PII: S0032-3861(96)00726-4

Polymer Vol. 38 No. 8, pp. 1949–1951, 1997

0032-3861/97/\$17.00+0.00

Polyether/salt hybrid: 6. Effect of sulfonamide ends having different alkyl groups on the bulk ionic conductivity

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(Received 10 May 1996; revised 19 June 1996)

Poly(ethylene oxide) (PEO)/salt hybrids having sulfonamide groups on the PEO chain ends ($PEO_{1000}-(SAR)_2M_2$; R = $-CF_3$, $-CH_3$ and $-C_6H_5$; M = Li, Na, K, Rb and C_s) were prepared, and the bulk ionic conductivity was measured as a new type of ion conductive matrix. Among these, the salt having a trifluoromethyl sulfonamide group showed the highest ionic conductivity (for example, $2.83 \times 10^{-5}\,S\,cm^{-1}$ at 303 K for potassium salt). Although there was little difference in the glass transition temperature (T_g) for these salts and the same average molecular weight of the PEO part, there was a considerable difference in the ionic conductivity. The difference was attributed to the dissociation constant of sulfonamide groups depending upon the terminal alkyl groups. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene oxide); ionic conductivity; sulfonamide)

INTRODUCTION

Poly(ethylene oxide) (PEO) has been extensively studied as a typical ion conductive polymer, since PEO dissolves a variety of inorganic salts and transports the dissociated ions. Ion conduction in a mixture of PEO and inorganic salts was first reported by Wright[1]. Generally, ionic conductivity is governed by the number of carrier ions and their mobility. For higher ionic conductivity, it is necessary to develop a system having both excellent solubility of carrier ions and high segmental motion. In recent years, the following two trends have been developed vigorously; one is to increase the number of carrier ions, and the other is to improve the segmental motion.

For the former case, the simplest method is to add excess salts to the PEO. However, a large amount of inorganic salts cannot be dissolved homogeneously in PEO[2]. To generate enough carrier ions in a limited amount, salts having a higher dissociation degree were developed. Lithium perchlorate ($LiClO_4$) had been generally used because of its high dissociation degree, in spite of its explosive characteristics[3]. Instead of this, lithium trifluoromethyl sulfonate ($LiSO_3CF_3$) has been applied because of its better properties[3]. Recently, lithium bis(trifluoromethanesulfonyl) imide ($LiN(CF_3SO_2)_2$) and lithium tris(trifluoromethanesulfonyl) methide ($LiC(CF_3SO_2)_3$) have been successfully reported as excellent salts[4–7]. The dissociation constant of these salts is high because of the electron-donating property of the trifluoromethyl group. The amount of carrier ions was indeed improved by these; however, the formula weight of the salt similarly increased. This means that a considerable amount of salts is required to obtain a certain concentration of carrier ions. A new type of salt is therefore still to be developed to generate enough numbers of carrier ions.

For the latter case, it is essentially important to keep the segmental motion high. The following two factors are effective for this: suppression of both the increase of glass transition temperature (T_g) and the crystallization of the matrix. However, it is difficult to dissolve a large amount of salts in PEO without decreasing the mobility of carrier ions[8].

We have already prepared PEO/salt hybrids having a variety of anionic groups such as carboxylate, benzenesulfonate and sulfonate[9–11]. These hybrids are amorphous when the molecular weight of the PEO part lies between 350 and 600. The cation concentration of these hybrids ranges from 13.8 to 15.1 mol% of the ether unit. It is quite hard to dissolve inorganic salts in PEO at over 10 mol% without stiffening the matrix. The introduction of sulfonamide groups on the PEO chain ends should be helpful in order to increase the number of carrier ions without increasing the T_g.

EXPERIMENTAL

Materials

The α,ω-diamino-PEO with an average molecular weight of 1000 was a gift from Kawaken Fine Chemical Co Ltd. The α,ω-diamino-PEO (1.000×10^{-2} mol) and alkyl sulfonyl chloride (RSO_2Cl; R = $-CF_3$, $-CH_3$ and $-C_6H_5$; 2.000×10^{-2} mol, respectively) were dissolved and mixed in N,N-dimethylformamide (DMF, 100 ml) for 30 min at room temperature. The solution was made to react in the presence of triethylamine (4.0×10^{-2} mol) at 333 K for 24 h. In the case of CF_3SO_2Cl, this was reacted at 273 K for 6 h because of its low boiling point

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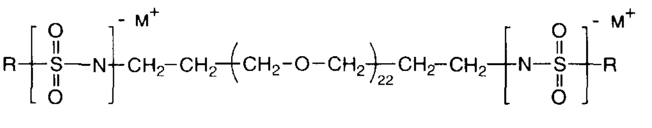

Scheme 1 Structure of $PEO_{1000}-(SAR)_2M_2$: $R = -CF_3$ (1-M), $-CH_3$ (2-M) and $-C_6H_5$ (3-M); M = Li, Na, K, Rb and Cs

(304 K). After reaction, the solution was cooled to form crystals of triethylammonium chloride, which was removed by filtration. Solvent DMF was removed by evaporation. The product was dissolved in cold benzene (300 ml) and filtered to remove triethylammonium chloride. This process was carried out several times, and the product was dried *in vacuo* at 333 K for 24 h.

