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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Single-Ionic Conductivity in Poly(Sodium 2-Methacryloyl 3-[ $\Omega$ -Methoxyl Oligo(Oxyethylene)]Propylsulfonate)

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**To cite this Article** Zhang, Sheng-Shui, Liu, Qing-Guo and Yang, Lei-Ling (1994) 'Single-Ionic Conductivity in Poly(Sodium 2-Methacryloyl 3-[ $\Omega$ -Methoxyl Oligo(Oxyethylene)]Propylsulfonate)', *Journal of Macromolecular Science, Part A*, 31: 5, 543 – 553

**To link to this Article:** DOI: 10.1080/10601329409349737

**URL:** <http://dx.doi.org/10.1080/10601329409349737>

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# **SINGLE-IONIC CONDUCTIVITY IN POLY(SODIUM 2-METHACRYLOYL 3- $[\omega$ -METHOXYL OLIGO(OXYETHYLENE)] PROPYLSULFONATE)**

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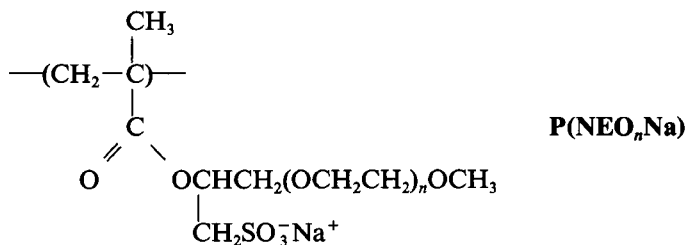
## **ABSTRACT**

Sodium 2-methacryloyl 3- $[\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate was synthesized, from which homopolymer-based polyelectrolyte was prepared. The polyelectrolytes thus obtained show single  $\text{Na}^+$  ionic conductivity at ambient temperature, neither adding plasticizer nor hybridizing small molecular salt. The conductivity depends considerably on the length of oligo(oxyethylene) side-chain. Optimally, the highest conductivity of  $6.0 \times 10^{-6}$  S/cm at 25°C is obtained when the number of  $(\text{CH}_2\text{CH}_2\text{O})$  repeating units equals 16. Results indicate that the conductivity data follow WLF and VTF equations. The WLF parameters

are found to be comparable with "universal" values, and analysis of the configurational entropy model suggests that the conduction of  $\text{Na}^+$  ions is carried out by an association mechanism.

## INTRODUCTION

Complexes of polyethers with alkali metal salts have extensive interest for theoretical study and for practical application in novel electrochemical devices. Previous emphasis was mainly on the enhancement of ionic conductivity at ambient temperature. For this purpose, much effort has been devoted to explore new types of polyether hosts that have a flexible macromolecular chain (low glass transition temperature). So far, complexes of alkali metal salts with ionic conductivities higher than  $10^{-5}$  S/cm at  $25^\circ\text{C}$  have been easily obtained from structure-modified polyethers such as comb-shaped and network polyethers [1, 2]. Unfortunately, most of them are better conductors of anions than of cations. If such a material is used in an electrochemical device involving direct current, the motion of the anions will offset the property of the device since it will lead to the formation of a polarized potential opposing the applied voltage. Therefore, there has recently been interest in developing solid polymer electrolytes that are single-ion conductors of cations [3–14]. The approach to immobilizing anions is to fix them on the macromolecular chain by covalent bonds. The study of single-ionic conductors has been reviewed in detail [3]. These materials can be divided into blends [4, 5], copolymers [6–10], networks [11–13], and homopolymer systems [14]. We report here the synthesis and single  $\text{Na}^+$  ionic conductivity of poly(sodium 2-methacryloyl 3- $[\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate) [P(NEO $_n$ Na)], whose structure is



In P(NEO $_n$ Na), the polar oligo(oxyethylene) short chains act as a "solid solvent" to solvate the salt species, the  $\text{---SO}_3\text{Na}$  group provides the charge carrier ( $\text{Na}^+$ ), and the segmental motion of the flexible macromolecular chains drives the migration of sodium ions. As a result, P(NEO $_n$ Na) should display single ionic conductivity of  $\text{Na}^+$  ions without the use of other additives.

