Poly{sodium 2-[ω-methacryloyl oligo(oxyethylene)] ethylsulfonate} as a new type of polymer electrolyte with Na^+ single-ionic conductivity

Sheng-shui Zhang*
Institute of Chemistry, Academia Sinica, Beijing 100080, People's Republic of China

and Qing-guo Liu
Laboratory of Solid State Ionics, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

and Lei-ling Yang
Beijing Research Institute of Chemical Industry, Beijing 100013, People's Republic of China
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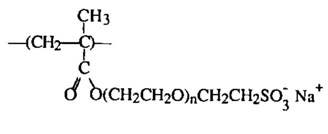
Sodium 2-[ω-methacryloyl oligo(oxyethylene)] ethylsulfonate has been synthesized and polymerized to prepare a polymeric solid electrolyte with Na^+ single-ionic conductivity. The length of oligo(oxyethylene) side chain determines the glass transition temperature and salt concentration of the homopolymers, and consequently influences the conductivity. The highest conductivity of 3.5×10^{-6} S cm^{-1} at 25°C is obtained when the number of CH_2CH_2O repeat units in the side chain is equal to 14. The temperature dependence of the ionic conductivity shows a curved Arrhenius plot, suggesting that ionic conduction is closely associated with segmental motion of the polymer host. The Williams–Landel–Ferry (WLF) empirical equation, which is based on the free-volume theory, is found to be valid for describing the conductivity data, and the obtained WLF parameters are comparable with the universal values.

(Keywords: polymer electrolyte; ionic conductivity; oxyethylene macromer)

INTRODUCTION

In the past two decades great progress has been made in exploring polymeric solid electrolytes with high conductivity at ambient temperature[1]. Most of them are based on poly(oxyethylene) complexes with alkali-metal salts and are found to be bi-ionic conductors, in which both cations and anions contribute to ionic conduction. In the case of d.c. condition, the motion of anions opposite cations will lead to the formation of a polarization potential across the electrolyte, which offsets the imposed voltage and consequently decreases the ionic transport. It is, therefore, inconvenient that these materials are applied as practical electrochemical devices that employ an ion-inserting-type compound as the electrode. An efficient solution to this problem is to design single-ionic conductors with the opposite anions fixed covalently in the macromolecules[2–7].

So far, four forms of single-ionic conducting polymer electrolytes have been reported[2]. Blends of poly(oxyethylene) with polyanionic salts are the first[3], copolymers of oxyethylene macromer and salt-containing monomer are another[4], ionomeric networks that contain flexible oligo(oxyethylene) chains are the third[5], and polyelectrolytes (homopolymers) are the fourth[6,7]. Compared with a bi-ionic conductor, single-ionic conductors have much lower conductivity under the same conditions (generally in the range of 10^{-6}–10^{-8} S cm^{-1} at 25°C for alkali-metal ions), since in the latter only one kind of ion can serve as charge carriers. Typically, the highest conductivity of K^+ ions was reported to be 1.1×10^{-7} S cm^{-1} at 30°C for homopolymer-based polyelectrolytes[6], in which the terminal group of potassium carbonate acts as the carrier source and oligo(oxyethylene) as pendent side chain. We have recently synthesized another polyelectrolyte with sodium sulfonate as the carrier source and with a longer oligo(oxyethylene) chain as pendent group, and hence obtained higher conductivity due to the lower dissociation energy of the sulfonates and to the greater solubility of the long oligo(oxyethylene) side chain[7]. We report here the synthesis and Na^+ single-ionic conductivity of poly{sodium 2-[ω-methacryloyl oligo(oxyethylene)] ethylsulfonate}. For the sake of convenience, the polyelectrolytes are abbreviated as P(EEO$_n$Na), where n is the number of CH_2CH_2O repeat units in the side chain. The schematic structure of the polyelectrolytes is shown below:



$$-\!\!\left(CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O^{\nearrow\!\!\!\!/}\;\; \searrow O(CH_2CH_2O)_nCH_2CH_2SO_3^-\,Na^+}{C}}{\underset{|}{C}}}\right)\!\!-$$

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*To whom correspondence should be addressed. Present address: Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604, USA

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As can be seen from the structure, the polyelectrolytes should exhibit Na^+ single-ionic conductivity without using any additives because the short oligo(oxyethylene) chains facilitate the dissociation of sodium sulfonate and the flexible macromolecular chains promote the transfer of the Na^+ ions.

