

SINGLE-ION CONDUCTIVITY IN POLY (LITHIUM PROPIONATE METHYL SILOXANE)

FANG Shibi (方世璧), MA Yanguang (马延光), GUO Defan, (郭德凡)

LI Yongjun (李永军) and JIANG Yingyan (江英彦)

(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

HUANG Xuejie (黄学杰) and CHEN Liquan (陈立泉)

(*Institute of Physics, Academia Sinica, Beijing 100080*)

ABSTRACT

Poly(lithium propionate methyl siloxane) as a single-ion carrier source was synthesized. The crosslinked film showed lower lithium ionic conductivity at room temperature (about 10^{-10} S/cm). However, the lithium ionic conductivity was obviously increased by blending with high polar polymers such as polyethylene oxide, poly(methylsiloxane-co-ethylene oxide) and poly(methylsiloxane-g-ethylene oxide). In the blend system a high conductivity of 10^{-7} – 10^{-5} Scm^{-1} at room temperature was obtained and the single-ion conductivity was deeply influenced by the content of the poly(lithium propionate methyl siloxane). The dc ionic conductivity of the flexible crosslinked films is more stable over time.

INTRODUCTION

Polymer salt complexes with significant ionic conductivity have been received great attention as electrolyte materials in high energy density solid state batteries^[1–3]. For this application the polymer electrolyte has an additional advantage of being soft, which helps in making good and lasting interfacial contact between the electrolyte and various electrode materials.

The polymer solid electrolyte has been widely investigated in the polymer salt hybrid system. The material used has been focused on the polyether polymers complexes with various inorganic salts^[4–9], in which the polysiloxane containing high polar group electrolytes have a high ionic conductivity^[10–13]. The dc conductivity is decreased by long dc polarization in the bi-ion conductors.

Recently, only a few reports on the single-ion polymeric conductors appeared^[14–18], because it is required for such uses as dry batteries, sensory systems, and capacitors. Up to now the single-ion conducting polymers reported include the poly(diallyl dimethyl ammonium chloride) or poly(diallyl trifluoromethyl sulfonate)^[14], sodium salt of polystyrene sulfonate^[14], poly(alkali methyl methacrylate-co-oligo oxyethylene methacrylate)^[15–18], poly(2-sulphoethyl methacrylate-Li salt)^[6], poly(2-(4-carboxy hexafluoro-butanoyloxy) ethyl methacrylate-Li salt)^[17].

In the present paper, the poly(lithium propionate methyl siloxane) as single ion carrier source was synthesized. The electrochemical properties of the network films in the block copolymer of poly(lithium propionate methyl siloxane) and

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poly (oligoxyethylene methyl siloxane) were investigated. The plasticizer is known to increase ionic conductivity in polymeric solid electrolytes. The conductivity in a plasticized single ion conductor was also studied.

EXPERIMENTAL

1. Materials

Poly (β -carboxyethylmethylsiloxane), poly (methylsiloxane-*g*-ethylene oxide) [poly (MS-*g*-EO)] and poly (methylsiloxane-co-ethylene oxide) [poly (MS-co-EO)] were prepared according to the literature^{[19,20],[12],[11]}, respectively. In the copolymers, the molecular weight of PEO used was 400 and the T_g of poly (MS-*g*-EO) and poly (MS-co-EO) was determined to be about -70°C and -60°C respectively.

Lithium salt of poly (methyl carboxyethylsiloxane) was obtained by adding the stoichiometric amount lithium hydroxide in aqueous solution to poly (β -carboxyethylmethylsiloxane). The resulting mixture was dried and evacuated by vacuum at 50°C for 8h. By neutralizing with various amount of LiOH, the polymers containing different content of lithium ions were prepared. The IR spectra ($-\text{COOH}$, 1700cm^{-1} ; COOLi , 1560cm^{-1}) and ^1H NMR spectra also confirmed the structure of the polymers.

Polyethylene oxide (PEO), propylene carbonate (PC), LiOH and LiClO_4 was purchased without any further treatment.

2. Film preparation

The film of poly (lithium propionate methyl siloxane) was prepared by casting the viscous aqueous solution of the polymer on a Teflon plate and being allowed to evaporate at 80°C for 8h. The film was stored over P_2O_5 for 3 days and under vacuum at 50°C for 2 days before measurement.

