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The influence of the compatibility of plasticizers with polymer ionic conductors on ionic conduction

Abstract The influence of the compatibility of plasticizers on the aggregated structure and the ion-conductive behavior of poly(ethylene oxide)/lithium methoxy di(ethyleneoxy) phenylsulfonate (EO_2PSLi) complex were studied using two plasticizers with different polarity, γ-butyrolactone (BL) and 2,5-di(methyl diglycol)-1,4;3,6-dianhydrous sorbitol ether (DGS), a novel pincer-like plasticizer synthesized in this paper. The DGS can effectively destroy the PEO crystalline phase in PEO/EO_2PSLi complex and increase the amorphous area in which Li^+ cations transport, depending on polymeric segmental movement. However, in BL-plasticized PEO/EO_2PSLi complex, the highly polar BL hardly disrupts PEO crystals and only forms a BL-rich phase, a kind of liquid electrolyte tunnel in which Li^+ mainly transfers.

Key words Compatibility · Plasticizer · Ionic conduction · PEO · Lithium oligoether phenylsulfonate

Introduction

Solid polymer electrolytes (SPEs) have been given extensive attention since they were reported by Wright [1] and Armand [2] owing to their desirable characteristics such as light weight, easy film-formation, good compatibility with lithium metal, no leakage and low self-discharge when used in batteries. However, the conductivities of the ionic conducting polymers without solvents are very low (about 10^{-7}–10^{-5} S cm^{-1}), which limits their applications because the capacity and the discharge current density are too low when they are used as components of lithium batteries. The ionic conductivity can be improved by a large margin if organic plasticizers are added to these conducting polymers. Therefore, an efficient way to increase ionic conductivity for practical applications is to add organic plasticizers to polymer ionic conductors.

Generally, when plasticizers are added to polymer ionic conductors, they should: (1) be able to increase the ionic conductivity substantially, (2) have good compatibility with polymer matrix, and (3) have good chemical and electrochemical stability. Many studies on plasticized polymer electrolytes and polymer gel electrolytes based on the complexes of polymers and inorganic alkali metal salts have been reported [3–11]. The commonly used plasticizers are propylene carbonate (PC), ethylene carbonate (EC), γ-butyrolactone (BL), dimethyl carbonate (DMC), etc. It has been found that these plasticizers can easily migrate in and leak out of the polymer electrolytes. This phenomenon may result in the decrease of ionic conductivity with increasing storage time, simultaneously leading to the formation of a high resistance layer of electrolytic salt in the vicinity of polarized electrodes [12]. It is demonstrated from the phenomena of the migration of plasticizers in plasticized polymer electrolytes and polymer gel electrolytes that the presently used plasticizers such as PC, EC, BL, etc. have poor compatibility with polymer matrixes. This poor compatibility in turn influences the stability of the ionic conductivity of the polymer electrolytes.

In this paper, a novel kind of pincer-like plasticizer, 2,5-di(methyl diglycol)-1,4;3,6-dianhydrous sorbitol ether (abbreviated as DGS) has been designed and synthesized. The influence of this plasticizer and BL on the aggregated structure and the ionic conductivity of PEO/lithium methoxydi(ethyleneoxy)phenylsulfonate (abbreviated as EO_2PSLi) complex will be studied. The purpose of the employment of PEO/organic lithium salt complex as the studied matrix is to eliminate the influence of the interactions between the electrolytic salts such as $LiClO_4$ and the plasticizers.

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Experimental

Synthesis of 2,5-di(methyl diglycol)-1,4;3,6-dianhydrous sorbitol ether (DGS)
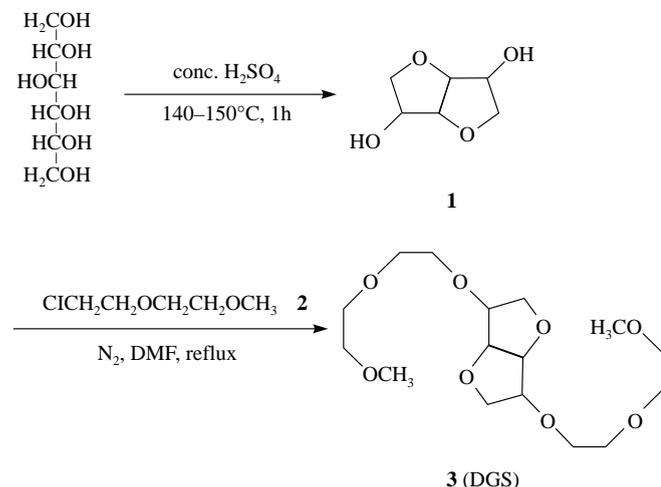
1,4;3,6-dianhydrous sorbitol (**1**) [13] and methyl di(oxyethylene) chloride (**2**) [14] were synthesized according to literature methods.

