

Polymer electrolytes based on hyperbranched polymers

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Abstract

A hyperbranched poly[bis(hexaethylene glycol)benzoate] with terminal acetyl groups was prepared, and ionic conductivity, thermal property, and electrochemical stability of the polymer electrolyte with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were investigated. Ionic conductivity of the polymer electrolyte exhibited a maximum value of $9 \times 10^{-5} \text{ S/cm}$ at a $[\text{LiN}(\text{CF}_3\text{SO}_2)_2]/[\text{repeat unit}]$ ratio of 0.6 (corresponding to a Li/O ratio of 0.04) and 80°C . The effect of a hyperbranched polymer, a poly[bis(triethylene glycol)benzoate] with terminal acetyl groups (poly-Ac1b), as an additive on ionic conductivity of a linear poly(ethylene oxide) (PEO)/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte was also investigated. Addition of 10 wt.% poly-Ac1b improved ionic conductivity and also ion transference number in the polymer electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

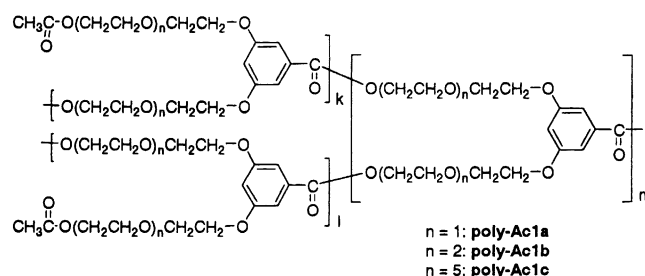
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1. Introduction

Solid polymer electrolytes based on linear polymers having ether, amine, ester, and sulfide bonds in their backbones have been widely studied because they have potential applications such as high-energy density batteries, electrochemical cells, and electrochromic devices [1–4]. However, crystallization in these electrolytes limits their practical uses. To eliminate any crystallinity, considerable attempts to modify the properties of linear polymers, for example, forming networks, copolymers with other units, and adding plasticizers such as propylene carbonate, ethylene carbonate, or oligomeric poly(ethylene glycols) and their derivatives have been made [5,6]. Hyperbranched polymers are interesting materials as a matrix for polymer-based electrolytes because they are completely amorphous, highly soluble, and highly processable, and also have many free chain ends which could greatly contribute to transportation of lithium ion. Our previous works, involving new polymer electrolytes based on hyperbranched polymers such as poly[bis(diethylene glycol)benzoate] ($n = 1$) (poly-Ac1a) and poly[bis(triethylene glycol)benzoate] ($n = 2$) (poly-Ac1b) with terminal acetyl groups showed that higher ionic conductivity is observed for the polymer electrolyte com-

posed of a hyperbranched polymer having a triethylene glycol chain rather than a diethylene glycol chain and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ rather than LiCF_3SO_3 [7,8] and, moreover, addition of ceramic fillers to the poly-Ac1b electrolyte with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ can increase ionic conductivity and mechanical strength of the polymer electrolyte and also improve the interfacial stability with lithium metal [9].

In this work, a hyperbranched polymer having hexaethylene glycol chain longer than triethylene glycol chain, poly[bis(hexaethylene glycol)benzoate] ($n = 5$) (poly-Ac1c), was prepared and some properties of the polymer electrolyte with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were investigated. In order to investigate the effect of a hyperbranched polymer as an additive, a blend-based polymer electrolyte composed of poly-Ac1b, linear poly(ethylene oxide) (PEO), and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, was also investigated.



Hyperbranched Polymers

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2. Experimental

2.1. Materials

Poly[bis(triethylene glycol)benzoate] ($n = 2$) (poly-Ac1b) with terminal acetyl groups was prepared according to the method reported previously [7] and the number of average molecular weight (M_n) of the polymer was determined to be 25,000 by gel permeation chromatography (GPC).

Poly[bis(hexaethylene glycol)benzoate] ($n = 5$) (poly-Ac1c), was prepared as follows: methyl 3,5-bis[(17'-hydroxy-3',6',9',12',15'-pentaoseptadecyl)oxy]benzoate (**1c**) (1.30 g, 1.86 mmol), prepared from 1-bromo-17-(*tert*-butyldiphenylsiloxy)-3,6,9,12,15-pentaoseptadecane [10] and methyl 3,5-dihydroxybenzoate, and di(*n*-butyl)tin diacetate (106 mg, 0.30 mmol) were placed in a flask and then the mixture was heated under dry nitrogen gas at the temperature range of 200–220°C for 120 min. The reaction mixture was dissolved in a small amount of tetrahydrofuran and the resulting solution was poured into hexane to obtain a hyperbranched polymer, poly[bis(hexaethylene glycol)benzoate] (poly-1c) (0.88 g, 68% yield; $M_n = 30,000$) as a rubbery solid, which was dried under reduced pressure at room temperature.