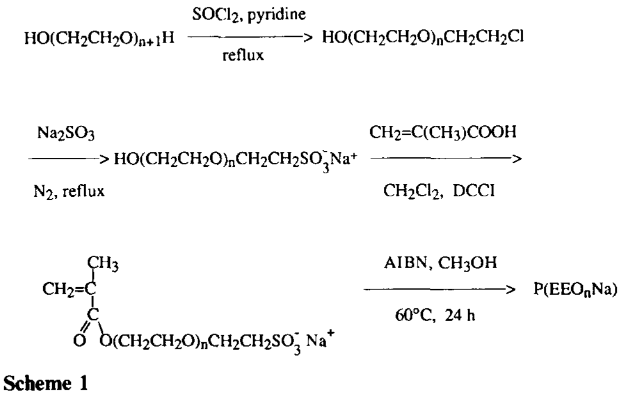
EXPERIMENTAL

Materials

Oligo(oxyethylene) glycols with different average molecular weight (*n* value) were purchased from Aldrich Chemical Co., and azeotropically distilled with benzene to remove residual moisture before use. Thionyl chloride, pyridine and other solvents were distilled prior to use. 2,2′-Azobisisobutyronitrile (AIBN; Beijing Chemical Co.) was recrystallized from methanol and dried at room temperature under reduced pressure. Dicyclohexylcarbodiimide (DCCI) and 4-dimethylaminopyridine (DMAP) supplied by Aldrich Chemical Co. and methacrylic acid from Beijing Chemical Co. were used in the commercial form. The synthesis route of P(EEO$_n$Na)s is shown in *Scheme 1* and a typical example for the synthesis of P(EEO$_8$Na) is now described. Polyelectrolytes with other *n* values are prepared according to the same procedures.

To a well stirred solution of oligo(oxyethylene) glycol (120 g, $\bar{M}_w = 400$, 0.30 mol), pyridine (24.3 ml, 0.30 mol) and benzene (100 ml) cooled in a water–ice bath, 22.0 ml (0.30 mol) of thionyl chloride was added dropwise over 30 min with vigorous stirring. The mixture was allowed to reflux for 24 h, after which gas evolution had nearly ceased. After cooling, the precipitate was filtered and 10 ml of hydrochloric acid (1:1 in volume) was dripped into the filtrate. The organic layer was separated and then dissolved in methanol/ethyl ether (1/4 in volume) solution, followed by extraction with pentane (3 × 30 ml) to purge bi-chlorinated ether. The product, ω-hydroxyoligo(oxyethylene) chloroethyl ether, in a yield of 41%, was crystallized from petroleum ether at lower temperature. The i.r. spectrum of the product shows absorption peaks at 3400 (O–H), 1106 (C–O–C) and 750 cm^{-1} (C–Cl), respectively. The Cl content of the product was determined to be 1.0 ± 0.05 mole per mole. ^{1}H n.m.r. ($CDCl_3$), δ (ppm): 2.87 (1 H, $O\underline{H}$), 3.6–3.8 (34 H, $C\underline{H}_2C\underline{H}_2O$), 4.13 (2 H, $ClC\underline{H}_2$). For the products with an *n* value of less than 8, reduced pressure distillation should be employed for the isolation and purification.

