-ionic” conductor. In such conductors, the migration of anions toward the cathode causes polarization and results in a serious decay of the direct current (DC) conductivity and the time-dependent increase of the cell impedance. These electrolytes are unsuitable for a rechargeable battery. To minimize the polarization, single-ionic conductors are studied because cations are the only carrier ions that can transmit electrons in which anions are fixed on polymer chains via a covalent bond and cations are free. In some reports, single-ionic conductors show very low polarization when they are used as a polymer electrolyte.<sup>8</sup> However, the conductivity of single-ionic conductors is lower than that of bi-ionic conductors because cations are the only ions that are transferred and they are of lower ionic concentration in single-ionic conductors.

Hyperbranched poly(glycidol) alkali sulfate (SHPG-M) was synthesized, according to a previous report,<sup>7</sup> by reacting hyperbranched poly(glycidol) and chlorosulfonic acid and then adding alkali to neutralize the acid. SHPG is a kind of single-ionic conductor because sulfonic groups are fixed on the top of poly(glycidol), but cations are free to transfer. In this case, the SHPG was used not only as a solvent for cation but also as an ionic source in the polymer electrolytes. PU was used to improve the dimensional stability of the polymer electrolyte. The ionic conductivity of the blend of SHPG and poly(ether polyurethane) (PEU) was studied.

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**Scheme 1** Synthesis of hyperbranched poly(glycidol) sulfate.

## EXPERIMENTAL

### Materials

The boron trifluoride diethyl etherate from Shanghai Chemical Reagent Company was dried by refluxing over  $\text{CaH}_2$  for 4 h under nitrogen and then distilling under

vacuum. The glycerol was similarly purified. The glycidol from Aldrich Chemical Company was used without further purification. The 4,4'-methylene bis(phenyl isocyanate) (MDI) was distilled under vacuum and used immediately. The chloride sulfonic acid from Shanghai Second Reagent Company was used without further purification.

**TABLE I**  
Elemental Analysis Results for SHPG-M

Sample <sup>a</sup>	Sulfur, %		M, %	
	Theory	Measured	Theory	Measured
SHPG-Na	16.67	16.26	7.19	7.08
SHPG-K	15.32	15.11	11.46	11.25
SHPG-Li	18.19	17.93	2.37	2.32

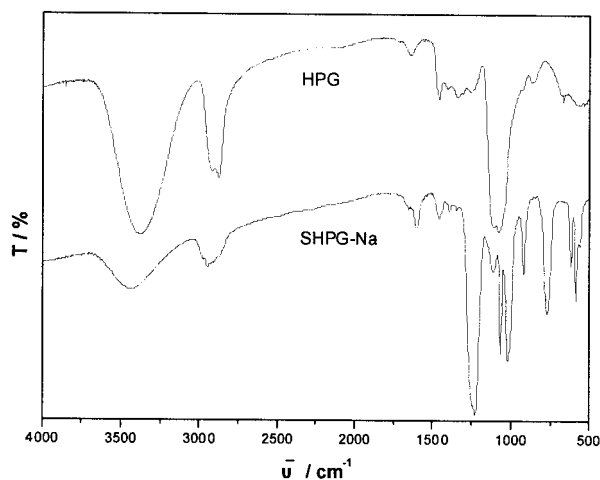
<sup>a</sup> The yield of esterifying reaction is 60%.

