

# Ionic conductivity of the hyperbranched polymer-lithium metal salt systems

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## Abstract

Terminal-acetylated hyperbranched poly(ethylene glycol) derivatives containing diethylene and triethylene glycols and 3,5-dioxybenzoate branching units were prepared and the ionic conductivities of these polymers complexed with lithium metal salts such as  $\text{LiCF}_3\text{SO}_3$  and  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  as polymer electrolytes were investigated. It was found that the hyperbranched polymer with a triethylene glycol chain and with  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  shows higher conductivity and also the number of charge carriers increases with  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  salt concentration. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Hyperbranched polymer; Ionic conductivity; Lithium metal salts

## 1. Introduction

The ionic conductivity of ether-, ester-, amine-, and sulfide-based linear polymers complexed with a variety of inorganic salts has been widely studied because these complexes as polymer electrolytes have potential applications such as high-energy density batteries, electrochemical cells, and electrochromic devices [1–6]. However, crystallization in these polymers limits their practical uses. To overcome this disadvantage, considerable efforts have been directed toward forming networks, comb-like polymers with short ethylene glycol side chains, and copolymers with other units and adding plasticizers such as propylene carbonate, ethylene carbonate, or oligomeric poly(ethylene glycols) and their derivatives [6,7].

Recently, studies on preparations and properties of unique structural polymers and well-defined polymers such as dendrimers and hyperbranched polymers have developed because they are expected to have new functions and properties different from linear polymers [8–11]. As one of unique properties of them, they are completely amorphous and highly soluble in common organic solvents and processible because of their highly branched nature. The effect such a structural feature and property on ionic

conductivity is interesting. However, such works are a few [12–15].

In this work, terminal-acetylated hyperbranched poly(ethylene glycol) derivatives containing diethylene and triethylene glycols and 3,5-dioxybenzoate branching units were prepared and the ionic conductivity of these polymers complexed with lithium metal salts such as lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) and lithium trifluoromethanesulfonimide ( $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ) as polymer electrolytes was investigated to know the effect of the kind of salt, salt concentration, and the chain length of ethylene glycol.

## 2. Experimental

### 2.1. Materials

Lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) or lithium trifluoromethanesulfonimide ( $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ) were dried under reduced pressure prior to use. Acetonitrile (bp 82°C) was refluxed over calcium hydride for 12 h and then distilled. The number-average molecular weights,  $M_n$ , of polymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as a reference and tetrahydrofuran (THF) as an eluent without correction. The glass transition temperatures,  $T_g$ , were determined by differential scanning calorimetry (DSC) at a scanning rate of 10°C/min under nitrogen atmosphere. <sup>1</sup>H-NMR measurements were

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carried out in chloroform-*d* with tetramethylsilane as an internal standard. A Yanaco CHN Corder MT-3 was used for elemental analysis, a GPC Tosoh HLC-803D with a series of Tosoh TSK-gel G2000H, G2500H, G3500H, and G4000H columns for measuring  $M_n$ , a JEOL JNM-EX 270 FT NMR spectrometer for  $^1\text{H-NMR}$  spectroscopy, Rigaku Denki DSC 8230 for measuring  $T_g$ , and a JASCO IR-700 spectrometer for infrared spectroscopy, respectively.

## 2.2. Preparation of monomers

Triethylene glycol monochlorohydrin or diethylene glycol monochlorohydrin (11.9 mmol), methyl 3,5-dihydroxybenzoate (6.0 mmol), potassium carbonate (11.9 mmol), bis[tri-*n*-butyltin(IV)]oxide (1.8 mmol) and 18-crown-6 (3.5 mmol) were dissolved in 50 ml of acetonitrile and the resulting solution was refluxed for 12 h. The deposited white solid was filtered off and the filtrate was placed under reduced pressure to remove solvent to obtain pale brown oil, which was dissolved in a small amount of ethyl acetate. The resulting solution was passed through silica-gel column by using a mixture solution of ethyl acetate/methanol (3/1 vol/vol) as an eluent. The third elution band was collected and placed under reduced pressure to remove solvent to obtain methyl 3,5-bis[5'-hydroxy-3'-oxopentyl]oxy]benzoate (**1a**) or methyl 3,5-bis[8'-hydroxy-3',6'-dioxooctyl]oxy]benzoate (**1b**) as colorless oils.