The precursory oligomers ($PEO_{1000}-(SAR)_2H_2$) were neutralized with alkali metal hydroxide (MOH; M = Li, Na, K, Rb and Cs) in pure water. The structure of $PEO_{1000}-(SAR)_2M_2$ is shown in *Scheme 1*. These hybrids are abbreviated as follows: 1-M, 2-M and 3-M (1: $R = -CF_3$; 2: $R = -CH_3$; $R = -C_6H_5$; M = Li, Na, K, Rb and Cs).

The $PEO_{1000}-(SAR)_2H_2$ and these hybrids were characterized by proton nuclear magnetic resonance spectroscopy (^{1}H-n.m.r.; JEOL LA-300). The proton peaks for terminal amino propylene groups ($-(C\underline{H}_2)_3-NH_2$) at 1.73, 2.80 and 3.55 ppm shifted to 1.97, 3.15 and 3.71 ppm, respectively. The sulfonamide proton ($-N\underline{H}SO_2R$) peak at 2.45 ppm disappeared after neutralization.

Methods

Ionic conductivity was measured by the complex impedance method with the Schlumberger Solartron 1260 impedance analyser over frequencies ranging from 10 Hz to 1 MHz. The temperature was swept from 333 K to 283 K at a rate of $3\,K\,min^{-1}$. The impedance data at each temperature were collected by custom-designed apparatus to record Arrhenius plots of the ionic conductivity[12]. A custom-designed cell was also constructed with a pair of parallel stainless steel plates, and a 0.50 mm thick Teflon spacer. All the cell preparations and the impedance measurements were carried out in a glove box filled with dry nitrogen gas.

D.s.c. measurement was carried out with a SEIKO Instruments Inc. DSC-120. The samples were annealed from room temperature to 153 K with liquid nitrogen, and then measured at a heating rate of $10\,K\,min^{-1}$ over the temperature range from 153 K to 393 K.

RESULTS AND DISCUSSION

The ionic conductivity of PEO/salt hybrids having sulfonamide groups was measured. The Arrhenius plots of ionic conductivity for 1-K, 2-K and 3-K are shown in *Figure 1*. These hybrids showed higher bulk ionic conductivity than other PEO/salt hybrids having a carboxylate group[9]. The hybrid with a trifluoromethyl sulfonamide group (1-K) showed the highest ionic conductivity, $2.83 \times 10^{-5}\,S\,cm^{-1}$ at 303 K. The 1-K and 3-K did not show any transition of ionic conductivity in the temperature measurement range from 283 K to 333 K. On the other hand, 2-K showed a transition at 288 K, attributed to the solidification of the PEO part. The structure of alkyl groups affected the number of carrier ions in the system and the mobility of these hybrids.

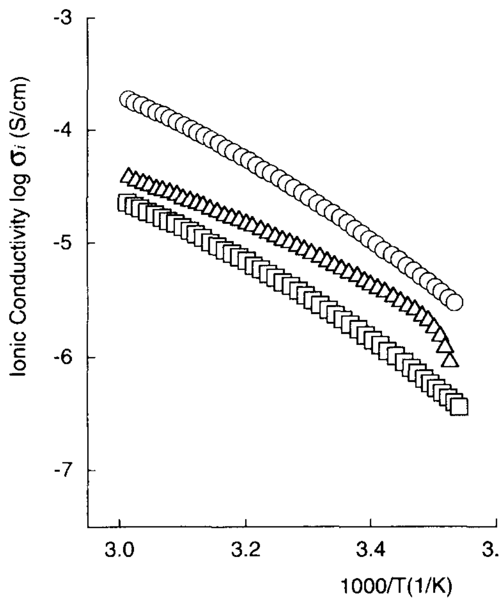

Figure 1 Arrhenius plots of the bulk ionic conductivity for $PEO_{1000}-(SAR)_2K_2$: ○, 1-K; △, 2-K; □, 3-K

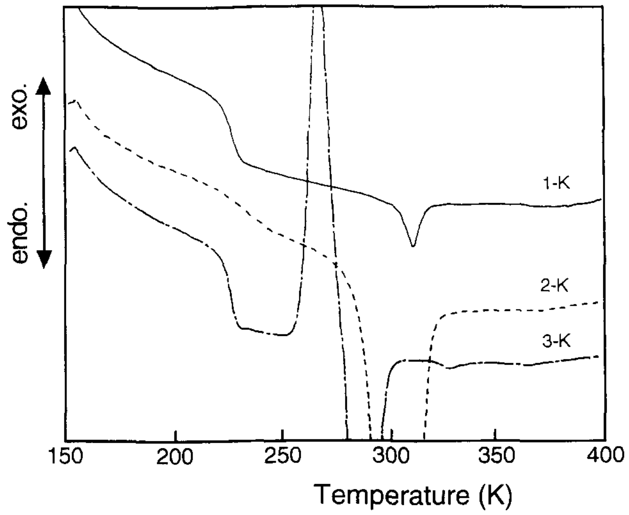

Figure 2 D.s.c. thermograms of $PEO_{1000}-(SAR)_2K_2$: $R = -CF_3$ (1-K), $-CH_3$ (2-K) and $-C_6H_5$ (3-K); heating rate = $10\,K\,min^{-1}$