### Instrumentation

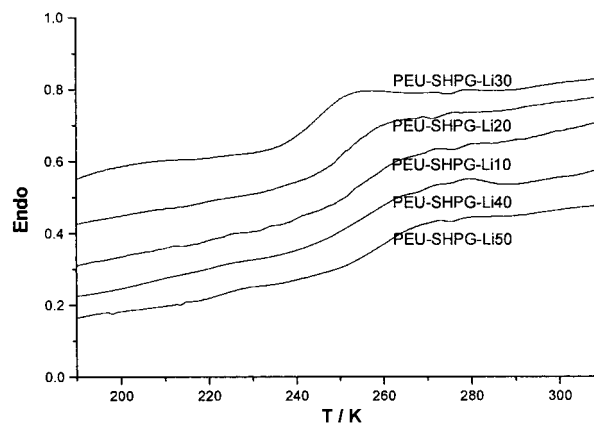
Fourier-transform infrared (FTIR) spectral analysis was performed with a Bruker Equinox 55 spectrometer with KBr. The elemental analyses were performed with an IRIS Advantage 1000 elemental analyzer. Atomic force microscopy (AFM) analysis was carried out on a Nano-Scope IIIa SPM analyzer from Digital Instruments at room temperature, with the tapping mode. The molecular weights of samples were measured on a vapor permeation osmometer (VPO; Eurosmo 7000). Differential scanning calorimetric (DSC) studies were conducted under nitrogen on a PE Pyris-1 DSC thermal analyzer. All samples were heated at 20°C/min heating rate from -120 to 80°C. The ionic conductivities of samples were measured with an impedance analyzer (Hewlett Packard HP 4192A LF IMPEDANCE ANALYZER).

### Synthesis and characterization

The synthesis reaction, which includes polymerization, esterification, and neutralization, is shown in Scheme 1. The polymerization of glycidol has been reported in previous papers.<sup>7,9,10</sup> The esterification between poly(glycidol) and chlorosulfonic acid was carried out in a three-necked bottle equipped with a mechanical stirrer. The lithium hydroxide (sodium



**Figure 1** IR spectra of the HPG and SHPG-Na.



**Figure 2** DSC curves of PEU-SHPG-Li.

hydroxide, or potassium hydroxide) solution was added slowly, in a dropwise manner, after esterification was finished. This procedure resulted in poly(glycidol) lithium (sodium or potassium) sulfate. A benefit of this poly(glycidol) esterifying reaction is the enhanced ionic conductivity of the resultant material, which is due to the higher concentration of ions in the polymer electrolyte. However, the reaction is not controlled very well when the yield of esterification is >70%. Also, the purification of poly(glycidol sulfate), with its high degree of esterification, is very difficult because few solvents are able to solvate samples with higher degrees of esterification very well.

To get pure polymer and easily control the polymerization reaction, it is necessary that the yield of poly(glycidol) sulfate be ~60%. SHPG-60, with a mean yield of 60%, can therefore be used as the polymer electrolyte. SHPG-60 was synthesized based on the hydroxyl group/chlorosulfonic acid molar ratio of 1:0.62. The element analysis (EA) results for SHPG-M when the yield of poly(glycidol) sulfate is 60%, summarized in Table I, indicate that the synthesis of poly(glycidol) sulfate was successful. The IR spectra of sodium hyperbranched poly(glycidol) sulfate, sodium salt (SHPG-Na) are shown in Figure 1. The following characteristic bands for sulfate are evident: 1235, 1020, and 772  $\text{cm}^{-1}$ . The characteristic absorption for hydroxyl groups in SHPG-Na is much lower than that in HPG because most of the hydroxyl groups in the former have reacted with chloride sulfonic acid. The approach for synthesis of PEU has been presented in previous reports.<sup>11-13</sup> The solid-state polymer electrolyte (SPE) was prepared by dissolving the appropriate amount of the PEU and SHPG-M in dimethyl acetamide (DMA) solvent and pouring the solution into a Teflon dish to allow the DMA to be evaporated at 60°C in an oven.