**1a:** Yield 44%. IR(NaCl):  $\nu_{\text{OH}}$  3370,  $\nu_{\text{CH}}$  2904,  $\nu_{\text{C=O}}$  1685,  $\nu_{\text{C-O}}$  1114  $\text{cm}^{-1}$ .  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  7.20–7.18 (m, 2H), 6.72–6.68 (m, 1H), 4.16 (s, 4H), 3.89 (s, 3H), 3.85–3.82 (m, 8H), 3.79 (s, 4H), 2.90 (br, 2H).  $^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta$  166.6(C=O), 159.5(Ar), 131.7(Ar), 107.8(Ar), 106.9(Ar), 72.6(CH<sub>2</sub>), 69.5(CH<sub>2</sub>), 67.8(CH<sub>2</sub>), 61.7(CH<sub>2</sub>), 52.1(CH<sub>3</sub>).

**1b:** Yield 56%. IR(NaCl)  $\nu_{\text{OH}}$  3372,  $\nu_{\text{CH}}$  2844,  $\nu_{\text{C=O}}$  1687,  $\nu_{\text{C-O}}$  1108  $\text{cm}^{-1}$ .  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  7.19 (d,  $J = 1.98$  Hz, 2H), 6.73 (d,  $J = 1.98$  Hz, 1H), 4.17–4.14 (m, 4H), 3.89 (s, 3H), 3.87–3.70 (m, 16H), 3.62–3.59 (m, 16H), 2.83 (br, 2H).  $^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta$  166.6(C=O), 159.6(Ar), 131.7(Ar), 107.9(Ar), 106.9(Ar), 72.4(CH<sub>2</sub>), 70.4(CH<sub>2</sub>), 70.2(CH<sub>2</sub>), 69.4(CH<sub>2</sub>), 67.5(CH<sub>2</sub>), 61.5(CH<sub>2</sub>), 52.1(CH<sub>3</sub>).

## 2.3. Preparation of terminal-hydroxyl hyperbranched polymer

Given amounts of monomer (**1a** or **1b**) and di-*n*-butyltin diacetate were placed in a flask and then the mixture was heated under dry nitrogen gas at the temperature range of 160 to 165°C for the reaction time of 10 to 20 min for the polymerization. The crude products were purified by precipitating from THF into hexane and then by precipitating from THF into methanol to give terminal-hydroxyl hyperbranched polymers (poly-**1a** and poly-**1b**) as rubbery solids,

which were dried under reduced pressure at room temperature until a constant weight was reached. Spectral data of typical hyperbranched polymers obtained are shown in below.

Poly-**1a:** IR(NaCl):  $\nu_{\text{OH}}$  3428,  $\nu_{\text{CH}}$  2840,  $\nu_{\text{C=O}}$  1681,  $\nu_{\text{C-O}}$  1115  $\text{cm}^{-1}$ .  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  7.19, 6.66, 4.46, 4.12, 3.88–3.64, 3.00.  $^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta$  166.0(C=O), 159.5(Ar), 131.7(Ar), 108.4(Ar), 106.7(Ar), 72.5(CH<sub>2</sub>), 69.3(CH<sub>2</sub>), 67.6(CH<sub>2</sub>), 64.1(CH<sub>2</sub>), 61.5(CH<sub>2</sub>).

Poly-**1b:** IR(NaCl):  $\nu_{\text{OH}}$  3388,  $\nu_{\text{CH}}$  2844,  $\nu_{\text{C=O}}$  1687,  $\nu_{\text{C-O}}$  1107  $\text{cm}^{-1}$ .  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  7.19, 6.69, 4.44, 4.12, 3.83–3.60, 2.66.  $^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta$  166.1(C=O), 159.6(Ar), 131.8(Ar), 108.1(Ar), 106.7(Ar), 72.5(CH<sub>2</sub>), 70.7(CH<sub>2</sub>), 70.2(CH<sub>2</sub>), 69.5(CH<sub>2</sub>), 67.6(CH<sub>2</sub>), 61.6(CH<sub>2</sub>).