Sodium ω-hydroxyoligo(oxyethylene) ethylsulfonate was prepared by refluxing the aqueous solution of ω-hydroxyoligo(oxyethylene) chloroethyl ether (43.3 g, 0.10 mol) and sodium sulfite (63.0 g, 0.50 mol) for at least 6 h, while a stream of nitrogen flushes air from the system. After the mixture was dried, a large amount of absolute ethanol was added to dissolve the desired product, followed by filtering the residual solids. The product, in a yield of 85%, was crystallized by cooling the concentrated filtrate. Further purification carried out by recrystallization from ethyl ether gave a white moist solid (b.p. 31°C). No C–Cl absorption peak at ca. 750 cm^{-1} was observed, while the characteristic peaks at 1216 and 1165 cm^{-1} for the $-SO_3Na$ group were monitored from the i.r. spectrum of the resultant product. ^{1}H n.m.r. ($CDCl_3$), δ (ppm): 2.81 (1 H, $O\underline{H}$), 3.60–3.70 (34 H, $C\underline{H}_2C\underline{H}_2O$), 3.72 (2 H, $C\underline{H}_2SO_3Na$). Analysis — calculated for $C_{18}H_{37}O_{12}SNa$: C 43.20%, H 7.40%, S 6.40%; found: C 43.08%, H 7.53%, S 6.32%.



Scheme 1

Sodium 2-[ω-methacryloyl oligo(oxyethylene)] ethylsulfonate (EEO$_n$Na) was prepared as follows. Sodium ω-hydroxyoligo(oxyethylene) ethylsulfonate (25 g, 0.05 mol), methacrylic acid (4.35 g, 0.05 mol), DMAP (6.40 ml, 0.05 mol) and DCCI (10.42 g, 0.05 mol) were dissolved in 140 ml of CH_2Cl_2 with vigorous stirring. After the reaction was left to proceed overnight (15 h), the formed dicyclohexylurea was filtered and the filtrate was carefully stripped to a viscous liquid on a rotary evaporator. The product, in a yield of 75%, was precipitated with dry ethyl ether and washed many times to remove impurities. I.r. absorption peaks of the product are assigned as follows: 1633 (C=C), 1710 (>C=O), 1106 (C–O–C), 1457 ($-CH_2O-$), 1220 and 1165 cm^{-1} ($-SO_3Na$). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.96 (3 H, $C\underline{H}_3$), 3.60–3.70 (32 H, $C\underline{H}_2C\underline{H}_2O$), 3.73 (2 H, $C\underline{H}_2SO_3Na$), 4.31 (2 H, $COOC\underline{H}_2$), 5.57 and 6.13 (2 H, $C\underline{H}_2=$).

Polymerization of the EEO$_n$Na was carried out in methanol solution with 2–4 mol% of AIBN vs. the monomers as initiator at 60°C under nitrogen atmosphere for 16 h. The mixture was allowed to evaporate to dryness followed by thermal polymerization for 1 day at 100°C. The resultant solids were extracted with 95% alcohol until no characteristic peak of vinyl bonds at about 1640 cm^{-1} was seen from the extracts. The final product was dried under vacuum at 80°C for at least 24 h.

Measurements

I.r. spectra were analysed on a Bruker IFS 113V FT-IR instrument and ^{1}H n.m.r. spectra on a Unity 200 NMR spectrometer. D.s.c. scan was conducted under a nitrogen atmosphere using a Perkin–Elmer DSC-7 Differential Scanning Calorimeter at a heating rate of 5°C min^{-1}. The glass transition temperature (T_g) was regarded as the midpoint temperature of the baseline shift observed during the transition from glassy to rubber-like state, and the melting or crystallizing point (T_m and T_c) as the onset temperature during phase change.

Ionic conductivity was determined with a Solartron 1170 Frequency Response Analyzer over the frequency of 1 Hz to 100 kHz. The cylindrical disc sample (10 mm in diameter and ca. 0.4 mm in thickness) was sandwiched between two platinum electrodes and sealed in a test tube filled with dry nitrogen. To obtain a close connection, the test tube was heated to 90°C followed by cooling naturally to the measured temperatures. Before each measurement was made, the sample was kept at constant temperature for at least 30 min.

