Solid polymer electrolytes based on oligo(ethylene glycol)methacrylates

1. Conductivity of plasticized networks containing a polar comonomer

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Summary

Complexes of LiCF₃SO₃ and a polymer obtained by polymerization of triethylene glycol dimethacrylate (TRGDMA) and its copolymerization with acrylonitrile (AN) at molar ratios of 0.67, 2.0 and 4.0, both in the presence of poly(ethylene glycol) dimethylether as a plasticizer, provides a.c. conductivities in the range between 10⁻⁵ and 10⁻⁴ S/cm at ambient temperature. An increase of conductivities has been found at growing ratios of [AN]:[TRGDMA] from 0 to 2.0 and molar ratios of ethylene oxide (EO) units : LiCF₃SO₃, ranging from 12 to about 26. The conductivity is nearly independent on the content of AN at [EO]:[Li⁺] = 52.

The temperature-dependence of the conductivity shows an Arrhenius-type behaviour when the content of the salt and/or acrylonitrile in the network was high.

Introduction

In connection with the search for materials of high ionic conductivity at ambient temperature, a variety of possibilities to prevent the crystallization of poly(ethylene oxide) (PEO)-alkali salt complexes has been developed. For instance, by use of comb-like poly(siloxane)s, poly(methacrylate)s or poly(itaconate)s with side chains of relatively low molecular weight PEO, one can obtain nearly amorphous polymer-salt complexes for solid state electrolyte systems (1,2,3,4).

A minor comb density by random incorporation of styrene into the backbone of poly(methoxy poly(ethylene glycol) methacrylate) was reported to reduce the crystallinity and increase the conductivity of polymer complexes doped with alkali salts (4). A comparable behaviour could not be established for similar systems crosslinked via tetraethylene glycol dimethacrylate. ABA block copolymers of poly[oligo(oxyethylene)methacrylate] and poly(styrene) showed a significant decrease in the amount of the conducting phase by the less polar poly(styrene) middle block B (7).
However, the substitution of styrene by the more polar N-vinylpyrrolidone or N-vinylpyridine in unsaturated polyester networks containing LiClO₄ resulted in lower conductivities by about one order of magnitude (15).

Most recently, Florjanczyk et al. (8) have revealed that polar comonomers, such as sulphur dioxide and acrylamide, in copolymer electrolytes seem to promote the interaction between polymer groups and metal cations resulting in high ambient temperature conductivities of about $10^{-3}$ - $10^{-4}$ S/cm. A lithium salt complex of a mixture of ethylene and propylene carbonate in poly(acrylonitrile) with extraordinarily high conductivity investigated by Hong et al. (9) was discussed to be in line with the properties of actually intensively studied gels of a polar solvent and a polymer suitable to impart mechanical stability to the electrolyte system. Conductivity values at ambient temperature reported by Abraham et al. (10) dealing with similar systems do not indicate that there is a significant contribution of the PAN-host to ionic conduction.

To elucidate the role of additional polarity of the polymer host, ionic conductivity of a plasticized LiCF₃SO₃ containing network structure formed by crosslinking of triethylene glycol dimethacrylate in the presence and absence of acrylonitrile has been studied.

**Experimental part**

Materials:
Poly(ethylene glycol)dimethylether (PEGDME, Mol.wt.= 500, Merck-Schuchardt) and triethylene glycol dimethacrylate (TRGDMA, Aldrich Co.) were dried prior to use over a molecular sieve type 4A. Anhydrous lithium trifluoromethane sulfonate (LiCF₃SO₃, Fluka) was treated under reduced pressure at 130°C for 12 h. Inhibitor-free acrylonitrile (AN) was distilled from calcium hydride. Dibenzoylperoxide (DBPO) and N,N'-dimethyl-p-toluidine (DMpT) were purified by conventional methods.

Film preparation:
Films of 100-300 μm in thickness were prepared by crosslinking homopolymerization of TRGDMA and copolymerization of TRGDMA and AN in the presence of PEGDME and LiCF₃SO₃ by the following procedure:

PEGDME was mixed with the corresponding amount of salt at 50°C. After cooling in a dessicator, a TRGDMA-DBPO master solution and, in the case of copolymerization, acrylonitrile was added to the mixture. At least an amount of DMpT as redox activator equimolar to DBPO was dropped into the solution using a microlitre syringe. Thus prepared viscous liquids were thoroughly stirred for 30 seconds and then pressed between two Teflon® plates equipped with a distance holder of different thickness (100-300 μm). The films formed at ambient temperature in a period of 10-15 minutes were annealed at 80°C in vacuo for 10 h and stored in a dry box for several days.
Films formed at molar ratios of [AN]:[TRGDMA] > 4 were not taken into account because their formation was accompanied by a longer...