The methanol solution of poly (lithium propionate methyl siloxane) was mixed with PEO or poly (MS-*g*-EO), crosslinking agent (polymethyltriethoxysiloxane or tetraethylorthosilicate) and a few dibutyltin dilaurate, PC (if any), and vulcanizing at room temperature. The network film was stored over P_2O_5 for 3 days and under vacuum at 50°C for 2 days.

The methanol solution of poly (lithium propionate methyl siloxane) was mixed with poly (MS-co-EO). After well-mixing, the viscous liquid was casted into Teflon plate and vulcanized at room temperature. The film was laid under vacuum at 50°C for 2 days and stored over P_2O_5 for 3 days.

3. Measurement

The conductivity of the single-ionic electrolyte measured by HP4192A LF Impedance Analyzer. Stainless steel was used as electrode. DSC was measured by Dupont 1090. Solartron Model 1174 Frequency Response Analyzer was used to measure impedance behavior.

The lithium ion transference number (t_{Li^+}) was determined from the impedance of cell $\text{Li}/\text{sample}/\text{Li}$ according to the $t_{\text{Li}^+} = R_b / [V/I_\infty - R_c]$ equation^[22-23],

Here R_b is the bulk resistance and R_c is the charge transfer resistance. I_∞ can be obtained from potentiostatic polarization measurements.

RESULTS AND DISCUSSION

1. Cation conductivity of various lithium salifying content of poly(methylcarboxyethyl siloxane)

Various lithium salifying contents of poly(methyl carboxyethyl siloxane) were prepared by reaction of various molar ratio of LiOH and poly(methyl carboxyethyl siloxane). The single-ion conductivity and glass transition temperature (T_g) for various lithium salifying contents of poly(methyl carboxyethyl siloxane) are shown in Fig. 1

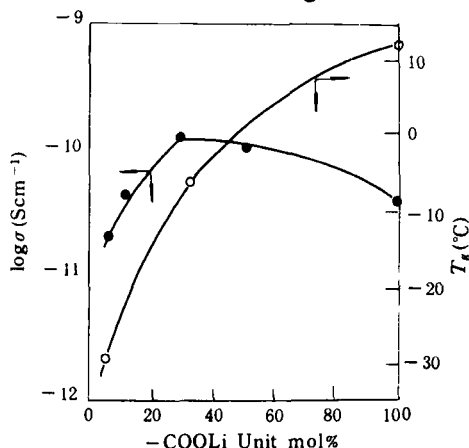


Fig. 1 Cation conductivity and T_g of various lithium salifying content of poly(methyl carboxyethyl siloxane)

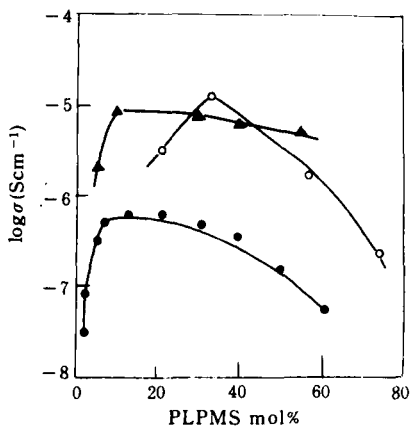


Fig. 2 Dependence of ionic conductivity on content of PLPMS for poly(MS-co-EO) (○); PEO-400 (●); poly(MS-g-EO) (▲) systems

100% lithium salifying of poly(methyl carboxyethyl siloxane), also refers to the polymer as poly(lithium propionate methyl siloxane)(PLPMS), has a very low ionic conductivity (about $10^{-11} \text{ S cm}^{-1}$) because the lithium carboxylate bonding on polymer possesses larger disassociation energy and higher glass transition temperature (as shown in Fig. 1). However, partly lithium salifying poly(methyl carboxyethyl siloxane) has a higher ionic conductivity (about $10^{-10} \text{ S cm}^{-1}$) than poly(lithium propionate methyl siloxane). It may be attributed to the interaction between the carboxylic acid group and the lithium propionate group, the near polar group can associate the diassociation of lithium propionate group. As the lithium salifying poly(methyl carboxyethyl siloxane) increases, the number of carrier ions increases while the microviscosity at the conduction column in the film increases (as Fig. 1 the T_g increases). The ionic conductivity of 30% lithium salifying poly(methyl carboxyethyl siloxane) reached maximum.