## EXPERIMENTAL

### Materials

Epichlorohydrin (from Beijing Chemical Co.) and methacryloyl chloride (from Aldrich Co.) were distilled before use. Monomethoxyl oligo(oxyethylene)s with different average molecular weights, supplied by Aldrich Co., were used in

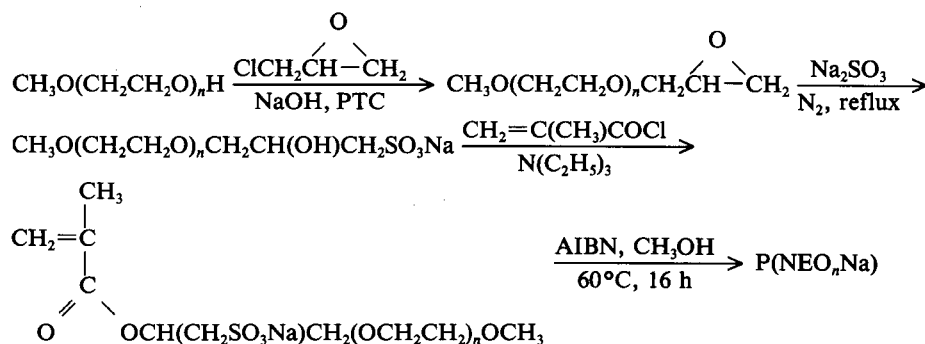
their commercial form. The synthesis route of poly(sodium 2-methacryloyl 3- $[\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate) is shown in Scheme 1. All the experimental procedures have been described in detail elsewhere [15], and only an outline is given here.

Methoxyl oligo(oxyethylene) oxirane was prepared by the reaction between epichlorohydrin and monomethoxyl oligo(oxyethylene) in an alkali medium with tetrabutyl ammonium iodide as the phase transference catalyst. The structure of the product was checked by its IR spectrum which showed the characteristic peaks of oxirane at 3040, 1250, and 830  $\text{cm}^{-1}$ , respectively.  $^1\text{H-NMR}$  ( $\text{CD}_3\text{Cl}$ )  $\delta$  ppm: 2.68/2.88 ( $\text{CHCH}_2\text{O}$  in cyclic ether), 3.30 ( $\text{OCH}_3$ ), 3.6–3.7 ( $\text{CH}_2\text{CH}_2\text{O}$ ), and 3.88 ( $\text{CHCH}_2\text{O}$  in cyclic ether).

Sulfonation of methoxyl oligo(oxyethylene) oxirane with sodium sulfite gave sodium 2-hydroxyl 3- $[\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate, which was purified by crystallization from a mixed solvent of ethyl alcohol and ethyl ether. The complete sulfonation was confirmed by the absence of peaks of oxirane in the IR spectrum of the product.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  ppm: 3.04 ( $\text{OH}$ ), 3.31 ( $\text{CH}_2\text{SO}_3\text{Na}$ ), 3.38 ( $\text{OCH}_3$ ), and 3.5–3.7 ( $\text{OCH}_2\text{CH}_2\text{O}$ ).

Sodium 2-methacryloyl 3- $[\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate was synthesized by esterification of the sodium salt obtained above and methacryloyl chloride in a chloroform solution with triethylamine as catalyst at room temperature. After filtering the precipitate that formed during reaction, the filtrate was carefully lyophilized to give the crude product. Further purification was done by flowing its chloroform solution through a silica gel column with the same solvent as eluant. The eluate was carefully evaporated to obtain the final product, which contained no Cl atoms according to elemental analysis. The important IR peaks of the product may be assigned to  $\text{C}=\text{C}$  (1630),  $>\text{C}=\text{O}$  (1710),  $\text{C}-\text{O}-\text{C}$  (1100),  $\text{CH}_2\text{O}$  (1440), and  $-\text{SO}_3\text{Na}$  groups (at 1220 and 1200  $\text{cm}^{-1}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.88 ( $\text{CH}_3$ ), 3.20 ( $\text{CH}_2\text{SO}_3\text{Na}$ ), 3.32 ( $\text{OCH}_3$ ), 3.5–3.8 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 3.92 ( $\text{COOCH}$ ), and 5.64 and 6.08 ( $\text{CH}_2=$ ).

