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Ionic conductivity in crosslinked poly(β-cyanoethylmethylsiloxane) network films containing lithium perchlorate

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SUMMARY

Polymeric solid electrolytes with high ionic conductivity, excellent mechanical strenght and flexibility were prepared by dispersing homogeneously lithium perchlorate in the crosslinked poly(β-cyanoethylmethylsiloxane) and poly(β-cyanoethylmethylsiloxane-co-dimethylsiloxane) network films. The ionic conductivity of the network films was close to 10^{-5} Scm^{-1} at room temperature and affected by the content of cyanoethylmethylsiloxane unit in the copolymers and the species and content of the crosslinking agents.

INTRODUCTION

Polymeric solid electrolytes have aroused interests widely because of the high ionic conductivity and excellent application prospects. On the materials used, the alkaili salt complexes of poly(ethylene oxide) and poly(propylene oxide) were plentifully investigated (1-3). More recent work has focussed on polymers such as polyethyleneimine (4) and poly(ethylene succienate) (5) as well as on polymers with pendent ω-methoxypoly(oxyethylene) chains anchored to polymethacrylate (6,7), polyphosphazene (8), polysiloxane (9,10) etc.

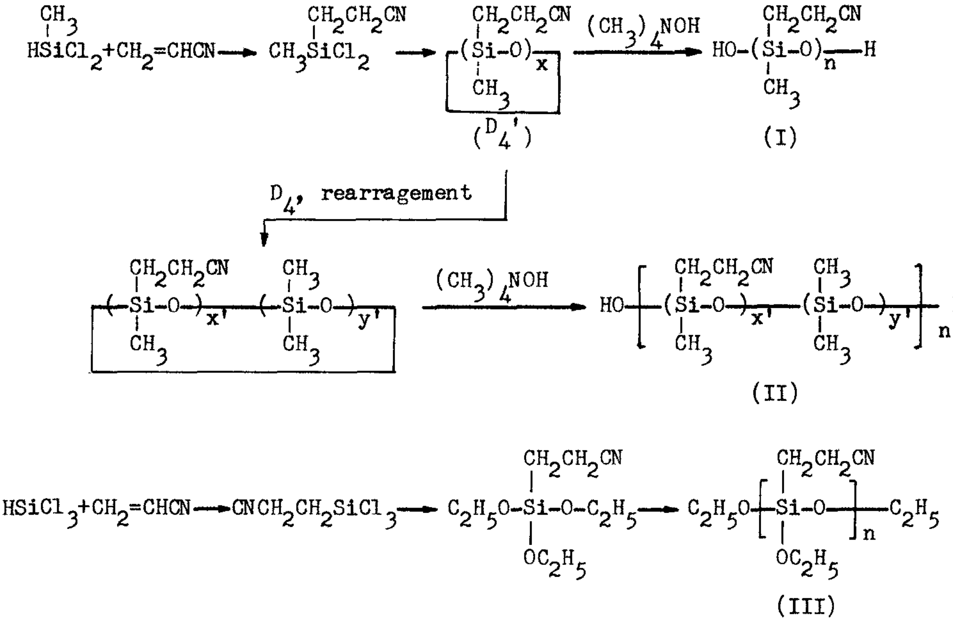
It has been known that the ionic conductivity of polymeric solid electrolytes closely related on the polarity and motion of chain segments of the polymer used, and the dissociation energy of metal salts. The results of our preliminary investigation demonstrated that the ionic conductivity also related on the regularity of arrangement of the polymer complexes (11,12). As well known, the polysiloxane has excellent flexibility and the polysiloxane containing polar group has high dielectric constant, therefore it may be expected that this polymeric system can be used as an ideal materials for the polymeric solid electrolytes.

