Polymer Bulletin 18, 143–148 (1987)

Polymer Bulletin

Ionic conductivity of polyelectrolyte derivatives of poly(vinyl alcohol) – lithium ion complex films

Guan-Ling Bao[1], Wei-Qin Yun[1], Shi-Bi Fang[2], and Ying-Yan Jiang[2]

[1] Xian Modern Chemistry Research Institute, Xian, China
[2] Institute of Chemistry, Academia Sinica, Bejing, China

Summary

Ionic conductivity of various polymeric hybrid complexes made from the polyelectrolytes carboxymethylated poly(vinyl alcohol) (PVAC), poly(vinyl alcohol) acetalized with glyoxylic acid (PVAG) and poly(vinyl alcohol) acetalized with iodine N-methyl-4-pyridyladehyde (PVAP) were investigated. It was found that when the content of carboxyl group in PVAC reaches 5.3% and the content of carboxyl group in PVAG is more than 9.7%, the ion conductivity of polymeric hybrid complexes rises sharply. These polymer—Li^+ complex hybrids gave the ionic conductivity of 10^{-6} Scm^{-1} at room temperature.

Introduction

Complexes consisted of the polymer and electrolyte exhibit high ionic conductivity and possess the advantages of small size and light mass, structural stability and low volatility (TSUCHIDA,1982). Polymeric electrolytes may also have flexibility which greatly facilitates the design of an all-solid-state rechargeable battery. Hence they have been widely used for solid batteries, big volume container, ionic concentration sensors and long cell etc. The polymer materials having the ionic conductivities, organic lithium ion conductors, in particular, are currently attracting considerable interest.

It is well known that the most promising examples of solid electrolytes to date are based on the poly(ethylene oxide) (LEE,1982), polyacrylonitrile

(WATANABE,1982) and poly(vinylidene fluoride) (TSUNEMI,1983) doped with alkali metal salts. MIKAWA et al. synthesized poly(sodium acrylate), polybreme and poly(2-acrylamino-2-methylpropane sulfonate)—Li^+ complexes. Their ionic conductivity varied 10^{-3}—10^{-8} Scm^{-1} at 100—200°C (MIKAWA,1984).

Recently, in order to get a hybrid film of higher mechanical strength, various polycation and polyanion based on poly(vinyl alcohol) were prepared in our laboratory and their properties were examined. In the present paper, the ionic conductivity of polyelectrolyte derivatives of poly(vinyl alcohol) —Lithium ion complex films was studied.

Experimental

Materials

The polyelectrolyte derivatives of poly(vinyl alcohol) (PVA) such as carboxymethylated PVA (HOSONO,1977) and acetalized PVA with glyoxylic acid (NAKAJIMA,1957) were prepared according to the literatures. The polymers obtained were purified by reprecipitation from water-acetone system and through cation and anion ionic exchange resin.

Preparation of Iodine N-methyl-4-pyridylaldehyde

28.6g of 4-pyridylaldehyde (0.27mol) and 25ml of ether were placed in a flask equipped with a thermometer reflux condenser and dropping funnel. The 87 ml of iodomethane was added dropwise at room temperature and the solution was stirred for 7 h in the dark. The sediments were filtered and dried under vacuum to give a red powder (62.5g, 93%).

Preparation of PVAP

To a 500ml of three-necked flask equipped with a reflux condenser, stirrier and thermometer was added 5g of PVA, 190ml of water and 21.5ml of sulfuric acid (95-98%) and heated to dissolve at 65°C. Then 12.5g of iodine N-methyl-4-pyridylaldehyde was added with stirring. The reaction was kept at 65°C for 4 h and the colour of the reaction mixture changed to deep blue.

170ml of water was added and the mixture poured into acetone. The polymer was dried to give a white product (12.4g). The degree of acetalization is 22.0 mol% by elemental analysis.

The polymer obtained was purified through ionic exchange resin.

Preparation of the polymeric hybrid films

The ionless aqueous solution of polyelectrolyte was mixed with the ionless aqueous solution of $LiClO_4$. After complete homogenization, the solution was evaporated and poured into a silicone mould of 3 cm in diameter. The solution was allowed to slowly evaporated in dry atmosphere to leave a film about 0.01 cm thick. The film was peeled off from the silicone substrate and dried over P_2O_5 for 3 days.

Measurement of the ionic conductivity

A disc of hybrid membrane of 2 cm in diameter was placed between two polished stainless-steel cylindrical electrodes in a apparatus. This apparatus provided an inert atmosphere, a controlled temperature, and a pressure loading to ensure good contact between the sample and electrodes. The ionic conductivity of the hybrid films was determined using TR-10C dielectric Loss Measuring Set and QF-2790 RCL Bridge at room temperature under vacuum and inert atmosphere by 1 KHz frequency.

