

SINGLE IONIC CONDUCTION OF POLYSILOXANE CONTAINING PROPYLENE CARBONATE GROUP AND LITHIUM POLYMERIC SALTS*

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ABSTRACT

The polysiloxane containing propylene carbonate side group and several lithium polymeric salts were synthesized. The structure were confirmed by IR, NMR and XPS. The blending systems of polysiloxane containing propylene carbonate group with different lithium polymeric salts were studied by ion conductivity, XPS and DSC. Different lithium polymeric salts in the blending system lead to conductivity arranged in the following sequence: poly(lithium ethylenebenzene sulfonate methylsiloxane) > poly(lithium propionate methylsiloxane) > poly(lithium propylsulfonate methylsiloxane) > poly(lithium styrenesulfonate). In the blending system the best single ion conductivity was close to 10^{-5} Scm^{-1} at room temperature. XPS showed that at low lithium salt concentration the conductivity increased with the increasing content of lithium salt, in consequence of the increase of free ion and solvent separated ion pair. At high lithium salt concentration the free ion was absent and the solvent-separated ion pair functioned as carrier.

INTRODUCTION

It is well known that propylene carbonate is one of the best materials used in liquid electrolyte used in lithium batteries. It has both high polarity and high donor capability. The chain structure of poly(vinyl carbonate) has similarity to propylene carbonate. The ionic conductivity of poly(vinyl carbonate) and lithium triflate blending system was only 10^{-7} Scm^{-1} at room temperature^[1]. Introduction of propylene carbonate unit into flexible polysiloxane backbone may result in polymer matrix with high polarity and high donor capability, as well as low glass temperature. It may be expected that these polymers can be used as a good material for the solid polymer electrolytes.

The single ionic solid polymer electrolytes have a stable ion transferring property and it has received great attention as electrolyte materials in the solid state

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rechargeable battery. Several research groups have reported the single ion conductors. For example, Bannister^[2] reported two kinds of polyelectrolytes, poly(2-(4-carboxyhexafluorobutanoloxy)ethyl methacrylate) and poly(2-sulfoethylmethacrylate); Cheradame^[3] studied the crosslinking networks; Okamoto, et al.^[4-6] investigated the hindered phenol metal salt system. These single conductors have the enhance cation mobility, the transference number of cation was close to unity. But at the same time the conductivity is lower than that of double ion conductor. In order to obtain high conductivity and to get deep insight into the effect of polymeric salt structure and the interaction between the salt and polymeric matrix, in this paper the blending systems of polysiloxane containing propylene carbonate group with different polymeric lithium salts which have different main chain structure and different anion species were designed. The effects were studied by XPS and ion conductivity.

EXPERIMENTAL

1. Materials

3-Allyloxy-1, 2-propanediol (99%), Lithium perchlorate, Cyclopentadiene, Diethyl carbonate and Poly(methylhydrogen siloxane) ($d = 1.006$, $n_D^{20} = 1.3980$) were purchased from Aldrich Chemical Company.

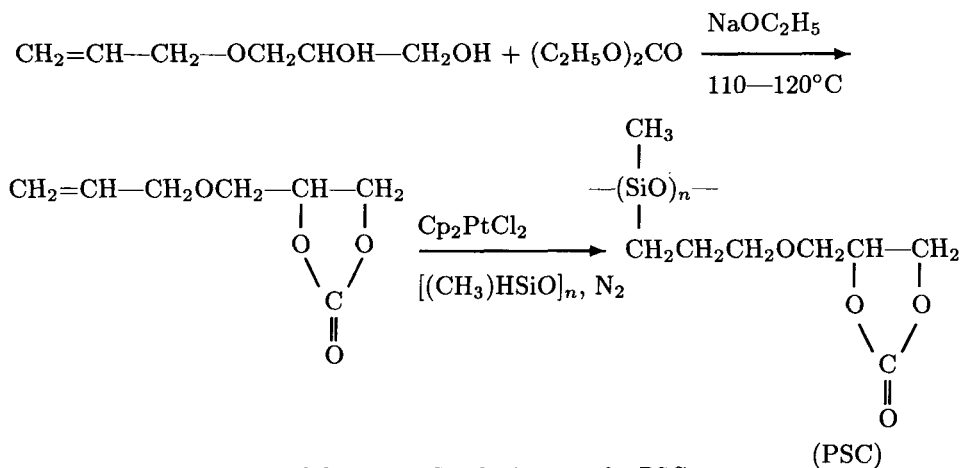
Poly(lithium propionate methylsiloxane) (PSiO-COOLi) was synthesized according to the literature method^[7].