## 2.4. Acetylation of terminal-hydroxyl hyperbranched polymers

Terminal-hydroxyl hyperbranched polymer [poly-**1a** ( $M_n = 8800$ ) and poly-**1b** ( $M_n = 20,000$ )] and acetyl chloride were dissolved in dichloromethane at room temperature. To the resulting solution was added a triethylamine solution in dichloromethane and then stirred for 2 days at room temperature. The reaction mixture 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 the acetylated hyperbranched polymers. Purification was carried out in three or more cycles of a redissolution–reprecipitation method. Dichloromethane and diethyl ether were used as a solvent and a precipitant, respectively. The polymeric products were dried under reduced pressure at room temperature until a constant weight was reached.

Terminal-acetylated poly[bis(diethylene glycol)benzoate] (poly-**Ac1a**): Yield 82%. IR(NaCl):  $\nu_{\text{CH}}$  2844,  $\nu_{\text{C=O}}$  1698,  $\nu_{\text{C-O}}$  1118  $\text{cm}^{-1}$ .  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  7.21, 6.69, 4.48, 4.24, 4.14, 3.89–3.76, 2.07.  $^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta$  170.9(C=O), 166.0(C=O), 159.5(Ar), 131.7(Ar), 108.1(Ar), 106.6(Ar), 69.3(CH<sub>2</sub>), 69.2(CH<sub>2</sub>), 67.5(CH<sub>2</sub>), 64.0(CH<sub>2</sub>), 63.3(CH<sub>2</sub>), 20.8(CH<sub>3</sub>).

Terminal-acetylated poly[bis(triethylene glycol)benzoate] (poly-**Ac1b**): Yield 87%. IR(NaCl):  $\nu_{\text{CH}}$  2846,  $\nu_{\text{C=O}}$  1689,  $\nu_{\text{C-O}}$  1105  $\text{cm}^{-1}$ .  $^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta$  7.19, 6.68, 4.44, 4.19, 4.13, 3.84–3.68, 2.06.  $^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta$  170.9(C=O), 166.1(C=O), 159.6(Ar), 131.8(Ar), 108.1(Ar), 106.6(Ar), 70.7(CH<sub>2</sub>), 70.5(CH<sub>2</sub>), 69.5(CH<sub>2</sub>), 69.1(CH<sub>2</sub>), 67.6(CH<sub>2</sub>), 63.5(CH<sub>2</sub>), 20.9(CH<sub>3</sub>).

## 2.5. Preparation of terminal-acetylated hyperbranched polymer-lithium metal salt samples

All preparation procedure was carried out in dry box under argon gas flow. Polymer electrolyte samples were prepared by mixing the weighed hyperbranched polymer (poly-**Ac1a** and poly-**Ac1b**) and lithium metal salt

[LiCF<sub>3</sub>SO<sub>3</sub> or Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] in acetonitrile and stirring at room temperature until the salt dissolved completely. The solution was cast on a Teflon sheet and the solvent was removed at room temperature under dry argon flow. The samples were dried completely under vacuum (0.1 mm Hg) at 60°C for 24 h by using electric furnace equipped in a dry box.

## 2.6. Conductivity measurements

Electrical conductivities of the hyperbranched polymer-lithium metal salt systems were measured using stainless steel blocking electrodes in the temperature range 30–80°C in a dry argon gas flow. The conductivities were obtained by ac impedance measurement with a Solartron 1260 frequency response analyzer over a frequency range 0.1 Hz to 10<sup>6</sup> Hz. Resistances were derived by interpretation of the complex impedance plane diagram of the data.

