

IONIC CONDUCTIVITY OF POLY (β -ALKOXYCARBONYLETHYLMETHYLSILOXANE) - LiClO_4 CROSSLINKED FILMS

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ABSTRACT

Poly (β -carboxyethylmethylsiloxane) - LiClO_4 and poly (β -alkoxyethylmethylsiloxane) - LiClO_4 crosslinked films have been prepared. The ionic conductivity of the films depends on the polymer species, concentration of lithium perchlorate, temperature and content of crosslinking agent. The effect of high polar organic solvent 1, 4-butyrolactone on the ionic conductivity and mechanical properties of poly (β -carboxyethylmethylsiloxane) - LiClO_4 system was also investigated.

INTRODUCTION

Fast-alkali ion transport in complexes formed by alkali metal salts and poly (ethylene oxide) (PEO) was first observed by Wright and co-workers^[1, 2]. Armand et al. reported more extensive studies on the alkali metal salts of polyethers and proposed the application of these complexes to solid-state devices^[3, 4]. After that polymeric solid electrolytes with high ionic conductivity have been of great interest in theoretical research for their important potential application in high energy density dry batteries, capacitors, specific ion sensors, electrochromic displays and other electrochemical devices because of their advantageous mechanical properties and ease of fabrication to thin films^[5, 6, 7].

Vibrational spectroscopy^[8], X-ray diffraction^[9], and EXAFS spectroscopy^[10] studies have provided structure information for PEO-salt complexes. For sodium and lithium complexes, the cations are coordinated to the lone-pair electrons on the polyether oxygen atoms and reside within the helical tunnel of PEO^[9]. In this respect, they are similar to the complexes formed between alkali metal salts and crown-ethers^[11]. However, at room temperature the ionic conductivity of alkali cation-PEO complexes is not high enough for practical application (10^{-6} Scm^{-1}). And the ionic transport was found to occur mostly in amorphous region^[12, 13].

Efforts to improve ionic conductivity in polymer-salt systems generally fall into three categories, which include (1) the PEO system is modified by grafting, copolymerizing and so on^[14, 15]; (2) different types of polymers are synthesized such as poly (ethylene succinate)^[16, 17], poly (ethylenimine)^[18], and poly (alkylene sulfides)^[19], and (3) organic polar polymer/additive systems are investigated^[20, 21].

It has been found that the ionic conductivity of polymeric solid electrolytes is closely related to the polarity and segmental motion of the polymer used, as well as the dissociation energy of metal salts. The high polar groups in polymer are responsible

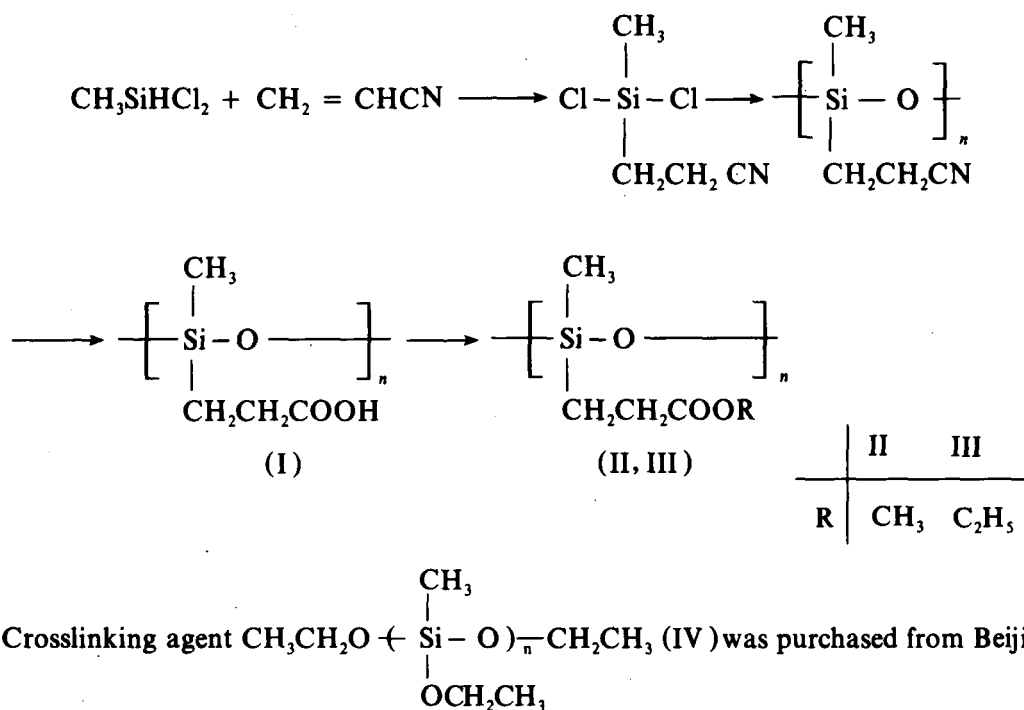
for the hopping-site of carrier ions, and large segmental motion of polymer chain can decrease potential barrier for ion transport. As well known, polysiloxanes have excellent flexibility and very low glass transition temperature and their dielectric constant can be greatly improved if high polar groups are attached to the polymer backbone. Thus, high ionic conductivity may be obtained from polysiloxane system hybridized with alkali metal salts of low lattice energy^[24, 25, 26].