RESULTS AND DISCUSSION

Thermal behaviour of P(EEO$_n$Na)s

D.s.c. curves of the P(EEO$_n$Na)s with different n values are illustrated in *Figure 1*. When n is equal to or less than 14, only one glass transition is observed over the temperature range from −100 to 80°C, showing a characteristic of completely amorphous polymers. Poly(oligo(oxyethylene) methacrylate) (P(MEO$_{12}$)), which has the same structure as the P(EEO$_n$Na) except for no sodium sulfonate, is a slightly crystalline polymer[8]. This is not surprising because the interaction between Na$^+$ ion and ether oxygens in the P(EEO$_{14}$Na) hinders the crystallization of oligo(oxyethylene) side chains. On the contrary, in addition to the glass transition at −37°C there is respectively an endothermal peak at 23.6°C and an exothermal peak at −7.4°C in P(EEO$_{22}$Na). Interestingly, the exothermal peak cannot be observed any more in the P(MEO$_{22}$) although there is the same length of oligo(oxyethylene) side chain between them[8]. Therefore, the endothermal peak in the P(EEO$_{22}$Na) may be ascribed to the melting of oligo(oxyethylene) crystals and the exothermal one to cooling crystallization of oligo(oxyethylene) side chains during rapid cooling followed by slow heating. The cooling crystallization of P(EEO$_{22}$Na) is probably caused by the interaction of metal ion and ether oxygens. This phenomenon has also been observed from another homopolymer-based polyelectrolyte containing short oligo(oxyethylene) chains and sodium sulfonates[7].

Correlation between ionic conduction and length of side chain

As seen from the structure of P(EEO$_n$Na)s, the n value represents precisely the ratio of ether oxygens to sodium ion (O/Na). In other words, the length of oligo(oxyethylene) side chains determines the salt concentration and the T_g of the polyelectrolytes, and consequently influences ionic conductivity. The dependence of isothermal conductivity and T_g of P(EEO$_n$Na)s on the n value is estimated in *Figure 2*. The polyelectrolytes with lower n value display poor conductivity due mainly to the high T_g caused by more salt species, while the larger n value also results in low conductivity because of too low salt concentration and slightly higher T_g. When n is equal to 14, the T_g of polyelectrolyte becomes lowest and accordingly the conductivity reaches an optimum value as high as 3.5×10^{-6} S cm^{-1} at 25°C.

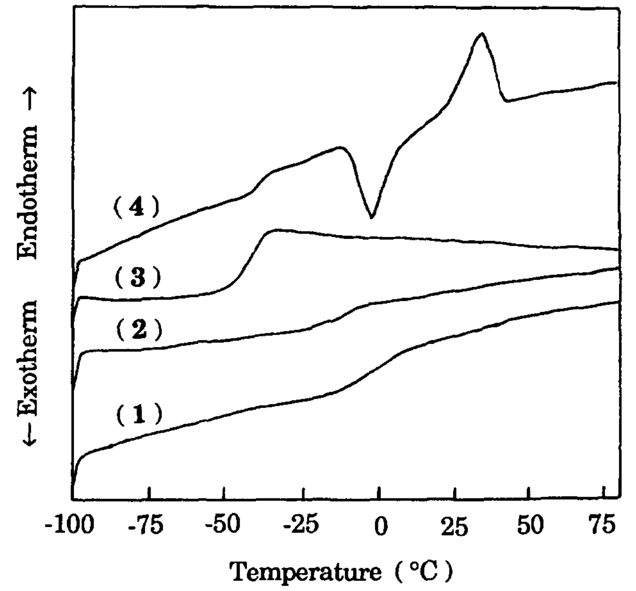


Figure 1 D.s.c. curves of P(EEO$_n$Na)s with $n = 5$ (1), 9 (2), 14 (3) and 22 (4)

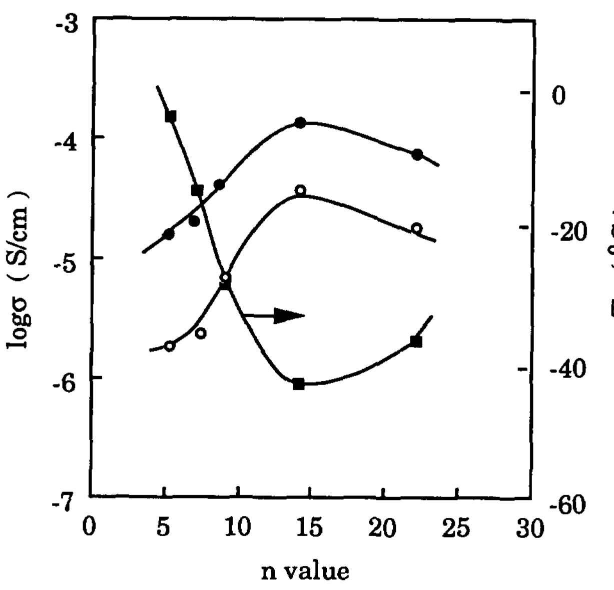


Figure 2 Effect of n value on the isothermal conductivity and glass transition temperature for P(EEO$_n$Na)s: conductivity at 50°C (○) and at 80°C (●); glass transition temperature (■)

