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Communications

Ion-Conducting Hyperbranched PEG Electrolytes Derived from Poly(glycidol)

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Introduction

The introduction of many branch units into polymeric materials has been a topic of considerable interest.¹ Hawker *et al.* introduced the concept of hyperbranched polymer electrolytes for the first time.² A noticeable feature of the hyperbranched poly(ethylene glycol) [PEG] in the paper is its lack of crystallinity. However, the introduction of branch points into the polymeric electrolytes does not increase the flexibility of the polymeric chains significantly due to the rigidity of phenyl ring-based structures of the branch units, which eventually causes low ionic conductivity of the materials. In addition, the synthesis of hyperbranched PEG electrolytes introduced in the literature requires many steps, which is not desirable for the commercial application of the as-synthesized polymer electrolytes. In addition, almost all the polymer electrolytes, to date, are based on linear and/or branched PEG derivatives. While there were

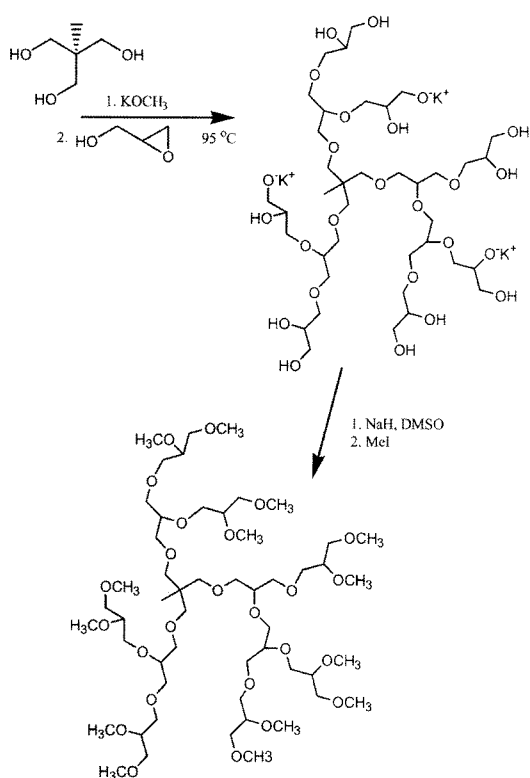
attempts to utilize hyperbranched poly(glycidol) [HPG] as a matrix for Li ions.³ However, HPG has many terminal hydroxyl groups. Strong H-bonding among OH groups increases the T_g of hyperbranched polymers significantly. In addition, the OH groups may not show an electrochemical stability during the redox cycle of Li/polymer complex. In this paper, new hyperbranched PEG electrolytes based on HPG were synthesized and characterized as a polymer electrolyte for the lithium/polymer secondary battery.

Results and Discussion

HPG was prepared from the synthetic method in the literature as shown in Scheme I.⁴ The polymerization was carried out in a three-neck flask equipped with a mechanical stirrer and a dosing pump under argon atmosphere. 1,1,1-Tris(hydroxymethyl)propane was partially deprotonated with potassium methylate solution (25 wt%, Fluka) in methanol by distilling off excess methanol from the melt. A 20 mL aliquot of glycidol was slowly added at 95 °C for 12 h, choosing suitable amount of the initiator according to the monomer/initiator ratio.^{4,5} The HPG in methanol solution was precipitated in acetone twice and the potassium ion was removed with cationic ion exchange resin. 11 g of HPG was dissolved in 200 mL of DMSO and 8.6 g of NaH was added in the solution to remove the protons of -OH groups. The reaction mixture was stirred at 45 °C overnight. 58.5 g of methyl iodide was then added slowly for 2 h. The solution was stirred for additional 5 h. DMSO was then removed by vacuum distillation and the product polymer was extracted with methylene chloride for several times. The remaining sodium iodide and iodine were removed by washing organic solution with sodium thiosulfate/NaCl solution. The organic layer was then dried and the methylated poly(glycidol) [hyperbranched PEG] was further purified with column chromatography.

Figure 1 shows the NMR spectrum of HPG (inset) and hyperbranched PEG obtained from the methylation of HPG. The methine and methylene peaks of poly(glycidol) appear as one broad resonance between 3.3 and 3.9 ppm.⁴ These

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Scheme I. Synthetic scheme of the hyperbranched PEG.

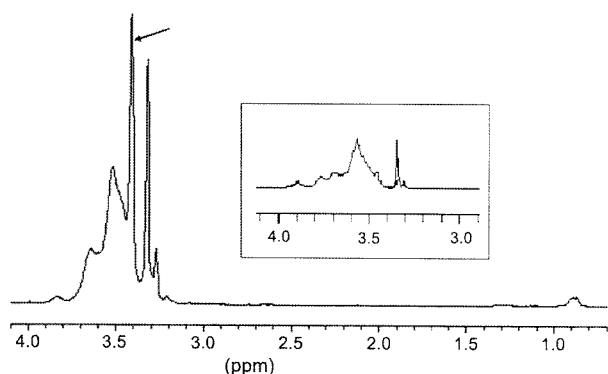


Figure 1. NMR spectrum of 2nd generated hyperbranched PEG. The arrow indicates the methoxy groups on the edge of polymers.

peaks appear almost at the same position when the OH groups of HPG are converted to methoxy groups. The sharp peak positioned at 3.31 ppm is due to methanol solvent. Meanwhile the new peak appearing at 3.41 ppm is due to the terminal methoxy groups of hyperbranched PEG.