Polymerization of sodium 2-methacryloyl 3- $[\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate was carried out as follows: A calculated amount of 2,2'-azobisisobutyronitrile was added to a methanol solution of the monomers with bubbling nitrogen and vigorous stirring. The polymerization was allowed to proceed for 24



SCHEME 1.

hours at 60°C. After concentrating the solution to a viscous liquid with a rotary evaporator, the resulting polymer was precipitated from a large amount of ethyl ether, washed with ethyl ether, and dried on a vacuum line at 80°C for 36 hours.

## Measurements

DSC analysis was conducted under a nitrogen atmosphere using a Perkin-Elmer DSC-7 Differential Scanning Calorimeter at a scan rate of 5°C/min. The glass transition temperature ( $T_g$ ) was taken as the midpoint temperature of the baseline shift observed during the transition from the glassy to the rubberlike state, and the melting or crystallizing points ( $T_m$  and  $T_c$ ) as the onset temperatures.

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

<sup>1</sup>H-NMR spectra were run on a JEOL JNM-FX100 spectrometer, and IR on a Bruker IFS 113V FI-IR instrument. A Waters ALC/GPC 224 column was used to analyze gel permeation chromatograms. The morphology of the polymer film was studied with a JEOL JEM-100CX II Electron Microscope.

## RESULTS AND DISCUSSION

### Morphology of Polyelectrolyte

DSC curves of P(NEO<sub>*n*</sub>Na)s with different *n* value are illustrated in Fig. 1. The curves reflect the effect of length of the oligo(oxyethylene) side-chain on the morphological structures of the polyelectrolytes, although they have not been normalized. For low *n* values the DSC curves show a glass transition over the whole temperature range, indicative of a completely amorphous structure. The polyelectrolytes begin to crystallize with increasing *n* values, and the DSC curves have an endothermic peak at 0–30°C. Interestingly, the melting peak is always accompanied by an exothermic peak on the low temperature side, which may be ascribed to cold crystallization of the oligo(oxyethylene) side-chains. This phenomenon has not been observed in salt-free poly[oligo(oxyethylene) methacrylate]s [P(MEO<sub>*n*</sub>)] that have a structure similar to P(NEO<sub>*n*</sub>Na) [6, 16], but it does occur in complexes of polyethers and alkali metal salts with high salt concentrations [17]. Thus, one may say that cold crystallization of P(NEO<sub>*n*</sub>Na)s is closely associated with interaction between metal ion and ether oxygens. DSC data demonstrate that both melting and crystallizing peaks shift toward high temperature, and their enthalpy rises as the *n* value increases. This is because long oligo(oxyethylene) chains favor the formation of large crystals.

Correlation of the *n* value with morphology may also be observed from transmission electron micrographs (Fig. 2). Both P(NEO<sub>12</sub>Na) and P(NEO<sub>16</sub>Na) form irregular, lamellar crystals, which are well distributed in amorphous media. However, P(NEO<sub>16</sub>Na) has larger size crystals and higher crystallinity compared with

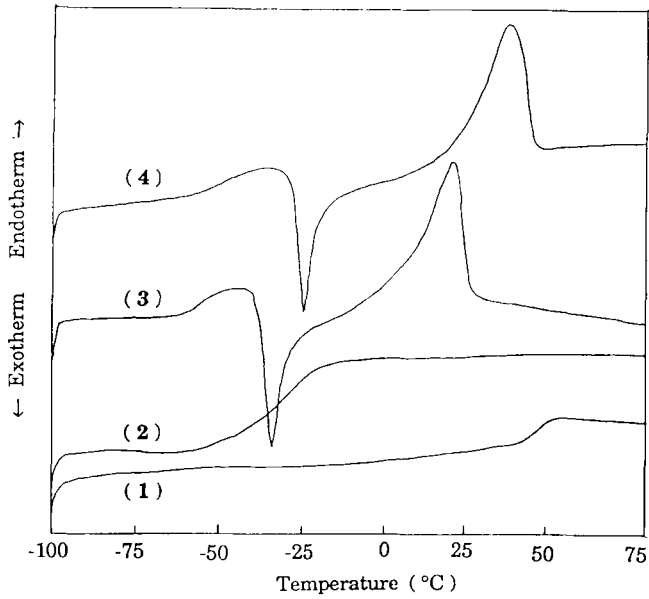


FIG. 1. DSC curves for the  $P(\text{NEO}_n\text{Na})$ s with  $n = 1$  (1), 7 (2), 12 (3), and 16 (4).