Poly(lithium styrenesulfonate) (PS-SO₃Li) was prepared from poly(styrene sulfonic acid)^[8] and lithium hydroxide.

Poly(lithium ethylenebenzene sulfonate methylsiloxane) (PSiO-ES-SO₃Li) was obtained according to the method in reference [9].

2. Polysiloxane containing propylene carbonate group (PSC)

The reaction was described as follows:



Scheme 1 Synthetic route for PSC

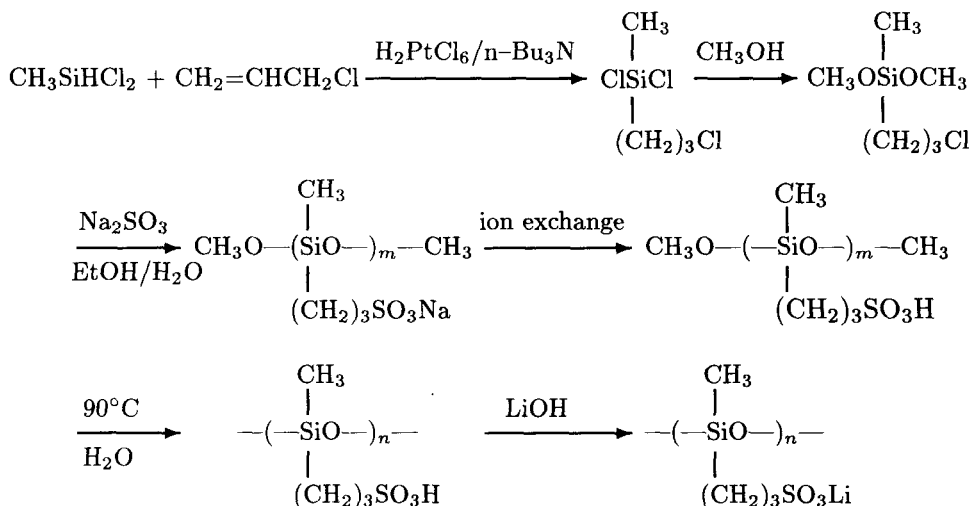
a. 4-(Allyloxy)methyl-1, 3-dioxolan-2-one was obtained by transesterification reaction from 3-allyloxy-1, 2-propanediol (33 g, 0.25mol) and diethyl carbonate (59g, 0.5mol) and sodium ethoxide (13 mmol) as a catalyst at 110–120°C for 24h. The product was collected at b.p. 106–108°C/0.4mmHg and purified by column to give colorless liquid (33g, 84%).

Anal. Calcd. for $C_7H_{10}O_4$: C 53.16%, H 6.37%. Found: C 53.45%, H 6.40%.

b. 4-Allyloxymethyl-1, 3-dioxolan-2-one in THF reacted with polymethyl hydrosiloxane at 70–80°C under the protection of nitrogen atmosphere and Cp_2PtCl_2 (prepared according to the method in reference [10]) as the catalyst. The polymer was confirmed by IR, NMR and XPS.

3. Poly(lithium propylsulfonate methylsiloxane) ($PSiO-SO_3Li$)

$PSiO-SO_3Li$ was prepared according to the following reaction:



Scheme 2 Synthetic route for $PSiO-SO_3Li$

Chloropropyl-dichloromethylsilane synthesized according to the method in reference [11] was collected at 80°C/18mmHg, yield 66%. Chloropropyldimethoxymethylsilane prepared according to literature [12] was collected at 103°C/70mmHg, yield 55%.

To a 1000ml flask were added 20.0g (0.11mol) the above obtained chloropropyldimethoxymethylsilane, 17.0g (0.13mol) anhydrous sodium sulfite, 140ml distilled water, and 30ml 95% ethanol. The mixture was slightly bulky. Then refluxed at 80–90°C for 48h. Cooled, filtered, the filtrate was evaporated and a brandy, candy solid was obtained, yield 83%. The product of methoxy terminated oligo (sodium propylsulfonate methylsiloxane) was confirmed by IR and ^1H NMR.