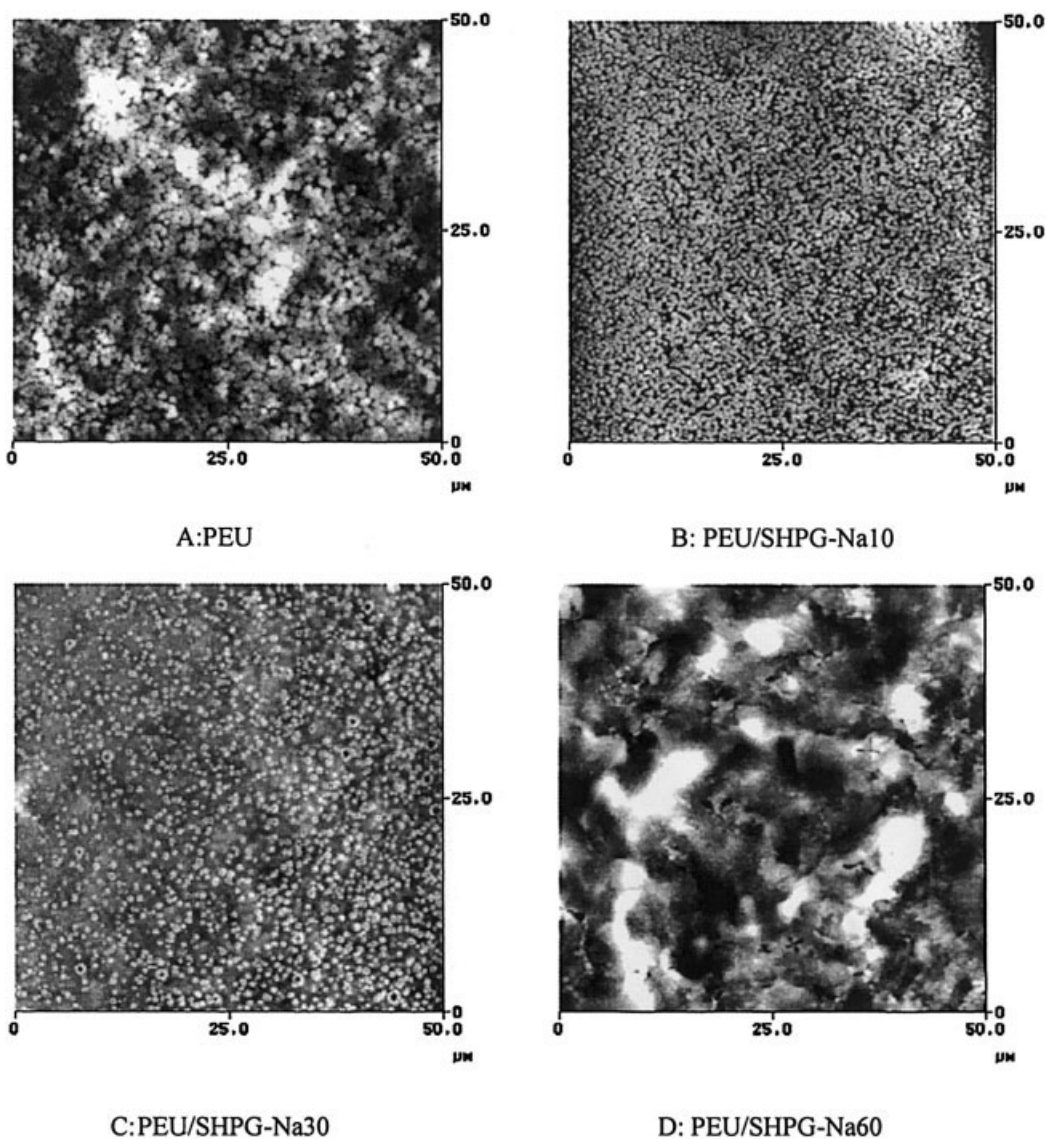


Figure 3 AFM photos of PEU-SHPG series.