Into a dry flask were added 0.05 mole 1,4;3,6-dianhydrous sorbitol (**1**), 0.50 mole methyl di(oxyethylene) chloride (**2**), 0.15 mole anhydrous K_2CO_3 and 250 ml dry DMF. After refluxing for seven days under dry N_2 atmosphere, the solid was filtered off. All DMF and unreacted methyl di(oxyethylene) chloride in the filtrate were removed on a rotary evaporator under reduced pressure. The residue was further fractionally distilled under reduced pressure, and the fraction, a pale yellow viscous liquid, of b.p. 140–142°C/0.5 mmHg was collected. The yield is 52.0%. FTIR (cm^{-1}): 2932 ($v_{as,C-H}$), 2874 ($v_{s,C-H}$), 1457 ($\delta_{as,C-H}$), 1355 ($\delta_{s,C-H}$), 1249 ($v_{as,C-O-C}$), 1199 ($v_{as,C-C-O}$), 1111 ($v_{s,C-C-O}$), 1011 ($v_{s,C-O-C}$). ^{1}HNMR (in D_2O) δ (ppm): 3.67 (s, 4H, $2 \times CH_2$ of ring), 3.59 (s, 16H, $8 \times CH_2$ of non-ring), 3.39 (s, 6H, $2 \times CH_3$), 2.28 (s, 4H, $4 \times CH$). Elemental analysis: calc for $C_{16}H_{28}O_8$ C 54.86%, H 8.57%; found C 54.22%, H 8.39%. It is shown that this compound is the required one, i.e., 2,5-di(methyl diglycol)-1,4;3,6-dianhydrous sorbitol ether (**3**, DGS).

Synthesis of lithium methoxy di(ethyleneoxy) phenylsulfonate (EO₂PSLi)

Lithium methoxy di(ethyleneoxy) phenylsulfonate (EO$_2$PSLi) was synthesized according to the former paper [15]. The structure is shown in the following:

$$LiO_3S \text{---} \bigcirc \text{---} OCH_2CH_2OCH_2CH_2OCH_3$$

Preparation of the plasticized complex films

Into anhydrous methanol solutions of PEO/EO$_2$PSLi complex with EO/Li$^+$ molar ratio of 25:1 were respectively added DGS, BL and DGS–BL mixtures (DGS/BL weight ratio of 3:7, 5:5 and 7:3, respectively). The plasticizers' contents in the complex are from 7.4 to 44.3 wt%. When all methanol was removed, the solid polymers were pressed into thin films with a thickness of about 100–200 mm. The films were then dried in a vacuum oven at a temperature of 40 °C for 24 h.

Measurements

An a.c. ionic conductivity measurement of PEO/EO$_2$PSLi/plasticizer complexes was carried out with a DDS-11 A type conductometer at 1100 Hz and in a temperature range of 10–70 °C. The thermal behavior was determined with a Perkin-Elmer DSC-7 system in the temperature range from −100 °C to 100 °C and the heating rate was kept at 20 °C/min. The crystalline morphology of the complex was photographed using a polarizing microscope. Before photographing, the films were annealed in an oven at 70 °C for at least 5 h.

Results and discussion

Plasticization of DGS and BL to PEO/EO₂PSLi complex

Figure 1 shows the influence of the content of plasticizers DGS and BL in PEO/EO$_2$PSLi/plasticizer complexes on the ionic conductivity at ambient temperature. It is seen that the ionic conductivity increases with increasing plasticizer content, which is in accordance with the normal understanding of the influence of plasticizer content on ionic conductivity of solid polymer electrolytes. Once the DGS content is higher than 20 wt%, the conductivity of the PEO/EO$_2$PSLi/DGS complex does not increases much, while the increase of the conductivity of PEO/EO$_2$PSLi/BL complex increases rapidly until the BL content is over 35 wt%. This reflects that different molecular structures of the plasticizers have different influence on polymer ionic conductivity.

