Synthesis of tetraethylene oxide–organosiloxane hybrid and the linear ionically conductive spectra of its membrane doped with $LiClO_4$

Yukihiko Ueno and Yoshiro Tajitsu
Department of Physics and Chemistry, Honjo Kotogakuin of Waseda University, Honjo-shi, Saitama 367, Japan

and Takeo Furukawa
Institute of Physical and Chemical Research, Wako-shi, Saitama 350-01, Japan
(Received 23 July 1991)

Tetraethylene oxide–organosiloxane hybrid (TEOS), a flat membrane, was obtained by mixing solutions of tetraethylene oxide and methyltrichlorosilane in a Teflon vessel. In the frequency spectra of the linear conductivity of the ionically conductive membrane using TEOS as a matrix (TEOS/$LiClO_4$), relaxations associated with the electrode and interfacial polarizations were observed.

(Keywords: siloxane; poly(ethylene oxide); polyelectrolyte; electric relaxation; ionic conductivity)

Introduction

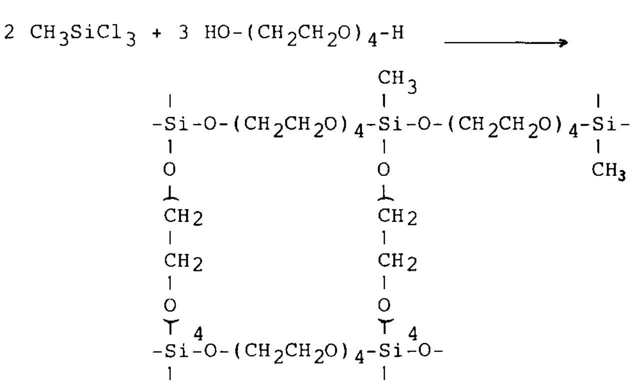
Ravaine *et al.*[1] reported the application of the sol-gel method for the preparation of a polyether–polysiloxane hybrid. (The sol-gel method is the condensation of alkoxymetals to prepare a metal oxide gel[2].) Recently, Fujita and Honda[3] reported the preparation of a new class of poly(ethylene oxide)–polysiloxane hybrid membrane, which is elastic, free-standing and excellent as a matrix in a solid polymer electrolyte. However, to prepare this hybrid membrane, allylation of oligo-(ethylene oxide) followed by hydrosilylation is needed; these procedures are very laborious.

This paper describes an easy method of preparing the tetraethylene oxide–methylsiloxane hybrid (TEOS). It is a single vessel reaction and produces a flat membrane. Also, the linear conductivities $\sigma_1^* = \sigma_1' + i\sigma_1''$ of the membrane containing $LiClO_4$ were measured.

Experimental

Preparation of the membrane. Tetraethylene oxide and methyltrichlorosilane were purchased and used without further purification. Tetrahydrofuran (THF) was distilled on sodium and $LiClO_4$ was dried at 100°C *in vacuo* before use.

The equation for the preparation of TEOS is shown in *Scheme 1*. Tetraethylene oxide 14.6 g (0.075 mol) in THF (20 ml) and methyltrichlorosilane 7.47 g (0.05 mol) in THF (20 ml) were mixed. The mixture was quickly stirred and poured into flat-bottomed Teflon vessels and allowed to stand for a few days in a dry atmosphere at room temperature. After the membrane formed, it was put in another Teflon vessel. Then it was heated at 140°C *in vacuo* for 1 day.



Scheme 1

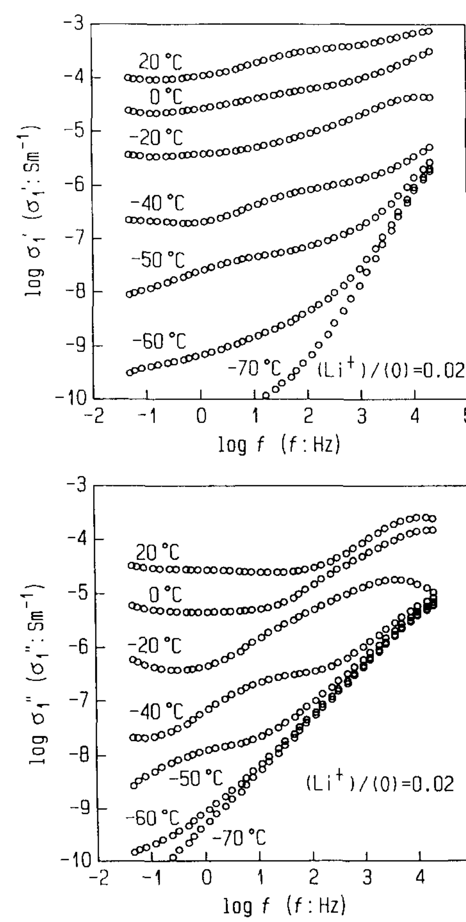


Figure 1 Plots of the logarithms of the linear conductivities σ_1' and σ_2'' against the logarithm of frequency

0032-3861/92/030665-02

In the case of the TEOS/$LiClO_4$ membrane, $LiClO_4$ (0.638 g, 0.006 mol) was dissolved in dry THF with tetraethylene oxide and it was mixed with methyltrichlorosilane solution. The procedures followed were the same as those above.

Measurement of conductivity. Gold was vacuum-deposited onto both sides of the film samples to serve for electrodes. The linear conductivities were measured by applying a sinusoidal electric field with amplitude E_0 and angular frequency ω, and detecting the in-phase and 90° out-of-phase components of the electric current with frequency ω, I'_1 and I''_1. The complex conductivity, $\sigma_1^* = \sigma'_1 + i\sigma''_1$ from $\sigma'_1 = I'_1/E_0$ and $\sigma''_1 = I''_1/E_0$, was obtained. Details of the experimental set-up have been described previously[4].

Results and discussion

The TEOS membrane ($\sim 100\,\mu m$ thick) is free-standing, flat and semitransparent.

Figure 1 shows the frequency spectra of the linear conductivity σ_1^* at temperatures between −70°C and 20°C. The plateau of σ'_1 in the low frequency range corresponds to the direct current conductivity. As the frequency increased, σ'_1 increases first gradually and then rapidly due primarily to the dielectric loss. The plateau of σ''_1 is attributed to the dielectric relaxations associated with the electrode and interfacial polarizations. These results are the same as those obtained for the Li^+-doped poly(ethylene oxide) membrane system[5].

References

1 Ravaine, D., Sominel, A., Charbouillot, Y. and Vincens, M. *J. Non-Cryst. Solids* 1986, **82**, 210
2 Sakka, S. 'Treatise on Materials Science and Technology' (Eds M. Tomozawa and R. H. Doremus), Vol. 22, Academic Press, New York, 1982, p. 129
3 Fujita, M. and Honda, K. *Polym. Commun.* 1989, **30**, 200; Honda, K., Fujita, M., Ishida, H., Yamamoto, R. and Ohgaki, K. *J. Electrochem. Soc.* 1989, **135**, 3151
4 Furukawa, T., Nakajima, K., Koizumi, N. and Date, M. *Jpn J. Appl. Phys.* 1987, **26**, 1039
5 Tajitsu, Y., Ueno, Y. and Furukawa, T. *Polym. Prepr. Jpn* 1990, **39**, E1464