## RESULTS AND DISCUSSION

### Effect of SHPG content on $T_g$ and Ionic Conductivity of PEU-SHPG

Generally, lower  $T_g$  is a benefit to enhance the mobility of polymer chains or achieve higher ionic conductivity a polymer electrolyte at room temperature. In Figure 2, the content of SHPG-Li has obvious influence on the  $T_g$  of the polymer electrolyte [PEU-SHPG-Li10 refers to a blend of PEU and SHPG-Li in which the content of SHPG-Li is 10% (wt %)]. The  $T_g$  of the polymer electrolyte decreases with the addition of SHPG-Li because of the hyperbranched structure and lower molecular weight of SHPG-Li which allows this blend to act as plasticizer. However, the coordination between metal ion and oxygen atom is a barrier for polymeric segment mobility and results in increase in  $T_g$  when the ionic concentration increases with the

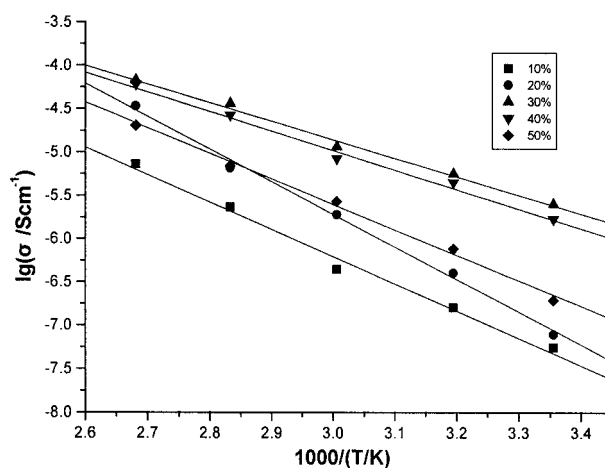
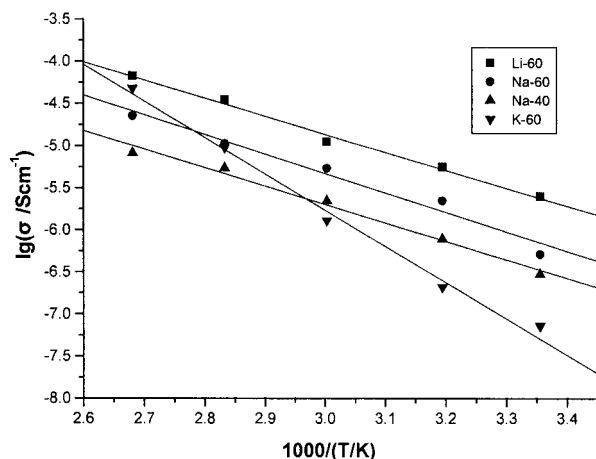


Figure 4 Dependence of conductivity on temperature with different SHPG-Li content.



**Figure 5** Effect of ionic species on ionic conductivity (30% SHPG-M content).

content of SHPG-Li. In this system, there is a balance between plastification and activity of coordination. The results in Figure 2 indicate that  $T_g$  is lowest when the content of SHPG-Li is 30%. DSC results show PEU-SHPG-Li30 should have higher ionic conductivity at room temperature because of its low  $T_g$  when it is used as a polymer electrolyte. The AFM images of PEU and the polymer electrolyte shown in Figure 3 indicate an obvious phase separation between two parts, a hard-segment and a soft-segment. Karbach and Drechsler indicated that the bright aggregates consisted of the hard-segment-rich phase in PU.<sup>14</sup> The compatibility of polymer electrolyte is improved with addition of SHPG-Li because the metal ions are able to coordinate with both the oxygen atoms in the soft-segment and the urethane group in the hard-segment and thereby improve compatibility between two phases. But, the ionic aggregate increases with an increase of SHPG-M content of >30%, resulting in bad compatibility and higher  $T_g$ . In previous reports, the AFM results show obvious phase separation (light dots) for the hard segments and a continuous phase for the soft segments in the PU electrolyte.<sup>14</sup> Generally, good compatibility of the PU electrolyte is desirable because it enhances the segment mobility, high ionic transfer, and therefore higher ionic conductivity. The AFM image of PEU/SHPG-Na60 shows very different aggregate or phase separation than the images of other samples because the concentration of salt is too high to be in solution. This result is attributed to the crystallization or aggregation of alkali metal salt. The results in Figure 3 indicate that the morphology of PEU/SHPG-Na30 has higher compatibility and that this compound is suitable to be used as a polymer electrolyte.