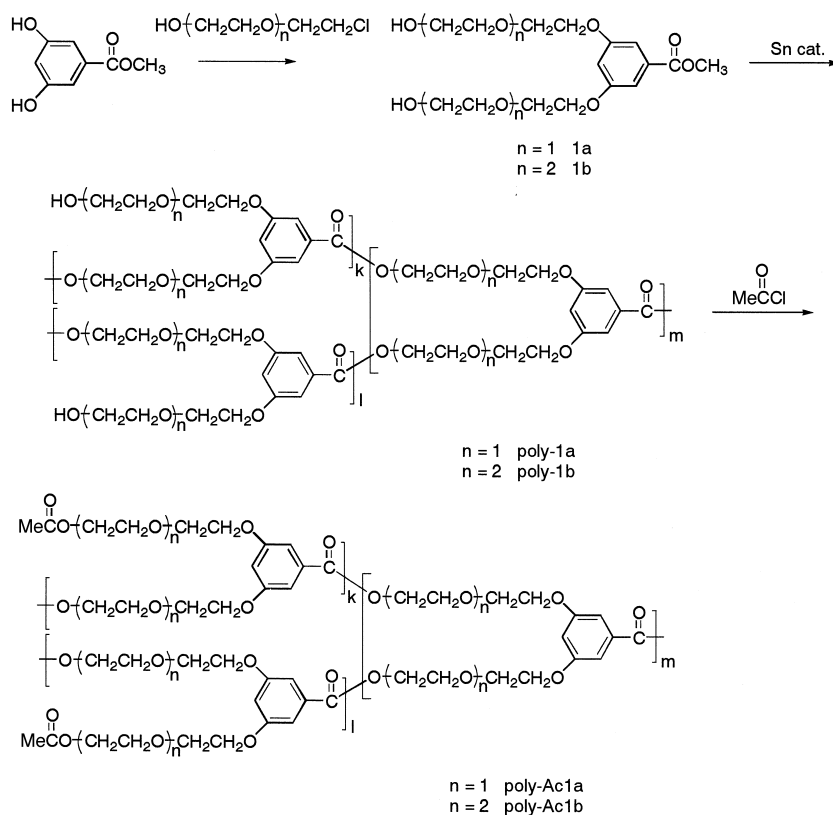
## 3. Results and discussion

### 3.1. Preparation of monomers and terminal-hydroxyl and terminal-acetylated hyperbranched polymers

Terminal-acetylated hyperbranched polymers (poly-**Ac1a** and poly-**Ac1b**) were prepared via the reaction routes as shown in Scheme 1.

Monomers **1a** and **1b** were prepared as colorless oils in 44% and 56% yields, respectively, by the reactions of methyl 3,5-dihydroxybenzoate with diethylene glycol monochlorohydrin and triethylene glycol monochlorohydrin in the presence of potassium carbonate, 18-crown-6, and bis[tri-*n*-butyltin(IV)]oxide. Preparations of both **1a** and **1b** were also carried out according to the procedure reported by Hawker et al. [12] and total yields of **1a** and **1b** via three steps were to be 13% and 14% yields, respectively. The structures of **1a** and **1b** obtained by both methods were confirmed by IR and NMR spectroscopy, and both were almost same. Therefore, our method is better than Hawker's one in the view of yields.

Bulk polymerizations of **1a** and **1b** in the presence of a catalytic amount of dibutyltin diacetate were carried out in various reaction conditions and the results are shown in Table 1. Heating at the temperature below 150°C produced only low molecular weights polymers even in prolonged reaction time. And also, prolonged heating at 165°C and heating at temperature in excess of 200°C resulted in the production of insoluble materials, presumably due to uncontrolled cross-linking reactions. Heating at 165°C for 25 min for **1a** and for 20 min for **1b** under nitrogen gas gave the best results at present in the view of the molecular weights of the soluble part in the polymers obtained, which are 8800 for poly-**1a** and 21,000 for poly-**1b**, respectively. Both polymers were purified by reprecipitating the THF solutions into methanol.



Scheme 1.

