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Synthesis and Ionic Conductivity of Network Polymer Electrolytes with Internal Plasticizers

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Abstract: Network polymer electrolytes with free oligo(oxyethylene) chains as internal plasticizers were prepared by cross-linking poly(ethylene glycol) acrylates. The effects of salt concentration and properties of internal plasticizers on ionic conductivity were studied.

Keywords: Polymer electrolyte, ionic conductivity, poly(ethylene glycol), acrylate.

Complexes of poly(ethylene oxide) (PEO) with alkali metal salts have been widely investigated for their potential application in electrochemical devices[1,2]. Unfortunately, these electrolytes suffer drawbacks from very low ambient ionic conductivity, because the crystalline domains in PEO will impede ion transport[3]. In order to suppress the crystallinity of PEO, network polymer electrolytes with short polyether chains as internal plasticizers have been designed and prepared[4-6]. Recently, network polymer electrolytes based on polyacrylates were reported[7]. However, the influences of the properties of internal plasticizers on ionic conductivity have not been studied. In this paper, we report the effects of the number and length of internal plasticizing chains on the ionic conductivity of the network polymer electrolytes prepared by cross-linking poly(ethylene glycol) acrylates.

Poly(ethylene glycol) diacrylate (PEGDA) and monomethoxy poly(ethylene glycol) acrylates (PEGMA350, 550, 750) were synthesized by esterification of poly(ethylene glycol) with average molecular weight 400 and poly(ethylene glycol) methyl ether with average molecular weight 350, 550 and 750, as shown in **Scheme 1**. The modified method was similar to that described in the literature[8].

Scheme 1 Synthesis of poly(ethylene glycol) acrylates

$$H(OCH_2CH_2)_nR \; + \; CH_2{=}CHCOCl \longrightarrow CH_2{=}CHCO(OCH_2CH_2)_nR'$$

R = OCH_3 or OH, R′ = OCH_3 or $CH_2{=}CHCOO$

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PEGDA, PEGMA, $LiClO_4$ and 2,2′-azobisisobutyronitrile (1.5 wt% with respect to the acrylates) were dissolved in tetrahydrofuran and stirred at room temperature for 2 h. The salt concentration is represented by the molar ratio of the salt to the repeating ethylene oxide units of the poly(ethylene glycol) acrylates ($[Li^+]/[EO]$). The mixture was then cast on a flat poly(tetrafluoroethylene) mold and cured at 80 °C for 4 h. After being dried at 60 °C for 48 h, the sample was sandwiched between two polished stainless steel electrodes and sealed in a testing cell. The ionic conductivity was measured using a HIOKI LCR 3520 Hi TESTER at 1 kHz.

Figure 1 Ionic conductivity as a function of salt concentration

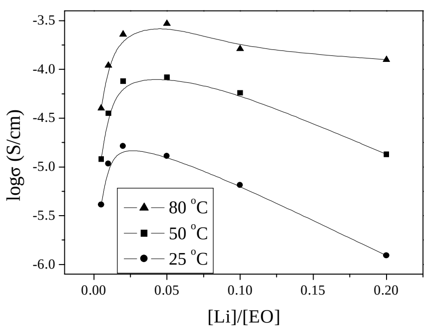
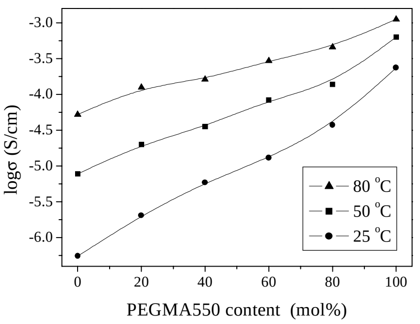


Figure 2 Effect of PEGMA550 content on ionic conductivity

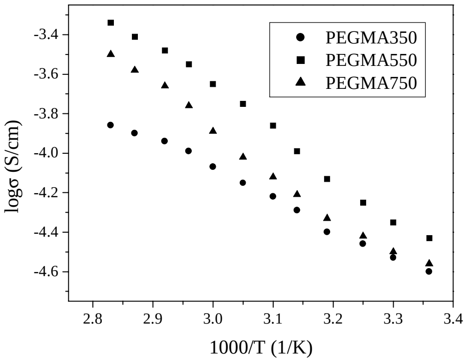


The influence of salt concentration on ionic conductivity is shown in **Figure 1**. There is an optimum salt concentration at which a maximum conductivity appears, showing a typical polymer electrolyte behavior[9,10]. At lower salt concentration, the build-up of charge carriers with the increase of salt concentration leads to an increase in ionic conductivity. However, this will be offset by the formation of ion clusters and decrease of chain flexibility at higher salt concentration. **Figure 1** also shows that the maximum ionic conductivity tends to appear at higher salt concentration and the dramatic drop of ionic conductivity at high salt concentration is reduced with increasing the temperature. This behavior could be rationalized by recognizing the free volume model[11].

Due to the restricted mobility of polymer chains, the ionic conductivity of the electrolyte prepared without PEGMA is as low as 10^{-7} S/cm at 25 °C. **Figure 2** shows the dependence of ionic conductivity on the content of PEGMA550 at $[Li^+]/[EO]=0.02$. The ionic conductivity rises with increasing number of internal plasticizing chains. The increase of ionic conductivity could be attributed to the reduction of cross-linking density and the enhancement of segmental movement in the network matrix. The ionic conductivity represented by overall mobility of ions and polymer chains increases with the introduction of more flexible internal plasticizing chains into the network. However, the mechanical strength of the samples decreases with the increase of PEGMA550 content. When the PEGMA550 content is 80 mol%, the ambient ionic conductivity reaches 3.73×10^{-5} S/cm while maintaining good processability and mechanical strength.

Dependence of ionic conductivity on temperature for the electrolytes with 80 mol%

Figure 3 Temperature dependence of ionic conductivity for network polymer electrolytes



PEGMA at [Li$^+$]/[EO]=0.05 is shown in **Figure 3**. It is noted that the electrolyte prepared with PEGMA550 exhibits the highest conductivity in the overall range of the temperature studied. The high conductivity could be contributed to the enhanced segmental movement as increasing the length of plasticizing chains. The plasticizing chains in PEGMA550 system are more flexible and sufficiently long to solvate more salt, thus the conductivity is higher than that of PEGMA350 system. Unfortunately, the longer polyether chains have a tendency to crystallize and onset of crystallinity occurs[12], which will ultimately decrease the ionic mobility. The relatively low ambient conductivity of the electrolyte based on PEGMA750 could be therefore rationally interpreted. In conclusion, the transport of charge carriers in network polymer electrolytes could be promoted by introduction of free linear oligo(oxyethylene) chains with moderate molecular weight, which could act as internal plasticizers.

Acknowledgments

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