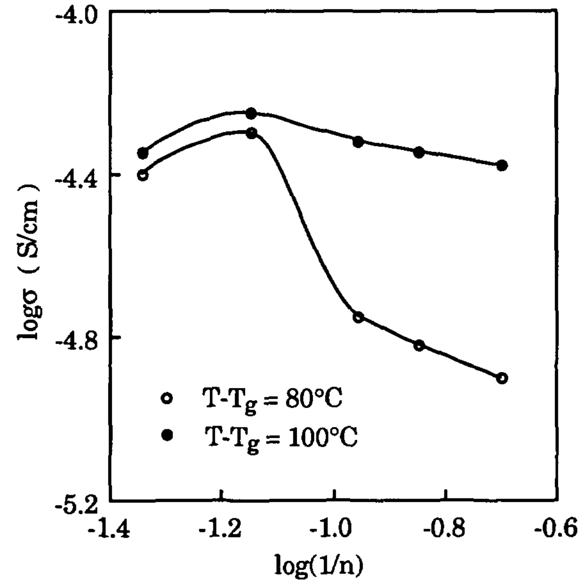


Figure 3 Conductivity of P(EEO$_n$Na)s at the same $T-T_g$

Figure 3 indicates the effect of salt concentration on the conductivity of P(EEO$_n$Na)s at the same temperature of $T-T_g$. In general, the conductivity (σ) of single-ionic conducting polymer electrolytes can be expressed as:

$$\sigma = nq\mu \qquad (1)$$

where n is the total number of charge carriers, q is the elemental charge of an electron and μ is mobility of the carriers. According to free-volume theory, the segmental motion for different polymers should be similar to each other at the same $T-T_g$. Thus, the difference in the conductivity of P(EEO$_n$Na)s at the same $T-T_g$ should reflect the change in the total number of charge carriers. It can be noticed from *Figure 3* that with increasing salt concentration the conductivity of P(EEO$_n$Na)s shows an initial increase followed by a decrease. This result suggests that the number of charge carriers will be decreased after the salt concentration exceeds a certain value. This may be due to the fact that the short oligo(oxyethylene) chains are less capable of complexing metal ions and then decrease dissociation degree of the salt species.

Interpretation of ionic conductivity

Arrhenius plots of conductivities of P(EEO$_n$Na)s are shown in *Figure 4*, which are all curves and independent of the n values. This behaviour is a characteristic of amorphous materials and implies that the process of ionic conduction is associated with the renewal of free volume of polymers. Therefore, the WLF (Williams–Landel–Ferry) equation, which has proven to be universally available for describing properties related to the relaxation of free volume of amorphous polymers, may be used to analyse the conductivity data[9]:

$$\log\left(\frac{\sigma(T)}{\sigma(T_g)}\right)=-\frac{C_1(T-T_g)}{C_2+(T-T_g)} \qquad (2)$$

where C_1 and C_2 are constants, and $\sigma(T)$ and $\sigma(T_g)$ are conductivity at temperature T and glass transition temperature T_g, respectively. In this work, the $\sigma(T_g)$ is determined by a non-linear least-squares analysis of the conductivity data using a computer, since it is too small to be measured with an ordinary apparatus. Based on the obtained $\sigma(T_g)$ values, the WLF parameters C_1 and C_2 are derived from the intersection and slope of the straight line of $\log^{-1}[\sigma(T)/\sigma(T_g)]$ vs. $(T-T_g)^{-1}$. The WLF parameters are listed in *Table 1* together with the free-volume fraction (f_g) at T_g and the coefficient of thermal expansion (a_f), which are calculated according to the formulae $f_g=1/2.303C_1$, $a_f=1/2.303C_1C_2$, respectively. The WLF parameters of conductivity of P(EEO$_n$Na)s with different n value are roughly consistent and comparable with the 'universal' values ($C_1=17.4$, $C_2=51.6$), which verifies the close relationship between ionic conduction and segmental motion of polymeric hosts.