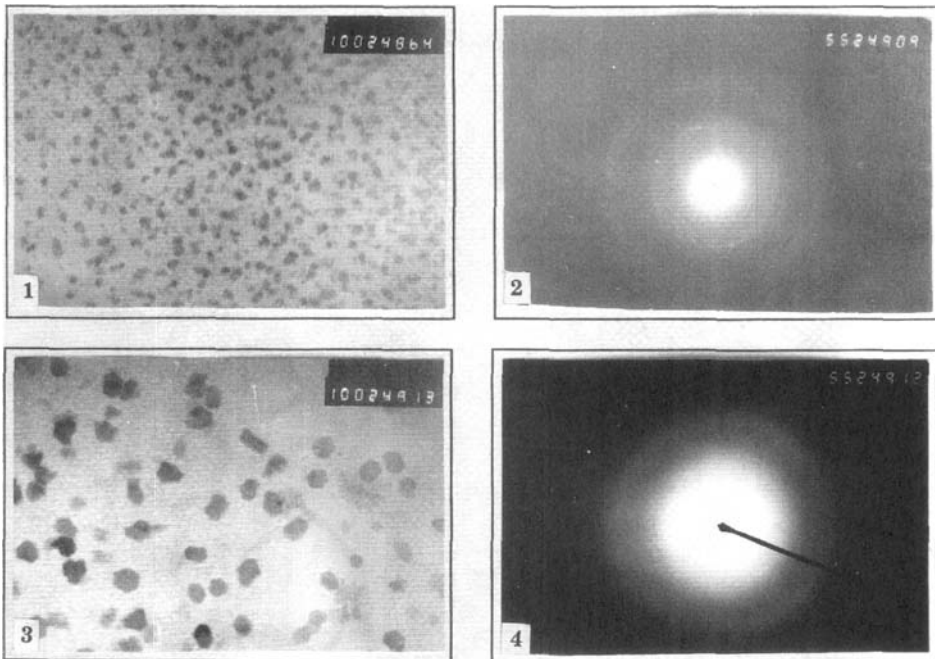


FIG. 2. TEM photos and patterns of electron diffraction for  $P(\text{NEO}_{12}\text{Na})$  (1, 2) and  $P(\text{NEO}_{16}\text{Na})$  (3, 4).

P(NEO<sub>12</sub>Na). The reason may be the contribution of the longer oligo(oxyethylene) side-chain and the lower salt concentration in P(NEO<sub>16</sub>Na) since  $n$  is equal to the O/Na value in P(NEO <sub>$n$</sub> Na). The electron diffraction patterns for P(NEO<sub>12</sub>Na) and P(NEO<sub>16</sub>Na), as shown in Fig. 2, are composed of a diffraction ring with bright spots distributed around it. This is a characteristic of partially crystalline polymers.

### Single-Ionic Conductivity in the Polyelectrolyte

Ionic conductivities of P(NEO <sub>$n$</sub> Na)s with different  $n$  values are evaluated in Fig. 3 over the 25–90°C temperature range. The curved dependence of conductivity on temperature suggests that there is a close relationship between the migration of ions and the segmental motion of the polyelectrolyte matrix. To shed light on how the length of the oligo(oxyethylene) side-chain influences conductivity, the isothermal conductivity and  $T_g$  of the P(NEO <sub>$n$</sub> Na)s were determined as a function of the  $n$  value (Fig. 4). A minimum value of  $T_g$  appears at  $n$  of 12. This phenomenon is similar to the observation in the P(MEO <sub>$n$</sub> ) system [16], and it might be explained as follows: P(NEO <sub>$n$</sub> Na) with a lower  $n$  value contains more salt species, which affords more chance for the chelation of a cation with ether oxygens, and hence leads to a higher  $T_g$ . On the other hand, an increase in the length of the oligo(oxyethylene) side-chain strengthens the dipole-dipole interaction between side-chains, and this also results in a higher  $T_g$ . The compensation of these two factors yields a minimum  $T_g$  of  $-55.3^\circ\text{C}$  at an  $n$  value of  $\sim 12$  (Fig. 4). It can be seen from Fig. 4 that the ionic conductivity of P(NEO <sub>$n$</sub> Na)s is monotonously enhanced with increasing  $n$  value. P(NEO<sub>16</sub>Na) displays better conductivity than P(NEO<sub>12</sub>Na), although it has a slightly higher  $T_g$ . This is because its long oligo(oxyethylene) side-chain is more capable of complexing with a cation, which favors dissociation of the salt species in the polyelectrolyte.