Table 1

Polymerizations of **1a** and **1b** in the presence of dibutyltin diacetate at various conditions

Run no.	Temperature (°C)	Time (min)	Yield (%)	$M_n$
<b>1a</b>				
1	160	15	68.9	4500
2	160	20	81.3	7400
3	165	25	97.6	8800
<b>1b</b>				
4	160	15	32.3	16,000
5	160	20	34.9	18,000
6	165	15	46.2	20,000
7	165	20	32.1	21,000

[**1a**] = [**1b**] = 0.5 mmol; [Sn(OAc)<sub>2</sub>] = 0.05 mmol.

Acetylation of poly-**1a** and poly-**1b** was performed by the reaction with acetyl chloride in the presence of triethylamine in dichloromethane at room temperature. Polymers of run no. 3 ( $M_n = 8800$ ) and run no. 6 ( $M_n = 20,000$ ) were used for acetylation reaction. By <sup>1</sup>H-NMR spectroscopy, the broad peaks due to terminal hydroxyl group at 3.00 ppm for poly-**1a** and at 2.66 ppm for poly-**1b** disappeared completely after the reaction and instead new sharp singlet peak appears at 2.07 ppm for poly-**1a** and at 2.06 ppm for poly-**1b**, respectively. This indicates that the acetylation reaction took place completely. Terminal-acetylated hyperbranched polymers, poly-**Ac1a** and poly-**Ac1b**, were obtained in 81 and 87% yields, respectively, and purified by reprecipitating the dichloromethane solutions into diethyl ether. Examination of DSC traces for both polymers shows no evidence of melting transitions, indicating completely amorphous structures. And also, glass transition temperatures of poly-**Ac1a** and poly-**Ac1b** were determined to be 3.3°C and -14.3°C, respectively.

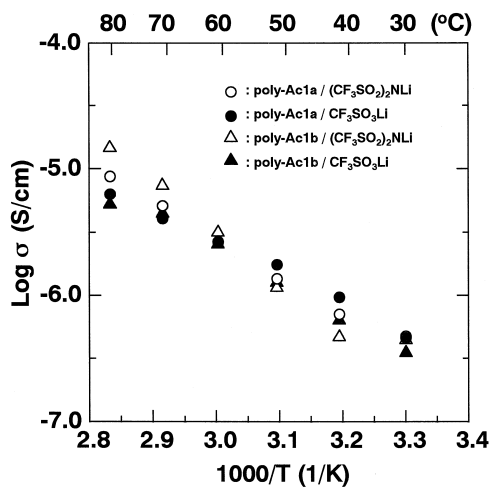


Fig. 1. Temperature dependence of the conductivity,  $\sigma$ , for poly-**Ac1a**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, poly-**Ac1a**/LiCF<sub>3</sub>SO<sub>3</sub>, poly-**Ac1b**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, and poly-**Ac1b**/LiCF<sub>3</sub>SO<sub>3</sub> systems at a fixed ratio of [Li salt]/[repeat unit] of 0.6.

Table 2

Ionic conductivity of polymer-lithium metal salt systems at a fixed ratio of [Li salt]/[repeat unit] of 0.6 at 30 and 80°C and their glass transition temperatures

Polymer	Salt	$T_g$ (°C)	Conductivity $\times 10^6$	
			30°C	80°C
Poly- <b>Ac1a</b> ( $n = 1$ )	Li(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N	-12.5	0.47	8.7
	LiCF <sub>3</sub> SO <sub>3</sub>	-3.5	0.46	6.3
Poly- <b>Ac1b</b> ( $n = 2$ )	Li(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N	6.5	0.44	14.6
	LiCF <sub>3</sub> SO <sub>3</sub>	13.5	0.35	6.3