2. Single ion properties in polar matrixes

Increasing the polarity of the matrix is known to increase ionic conductivity of the polymer solid electrolytes. Poly(methylsiloxane-g-ethylene oxide)[poly(MS-g-EO)], poly(methylsiloxane-co-ethylene oxide)[poly(MS-co-EO)] and PEO was used as plasticizer. The formers, polysiloxane derivatives, can be vulcanized together with poly(lithium propionate methyl siloxane) to form films. The latter, PEO acted only as plasticizer, which is known to increase polymer chain flexibility,

increases free volume and decreases the T_g . The dependence of ionic conductivity on the content of PLPMS for PEO, poly(MS-co-EO) and poly(MS-g-EO) were shown in Fig. 2.

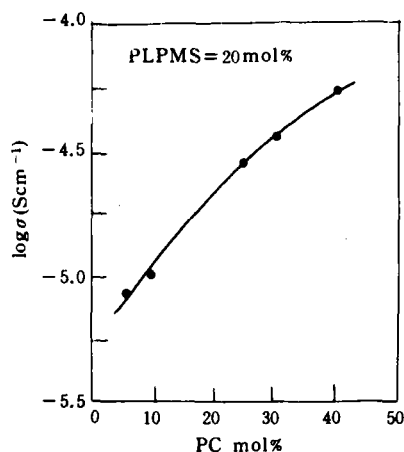


Fig. 3 Dependence of ionic conductivity on PC content of Poly(MS-g-EO)-PLPMS system

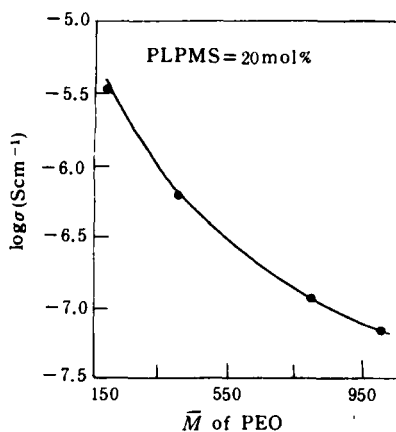


Fig. 4 Dependence of the molecular weight of PEO on the conductivity in the PEO-PLPMS system

It showed that the ionic conductivity of the PLPMS was increased by producing blends of poly(MS-co-EO), poly(MS-g-EO) and PEO. The polymethylsiloxane containing ethylene oxide polar chain units, poly(MS-co-EO) and poly(MS-g-EO) are more effective than PEO because the formers have a higher flexibility of the polymer chain (lower T_g) and a better solubility with PLPMS than PEO. The PLPMS content for maximum ionic conductivity was 10 mol%, 30 mol% and 10 mol%, respectively. The high PLPMS content of maximum ionic conductivity for poly(MS-co-EO) system may be attributed to the very good solubility, in the system the PLPMS can be fully dispersed. It is worth noting that the single-ion conductivity in the polyorganosiloxane system is as high as 1.4×10^{-5} S cm⁻¹ at room temperature without high polar organic solvent and increased by 5 orders magnitude than that of only PLPMS system. It exhibited well that the polyorganosiloxane ion-conductor is a kind of excellent polymer solid electrolyte.

The aprotic solvent with large dielectric constant, propylene carbonate (PC), was selected as additive. The ionic conductivity of the poly(MS-g-EO)-PLPMS system by addition of PC is shown in Fig. 3. It exhibits the increase of the conductivity with an increase in PC amount added in this system. It may be ascribed to predict that the PC further promotes the dissociation of PLPMS.

Using PEO as the plasticizer, the effect of the molecular weight of PEO on the conductivity is shown in Fig. 4. It shows that the lower molecular weight of PEO is preferable for that ion-conductor belong to the good solubility with PLPMS and the amorphous structure. In this system the addition of PC has no effect on the conductivity.

3. Temperature characteristics

The temperature dependence of ionic conductivity in poly (MS-co-EO) - PLPMS Poly (MS-g-EO) - PLPMS and PEO-PLPMS was summarized in Fig. 5(a), (b) (c), respectively.