The inverse gated (IG) NMR experiment was used to integrate the intensity of each structural unit of HPG and hyperbranched PEG. DEPT spectra were employed to distinguish methylene and methine carbons. The degree of branching of HPG estimated from IG NMR and DEPT was about 57%.⁴ The degree of polymerization (DP) and estimated MW were obtained by comparing the intensity of the methyl protons of the core molecule with that of the C-H, C-H₂, and C-H₃

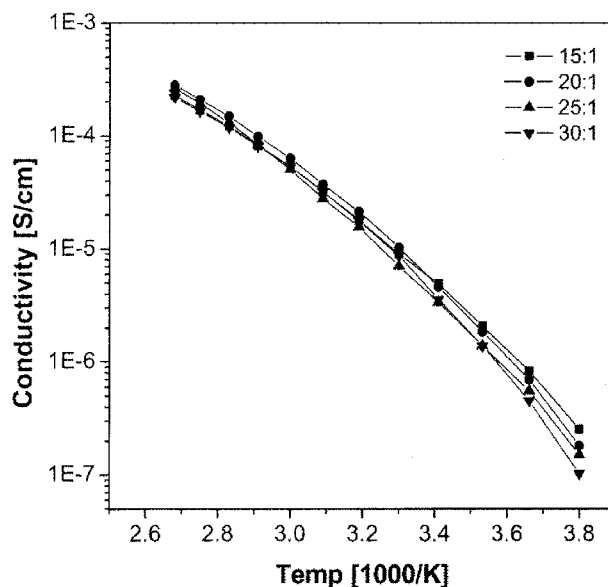


Figure 2. Temperature dependence of ionic conductivity at different O/Li ratios.

next to the oxygen appearing from 3.3 to 3.9 ppm in proton NMR spectra. Terminal CH₂ and CH₂ in L₁₃ disappeared completely after methylation of hydroxyl groups. However, DEPT showed that 12% of CH₂ in L₁₄ is still present after methylation, which suggests that the methylation of the OH group was not complete. The overall degree of methylation of all hydroxyl groups was 94% for the first methylation. Hyperbranched PEG shows a dramatic reduction of the *T_g* (-72 °C) with respect to HPG (*T_g*: -17 °C) after the methylation.

The molecular weight of hyperbranched PEG obtained from GPC was 1,225/1,813 (*M_n*/*M_w*) with PDI of 1.48. The MW of hyperbranched PEG was also estimated from ¹H NMR. However, the approximate value of MW calculated by the method mentioned above was 1,670. The small value of MW obtained from GPC might be related with the different radius of gyration of hyperbranched polymer with respect to the linear polymer.⁴

Figure 2 shows the ionic conductivity of hyperbranched PEG/Li complexes. LiCF₃SO₃ was used as a source for Li ions. The ionic conductivity increases with increasing temperature and shows the highest value when the [O/Li] ratio is 20:1 at temperature above 30 °C. However, *T_g* increases linearly with increasing salt concentration. The increase of *T_g* with increasing salt concentration is ascribed to the tight coordination of ether dipole with Li ion, which may act as transient cross-linking points in the polymer electrolytes.

Arrhenius plots showed a typical Vogel-Tamman-Fülcher (VTF) relationship in the temperature range of -10~100 °C.

$$\sigma = AT^{\frac{1}{2}} \exp\left(-\frac{E_a}{R(T-T_0)}\right) \quad (1)$$

Table I. Ionic Conductivities and VTF Fitted Parameters for Li/Polymer Complex at 30 °C

O/Li Ratio	T_g (°C)	Conductivity (S/cm)	A (SK ^{0.5} /cm)	E_a (KJ/mol)
15	-60.4	9.00×10^{-6}	1.1	9.2
20	-57.9	1.03×10^{-5}	2.1	9.8
25	-54.3	7.02×10^{-6}	2	10
30	-47.0	8.75×10^{-6}	2.3	10.2

A , E_a and T_0 shown in eq. (1) are fitted parameters which are related to the charge carrier density, pseudo-activation energy and the temperature where the segmental motion of polymer chains starts, respectively. The VTF relationship is based on that the mechanism of ionic conduction is related to the free volume theory.⁶ The fitted parameter, A , E_a , T_g , and ionic conductivity of Li complexes are shown in Table I.

The values of E_a were somewhat higher than those obtained from gel-type network polymers due to higher T_g of the hyperbranched PEG limiting the mobility of Li ions.⁷ Although Li/hyperbranched PEG has lower conductivity than the gel-type network polymer swelled with electrolyte solution, the values of ionic conductivity are comparable to or higher than those of the hyperbranched polymers having phenyl branch points.^{2,8}

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