The effect of temperature on ionic conductivity of PEU-SHPG-Li with different SHPG-Li contents is shown in Figure 4. The results indicate that the ionic conductivity is the highest when the content of SHPG-Li in the blend is 30%, in agreement with the DSC

data. PEU-SHPG-Li blends with an SHPG-Li content of >40% or <20% are not suitable for good ionic conductivity, possibly because there are more coordination bands to hinder ionic transfer at the higher content levels or there is lower ionic concentration at the lower content levels, respectively. The ionic conductivity of all samples increases with increases of temperature. The relationship between the ionic conductivity and the temperature of PEU-SHPG-Li is in agreement with the Arrhenius equation over the experimental temperature range 293–333 K.

### Effect of Ionic Species on Ionic Conductivity of PEU-SHPG

In polymer electrolytes, the ionic species have a remarkable influence on ionic conductivity. In polymer electrolytes, ionic dissociation energy and transfer are the main properties influencing the ionic motion or ionic conductivity. The results in Figure 5 show that the ionic conductivity ( $\sigma$ ) of the polymer electrolyte is decreased with an increase of ionic diameter from lithium to potassium at most of the measured temperatures. The ionic transfers in the polymer electrolyte are more difficult when the ionic diameter is larger because the free volume is small and results in lower ionic conductivity. The ionic conductivity of PEU-SHPG-Li is the highest in all samples because the lithium ion has the smallest diameter. The ionic conductivity increases with an increase in temperature because the motion of the ion and mobility of polymer chain is improved or because the free volume increases. The motion of potassium ions, whose diameter is the largest in these samples, is obviously influenced by the change of free volume. The results in Figure 5 indicate that the ionic conductivity is  $\sigma_{\text{SHPG-Li}} > \sigma_{\text{SHPG-Na}} > \sigma_{\text{SHPG-K}}$  with same SHPG content in the polymer electrolyte when the measurement temperature is <80°C. The activity energy of the polymer electrolytes with potassium ion is the highest, as shown in Table II. Therefore, the effect of temperature on the mobility of potassium ion is the most significant, which results in the ionic conductivity of PEU-SHPG-K being higher than that of PEU-SHPG-Na

**TABLE II**  
Summary of Results According to Arrhenius Equation and Parameters of Various Polymer Electrolytes in Figure 5

Source	Sample	$A^a$	$E_a/k^b$
Figure 5	PEU-SHPG-Li-60	1.524	2.128
	PEU-SHPG-Na-40	0.873	2.189
	PEU-SHPG-Na-60	1.512	2.122
	PEU-SHPG-K-60	7.147	4.303

<sup>a</sup>  $A$  is related to the pre-exponential factor of the Arrhenius equation.

<sup>b</sup>  $E_a/k$  is related to the activation energy.

when the measurement temperature is  $>80^{\circ}\text{C}$ . In PEU-SHPG-Li and PEU-SHPG-Na (40 or 60), the activation energies are very approximate and their difference in ionic conductivity is attributable to two facts; they are, ionic diameter and ionic concentration. The results show that higher sulfate content is advantageous to enhance the ionic conductivity when the SHPG-M content is 30%.

### CONCLUSIONS

Hyperbranched poly(glycidol) sulfate (SHPG-M) was prepared and characterized. The results show that SHPG-M can be used as a single-ionic polymer electrolyte with an ionic conductivity of  $\sim 3 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$  at room temperature. The ionic conductivity of SHPG-M is affected by temperature, ionic species, and SHPG-M content or ionic concentration in the polymer electrolyte.

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