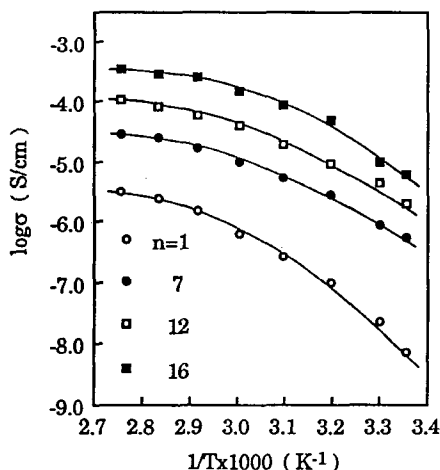


FIG. 3. Temperature dependence of ionic conductivity for the P(NEO <sub>$n$</sub> Na)s.

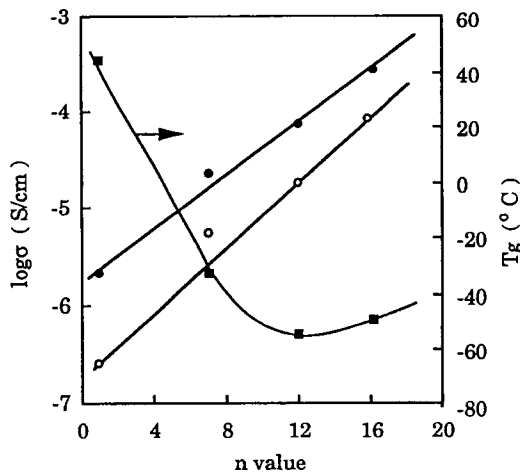


FIG. 4. Effect of  $n$  value on the isothermal conductivity and glass transition temperature for the P(NEO <sub>$n$</sub> Na)s. Conductivity at 50°C (○) and at 80°C (●); Glass transition temperature (■).

### Interpretation of Ionic Conduction in the Polyelectrolyte Host

As suggested by the curved Arrhenius plot of the conductivity, the migration of ions depends on the segment motion of the polymer host. Thus, the WLF (Williams-Landel-Ferry) equation, which describes the behavior of segmental relaxation for amorphous polymers, was used to analyze the conductivity data [18]:

$$\log \left[ \frac{\sigma(T)}{\sigma(T_g)} \right] = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

where  $C_1$  and  $C_2$  are constants,  $\sigma(T)$  and  $\sigma(T_g)$  are the conductivities at temperature  $T$  and the glass transition temperature ( $T_g$ ), respectively. In this work,  $\sigma(T_g)$  is determined by a nonlinear least-squares analysis of the conductivity data using a computer because  $\sigma(T_g)$  is too small to be measured with an ordinary apparatus. The WLF plot of ionic conductivity for P(NEO <sub>$n$</sub> Na)s shows that all the points are on similar curves (Fig. 5) which may be made to coincide by the use of a shift.

On the basis of the  $\sigma(T_g)$  obtained, the WLF parameters  $C_1$  and  $C_2$  in Eq. (1) 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 formulas  $f_g = 1/2.303C_1$ ,  $a_f = 1/2.303C_1C_2$ . The WLF parameters obtained for various P(NEO <sub>$n$</sub> Na)s are comparable with the "universal" values ( $C_1 = 17.4$ ,  $C_2 = 51.6$ ).