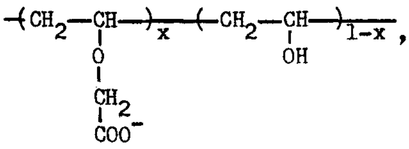
Measurement of DSC

Differential scanning calorimetry (DSC) was measured with a Du Pout Instruments 1090 Thermal Analyzer at a heating rate of $10^{o}C/min$.

Results and Discussion

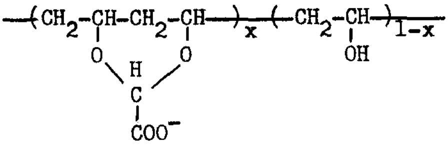
The PVAC, PVAG and PVAP were shown as follows:

Varying the molar ratio of the PVA with the glyoxylic acid or the monochloroacetic acid, the PVAG (or PVAC) containing different carboxyl group content were prepared (Table 1, 2). And the degree of acetalization for PVAP

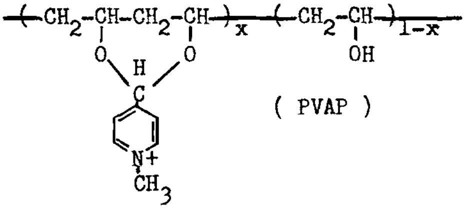


$$-\!\!\left(CH_2-\underset{\underset{\underset{\underset{COO^-}{|}}{CH_2}}{O}}{CH}\right)_x\!\!-\!\!\left(CH_2-\underset{OH}{CH}\right)_{1-x}$$

(PVAC)



(PVAG)



(PVAP)

is 22.0% . The $LiClO_4$ was used as charge carrier.

Table 1 Characteristics of PVAG *

Sample	Glyoxylic acid/PVA (mol./mol.)	Degree of acetalization for PVA (mol.)
PVAG-1	0.7	7.1
PVAG-2	1.0	9.7
PVAG-3	1.4	15.2
PVAG-4	2.0	22.0

* The degree of polymerization for PVA is 1700.

Table 2 Characteristics of PVAC *

Sample	Degree of carboxymethylation for PVA (mol.%)
PVAC-1	0.8
PVAC-2	2.5
PVAC-3	4.5
PVAC-4	5.3
PVAC-5	5.9

*The degree of polymerization for PVA is 1700.

The relation between the ionic conductivity(σ) and the composition of PVAC-PVAP-Li^+ hybrid film is shown in Fig.1. It was found that the ratio of polyanion to polycation was about 1:1, the ionic conductivity of the hybrid film exhibited the maximum value. It indicated that the interpolymeric cooperative efficiency effects on the ionic conductivity of polymeric hybrid complex.

Fig.2 shows the relation between σ and Li^+ content, in this figure, the highest value of the ionic conductivity was observed at about 10 wt% of

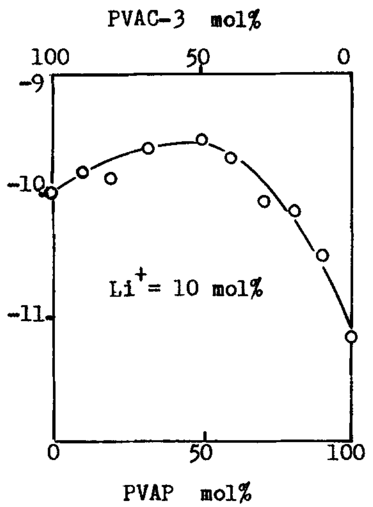


Fig.1 Relation between σ and composition of hybrid film

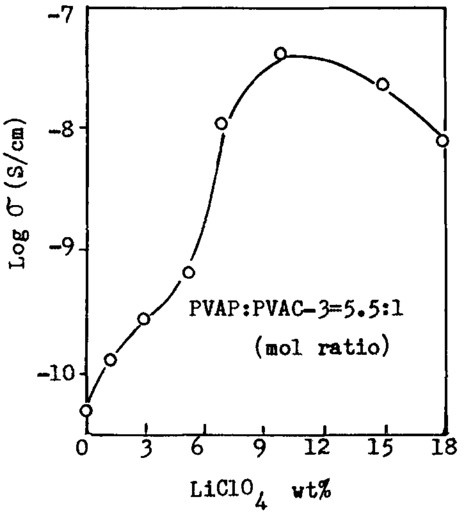


Fig.2 Relation between σ and Li$^+$ content

$LiClO_4$ in the hybrid film.