In this presentation the ionic conductivity in crosslinked poly(β-cyanoethylmethylsiloxane) and poly(β-cyanoethylmethylsiloxane-co-dimethylsiloxane) network films containing lithium perchlorate was studied. We maily approached the influence of the content of the cyanoethylsiloxane unit in the copolymers , the species and content of the crosslinking agents on the ionic conductivity of the network films.

EXPERIMENTAL

Materials

Poly(β-cyanoethylmethylsiloxane)α,ω-diols (PCMS), poly(β-cyanoethylmethylsiloxane-co-dimethylsiloxane)α,ω-diols (PCMS-co-DMS) and poly(β -cyanoethyltriethoxysiloxane) (PCTEOS) were prepared according to the following reaction (13-16).



Varing the ratio of D_4 and D_4', the copolymers containing different content of the cyanoethylsiloxane unit were obtained.

The intrisic viscocity of polymers (I), (II) system and (III) were measured, and are 5, 5-40 and 2.5 ml/g in acetone at 20°C, respectively. The structures of the polymers were confirmed by the H^1 NMR spectra and shown in the Figure 1. The IR spectra (NaCl, 2120 cm^{-1}) also confirmed the structure of the polymers containing cyano group.

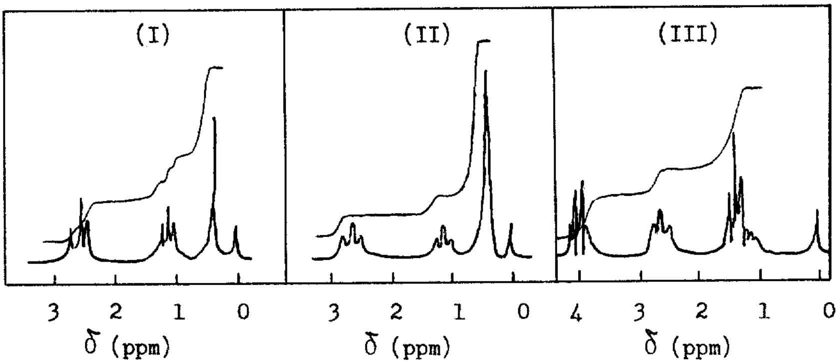


Fig. 1 H^1 NMR spectra of polymers (I), (II) and (III) in $CD_3\overset{O}{\overset{\|}{C}}CD_3$

Preparation of the network films containing lithium perchlorate

Crosslinked complex films were prepared by mixing stoichiometric amounts of the acetone solution of the polymer (I) or (II), crosslinking agent (polymer (III) etc.), lithium perchlorate and few dibutyltin dilaurate, and vulcanizing at room temperature or about 100°C. The network films were stored over P_2O_5 for 3 days and under vacuum at 100°C for 24 h.

Measurements

The ionic conductivity of the network films was determined with QF-2790 RCL Bridge under vacuum and argon atmospheres by 1 KHz frequency. Tg of the complex films was measured with a Du Pont Instruments 1090 Thermal Analyzer at a heating rate of 20°C/min. And the H^1 NMR spectra were recorded on a EM-360L in CD_3COCD_3. IR spectra were obtained with a JASCO A-100.

RESULTS AND DISCUSSION

The PCMS-co-DMS network films containing 10 wt% $LiClO_4$ were prepared with PCTEOS as a crosslinking agent (PCMS-co-DMS : PCTEOS = 4 : 6 wt). The relationship between the ionic conductivity (σ) and the content of the cyanoethylsiloxane unit in the copolymers is shown in Figure 2. The experimental results exhibited that the ionic conductivity of the polymeric solid electrolytes increased with an increase of the content of cyanoethylsiloxane unit in the copolymers. However, DSC analysis of the copolymer-Li^+ network films indicated that increasing the content of cyanoethylsiloxane unit, Tg of the polymeric solid electrolytes increased. It is well known that the ionic conductivity of polymeric solid electrolytes is closely related with