Poly-1c (1.3 g) and acetyl chloride (3.1 g, 39 mmol) were placed in a flask, and to the mixture was added dropwisely a triethylamine (5.4 g, 53 mmol) solution in 35 ml of chloroform at room temperature. After stirring for 48 h, the reaction mixture was added with 50 ml of chloroform and then the resulting solution was washed well with water and dried over anhydrous magnesium sulfate. The filtrate was concentrated and then poured into excess of diethyl ether to deposit a hyperbranched polymer, poly[bis(hexaethylene glycol)benzoate] with terminal acetyl groups (poly-Ac1c). Purification was carried out in three or more cycles of a redissolution–reprecipitation method. Chloroform and diethyl ether were used as solvent and a precipitant, respectively: yield 1.1 g (85% yield); ν_{CH} 2844 cm^{-1} , $\nu_{\text{C=O}}$ 1690 cm^{-1} , $\nu_{\text{C-O}}$ 1090 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.19, 6.66, 4.46, 4.24, 4.14, 3.88, 3.64, 2.07; $^{13}\text{C NMR}$ (CDCl_3) δ 170.9 (C=O), 166.0 (C=O), 159.6 (Ar), 131.7 (Ar), 108.0 (Ar), 106.5 (Ar), 72.6 (CH_2), 70.4 (CH_2), 69.4 (CH_2), 69.3 (CH_2), 68.9 (CH_2), 67.5 (CH_2), 64.0 (CH_2), 63.4 (CH_2), 20.8 (CH_3). Both poly-Ac1b and poly-Ac1c were dried under vacuum at 80°C overnight for preparation of the polymer electrolytes.

Commercial PEO (Aldrich Co.) with M_n of 5×10^6 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Aldrich Co.) were used after drying under reduced pressure of 0.1 mmHg at 50 and 120°C, respectively.

2.2. Preparation of polymer electrolytes

Free standing films of poly-Ac1c/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and poly-Ac1b/PEO/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolytes were formed

by solvent casting technique at room temperature. All procedures were performed inside an argon-filled glove box with a dew point of -95°C , to avoid moisture contamination. Given amounts of a hyperbranched polymer (poly-Ac1b or poly-Ac1c), of a PEO if necessary, and of a lithium salt were dissolved completely in acetonitrile and the resulting solution was poured onto a Teflon sheet and the solvent was allowed to evaporate slowly, and then finally dried under reduced pressure of 0.1 mmHg at 60 or 100–120°C for 24 h.

2.3. Measurements

Thermal properties such as glass transition temperature (T_g) and decomposition temperature of polymer and polymer electrolytes were determined by DSC and TGA measurements. Ionic conductivity was measured with a two probe method after the sample was immobilized inside a Teflon O-ring spacer with known thickness for the poly-Ac1c/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte (without a Teflon O-ring for the poly-Ac1b/PEO/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte), sandwiched between stainless steel discs acting as blocking electrodes and then set in a thermostat oven chamber. An ac impedance measurement was carried out by using a Solartron 1260 frequency response analyzer over a frequency range of 1– 10^6 Hz and a temperature range from 30 to 80°C with an amplitude of 10 mV. Electrochemical stability of polymer electrolytes was evaluated by the cyclic voltammetry (CV) measurement. Lithium ion transference number was determined by the two-impedance polarization coupling technique developed by Evans et al. [11].

3. Results and discussion

3.1. Preparation of hyperbranched polymers with terminal acetyl groups

Monomers (methyl 3,5-bis[(8'-hydroxy-3',6'-dioxooctyl)oxy]benzoate (**1b**: $n = 2$) and methyl 3,5-bis[(17'-hydroxy-3',6',9',12',15'-pentaoseptadecyl)oxy]benzoate (**1c**: $n = 5$)) for production of hyperbranched polymers were prepared according to the procedure reported [10], and then were polymerized in the presence of a di(*n*-butyl)tin diacetate catalyst at 200–220°C for 120 min, to give corresponding hyperbranched polymers (poly-1b and poly-1c) with M_n of 25,000 for **1b** and of 30,000 for **1c**, respectively, in 70–90% yield. Terminal hydroxy groups of the resulting polymers were acetylated by the reaction with acetyl chloride in the presence of triethylamine in dichloromethane at room temperature, and both poly-Ac1b and poly-Ac1c were obtained as brown rubber-like solids in 70–90% yields, and purified by redissolution–reprecipitation method using chloroform as a solvent and diethyl ether as a precipitant.