It may be found from Table 1 that the  $\sigma(T_g)$  rapidly decreases with increasing  $n$  value. In general, conductivity can be expressed as

$$\sigma(T) = \sum_{i=1}^k n_i q_i \mu_i \quad (2)$$



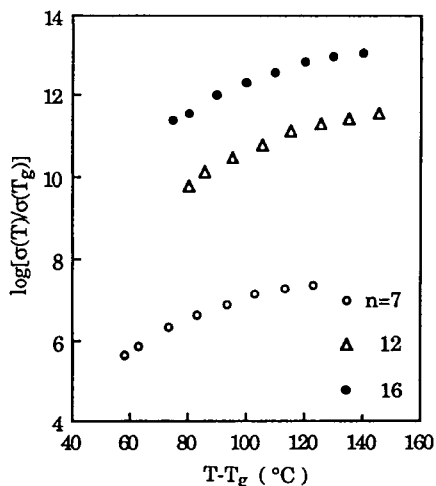


FIG. 5. WLF plots of ionic conductivity for the P(NEO<sub>n</sub>Na)s.

where  $i$  represents the kind of charge carriers,  $n$  is the number of charge carriers,  $q$  is the elemental electric charge, and  $\mu$  is the carrier mobility. In the P(NEO<sub>n</sub>Na) system, only Na<sup>+</sup> ions act as charge carriers and  $q$  is a constant; therefore, the conductivity is directly influenced by the terms of  $n$  and  $\mu$ . At  $T_g$ , segmental motion of the polymers has been frozen and the mobility of ions is vanishing, thus the salt content becomes more important in determining conductivity. It is evident that at  $T_g$  the P(NEO<sub>n</sub>Na) with the lower  $n$  value should exhibit higher conductivity due to its high salt content.

In addition, plots of  $\log[\sigma(T)/\sigma(T_g)]$  values vs shift factor [ $\log(a_T) = -C_1(T - T_g)/(C_2 + T - T_g)$ ] for the P(NEO<sub>n</sub>Na)s are all straight lines with a slope of unity (Fig. 6). This is in good agreement with what Eq. (1) predicts. Again, this verifies that the free volume theory is valid for interpreting conductivity data of the polyelectrolytes. In other words, the migration of ions is closely related to the renewal of free volumes caused by segmental motion of polyelectrolyte hosts.

More often, ionic conductivity in the viscous materials is described by the Vogel-Tammann-Fulcher (VTF) equation [19]:

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

TABLE 1. WLF Parameters of the Ionic Conductivity for the P(NEO<sub>n</sub>Na)s

P(NEO <sub>n</sub> Na), with $n =$	$T_g$ , °C	$\sigma(T_g)$ , S/cm	$C_1$	$C_2$ , °C	$f_g$	$a_f \times 10^{-4}$
7	-33.3	$1.3 \times 10^{-12}$	10.4	49.0	0.042	8.9
12	-55.3	$2.9 \times 10^{-16}$	14.9	40.8	0.029	7.2
16	-49.8	$2.3 \times 10^{-18}$	16.1	30.8	0.027	8.8
WLF			17.4	51.6	0.025	4.8

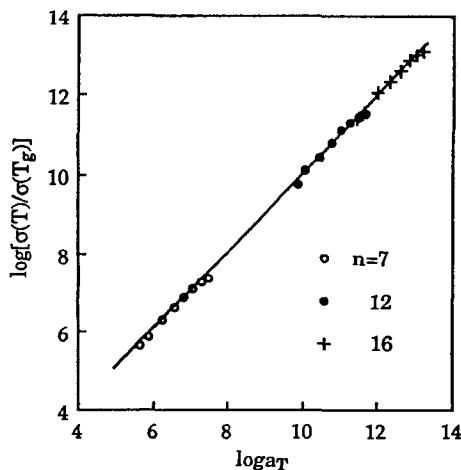


FIG. 6. Relationship between conductivity and shift factor for the P(NEO<sub>n</sub>Na)s.

where  $A$  and  $B$  are constants, and  $T_0$  is the thermodynamically limited glass transition temperature at which the configurational entropy vanishes. The parameters  $T_0$ ,  $A$ , and  $B$  obtained by a nonlinear least-squares analysis of the conductivity data are listed in Table 2. Substitution of these parameters into Eq. (3) gives a series of straight lines with a regression factor of more than 0.998 (Fig. 7), revealing a considerable dependence of ionic conductivity on the segmental motion of the polyelectrolyte hosts.