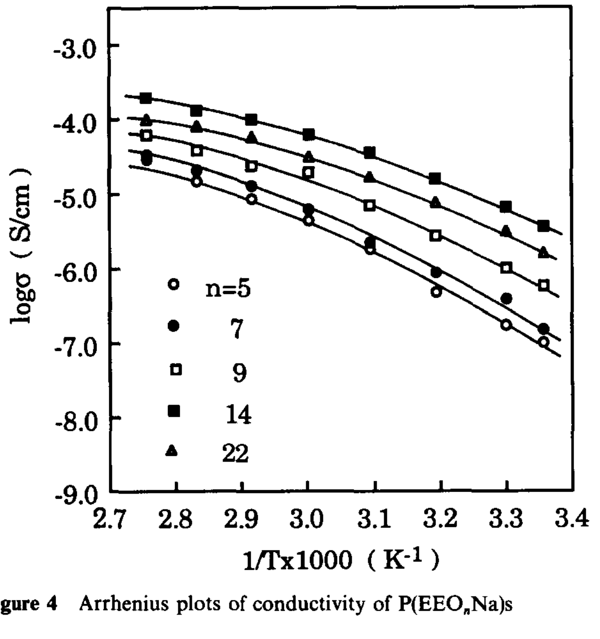


Figure 4 Arrhenius plots of conductivity of P(EEO$_n$Na)s

Table 1 WLF parameters of conductivity of P(EEO$_n$Na)s

n value	T_g (°C)	$\sigma(T_g)$ (S cm^{-1})	C_1	C_2 (°C)	f_g	a_f ($\times 10^{-4}$)
7	−15.0	6.1×10^{-11}	10.4	80.6	0.042	5.2
9	−28.7	2.5×10^{-13}	11.6	46.2	0.037	8.1
14	−43.2	1.5×10^{-13}	11.0	49.0	0.040	8.1
22	−36.7	2.5×10^{-13}	11.9	45.5	0.037	8.0
WLF			17.4	51.6	0.025	4.8

Table 2 VTF parameters of conductivity of P(EEO$_n$Na)s

n value	A	B	T_0 (°C)	$T-T_0$ (°C)	ΔC_p (J g^{-1} C^{-1})	$\Delta\mu$ (kJ g^{-1})
7	0.5152	5094	−58	43.0	0.510	4.5
9	0.4546	5560	−60	31.3	0.511	4.7
14	3.248	5532	−70	26.8	0.513	4.6
22	0.7570	5724	−65	28.3	0.612	5.7

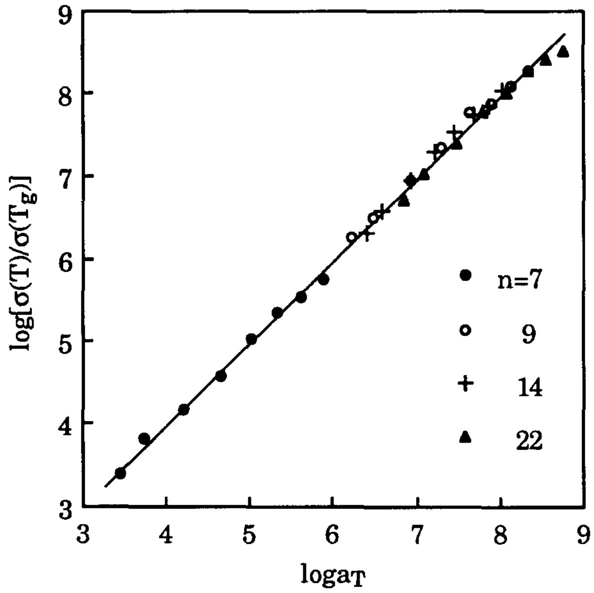


Figure 5 Conductivity as a function of the shift factor for P(EEO$_n$Na)s

It should be pointed out that the right term of equation (2) is referred to as a shift factor, $\log(a_T)$. The correlation of $\log[\sigma(T)/\sigma(T_g)]$ with the shift factor is plotted in *Figure 5*, from which it is observed that all the points fall on the straight line with slope of unity. This is in good agreement with what equation (2) predicts. Again, it is confirmed that the migration of ions is closely related to the renewal of free volume caused by segmental motion of polymeric hosts.