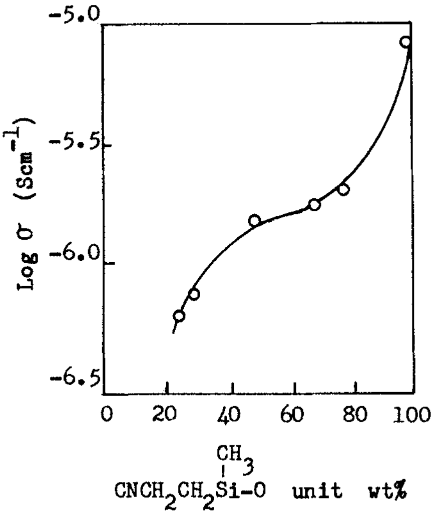


Fig. 2 Effect of content of cyanoethylmethylsiloxane unit in the copolymer on ionic conductivity.

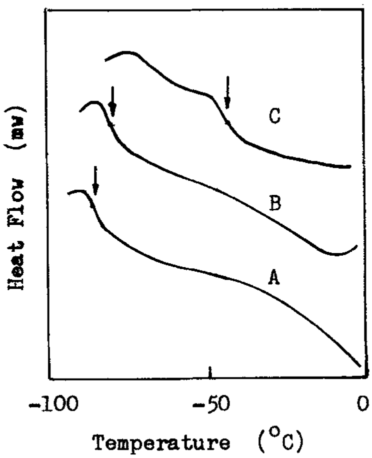


Fig. 3 DSC curves for the copolymer-Li^+ complexes. Systems A, B and C contain 25%, 50% and 100% cyanoethylmethylsiloxane unit, respectively.

the polarity and motion of the chain segments of the polymer. Generally, the polymer which have high polarity and low glass transition temperature is favourable for the ion motion in the polymeric solid electrolytes. The experimental results mentioned above clearly demonstrated that the polarity of polymer other than Tg factor occupied an important place.

Except PCTEOS, the cyanoethyltriethoxysilane, polymethyltriethoxysiloxane and methyltriisopropenyloxysilane were also used as a crosslinking agent . The influence of the structure of the crosslinking agents on the ionic conductivity showed as Table 1. From the table, it is clear that the conductivity of the network films was unaffected by the chain lenght of the crosslin-

Table 1 Influence of the crosslinking agents on the conductivity*

Crosslinking agents	Ionic conductivity (Scm^{-1})
cyanoethyltriethoxysilane	1.44×10^{-6}
PCTEOS	1.45×10^{-6}
methyltriisopropenyloxysilane	1.38×10^{-6}
polymethyltriethoxysiloxane	0.77×10^{-6}

* polymer : crosslinking agent : $LiClO_4$ = 4 : 6 : 1 (wt)
the polymer contain 50% cyanoethylmethylsiloxane unit.