DSC measurement was carried out in a temperature range from -50 to 100°C , and DSC traces for both polymers

show only glass transition and no evidence of melting transition, indicating that both polymers are completely amorphous. Glass transition temperatures of poly-Ac1b and poly-Ac1c were determined to be -14.3 , and -34.5°C , respectively.

3.2. Characterization of the poly-Ac1c/LiN(CF₃SO₂)₂ electrolyte

Previously, we reported lithium salt concentration dependence of ionic conductivity for the poly-Ac1b/LiN(CF₃SO₂)₂ electrolyte at various temperatures, in so much as the ionic conductivity increased monotonally with [Li salt]/[repeat unit] ratios [7,8].

Fig. 1 shows ionic conductivities at 30, 40, 50, 60, 70, and 80°C against lithium salt concentration in a range of a [Li salt]/[repeat unit] ratio of 0.3–4.2 (corresponding to a Li/O ratio of 0.02–0.28) for the poly-Ac1c/LiN(CF₃SO₂)₂ electrolyte. Here, the chemical structure in bracket is defined as a repeat unit, containing 15 oxygen atoms. Fig. 1 shows that at all temperatures, the ionic conductivity of the polymer electrolyte rises, reaches a maximum value at a [Li salt]/[repeat unit] ratio of 0.6 (corresponding to a Li/O ratio of 0.04), and then decreases gradually with increasing lithium salt concentration. This behavior is very different from that of the poly-Ac1b/LiN(CF₃SO₂)₂ electrolyte reported previously, but similar to those of any other reported PEO-based polymer electrolytes with lithium salts such as LiN(CF₃SO₂)₂, LiCF₃SO₃, LiBF₄, and LiClO₄. This indicates that, on even hyperbranched polymers, the longer is length of glycol chain (ethylene oxide chain) in a repeat unit, the more approximates the performance closely to that of linear PEO. However, the decrease in the ionic conductivity with increasing lithium concentration after the maximum value is relatively slow in comparison with that of the linear PEO-based polymer electrolytes, probably due to the specific hyperbranched structure. At a [Li salt]/[repeat unit] ratio of 0.6, the ionic conductivity shows a maximum value of 9×10^{-5} S/cm at 80°C.

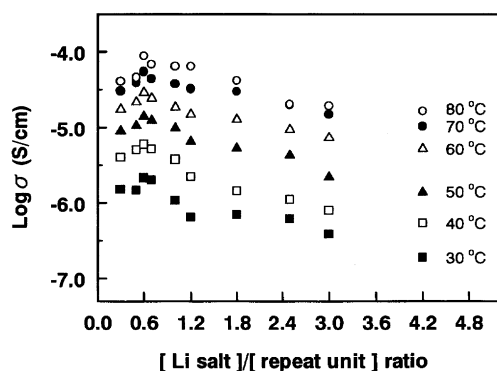


Fig. 1. LiN(CF₃SO₂)₂ concentration dependence of the ionic conductivity of poly-Ac1c/LiN(CF₃SO₂)₂ electrolyte at 30, 40, 50, 60, 70, and 80°C.

The electrochemical stability of the poly-Ac1c/LiN(CF₃SO₂)₂ electrolyte was determined by CV measurement using a lithium metal/polymer electrolyte/stainless steel cell at 70°C and found to extend to 4.9 V versus Li.

All samples of the poly-Ac1c/LiN(CF₃SO₂)₂ electrolyte show only glass transition and no evidence of melting transition by DSC measurement, indicating that they are completely amorphous, and also the T_g increased progressively from -28 to $+2.8^\circ\text{C}$ with increasing lithium salt content in the [Li salt]/[repeat unit] range of 0.3–4.2. TGA measurement indicated that the poly-Ac1c/LiN(CF₃SO₂)₂ electrolyte is stable until 320°C under air and undergoes 10% weight loss at 340°C.