More often, ionic conductivity in elastic materials is described by the VTF (Vogel–Tammann–Fulcher) equation[10–12]:

$$\sigma=AT^{-1/2}\exp\left(-\frac{B}{T-T_0}\right) \qquad (3)$$

where A and B are constants and T_0 is an ideal temperature, at which the configurational entropy becomes vanishing. The parameters T_0, A and B obtained by a non-linear least-squares analysis of the conductivity data are listed in *Table 2*. Substitution of these parameters into equation (3) gives a series of straight lines with a

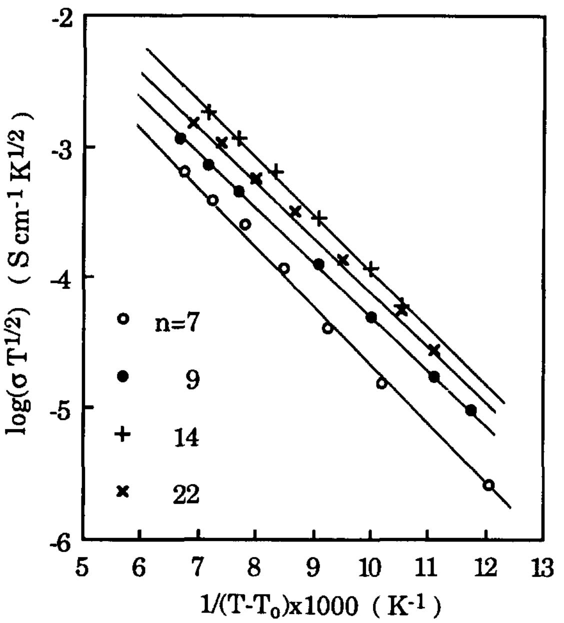


Figure 6 VTF plots of conductivity of P(EEO$_n$Na)s

regression factor of more than 0.997 (*Figure 6*), revealing the considerable dependence of ionic conductivity on the segmental motion of polyelectrolyte hosts.

According to the configurational entropy theory of Gibbs *et al.*, the parameter B of the VTF equation may be written as[13]:

$$B=\frac{T_0 S_c^* \Delta\mu}{k \Delta C_p T} \tag{4}$$

where ΔC_p is the change in heat capacity during the glass transition, $\Delta\mu$ is the molar energy barrier of segmental rearrangement, and S_c^* is the minimum configurational entropy required for such a rearrangement. An approximation of S_c^* is $k \ln 2$ where k is the Boltzmann constant. Using ΔC_p values determined from d.s.c. results, $\Delta\mu$ is calculated and also listed in *Table 2*. The $\Delta\mu$ values of the completely amorphous P(EEO$_n$Na)s are independent of the n value, revealing further that there is the same basic process between ionic transfer and segmental motion.

The availability of WLF and VTF equations for describing the conductivity data may let us conclude that conduction of Na$^+$ ions is carried out by segmental motion of polyelectrolyte hosts.

CONCLUSIONS

Poly{sodium 2-[ω-methacryloyl oligo(oxyethylene)] ethylsulfonate} was prepared as a new type of polymeric solid electrolyte that shows Na$^+$ single-ionic conductivity without liquid additives and low-molecular-weight salts. The length of oligo(oxyethylene) side chain influences considerably the ionic conductivity because it determines both the glass transition temperature and the salt concentration of the polyelectrolytes. The results indicate that P(EEO$_{14}$Na) has the lowest T_g and hence displays the highest conductivity of 3.5×10^{-6} S cm^{-1} at 25°C. The curved Arrhenius plots of conductivity suggest that there is a close correlation between ionic conduction and segmental motion, which is verified by the validity of WLF and VTF empirical equations for analysing the obtained conductivity data.

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