

IONIC CONDUCTIVITY OF METHYLSILOXANE TERMINATED POLYETHYLENE OXIDE WITH LITHIUM PERCHLORATE NETWORK FILMS

LI Yongjun(李永军), FU Yingwen(付英文)
FANG Shibi(方世璧) and JIANG Yingyan(江英彦)
(*Institute of Chemistry, Academia Sinica, Beijing*)

ABSTRACT

Complex films of crosslinked poly(methylsiloxane-co-ethylene oxide) and lithium perchlorate were prepared. These solid state polymeric electrolytes show a markedly higher ionic conductivity, and excellent flexibility. The ionic conductivity of the network films closed to 10^{-5} Scm^{-1} at room temperature. The effects of Li^+ content, species and contents of crosslinking agents, molecular weight of poly(ethylene oxide) and temperature on the ionic conductivity of the network films were also investigated.

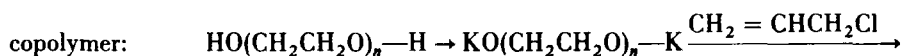
INTRODUCTION

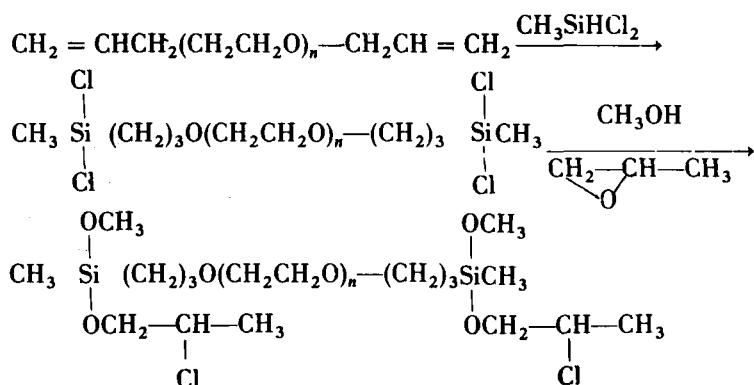
Recently, some progresses have been made on the solid electrolytes suitable for manufacturing of all solid state batteries of high energy density^[1,2]. A new kind of polymeric solid electrolytes with fast ion transport were obtained by hybridizing inorganic salts in a polymer matrix. Poly (ethylene oxide) (PEO) of high molecular weight has been widely used with various salts^[3,4]. The polymer electrolytes offer several advantages compared with liquid electrolytes, such as higher thermal stability, wider range of electroactivity, higher plasticity and so on. Secondary electrochemical cells have been made using lithium anode, PEO electrolyte and lithium intercalation cathode^[5].

Ionic conductivity of polymeric solid electrolytes is associated with the flexibility of the polymer backbone caused by the polymer's low glass transition temperature (T_g). Since polydimethylsiloxane derivatives have lower glass transition temperature, it is used for polymer backbone material. This paper is concerned with the ionic conductivity of the block poly-(methylsiloxane-co-ethylene oxide) with lithium perchlorate network films. The effects of Li^+ content, species and contents of crosslinking agents, molecular weight of PEO and temperature on the ionic conductivity of the polymeric solid electrolytes were investigated.

EXPERIMENTAL

The methylsiloxane terminated polyethylene oxide was prepared according to the method described in the literature^[6]. This may be expressed in the following scheme.





The crosslinking agent (I) is shown in the following scheme:

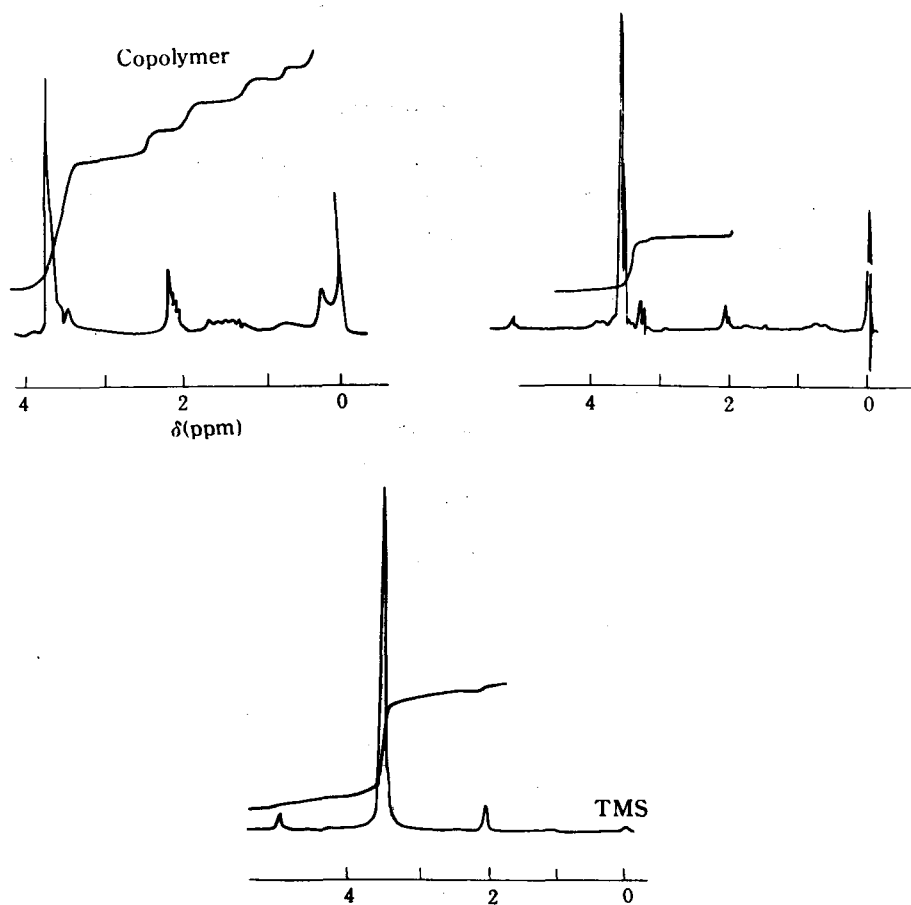
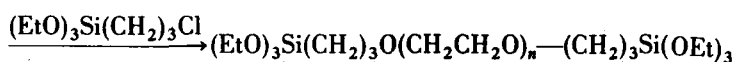
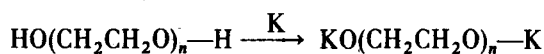


Fig. 1 ¹H NMR spectra of the copolymer, crosslinking agent and PEO in CD₃COCD₃

To the solution of poly (ethylene oxide) ($M=400$, 0.1mol) in 20 mL of benzene, potassium (0.22mol) was gradually added under nitrogen and the mixture was stirred for 4 hrs at room temperature. The γ -chloropropyltriethoxysilane (0.2mol) was added to the reaction mixture and stirred for 12 hrs at 80°C. The insoluble matter was removed by filtration. The solvent was evaporated with a rotaevaporater. The crosslinking agent (I) was purified by precipitation from 5:6 (by vol.) hexane/THF mixture in which the carbowax remained soluble.

The structures of the copolymer, crosslinking agent (I) and PEO were confirmed by NMR spectra and shown in Figure 1.

Preparation of network films containing lithium perchlorate

Known amount of acetone solution of LiClO_4 , block copolymer, crosslinking agent and a few amount of dibutyltin dilaurate were mixed and poured onto a glass retaining ring. The solvent was evaporated and the flexible network films were vulcanized at room temperature. The films were dried over P_2O_5 for 2 days and under vacuum oven at 70°C for 12 hrs.

Measurements

The measurement of the ionic conductivity was carried out on QF-2790 RCL Bridge by 1 KHz frequency under argon atmosphere. Differential Scanning Calorimetry (DSC) was performed on Du Pont Instruments 1090 Thermal Analyzer at a heating rate of 20°C/min. The ^1H -NMR spectra were recorded on a EM-360L in CD_3COCD_3 .

RESULTS AND DISCUSSION

The copolymer network films were prepared using crosslinking agent (I), ortho-silicate and polymethylethoxysiloxane- α , ω -diethoxy as crosslinking agents with a content of 2 wt%. The results of DSC indicate that these materials have a low glass transition temperature (about -60°C). The

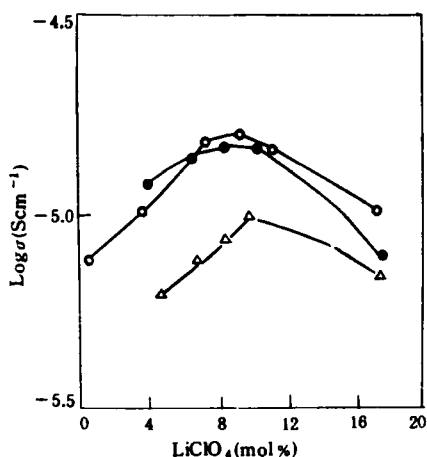
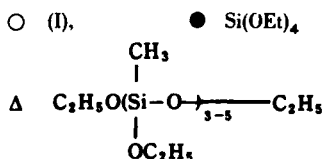