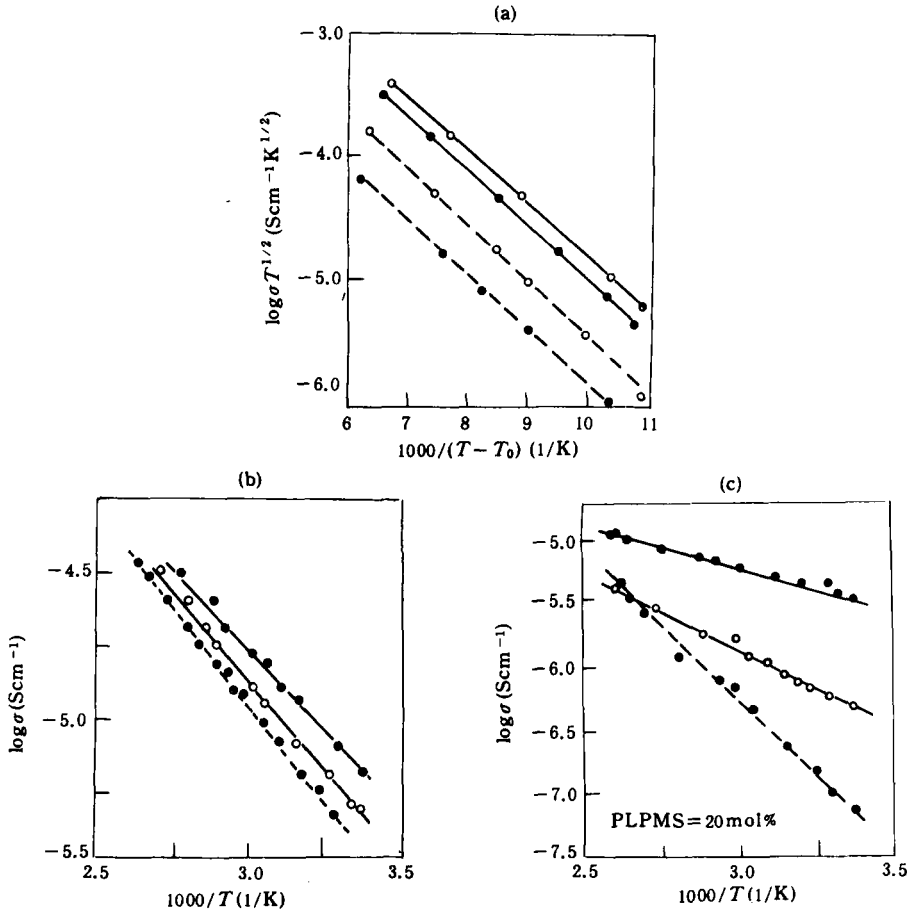


Fig. 5 The temperature dependence of the conductivity in poly (MS-co-EO)-PLPMS (a), poly (MS-g-EO)-PLPMS (b) and PEO-PLPMS (c)

The temperature dependence of the conductivity in poly (MS-g-EO)-PLPMS and PEO-PLPMS was as line obeyed Arrhenius equation (1), but in poly (MS-co-EO)-PLPMS system (different incorporation) did not follow Arrhenius equation. However the curve could be interpreted by using the Vogel-Tamman-Fulcher (VTF) equation (2), so that the linear VTF plots are obtained. (Fig. 5(a))

$$\sigma = A \exp (-E_a / K T) \tag{1}$$

$$\sigma = (A / T^{1/2}) \exp [-E_a / R(T - T_0)] \tag{2}$$

Where T_0 is defined as $T_g - 50 \text{ }^\circ\text{C}$ [21]. T is the absolute temperature, A , K , R , a constant, E_a an apparent activation energy.

From the slope of the straight lines in Fig. 5(b), it is shown that the

activation energy for ionic conduction, E_a increases with an increase of PLPMS content in the poly (MS-*g*-EO)-PLPMS system due to the increase of the $T_g^{[12]}$.

From Fig. 5(c), it is shown that the activation energy for ionic conduction, E_a increases with increasing molecular weight of PEO because of the increase of the degree of crystallization.