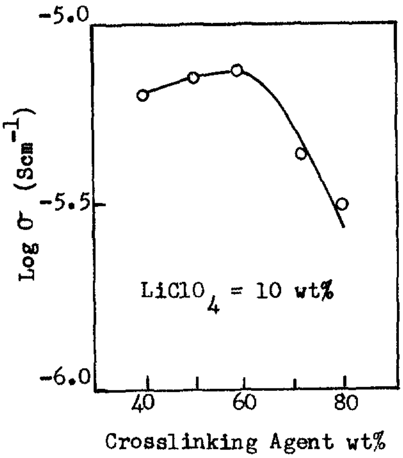


Fig. 4 Dependence of σ of PCMS-Li^+ film on PCTEOS content

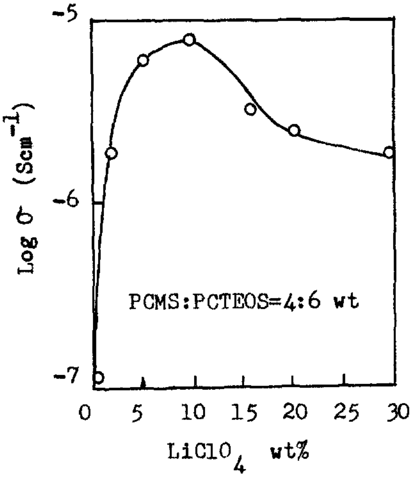


Fig. 5 Dependence of σ of PCMS-Li^+ network film on Li^+ content

king agents for the cyanoethylsiloxane system. When the poor polar methyloxane system was used as a crosslinking agent, the conductivity was influenced by the chain length because the long chain of the poor polar crosslinking agent cut off the siloxane chain containing polar cyanoethylsiloxane group. It is unfavourable to the motion of the ion.

Figure 4 shows the effect of the content of PCTEOS crosslinking agent on the ionic conductivity of the network films. When the content of PCTEOS was lower than 60%, the conductivity almost unchanged. When that was more than 60%, the conductivity decreased. The polymer (I) (contain 100% cyanoethylsiloxane unit) was used in the network films, therefor the polarity of the hybrid films almost unchanged with the variation of the content of PCTEOS. The decrease in conductivity may be attributed to the increase in the crosslinking degree and the decrease in the flexibility (Tg from -50 to -23°C).

The effect of the ionic carrier content on the conductivity is shown in Figure 5. The maximum conductivity appears at low concentration of $LiClO_4$ (about 10 wt%). It is well known that the ionic conductivity is represented by $\sigma = \sum ne\mu$, where n is the number of carriers, e is the charge of a carrier, and μ is the carrier mobility. Thus, the increasing ionic conductivity in the low concentration region might be attributed to the increase in the number of ionic carrier. In the high concentration region, when the $LiClO_4$ concentration increased, the number of ionic carriers increases, while the motion of the chain segment of polymer decreased because of the stroger interaction between the Li^+ and cyanoethylsiloxane chains. The DSC thermograms of the polymeric solid electrolytes revealed that the Tg raises from -52°C to -33°C according to the above explanation.

Figure 6 shows the temperature dependence of the ionic conductivity in PCMS-Li^+ network film (PCMS : PCTEOS : $LiClO_4$ = 4 : 6 : 1 wt). This curve basically according to Vogel-Tammann-Fulcher equation (17)

$$\sigma = A_o T^{-1/2} \exp[E_a/k(T-T_o)],$$

where T_o is the ideal glass transition temperature and A_o, E_a, k are constants (2). At 35°C the ionic conductivity reached 10^{-5} Scm^{-1} and obviously increased with a raise in temperature. At 140°C the conductivity reached 10^{-2} Scm^{-1}.

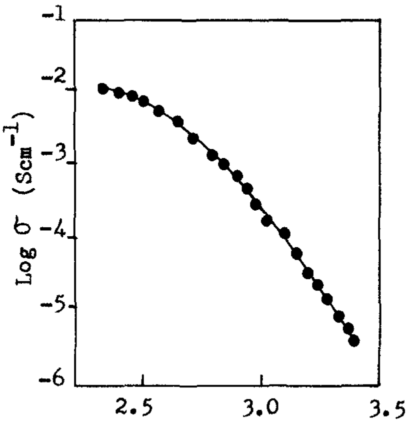


Fig. 6 Arrhenius plots for σ in PCMS-Li^+ network film

In conclusion, the conductivity of poly(β-cyanoethylmethylsiloxane)-Li^+ complex films which is crosslinked with a high polar crosslinking agent (PCTEOS) closed to 10^{-5} Scm^{-1} at room temperature. The high polarity of polymer and crosslinking agent used can accelerate the ionic carrier generation and favore the increase in the conductivity of polymeric solid electrolytes. However, when excess crosslinking agent was used, the increse in crosslinking degree is unfavourable to the motion of ionic carriers. The experimental results also showed that the polarity of polymers is more important than Tg for ionic conductivity of polymeric solid electrolytes.

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