It is difficult to purify the above obtained oligo (sodium propylsulfonate methyl-

siloxane) which contains small amount of inorganic salt. So it was treated through 732-type cation exchange resin, then the sulfonic acid type siloxane was concentrated and further taken condensation reaction at 90°C for 24h, a viscous material was obtained. The stoichiometric amount of LiOH solution was added to adjust to neutral, finally separated the low molecular weight inorganic salts by dialyse. The result was confirmed by elemental analysis, IR and ^1H NMR to be the desired product of poly(lithium propylsulfonate methylsiloxane).

4. Preparation of the film

A given amount of PSC and polymer lithium salt in THF was blended under the magnetic stirring and then evaporated. The film was pressed between two Teflon films and dried under vacuum at 60°C for 3 days, finally stored over P_2O_5 for 2 days.

5. Measurement

The ionic conductivity was measured with the QF-2700 type RCL electric bridge at 1kHz frequency between two stainless-steel blocking electrodes.

DSC was performed with Pekin-Elmer 7 Series Thermal Analysis System. The rates of heating and cooling were 20°C/min.

FT-Raman spectra were taken with the FRA 106 FT-Raman accessory mounted on a Bruker IFS 66 FT-IR Spectrometer. The resolution is 4 cm^{-1} .

XPS spectra were taken with PHI 5300 ESCA (Pekin-Elmer). The binding energy is calibrated by assuming the binding energy of the carbon in the polymer to be 284.6 eV in its lower binding energy region.

RESULTS AND DISCUSSION

The polysiloxane containing propylene carbonate group (PSC) has flexible main chain, high polar and strong donor capability of its side chain propylene carbonate group. It could be used as polymer matrix to blend with a polymer lithium salt to compose a single ion conductor. The dependence of single ionic conductivity on temperature for PSC blended with polymer lithium salts, $\text{PSiO-ES-SO}_3\text{Li}$, PSiO-COOLi , $\text{PSiO-SO}_3\text{Li}$ and $\text{PS-SO}_3\text{Li}$ was summarized in Fig. 1 (a), (b), (c), (d) respectively. The temperature dependence of the single ionic conductivity in the blending systems obeyed Arrhenius equation for the most part:

$$\sigma = A \exp(-E_a/kT)$$

where T is the absolute temperature, A and k constants, E_a an apparent activation energy.

The polymer lithium salt concentration dependence of single ionic conductivity in the blended systems are shown in Fig. 2. Each blend system has a maximum

conductivity around $[Li^+]/[MDO]=0.13$. MDO represents the propylene carbonate group in the polymer. The conductivity dependence is arranged in the following sequence for various lithium polymeric salts: poly(lithium ethylenebenzene sulfonate