4. Single ion characteristics

Time dependence of the dc ionic conductivity in poly (MS-*co*-EO)-PLPMS, poly (MS-*g*-EO)-PLPMS and PEO-PLPMS single-ion conductor systems and corresponding bi-ion conductor with LiClO_4 systems were shown in Fig. 6(a), (b), (c), respectively. It should be noted that the ionic conductivities in the single-ion conductor system have better time stability. While that in corresponding bi-ion conductor systems decreased markedly with prolonged supply of dc potential. It is attributed to that in the single-ion systems as carboxylate anions were covalently bonded on polysiloxane chain in PLPMS and difficult to move under dc polarity.

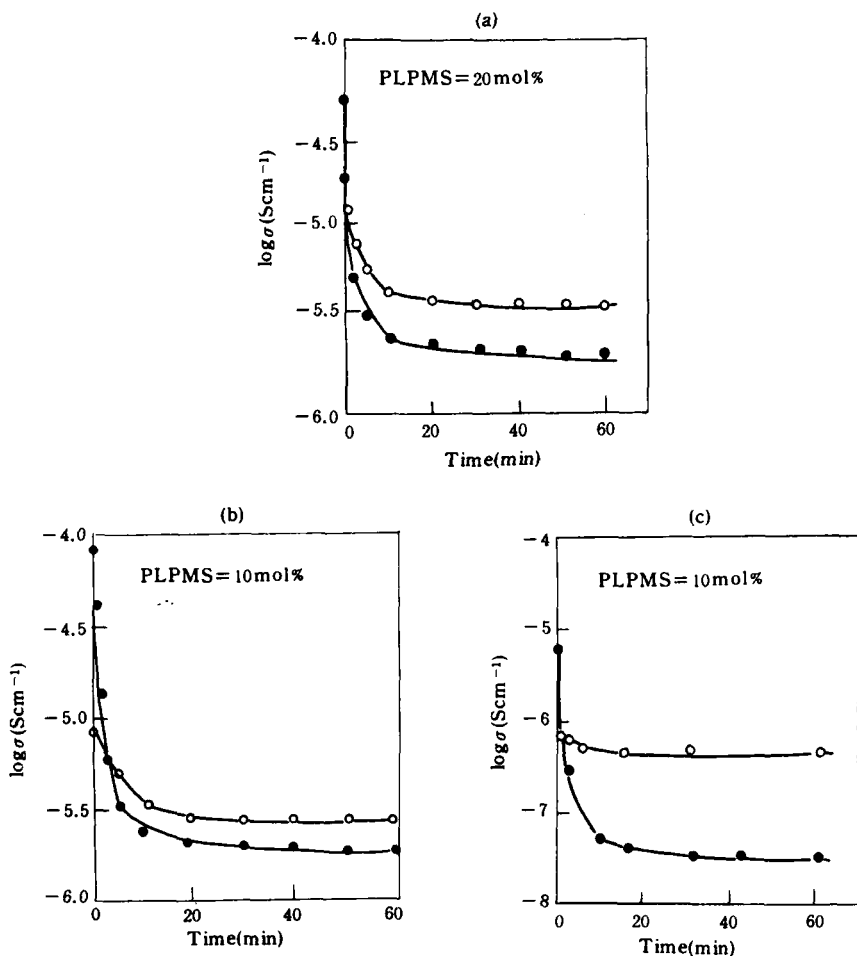


Fig. 6 Time dependence of the dc ionic conductivity in poly (MS-*co*-EO)-PLPMS (a), poly (MS-*g*-EO)-PLPMS (b) and PEO-PLPMS (c). Single-ion conductor systems (○) and corresponding bi-ion conductors (●).

In the poly (MS-co-EO)-PLPMS system the transference number was determined by method proposed by Ogata^[22,23]. The transference number of cation was therefore calculated to be 0.91, which closed to 1. It is concluded to be a cationic single-ion conductor.

5. Conclusion

The single-ion conductors were prepared by the copolymerization or blend of PLPMS and polysiloxane containing high polar chain unit or PEO. The single-ion conductor system, particularly the poly (MS-co-EO)-PLPMS system showed high ion conductivity, which reached to $1.4 \times 10^{-5} \text{ Scm}^{-1}$ at room temperature without any high polar organic solvent, and the ionic conductivity for Li ions was more stable over time.

Key words:

Single-ion conductor; Polysiloxane derivatives; poly (lithium propionate methyl siloxane)

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