

Short communication

# Ionic conductivities of cross-linked polymer electrolytes prepared from oligo(ethylene glycol) dimethacrylates

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## Abstract

Cross-linked polymer electrolytes are prepared from oligo(ethylene glycol) dimethacrylates (OEGDMA) with different ethylene oxide repeating units in the presence of lithium perchlorate as a lithium salt, ethylene carbonate–propylene carbonate as a mixed plasticizer, and poly(ethylene oxide) as a polymer matrix. The ionic conductivities of polymer electrolytes increase with an increasing amount of the ethylene oxide repeating unit in the OEGDMA. Conversely, the glass transition temperatures of the polymer electrolytes decrease with an increasing amount of the unit. The increased ionic conductivity can be explained by the sites of the spaces surrounded by the main chains and the cross-linking spacers in the polymers. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Cross-linked polymer; Ionic conductivity; Glass transition temperature; Cross-linking spacer

## 1. Introduction

Many solid polymer electrolytes have been studied since Armand et al. [1] first proposed the application of poly(ethylene oxide) (PEO)–lithium complexes in electrochemical devices. As linear PEO electrolytes show low ionic conductivity due to their high crystallinity, graft or block copolymers containing PEO have been prepared to increase ionic conductivity by destroying the PEO crystallization regions. In addition, poly(methacrylate)s with ethylene oxide units as side chains have been prepared [2,3]. The ionic conductivities of all these polymers, however, were also found to be low. Practically, an ionic conductivity of about  $10^{-3}$  S cm<sup>-1</sup> is required to apply solid polymer electrolytes to lithium–polymer batteries. Accordingly, plasticized polymer electrolytes have been recently prepared [4–7] and they exhibited ionic conductivities of  $10^{-3}$  S cm<sup>-1</sup>. Unfortunately, however, their mechanical properties are weak and the plasticizers leak from the polymer electrolytes. To overcome these problems, cross-linked polymers with lithium salts and plasticizers have

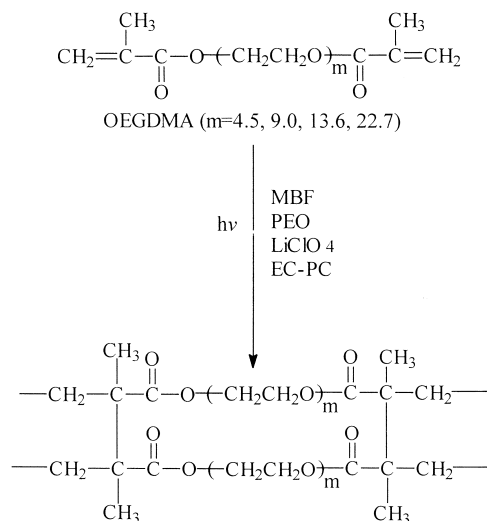
been produced [8–10]. The relationship between the ionic conductivity and the size of the spaces surrounded by the main chains and the cross-linked bridges of these polymers has not been studied. Accordingly, cross-linked polymer electrolytes have been prepared in this work by the photopolymerization of oligo(ethylene glycol) dimethacrylates (OEGDMA) with different ethylene oxide units in the presence of lithium perchlorate, ethylene carbonate (EC)–propylene carbonate (PC) as a mixed plasticizer, and PEO as a polymer matrix, and their ionic conductivities have been investigated.

## 2. Experimental

### 2.1. Materials

OEGDMAs with molecular weights of 354, 554, 754 and 1154 (Polyscience), lithium perchlorate (Aldrich; purity, 95%), PEO with a molecular weight of 2,000,000 (Aldrich), and methylbenzylformate (Aldrich) (MBF) as a photoinitiator were used as received. EC (Aldrich; purity, 98%) and PC (Aldrich; purity, 98%) were used after eliminating moisture using a molecular sieve. Stainless-steel (thickness: 100 μm) (SUS) and lithium foil (FMC; thickness, 100 μm) were also used.

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Scheme 1. Preparation of cross-linked polymer electrolytes (films). One structure of the cross-linked polymer electrolytes.

## 2.2. Preparation of the cross-linked polymer electrolytes

Lithium perchlorate (0.57 g) was dissolved in a mixed plasticizer (4.5 g) of EC-PC (molar ratio 1:1). In this solution, 10 mol (3 g) of OEGDMA ( $m = 13.6$ ) was added to the lithium salt. Also, 5 wt.% (0.15 g) of PEO was added to OEGDMA to improve the mechanical properties. The mixture was then stirred for 6 h. To this solution, 1.5 wt.% ( $4.5 \times 10^{-2}$  g) of MBF (with respect to OEGDMA) was finally added. The MBF was used as a radical-generating photoinitiator. The solution was then poured onto a glass plate and photopolymerized in an argon atmosphere using a high-pressure mercury lamp for 5 min (Scheme 1).