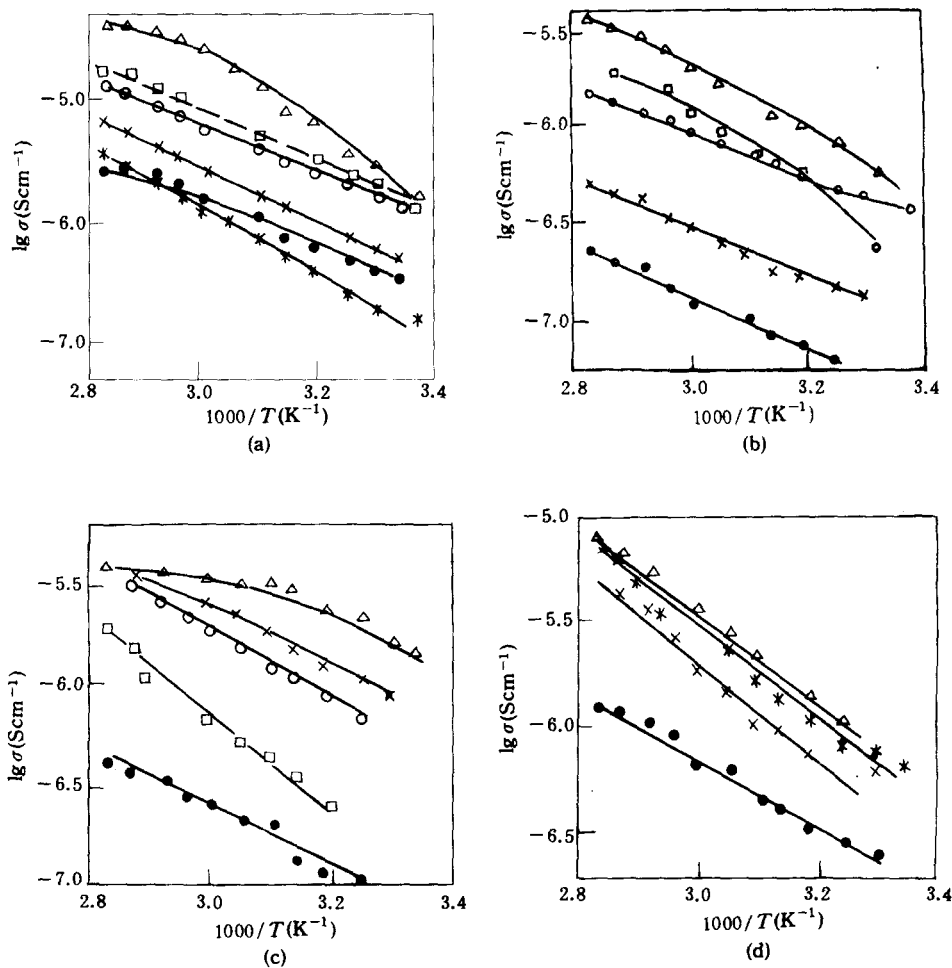


Fig. 1 The dependence of single ionic conductivity on temperature for PSC blended with (a) PSiO-ES-SO₃Li; (b) PSiO-COOLi; (c) PSiO-SO₃Li and (d) PS-SO₃Li
Li⁺/MDO: (●) 5%; (×) 6.7%; (○) 10%; (Δ) 12.5%; (□) 20%; (*) 25%

methylsiloxane) > poly(lithium propionate methylsiloxane) > poly(lithium propyl-sulfonate methylsiloxane) > poly(lithium styrenesulfonate). From this result we can see that with the same kind of aromatic sulfonate the polysiloxane system has the higher ionic conductivity than the rod main chain poly(lithium styrene sulfonate) system. It clearly explained that the former system has similar structure on main chain, leading to a better compatible system. And among three kinds of polymer lithium salts PSiO-ES-SO₃Li, PSiO-COOLi and PSiO-SO₃Li, PSiO-ES-SO₃Li has the highest conductivity because it has low dissociation energy resulting from the

conjugated benzene structure. While blended with the same content of polymer lithium salt, the T_g of the blending system of PSC with PSiO-COOLi is -18°C which is lower than that of the blending system with PSiO-SO₃Li (-14°C). In consequence it showed the above principle of ion conductivity.

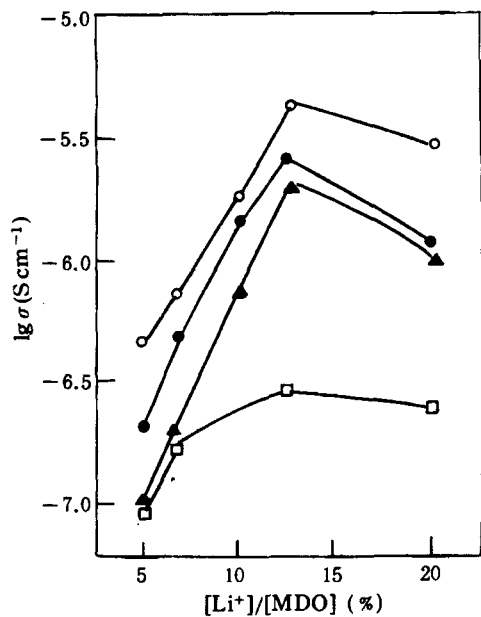


Fig. 2 Dependence of ionic conductivity (35°C) on the salt concentration for PSC blended with (O) PSiO-ES-SO₃Li; (●) PSiO-COOLi; (▲) PSiO-SO₃Li; (□) PS-SO₃Li

Table 1 ESCA data for PSC blended with various lithium polymeric salts and related system

Lithium ion source	Li1s	
[Li ⁺]/[MDO]=0.125	(peak width, percentage of total peak area)	
PSiO-ES-SO ₃ Li	51.7eV	55.6eV
	(2.50, 55.4%)	(2.81, 44.6%)
PSiO-SO ₃ Li	53.5eV	55.8eV
	(2.50, 55.4%)	(2.81, 44.6%)
PSiO-COOLi	52.0eV	55.4eV
	(3.00, 44.9%)	(3.21, 55.1%)
LiClO ₄ (10%)	50.0eV	52.8eV
	(2.20, 43.1%)	(2.41, 56.9%)
Pure LiClO ₄ crystal	56.7eV	
Li metal	48.8eV	