According to the configurational entropy model of Gibbs et al., parameter  $B$  of the VTF equation may be written as [20]

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

where  $\Delta C_p$  is the change in heat capacity at temperature  $T$  as the system transforms from a glass to a rubberlike state,  $\Delta\mu$  is the molar energy barrier opposing a segmental rearrangement, and  $S_c^*$  is the minimum configurational entropy required for such a rearrangement. A reasonable approximation for  $S_c^*$  is  $k \ln 2$ , where  $k$  is the Boltzmann constant. Using  $\Delta C_p$  values estimated from DSC analysis,  $\Delta\mu$  was also calculated and is listed in Table 2. The comparable  $\Delta\mu$  values among the P(NEO<sub>n</sub>Na)s with different  $n$  values imply that  $\Delta\mu$  should be a characteristic of

TABLE 2. VTF Parameters of the Ionic Conductivity for the P(NEO<sub>n</sub>Na)s

P(NEO <sub>n</sub> Na), with $n =$	$A$	$B$	$T_0, ^\circ\text{C}$	$T_g - T_0,$ $^\circ\text{C}$	$\Delta C_p,$ $\text{J/g}\cdot^\circ\text{C}$	$\Delta\mu, \text{kJ/g}$
7	0.0905	702	-52	18.7	0.122	0.134
12	0.8393	925	-68	12.7	0.281	0.398
16	0.6132	677	-64	14.2	0.361	0.377

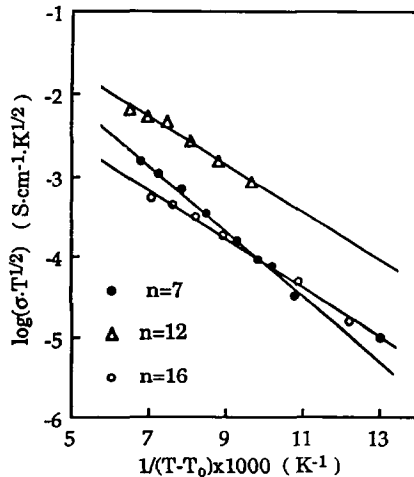


FIG. 7. VTF plots of ionic conductivity for the P(NEO<sub>n</sub>Na)s.

segmental motion but it does not tell us much about the energetics of ion transport where one would expect some energy change to be involved in moving the ion from one set of coordination sites to another.

The  $\Delta\mu$  value of Na<sup>+</sup> ionic conductivity is much smaller than the interaction energy of O<sup>-</sup>···Na<sup>+</sup>, but comparable with the activation energy of rearrangement of macromolecular chains. It may therefore be concluded that in the P(NEO<sub>n</sub>Na) media, the migration of Na<sup>+</sup> ions probably occurs through an associative mechanism. This mechanism considers that during the process of ionic conduction, one or two "free" oxygens move close to the coordinated cation. The cation then shifts a short distance, and one or two ether oxygens move away. Ionic transport is successful as long as the oxygens involved before and after are different. The above analyses reveal that there is a similar process between ionic conduction and segmental motion, and that conduction of Na<sup>+</sup> ions is carried out by segmental motion of the polyelectrolyte hosts.

## CONCLUSION

Poly(sodium 2-methacryloyl 3-[ $\omega$ -methoxyl oligo(oxyethylene)] propylsulfonate) has single-ionic conductivity of sodium ions without adding any additives. The ionic conductivity is greatly affected by the length of the oligo(oxyethylene) side-chains since it determines both the salt concentration and the morphology of the polyelectrolytes. An optimum conductivity as high as  $6.0 \times 10^{-6}$  S/cm at 25°C was achieved for P(NEO<sub>16</sub>Na). WLF and VTF empirical equations are valid for describing the conductivity data, revealing that the conduction of Na<sup>+</sup> ions in the polyelectrolyte host is closely coupled with segmental motion. Analysis of the configurational entropy model supports the assumption that ionic conduction occurs through an association mechanism.

## ACKNOWLEDGMENTS

The authors would like to thank Prof. S. Z. Jin and Ms. X. Q. for their helpful discussions regarding the structural analyses, and also Prof. G. C. Farrington of the University of Pennsylvania for helpful discussions. This work was supported by Beijing Zhongguancun Associated Center of Analysis and Measurement under Contract 92J31FQ-881.

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Received June 21, 1993