The temperature dependence of ionic conductivity of DGS- and BL-plasticized PEO/EO$_2$PSLi complexes is plotted in Fig. 2. Obviously, the correlation between ionic conductivity and temperature for DGS-plasticized complex gives positive curves despite the DGS content. The temperature dependence of ionic conductivity for BL-plasticized complex, however, is a positive curve only when the BL content is smaller than a certain concentration and shows a straight line when BL is in
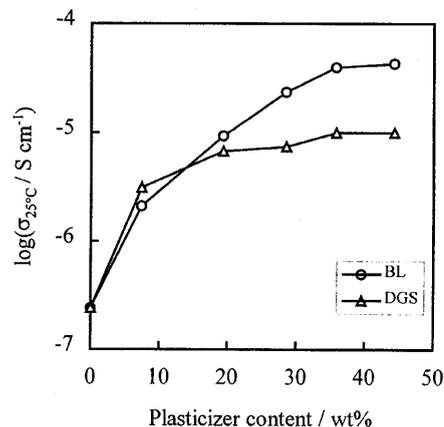
Fig. 1 Influence of plasticizer content on the ambient temperature ionic conductivity of plasticized PEO/EO$_2$PSLi complex with EO/Li$^+$ = 25 : 1

high concentration. It is demonstrated that the ionic conduction in PEO/EO$_2$PSLi/DGS complex follows the WLF [15] equation which describe the temperature dependence of the conductivity in terms of the chain segment mobility of the polymer host material, while the ionic conduction in PEO/EO$_2$PSLi/BL complex changes from WLF type at low BL content to Arrhenius behavior at high BL content.

The polarizing microscopic photographs (Fig. 3) reveal that a large difference exists in the micromorphologies of DGS- and BL-plasticized PEO/EO$_2$PSLi complexes. When the plasticizer content reaches 44.3 wt%, the spherulitic crystalline structure of PEO in DGS plasticized complex disappears, while the spherulitic crystals in BL plasticized complex only becomes smaller. However, in the latter complex, a plasticizer-rich phase appears around the spherulitic crystals. It can be deduced that, in the high BL content complexes, the ionic conductivity mainly comes from the contribution of lithium ions transporting in the plasticizer-rich phase. The relationship between the ionic conductivity and temperature follows the Arrhenius behavior as in the usual liquid electrolyte complexes. This also demonstrates that the compatibility of DGS with PEO is better than that of BL with PEO.
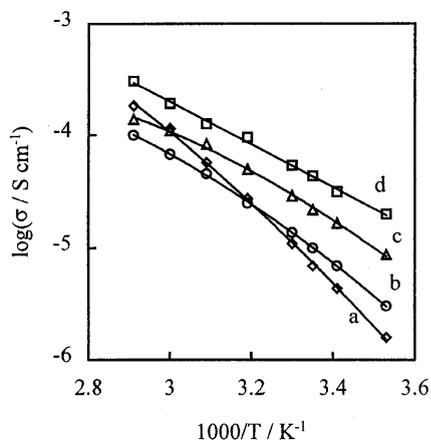
From the DSC curves of DGS- and BL-plasticized PEO/EO$_2$PSLi complexes, the glass transition temperature (T_g) and the melting temperature (T_m) of these complexes are obtained, and these are listed in Table 1. It can be seen that the T_g and T_m of PEO/EO$_2$PSLi/DGS-plasticized complexes drop sharply compared to those of unplasticized complexes. However, BL has little effect on T_g and T_m for BL-plasticized complexes. This also demonstrates that the compatibility of DGS with PEO is better than that of BL with PEO.

The above results indicate that the difference of the ionic conduction in DGS- and BL-plasticized PEO/EO$_2$PSLi complexes chiefly results from the difference of the compatibility of these two plasticizers with the polymer matrix PEO. In the complex of PEO/EO$_2$PSLi/DGS, the good compatibility of DGS with PEO means that DGS can permeate through the inside of PEO macromolecular coils, degrade the short-range interactions among polymer chains, efficiently destroy the PEO crystals and decrease the viscosity of segmental movement. As a result, the T_g and T_m of the complex decrease sharply, which in turn increases the ionic conductivity. The change of crystalline phase can be seen from Fig. 3a,b. In the meantime, since DGS itself possesses two oligoether chains resembling two open 12-crown-4 ether structures, these pincer-like oligoether chains can mix well with PEO macromolecules to form a unique phase and improve the interactions between the polymer molecules and the plasticizer. Lithium cations transport depending on the segmental movements of PEO macromolecules, and the ionic conduction follows WLF behavior. Even at

Fig. 2 Temperature dependence of ionic conductivity for plasticized PEO/EO$_2$PSLi complex with EO/Li$^+$ = 25:1: **a** DGS 28.5 wt%, **b**

Table 1 DSC data for PEO/EO$_2$PSLi complex with EO/Li$^+$ = 25 : 1 before and after plasticization by DGS and BL