The resulting cross-linked polymer electrolyte was a film with a thickness of about 200  $\mu\text{m}$ . In addition,

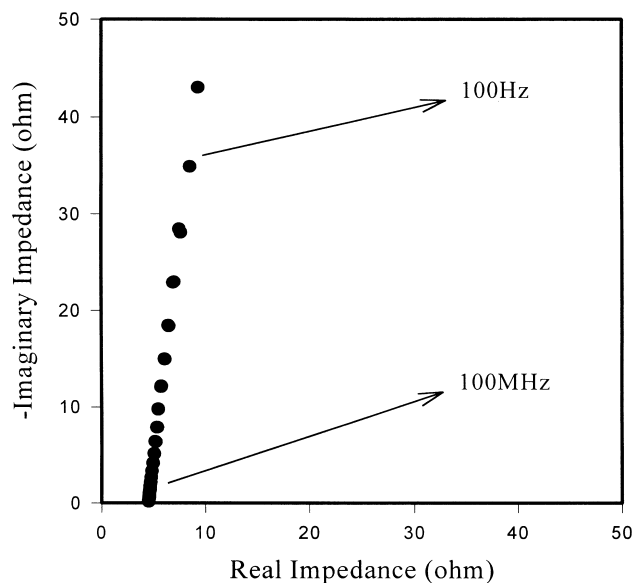


Fig. 1. Nyquist plot of SUS/SPE ( $m = 13.6$ )/SUS cell at 25°C.

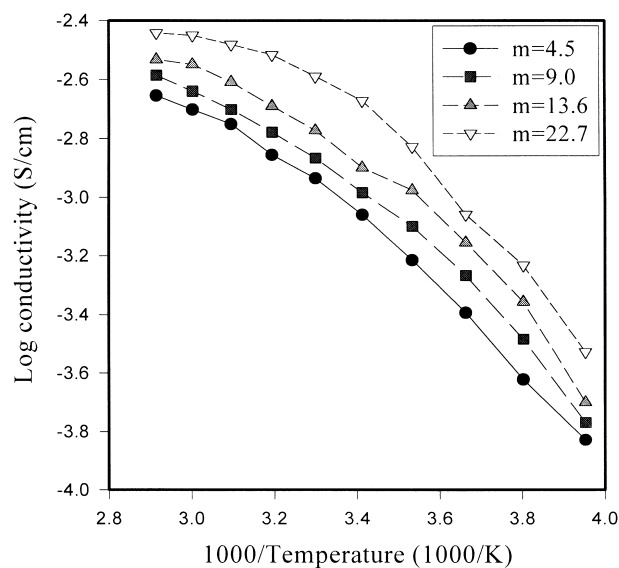


Fig. 2. Temperature dependence of ionic conductivity of SUS/SPE/SUS cells.

different films containing OEGDMA ( $m = 4.5, 9.0$  and  $22.7$ ) were also prepared in the same way as the above film.

## 2.3. Measurement of a.c. impedance of polymer electrolyte films

Cells were fabricated from SUS and the films. The a.c. impedance of these cells was measured by means of a 1M6 impedance measurement system (Zahner Electric). The amplitude was varied from 1 to 10 mV and the frequency ranged from 100 Hz to 100 MHz. The ionic conductivities

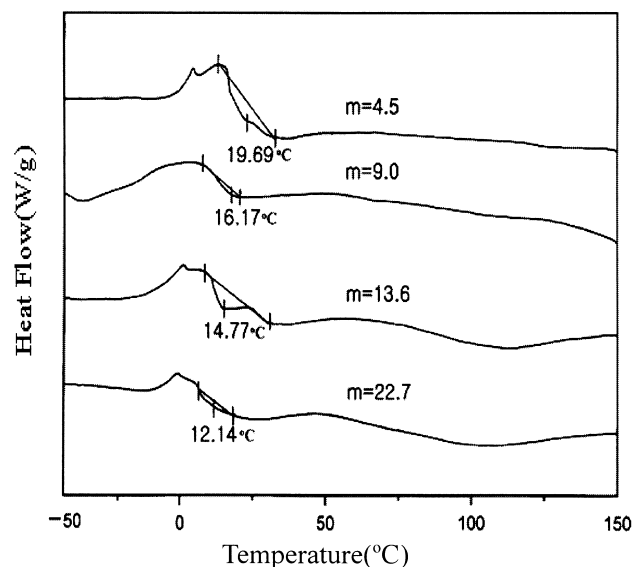


Fig. 3. Relation between glass transition temperatures and  $m$  values of cross-linked polymers.

were then calculated from the real impedance values on a Nyquist plot.

### 3. Results and discussion

The polymer films were somewhat sticky and very transparent. Also, they exhibited a tensile strength on a cell component level. The impedance spectrum of a typical cell constructed from the OEGDMA film ( $m = 13.6$ ) is given in Fig. 1. The ionic conductivity determined from this spectrum was  $1.89 \times 10^{-3} \text{ S cm}^{-1}$  at  $20^\circ\text{C}$ . The influence of temperature on the ionic conductivities of films with different ethylene oxide repeating units is presented in Fig. 2. The conductivity increases with increasing temperature, which could be due to the increased mobility of the films. Furthermore, the conductivity increases with an increasing amount of the ethylene oxide repeating unit of the OEGDMA within the temperature range. The size of the sites surrounded by the main chains and the cross-linking spacers of the polymers in the presence of the plasticizer should increase with an increasing amount of the repeating unit of OEGDMA. Accordingly, the increased conductivities may be related to the size of the spaces in the polymers. In order to demonstrate this phenomenon, the glass transition temperatures ( $T_g$ ) of the polymers are shown in Fig. 3. The value of  $T_g$  decreases with an increasing amount of the repeating unit of OEGDMA. This result indicates that the flexibility of the polymers increases as the size of the spaces increases. PEO with

dimethyl siloxane as the flexible group displays a higher ionic conductivity than PEO [11]. Therefore, the increase in conductivity with an increasing amount of the repeating unit can be explained by the size of the spaces in the polymers and the resulting increased mobility of lithium ions.

### Acknowledgements

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