In this paper, we have studied the ionic conductivity of crosslinked poly (β -carboxyethylmethyilsiloxane)–LiClO₄ and poly (β -alkoxycarbonylethylmethyilsiloxane)–LiClO₄ network films, as well as its dependence on polymer species, concentration of lithium ions, temperature, content of crosslinking agent, and content of high polar organic solvent 1, 4-butylolactone.

EXPERIMENTAL

Materials

Poly (β -carboxyethylmethyilsiloxane) (I) and poly (β -alkoxycarbonylethylmethyilsiloxane)s (II, III) were prepared as the following scheme according to the literature^[22, 23].



No. 2 Chemical Factory.

The structure of the polymers were confirmed by H¹ NMR spectra and IR spectra.

Preparation of the network films

The acetone solution of lithium perchlorate was added to the mixture of preweighed polymer, crosslinking agent (IV) and butylolactone (if any). Some more acetone was added to dissolve the mixture completely. Then, the solvent was evaporated and a small drop of dibutyltin dilaurate was added as catalyst. After well-mixing, the viscous liquid cast into a Teflon mode and vulcanized at room temperature. The film was laid under vacuum at 100 °C for 24 hours and stored in a

dryer with P₂O₅ for 3 days before measurement.

Measurements

The ionic conductivity of the network film was determined with QF-2790 RCL Bridge in argon atmosphere. T_g of the films was measured with Du Pont Instruments 1090 Thermal Analyser at a heating rate of 20 °C/min. ¹H NMR spectra were recorded on EM360L in CD₃COCD₃. IR spectra were obtained with JASCO A-100.

RESULTS AND DISCUSSION

The ionic conductivity of the thin films of I-LiClO₄, II-LiClO₄ and III-LiClO₄ are compared in Fig. 1 in respect to the content of lithium salts. It is shown that II and III-LiClO₄ hybrid films exhibited the ionic conductivity of 10⁻⁵ Scm⁻¹ at room temperature, while that of I-LiClO₄ films just reached 10⁻⁶ Scm⁻¹. The β-carboxyethyl group of poly(β-carboxyethylmethylsiloxane) can react with lithium ion and forms lithium carboxylate, which has a high dissociation energy^[27]. The lower ionic conductivity of I-LiClO₄ compared with II- and III-LiClO₄ may be attributed to the partly formation of the lithium carboxylate.

Table 1 T_g of hybrid films

Polymer	Li wt%	IV wt%	$T_g/^\circ\text{C}$
II	4	20	-25.0
II	16	20	-23.0
II	20	20	-22.5
II	10	16.2	-25.1
II	10	19.6	-23.3
II	10	28.1	-20.7
III	4	20	-45.0
III	8	20	-31.1
III	16	20	-28.0
III	10	13.4	-36.0
III	10	20.8	-25.8
III	10	29.4	-16.3