Fig. 2 Dependence of σ of network films on the Li^+ content crosslinking agent:



dependence of the ionic conductivity of the network films on Li⁺ content for different crosslinking agents is shown in Fig.2. The experimental results showed that the crosslinked poly (methylsiloxane-co-ethylene)-Li⁺ complex films have a higher ionic conductivity when using crosslinking agent (I) or orthosilicate as crosslinking agent than using polymethylethoxysiloxane- α,ω -diethoxy. This may be attributed to the long chain of the poor polar crosslinking agent that cut off the good polar poly-(methylsiloxane-co-ethylene oxide) chain, so it is unfavourable to the motion of ion. In point of the content of Li⁺, the maximum conductivity appeared at about 10 wt% of LiClO₄ whatever species of the crosslinking agent was used. Then the ionic conductivity decreased with increasing Li⁺ content because of the interaction between Li⁺ and the copolymer and the other Li⁺ being difficult dissociating the ionic compound.

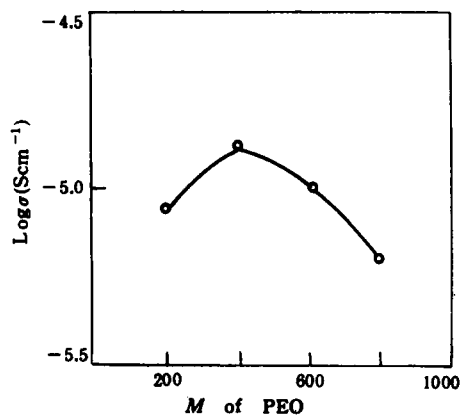


Fig. 3 Dependence of ionic conductivity (σ) on $\overline{M}$ of PEO

The dependence of the ionic conductivity on the molecular weight of PEO in the copolymer is shown in Fig. 3. The experimental results showed that when the molecular weight of PEO is 400, the

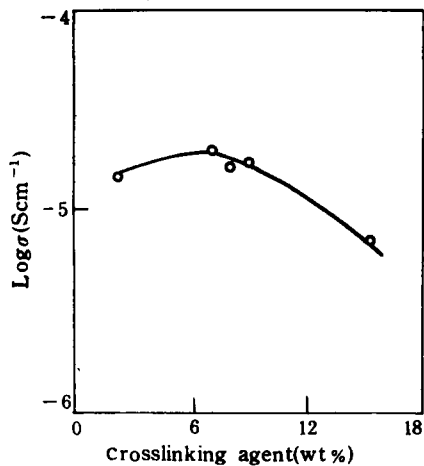


Fig. 4 Influence of the crosslinking content on the ionic conductivity of network films

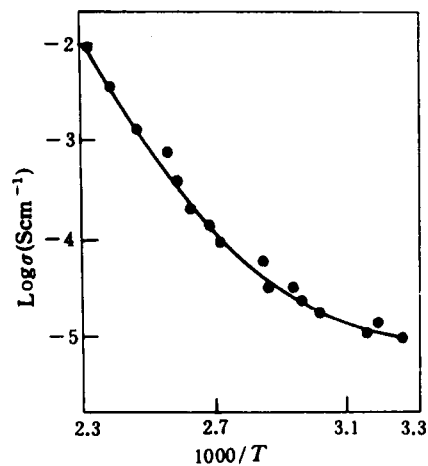


Fig. 5 Arrhenius plot for the conductivity of the network film

block copolymer network films have a higher ionic conductivity, which is similar to the results reported by Tsuchida and others^[7].

The influence of the content of the crosslinking agent on the ionic conductivity of the network films is summarized in Fig. 4. In the network complex films the crosslinking agent(I) was used and the content of LiClO_4 was 10 wt%. The ionic conductivity changes little when less than 8% crosslinking agent was used. Then the ionic conductivity decreases with increasing the content of the crosslinking agent. It may be due to the higher crosslinking degree in the network films, which restricts the transfer of the Li^+ ion.

The dependence of the ionic conductivity of the network complex films (poly(methylsiloxane-co-ethylene oxide): crosslinking agent (I): $\text{Li}^+ = 82:8:10$ wt. ratio) on the measurement temperature is shown in Fig.5. The ionic conductivity reached 10^{-5} Scm^{-1} at 25°C and then increased quickly with the increase of the temperature and finally reached 10^{-2} Scm^{-1} at 150°C .

Keyword:

Poly (methylsiloxane-co-ethylene oxide); Polymeric solid electrolyte; Network complex film

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