3.3. The effect of a hyperbranched polymer as an additive

As hyperbranched polymers are completely amorphous, highly soluble, and highly processable, it is expected that addition of a hyperbranched polymer as an additive to linear PEO-based polymer electrolytes might improve their ionic conductivity. Here, we selected a hyperbranched polymer, poly-Ac1b as an additive material because of the many experimental data available for poly-Ac1b, and related electrolytes. Table 1 shows ionic conductivity and lithium ion transference number of a blend-based polymer electrolyte, poly-Ac1b/PEO/LiN(CF₃SO₂)₂, having three different poly-Ac1b/PEO weight ratios; 10/90, 20/80, and 50/50 in wt.%, and a Li/O ratio of 0.125 at 80°C. Addition of 10 wt.% poly-Ac1b improved ionic conductivity of blend-based polymer electrolytes from 7×10^{-4} to 8.1×10^{-4} S/cm and also the ion transference number increased from 0.09 to 0.15, probably due to the reduction of crystallization in a PEO-based polymer electrolyte induced by addition of the amorphous and soluble hyperbranched polymer. Further addition, such as 20 and 50 wt.% poly-Ac1b, decreased the ionic conductivity to some extent, due to relatively low ionic conductivity of the poly-Ac1b/LiN(CF₃SO₂)₂ electrolyte. Fig. 2 shows temperature dependence of the blend-based polymer electrolyte composed of 10 wt.% poly-Ac1b, 90 wt.% PEO, and LiN(CF₃SO₂)₂ and of the PEO/LiN(CF₃SO₂)₂ electrolyte. For the blend-based polymer electrolyte, enhancement of the ionic conductivity is observed in the region of relatively low temperature. It is noteworthy that addition of a hyperbranched polymer is significantly effective for improvement of ionic conductivity in a low temperature region.

Table 1

Ionic conductivity (σ) and lithium ion transference number (t_{Li}) of the blend-based polymer electrolytes with a Li/O ratio of 0.125 at 80°C

Poly-Ac1b/PEO (wt.%)	0/100	10/90	20/80	50/50
σ ($\times 10^4$) (S/cm)	7.0	8.1	6.8	2.9
t_{Li}	0.09	0.15	0.20	0.37

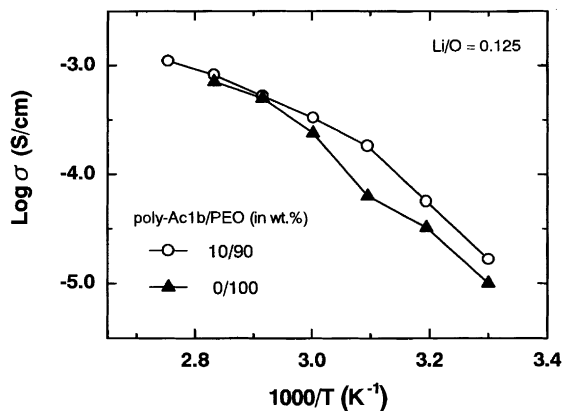


Fig. 2. Temperature dependence of the blend-based polymer electrolyte composed of 10 wt.% poly-Ac1b/90 wt.% PEO/LiN(CF₃SO₂)₂ and of PEO/LiN(CF₃SO₂)₂ electrolyte.

4. Conclusion

A hyperbranched poly[bis(hexaethylene glycol)benzoate] with terminal acetyl groups was prepared, and the ionic conductivity of the polymer electrolyte formed by its blend with LiN(CF₃SO₂)₂ exhibited a maximum value of 9×10^{-5} S/cm at a [Li(CF₃SO₂)₂N]/[repeat unit] ratio of 0.6 and at 80°C. Furthermore, the addition of a hyperbranched polymer to a PEO/Li(CF₃SO₂)₂N electrolyte was found to be considerably effective in improving the overall ionic conductivity.

Acknowledgements

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References

- [1] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews 1 and 2, Elsevier, London, 1987 and 1989.
- [2] P.G. Bruce (Ed.), Solid State Electrochemistry, Cambridge University Press, Cambridge, 1995, p. 95.
- [3] B. Scrosati (Ed.), Applications of Electroactive Polymers, Chapman & Hall, London, 1993, p. 251.
- [4] F.M. Gray, Polymer Electrolytes, The Royal Society of Chemistry, London, 1997.
- [5] F.M. Gray, Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH Publishers, New York, 1991.
- [6] J. Lipowski, P.N. Ross (Eds.), The Electrochemistry of Novel Materials, VHC Publishers, New York, 1994, p. 65.
- [7] T. Itoh, M. Ikeda, N. Hirata, Y. Moriya, M. Kubo, O. Yamamoto, J. Power Sources 81/82 (1999) 874.
- [8] Z. Wang, M. Ikeda, N. Hirata, M. Kubo, T. Itoh, O. Yamamoto, J. Electrochem. Soc. 146 (1999) 2209.
- [9] Z. Wen, T. Itoh, N. Hirata, M. Ikeda, M. Kubo, O. Yamamoto, J. Power Sources 90 (2000) 20–26.
- [10] C.J. Hawker, F. Chu, P.J. Pomery, D.J.T. Hill, Macromolecules 29 (1996) 3831.
- [11] J. Evans, C.A. Vincent, P.G. Bruce, Polymer 28 (1987) 2324.