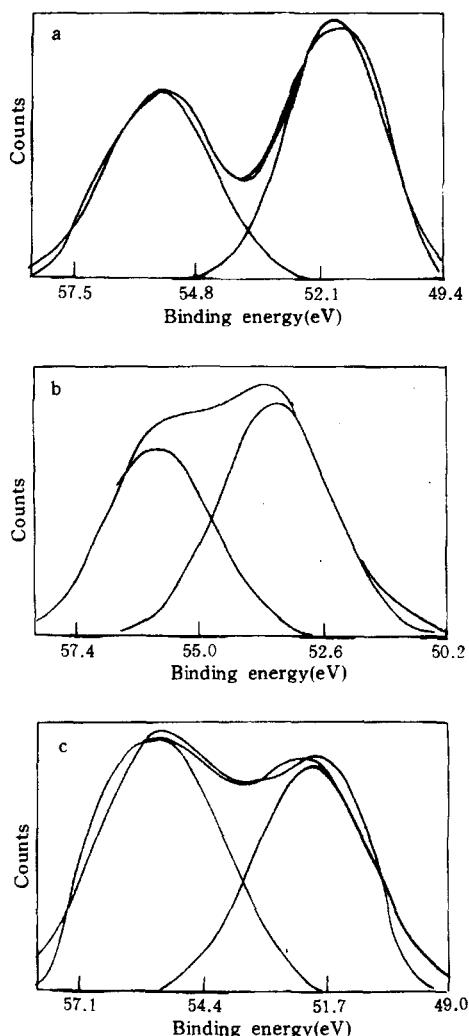


Fig. 3 Li_{1s} XPS spectrum for PSC blended with (a) $\text{PSiO-ES-SO}_3\text{Li}$; (b) $\text{PSiO-SO}_3\text{Li}$; (c) PSiO-COOLi $[\text{Li}^+]/[\text{MDO}]=0.125$

Many methods can be used to determine the interaction between the lithium ion and polymer matrix, for example, Raman spectroscopy, transfer number, dielectric relax, NMR. XPS is a very sensitive method to detect the electron density of an atom and thus also very useful to study the coordination. To our knowledge, this is the first to report the binding energy of Li_{1s} for single ionic conductor^[12]. The XPS data for PSC blended with different polymer lithium salts were shown in Table 1.

The results shown in Table 1 came from Fig. 3, in which the very low content part of Li_{1s} binding energy is to be neglected in the following discussion. From Table 1, it can be seen that every system has two kinds of Li_{1s} binding energy, the one with high Li_{1s} binding energy is assumed to be the state of ionic aggregation and the other with lower binding energy is to be the state of solvent-separated ion pair or compacted ion pair. Comparing with the double ion conductor system, there are no lower Li_{1s} binding energies near 50.0eV, which seem to be the state of free dissolved ion. All these single ion

conductor systems also have high ion conductivity [Fig. 1], this means the ion conduction also takes place in ion pair.

Comparing the ion conductivity and the Li_{1s} binding energy, it can be found that the lower Li_{1s} binding energy, the higher the conductivity. The aromatic sulfonate system has the lowest Li_{1s} binding energy among the three single ion sources in Table 1. This can be understood because aromatic sulfonate is the easiest to dissociate among these ions. Moreover the aliphatic sulfonate system has higher Li_{1s} binding energy than lithium carboxylate system. The results can further explain

the principle of ionic conductivity of polymer salts with different structure.

In conclusion, the polymer whose main chain is polysiloxane and side chain consists of propylene carbonate group with high polarity is a rather ideal matrix material for solid state polymer electrolyte. The blending systems of this kind of matrix material with various kinds of lithium ion polymeric electrolytes have high single ion conductivities. From the XPS results, it is shown that the ion conductivity is much affected by the coordination of Li ion with the oxygen. As the stronger the coordination is, the higher the ion conductivity in the blending system will be.

Keywords:

Single ionic conductor; Polysiloxane containing propyl carbonate group; Polymer Li salts; XPS

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