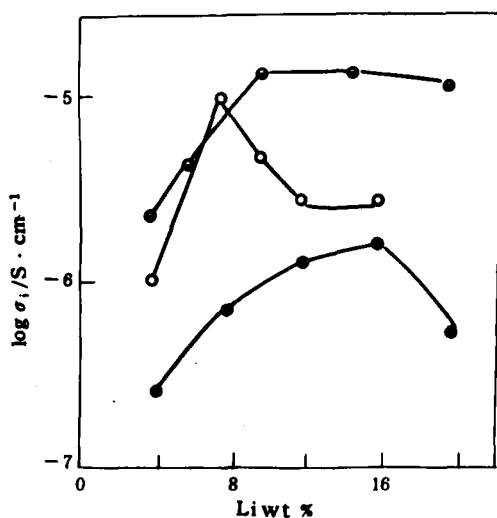


Fig. 1 Dependence of σ_i on lithium salt content

● I-LiClO₄; ○ II-LiClO₄; ◐ III-LiClO₄

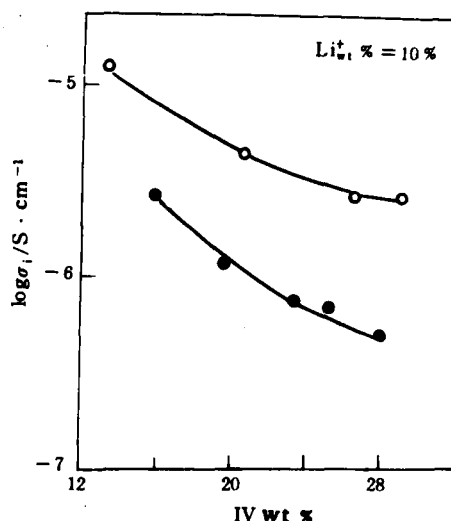


Fig. 2 Dependence of σ_i on crosslinking agent content

● I-LiClO₄; ○ II-LiClO₄

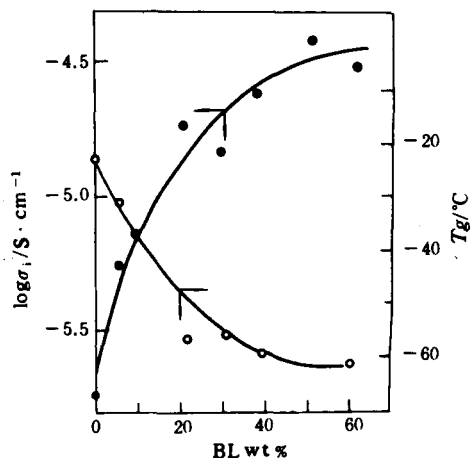


Fig.3 Dependence of σ_i and T_g of the films on BL content

From Table 1 it could be seen that the glass transition temperature (T_g) of the hybrid films increased with increasing lithium salt concentration. In the meantime, the flexibility of the polymeric film decreased and the microviscosity of the system increased. Thus, the transfer of carrier ions would become more difficult, and the mobility of the carrier ions decreased.

It has been known that the ionic conductivity is proportional to the number (n_i) and mobility (μ_i) of carrier ions, as indicated in equation 1.

$$\sigma = \sum_i n_i q_i \mu_i \quad (1)$$

wherein q_i is the charge of carrier ion.

Therefore, the two opposite effects of increasing n_i and decreasing μ_i give a maximum in conductivity at an intermediate salt concentration as shown in Fig. 1. The maximum appeared at different salt concentration depending on the different polymer matrix.

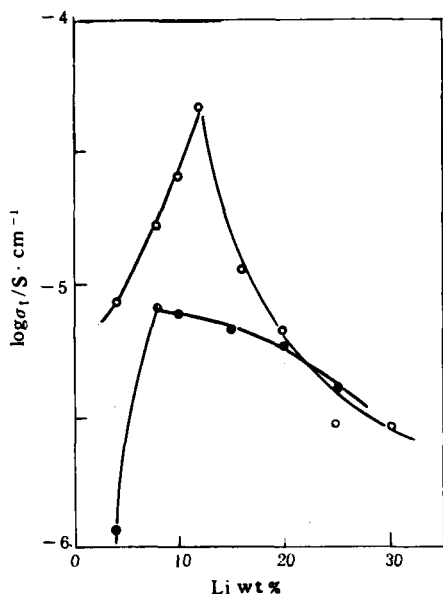


Fig.4 Dependence of σ_i on lithium salt concentration
○ BLwt% = 40%; ● BLwt% = 10%