Plasticizer		T_g (°C)	T_m (°C)
None		−55.2	49.6
BL	28.5%	−62.7	47.9
	44.3%	−64.9	51.5
DGS	28.5%	−80.0	38.4
	44.3%	−84.3	35.6

Fig. 3a–c Polarizing microscopic photographs of DGS- and BL-plasticized PEO/EO$_2$PSLi complex with EO/Li$^+$ = 25 : 1 (Amplification ×50): **a** No plasticizer, **b** DGS 44.3 wt%, and **c** BL 44.3 wt%
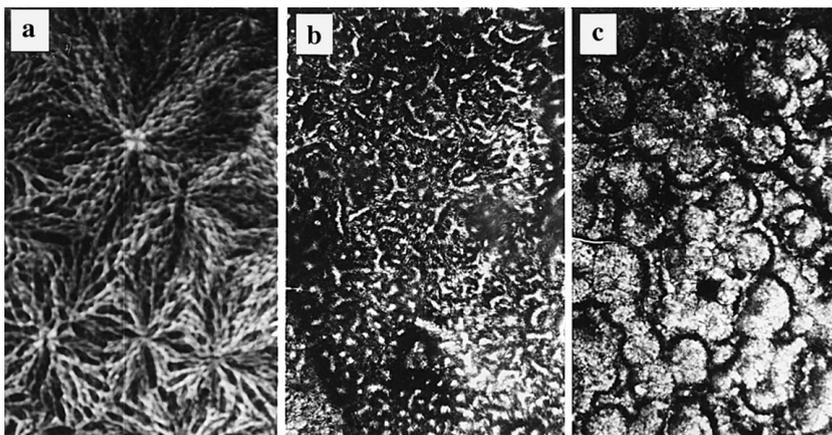
higher DGS content, the plasticized complex still maintains the characteristic of WLF conductive behavior.

However, in the complex of PEO/EO_2PSLi/BL, BL can hardly penetrate through the inside of PEO macromolecular coils and exists only in the regions among PEO macromolecular coils or in zones among the broken PEO crystalline edges to form passing tunnels similar to a liquid electrolyte: a BL-rich phase (shown as Fig. 3c). Therefore, BL has little influence on the T_g and T_m of the complex. When the BL content of the complex is low, BL dissolves only a little EO_2PSLi. Li^+ cations exist in the PEO/EO_2PSLi complex and BL tunnels simultaneously. The transport of Li^+ cations follows the WLF behavior in the complex, depending on polymer segmental movements and the Arrhenius type in BL tunnels (shown as Fig. 2c). When the BL content in the complex is high, BL can extract nearly all EO_2PSLi from the complex so that Li^+ cations mainly transport in BL tunnels, exhibiting the Arrhenius conducting behavior (Fig. 2d). Since the activation energy which the ions need to transport in BL tunnels is lower than that

in segmental movements, the ionic conductivity of BL-plasticized complex is higher than that of DGS-plasticized complex. However, because of the poor compatibility of BL with PEO, BL and PEO form two separate phases which do not completely dissolve in each other. BL may migrate easily out of the electrolyte. Therefore, the stability of ionic conductivity with the increase of storage time will be decreased.

Influence of DGS-BL mixture on ionic conductivity of PEO/EO_2PSLi complex

The good compatibility of DGS plasticizer with PEO/EO_2PSLi complex can effectively decrease the crystallinity of PEO and the migration of the plasticizer out of the polymer electrolyte. However, due to the higher freezing point and higher viscosity, DGS cannot improve the ionic conductivity of the complex as much as other plasticizers, such as PC, EC or BL. Therefore, the use of a DGS and BL mixture may improve the general properties of polymer ionic conductors by taking advantage of the good compatibility of DGS with PEO and the low viscosity and high polarity of BL.

Figure 4 shows the influence of changes in the content or composition of a DGS-BL mixture on the isothermal ionic conductivity of PEO/EO_2PSLi complex. With increasing DGS content and decreasing BL content in the DGS-BL mixture, the ionic conductivity of the plasticized PEO/EO_2PSLi complex increases gradually and reaches a maximum at the DGS-BL weight ratio of 3:7.