### 3.2. Ionic conductivity of terminal-acetylated hyperbranched polymer-lithium metal salt systems

Examination of DSC traces for the poly-**Ac1a**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, poly-**Ac1a**/LiCF<sub>3</sub>SO<sub>3</sub>, poly-**Ac1b**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, and poly-**Ac1b**/LiCF<sub>3</sub>SO<sub>3</sub> systems shows no evidence of melting transitions, indicating completely amorphous structures. The ionic conductivities of poly-**Ac1a**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N and poly-**Ac1a**/LiCF<sub>3</sub>SO<sub>3</sub> systems and of poly-**Ac1b**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N and poly-**Ac1b**/LiCF<sub>3</sub>SO<sub>3</sub> systems were investigated as a function of temperature at a fixed ratio of [Li salt]/[repeat unit] of 0.6 to know the effect of the kind of salt and the effect of the chain length of ethylene glycol. Fig. 1 shows the temperature dependence of the conductivity for these systems in temperature range 30–80°C and the conductivity values at 30 and 80°C for four systems are summarized in Table 2 along with the glass transition temperatures. The polymer with Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N salt shows somewhat higher conductivity and lower glass transition temperature than that of LiCF<sub>3</sub>SO<sub>3</sub>. The large and flexible (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> ion acts as a plasticizer on the polymer matrix [16], giving a higher mobility of the polymer chains in poly-**Ac1b**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N and poly-**Ac1a**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N systems than in poly-**Ac1b**/LiCF<sub>3</sub>SO<sub>3</sub> and poly-**Ac1a**/LiCF<sub>3</sub>

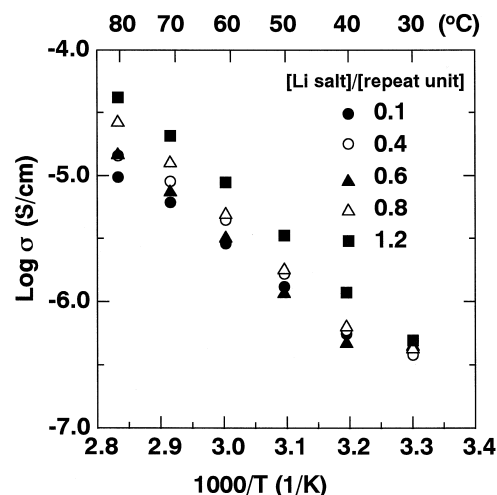


Fig. 2. Temperature dependence of the conductivity at various ratios of [Li salt]/[repeat unit] for the poly-**Ac1b**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N system.

Table 3

VTF parameters of the poly-**Aclb**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N system at various ratio of [Li salt]/[repeat unit] and their glass transition temperatures

[Li salt]/[repeat unit]	$T_g$ (°C)	VTF parameter	
		$A \times 10$	$B \times 10^2$ (eV)
0.1	-13.8	1.2	9.5
0.4	-13.1	4.2	10.6
0.6	-12.5	2.5	10.1
0.8	-6.1	11.7	11.4
1.2	-3.5	21.9	10.8

SO<sub>3</sub> systems. And also, poly-**Aclb**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N system exhibits higher ionic conductivities at 80°C than poly-**Aclb**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N one, probably due to high segmental mobility of triethylene glycol unit compared with diethylene glycol one. In the view of conductivity, polymer with longer ethylene oxide chain and the use of Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N as lithium metal salt probably improved the conductivity for hyperbranched polymer materials. The concentration of salt is another factor that affects the conductivity for the polymer-lithium metal salt systems. Fig. 2 shows the temperature dependence of the conductivity for the poly-**Aclb**/Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N in temperature range 30–80°C at various ratios of [Li salt]/[repeat unit]. The conductivity in the temperature range examined increases with increasing salt concentration over the whole lithium metal salt concentration range examined. Especially, at higher temperature the conductivity enhancement by addition of more amount of lithium metal salt is effective, probably due to increased chain mobility at a high temperature. With [Li salt]/[repeat unit] of 1.2, the conductivity at 30°C was  $4.9 \times 10^{-7}$  S/cm and at 80°C this value reached to  $4.17 \times 10^{-5}$  S/cm. The electrical conductivity for the amorphous materials is known to obey the Vogel–Tammann–Fulcher (VTF) equation [17–19]:

$$\sigma = AT^{-1/2} \exp[-B/(T - T_0)]$$

where  $\sigma$  and  $T$  are the conductivity and absolute temperature, respectively,  $A$  is proportional to the number of charge carriers,  $T_0$  is the temperature where the free volume vanishes, closely related to the glass transition temperature of the samples, usually about 50 K [20,21] below the glass transition temperature, and  $B$  is the activation energy for conduction. The VTF plots showed fairly good linearity when  $T_0$  is taken as  $(T_g - 50)^\circ\text{C}$  and the values of the corresponding parameters in the equation are summarized in Table 3 together with their glass transition temperatures,  $T_g$ . The  $B$ -values in Table 3 are almost constant, suggesting that conduction mechanism is not changing as salt concentration increases. While, the  $A$ -values increase, indicating that the number of charge carrier in the system increases with salt concentration. Usually, the maximum value of the conductivity can be observed

with increasing salt concentration in the poly(ethylene glycol)s, due to the formation of immobile multiple ions. However, this result suggests that carrier ions are available even at high concentration of Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, although all of added salt does not function as carrier ions and the formation of multiple ions is operative as shown by the increase in  $T_g$ -value. This difference is probably due to the feature of the structural effect of hyperbranched polymer.

#### 4. Conclusions

Acetylated hyperbranched poly(ethylene glycol) derivatives containing diethylene and triethylene glycols and 3,5-dioxybenzoate branching units were synthesized and they proved to be extremely soluble in a wide range of solvents and amorphous. The ionic conductivity of these polymers complexed with lithium metal salt such as LiCF<sub>3</sub>SO<sub>3</sub> and Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N was affected by the kind of salt, salt concentration, and the chain length of ethylene glycol. The results showed that the conductivity could be improved by using much longer ethylene glycol chain and much higher concentration of Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N for hyperbranched polymer materials. Further studies of conductivity of hyperbranched polymer with much longer ethylene glycol chain complexed with Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N are now in progress.

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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] M.A. Ratner, D.F. Shriver, *Chem. Rev.* 88 (1988) 109.
- [3] M. Watanabe, N. Ogata, *Br. Polym. J.* 20 (1988) 181.
- [4] P.G. Bruce (Ed.), *Solid State Electrochemistry*, Cambridge Univ. Press, Cambridge, 1995, p. 95.
- [5] B. Scrosati (Ed.), *Applications of Electroactive Polymers*, Chapman & Hall, London, 1993, p. 251.
- [6] F.M. Gray, *Solid Polymer Electrolytes: Fundamentals and Technological Applications*, VCH Publishers, New York, 1991.
- [7] J. Lipowski, P.N. Ross (Eds.), *The Electrochemistry of Novel Materials*, VHC Publishers, New York, 1994, p. 65.
- [8] D.A. Tomalia, *Aldrich Acta* 26 (1993) 91.
- [9] J.M. Fréchet, *Science* 263 (1994) 1710.
- [10] I. Gitsov, J.M. Fréchet, *Macromolecules* 26 (1993) 6536.
- [11] I. Gitsov, J.M. Fréchet, *J. Am. Chem. Soc.* 118 (1996) 3785.
- [12] C.J. Hawker, F. Chu, P.J. Pomery, D.J.T. Hill, *Macromolecules* 29 (1996) 3831.
- [13] K. Inoue, Y. Nishikawa, T. Tanigaki, *J. Am. Chem. Soc.* 113 (1991) 7609.

- [14] K. Inoue, H. Miyamoto, T. Itaya, *J. Polym. Sci., Polym. Chem.* 35 (1997) 1839.
- [15] H.R. Allcock, R. Ravikiran, S.J.M. O'Connor, *Macromolecules* 30 (1997) 3184.
- [16] J. Johansson, A. Gogoll, J. Tegenfeldt, *Polymer* 37 (1996) 1387.
- [17] H. Vogel, *Phys. Z.* 22 (1921) 645.
- [18] V.G. Tammann, W.Z. Hesse, *Anorg. Allg. Chem.* 156 (1926) 245.
- [19] G.S. Fulcher, *J. Am. Ceram. Soc.* 8 (1925) 339.
- [20] B.L. Pake, M.A. Ratner, D.F. Shriver, *J. Electrochem. Soc.* 129 (1982) 1694.
- [21] C.A. Angell, *Solid State Inoics* 9/10 (1983) 3.