The effect of the degree of carboxymethylation and degree of acetalization for PVA on the ionic conductivity of the hybrid film was studied (Fig.3 and Fig.4). As this figure, in PVAC-Li$^+$-PVAP system the ionic conductivity increased sharply, when the degree of carboxymethylation for PVA was more than 5.3 mol%. And in PVAG-Li$^+$-PVAP system the ionic conductivity also in-

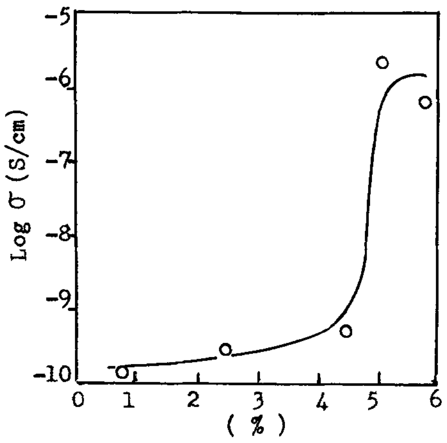


Fig.3 Relation between σ and degree of carboxymethylation in PVAC

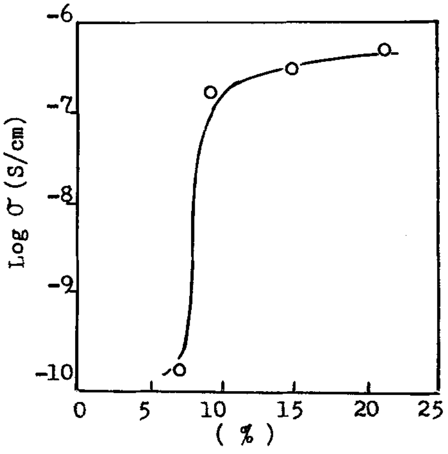


Fig.4 Relation between σ and degree of acetalization in PVAG

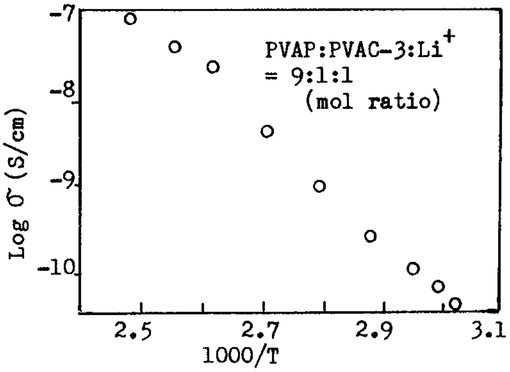


Fig.5 Relation between σ and temperature

creased sharply, when the degree of acetalization for PVA with glyoxylic acid was more than 9.7%. It is clear that the ionic conductivity of the polyelectrolyte derivatives of PVA-Li$^+$ hybrid film is closely related to the content of carboxyl group in the PVA derivatives. And the polyelectrolyte derivatives of PVA-Li$^+$ hybrid film have a high ionic conductivity at room temperature (10^{-6} Scm^{-1}).

The Tg of PVAC-5, PVAG-4 and PVAP were measured as 28.2, 29.9 and 21.7 °C respectively. The all are lower than that of PVA and the increase of modification degree cause Tg drop down gradually, while the Tg of PVAC—PVAP complex drop down to 20.1°C. This clearly show that the ionic conductivity of the polymer is badly affected by the motion of the chain segments.

Fig.5 gives the ionic conductivity in an Arrhenius plot. In the exerimental temperature range, the relation between $\log\sigma$ and 1/T close to linear.

Acknowledgment

The authors are grateful to Professor Ming-Nan Zang for his useful suggestion in this paper and acknowledge the support of S.Q. Liu for measuring the ionic conductivity.

References

1. TSUCHITA, E. : Kogyo Zairyo, 30, 109 (1982)
2. LEE, C. C. and WRIGHT, P. V. : Polymer, 23, 681 (1982)
3. WATANABE, M., KANBA, M., NAGAOKA, K. and SHINOHARA, I. : J. Appl. Polym. Sci., 27, 4191 (1982)
4. TSUNEMI,K., OHNO,H. and TSUCHIDA,E. : Electrochi. Acta, 28, 833 (1983)
5. MIKAWA, H., TOYOTA, S., NOGAMI, T. : Solid State Ionics, 13, 243 (1984)
6. HOSONO, M., SUGII, S., KITAMARU, R., HONG, Y. M. and TSUJI, W. : J. Appl. Polym. Sci., 21, 2125 (1977)
7. NAKAJIMA, A., ISHIDA, S., SAKURADA, I. : Kobunsi Kagaku, 14, 259 (1957)

Accepted June 5, 1987 S