In the PEO/EO_2PSLi complex, plasticized by DGS-BL mixture, DGS penetrates into the inside of PEO macromolecular coils and destroys the PEO crystals, so that the amorphous range in the complex increases. At the same time, the liquid electrolytic tunnels formed by BL among PEO crystals increases. Therefore, the transport of free ion carriers in the complex depends not only on the segmental movements of PEO macromolecules in the amorphous range but also on the migration in the BL liquid electrolytic tunnels. When the composition of DGS and BL reaches an optimum ratio, the ionic conductivity of PEO/EO_2PSLi complex plasticized
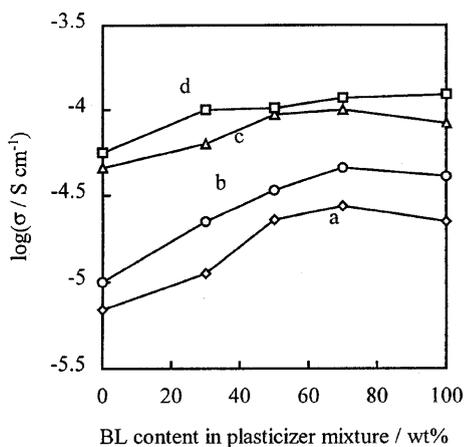
Fig. 4 Influence of the composition of DGS-BL mixture on the isothermal ionic conductivity of the plasticized PEO/EO_2PSLi complex with $EO/Li^+ = 25 : 1$: **a** DGS-BL 28.5 wt%, 25 °C, **b** DGS-BL 44.3 wt%, 25 °C, **c** DGS-BL 28.5 wt%, 50 °C, **d** DGS-BL 44.3 wt%, 50 °C

Fig. 5a–c Polarizing microscopic photographs of PEO/EO_2PSLi complex plasticized with DGS-BL mixture with $EO/Li^+ = 25 : 1$. Amplification ×50, plasticizer content 44.3 wt%. DGS-BL composition: **a** 7 : 3, **b** 5 : 5, and **c** 3 : 7
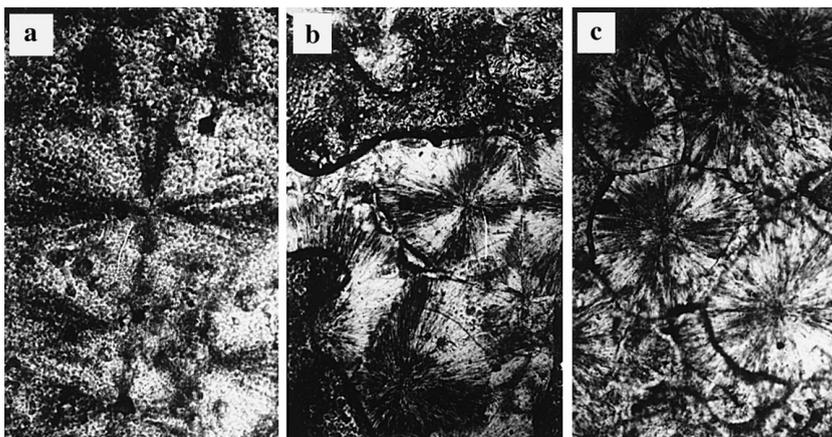
by DGS-BL mixture will be higher than that of a single-composition plasticized complex.

From the polarizing photographs of PEO/EO$_2$PSLi complexes plasticized by DGS-BL mixtures shown in Fig. 5, it is easy to observe that with the increase of DGS content, PEO spherulite crystals gradually get smaller, while the amorphous range increases. This change benefits the conduction of lithium cations based on segmental movement in the amorphous range and improves the ionic conductivity. Simultaneously, however, because of the decrease of BL content, the transport of lithium cations in liquid electrolyte decreases. These two contrary effects lead to a maximum ionic conductivity appearing when the weight ratio of DGS/BL is 3 : 7. Since the contribution of Li$^+$ transport to the ionic conductivity in BL liquid electrolyte is greater than that among polymer segments, the ionic conductivity of the plasticized complex will decrease macroscopically when the DGS content increases further in the mixture plasticizer.

Conclusions

Plasticizers with different polarity and different molecular structure have a significantly different influence on ionic conductive behavior for PEO/EO$_2$PSLi complexes. When the plasticizer has good compatibility with the polymer matrix, it is favorable to degrade the short-range interaction between polymer chains and in turn to improve the ionic conductivity.

The plasticizer DGS, synthesized in this paper, can efficiently destroy the spherulitic crystals of PEO in PEO/EO$_2$PSLi complex and increase the amorphous range in which transport of Li$^+$ cations is based on polymeric segmental movement. As a result, the ionic conductivity can be improved. However, in BL-plasticized PEO/EO$_2$PSLi complex, BL hardly penetrates through PEO macromolecular coils and forms a BL-rich phase, a kind of liquid electrolyte tunnel in which Li$^+$ cations mainly transport. Due to the poor compatibility of BL and PEO, BL may easily migrate out of the electrolyte and influence the stability of the conductivity. The use of DGS and BL mixture could improve the general properties of the polymer ionic conductors.

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