Figure 2 shows the results of d.s.c. measurement of 1-K, 2-K and 3-K. The T_g of these hybrids was observed at 228.5 K, 233.4 K and 228.2 K, respectively. Since the molecular weight of the PEO part, which affected the segmental motion, was the same, T_g was concluded to be little affected by the structure of the alkyl groups on the sulfonamide groups. The ionic conductivity of these three hybrids was different despite having the same T_g. The concentration of carrier ions in the system was strongly suggested as governing the ionic conductivity. However, the melting behaviour of these hybrids differed, depending on the alkyl groups. The d.s.c. thermogram for 1-K showed small melting enthalpy, and this hybrid was concluded to be amorphous. On the other hand, 2-K showed an endothermic peak for melting of the PEO part at 303.5 K. The 3-K showed an exothermic peak at 262.5 K and an endothermic peak at 282.6 K. Apart from the 2-K system, 3-K was a highly viscous liquid and was considered to have little fraction

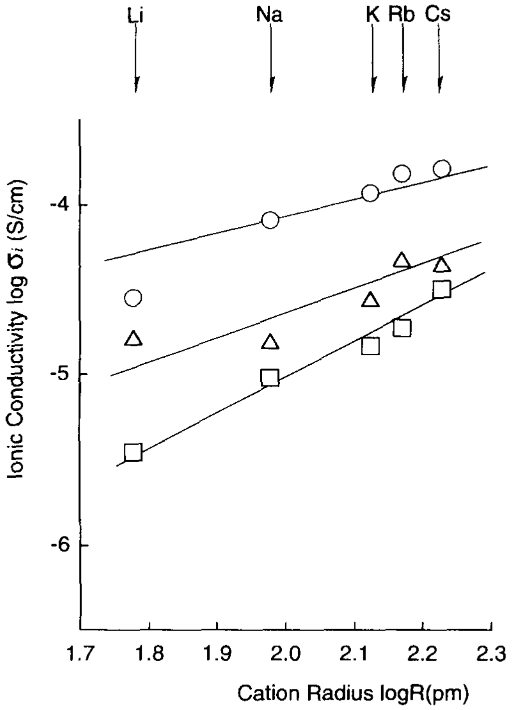

Figure 3 Effect of cation radius on the bulk ionic conductivity for PEO$_{1000}$ –(SAR)$_2$M$_2$ at 323 K: ○, 1-M; △, 2-M; □, 3-M

of crystalline phase at room temperature, since these hybrids were annealed by rapid cooling from room temperature to 153 K. At this stage, 3-K stayed amorphous even below its melting point. The exothermic peak at 262.5 K was attributed to crystallization.

It is possible to estimate the dissociation constant of sulfonamide groups by comparing tendencies between the ionic conductivity of these hybrids and cation radius. *Figure 3* shows the effect of cation radius on the ionic conductivity at 323 K for 1-M, 2-M and 3-M. The ionic conductivity of these hybrids increased with increasing cation radius. This was comprehensible in that the interaction between cations and ether oxygens decreased with increasing cation radius by reason of the lower surface charge density of the larger cations[13,14]. The dissociation degree of these sulfonamide groups is expected to be high since the dependence of cation radius on ionic conductivity for these hybrids is smaller than that of other hybrids having carboxylate or benzenesulfonate groups. The slope of the relation for these hybrids seen in *Figure 3* was also decreased by changing the alkyl groups on the sulfonamide ends. The ionic conductivity of 1-K was 8 times larger than that of 3-K, reflecting this effect. The difference of ionic conductivity between these hybrids was explained by the dissociation constant of the corresponding sulfonamide groups. The electron-donating characteristics of alkyl groups seemed to be the main factor in lowering the dissociation energy. The anionic stability of sulfonamide groups increases since these characteristics increase with changing alkyl groups such as trifluoromethyl, methyl and phenyl. Hence, these sulfonamide groups enhanced the production of carrier ions effectively and improved the ionic conductivity of these hybrids.

In conclusion, we prepared PEO/salt hybrids having sulfonamide groups on the PEO chain ends and measured their ionic conductivity. These hybrids showed higher ionic conductivity than other hybrids having carboxylate or benzenesulfonate groups. However, the T_g of these three hybrids was the same. The hybrid having a trifluoromethane sulfonamide group (1-M) showed the highest ionic conductivity among these hybrids. The electron-donating characteristics of alkyl groups were considered to improve the dissociation constant of the sulfonamide groups.

ACKNOWLEDGEMENTS

One of the authors (K. I.) acknowledges the financial support of the Japan Society for the Promotion of Science (Research Fellowships for Young Scientists). The present study was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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