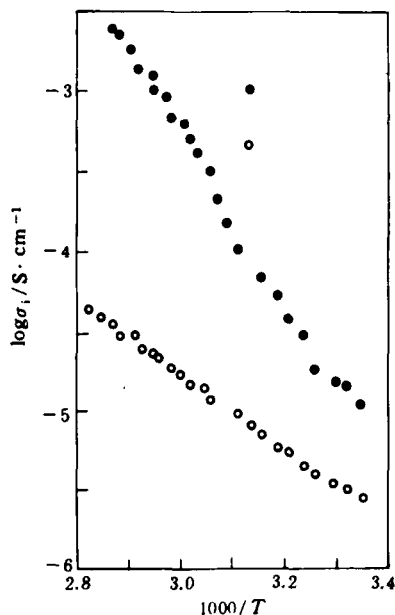


Fig.5 Arrhenius plot of hybrid films with different BL content
● BLwt% = 10% Li⁺ wt% = 20%
○ BL wt% = 40% Li⁺ wt% = 30%

It was found that the hybrid film of this system was hard to be cured with less than 15% of crosslinking agent (IV). However, as an increase of IV content, the ionic conductivity of the system decreased sharply, as shown in Fig. 2. The increase in crosslinking points may obstruct the transfer of carrier ions. DSC measurements of the hybrid films with different IV content (Table 1) indicated that, with increasing IV

concentration, the glass transition temperature (T_g) increased and the films became less flexible. Meanwhile, the polarity of the system may also be decreased with so large an amount of non-polar crosslinking agent.

The addition of high polar organic solvent with high boiling point to the general polymer-salt system is proposed to improve the ionic conductivity by the following three respects: (1) enhancing the dissociation of lithium perchlorate salt to increase the concentration of carrier ions (n_i), (2) providing hopping site by the solvent itself to increase the mobility of carrier ion (μ_i), and (3) plasticizing the polymer matrix to decrease the viscosity and T_g of the system. Here we choose 1, 4-butyrolactone (BL) as such a solvent. The dielectric constant of BL is as high as 39 at 20 °C and the boiling point is 204 °C. With the addition of BL to poly(β -carboxyethylmethoxysiloxane)-LiClO₄ system, the ionic conductivity increased from 10^{-6} to 5×10^{-5} S cm⁻¹, as shown in Fig. 3.

The plasticization effect of BL to the system can be seen clearly from Fig. 3, in which T_g is decreased with the addition of BL. This is quite in accordance with the increase of ionic conductivity in Fig. 3.

Fig. 4 indicates the lithium salt content dependence of the ionic conductivity of hybrid films containing different amount of BL. It seems that the organic solvent not only improves the overall ionic conductivity of the system but also shifts the maximum to higher salt concentration. The plasticization effect of BL to the film makes the T_g decrease at even higher salt concentration.

The temperature dependence of ionic conductivity of polymeric electrolytes is generally explained by a free volume model, that is, Vogel-Tamman-Fulcher equation (equation 2) for amorphous polymer systems and the simple Arrhenius equation (equation 3) for crystalline polymer electrolytes.

$$\sigma_i = AT^{-1/2} \exp(-B/(T - T_0)) \quad (2)$$

$$\sigma_i = AT^{-1} \exp(-E_a/RT) \quad (3)$$

wherein A is proportional to the charge carrier concentration, B in (2) and E_a in (3) are the apparent activation energy, and T_0 is a parameter closely related to T_g of the sample. Fig. 5 is the Arrhenius plot of the hybrid films with different amount of BL. As the increase of BL content, the activation energy was lowered and thus the ionic conductivity became less sensitive to temperature as indicated in Fig. 5.

In conclusion, polymers with high polarity and good flexibility give higher ionic conductivity for complexes with alkali metal salts. The ionic conductivity exhibits a maximum at an intermediate salt concentration and this maximum shifts with different polymers and 1, 4-butyrolactone content. Increase of crosslinking agent is unfavourable to the motion of carrier ions. 1, 4-Butyrolactone is a good plasticizer, and the ionic conductivity has been increased about 15 times by adding BL. The system with more butyrolactone content becomes less sensitive to temperature.

Keywords :

Ionic conductivity : Poly(β -alkoxycarbonylethylmethoxysiloxane)-Lithium Complex ; 1, 4-butyrolactone ; Crosslinked film.

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