

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 LiCF_3SO_3 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 $[\text{AN}]:[\text{TRGDMA}]$ from 0 to 2.0 and molar ratios of ethylene oxide (EO) units : LiCF_3SO_3 , ranging from 12 to about 26. The conductivity is nearly independent on the content of AN at $[\text{EO}]:[\text{Li}^+] = 52$.

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).

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However, the substitution of styrene by the more polar N-vinylpyrrolidone or N-vinylpyridine in unsaturated polyester networks containing LiClO_4 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^{-5} - 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 LiCF_3SO_3 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 (LiCF_3SO_3 , 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 LiCF_3SO_3 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 micro litre 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 $[\text{AN}]:[\text{TRGDMA}] > 4$ were not taken into account because their formation was accompanied by a longer

period of polymerization yielding very brittle films after annealing.

Impedance measurements:

The measurements in the frequency range of 0,1Hz -100 kHz were performed from ambient temperature to approximately 75°C using a transfer function analyzer (Schlumberger, SI 1255). The impedance of the working electrode was determined at its equilibrium potential by means of a potentiostat-galvanostat (EG&G Princeton Applied Research, PAR 273). The working and counter electrode area of the two electrode lithium cells built for electrochemical experiments was 2 cm².

Results and discussion

Redox-initiated, solvent-free preparation of LiCF₃SO₃-doped network structures of compositions given in Table 1 provides yellowish-transparent and homogeneous films. Initiator concentration and concentration of the plasticizer were kept constant and chosen to give not too strongly crosslinked polymers in order to avoid brittle materials but guaranteeing sufficient mechanical stability. Polymerizations were carried out at a constant molar concentration of C=C-double bonds by stepwise replacement of TRGDMA by acrylonitrile.

The plots of conductivity, σ , versus the [EO]/[LiCF₃SO₃] ratio for a TRGDMA-network and three TRGDMA-AN copolymer films all prepared in the presence of PEGDME show a dependence on the content of acrylonitrile. A maximum is observed at a [EO]/[LiCF₃SO₃] ratio of approximately 26 in the cases of experiments a-c, whereas a maximum of conductivity for experiment d is found in the range between 15 and 17. A shift in the conductivity maximum has already been pointed out in a flatter slope of curve c in the range of high salt concentrations. The appearance of a conductivity maximum is not surprising and widely discussed in literature (11,12,13). In the range of low salt concentration ([EO]/[LiCF₃SO₃]=52-55), the conductivity is nearly independent on the content of acrylonitrile, and it is relatively good in accordance with measurements of Wright et al.(15) for unsaturated polyester networks.

Table 1. Composition of the initial mixtures (4.2·10⁻³ mol C=C-double bonds; 2 mole% DBPO and DMpT referring to C=C-double bonds; [PEGDME] / [C=C-double bonds] = 0.56; [EO]/[Li⁺] = 12 - 55

Exp.	a	b	c	d
[AN] / [TRGDMA] [mole/mole]	0	0.67	2.00	4.00

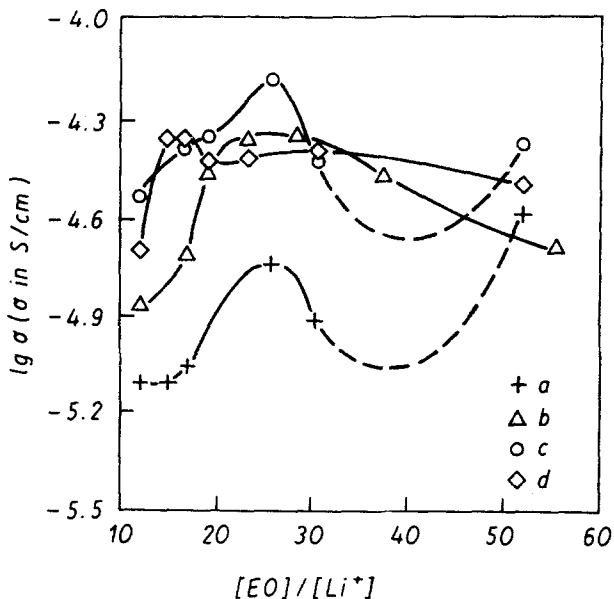


Fig.1 Log σ versus $[EO]/[Li^+]$ for plasticized networks at various contents of AN at ambient temperature

Furthermore, Fig.1 illustrates that the conductivities are increased when the crosslinking monomer TRGDMA is replaced by the comonomer acrylonitrile in the range of $[AN]/[TRGDMA]$ from 0 to 2 and $[EO]/[LiCF_3SO_3]$ from 12 to about 26. This result is suitable to confirm the supposition that ion conduction in a polymer which contains a relatively great part of strongly polar units in addition to EO-sequences is promoted by an improved salt dissociation. In fact, an intensive interaction between the nitrile group of acrylonitrile and $LiCF_3SO_3$ has been evidenced by I.R.spectroscopy (14). On the other hand, it has to be noted that this kind of association may contribute to a restricted movement of the charge carriers. The balance in polymer-ion interaction in the complexes investigated seems to appear in the films prepared with a molar ratio $[AN]:[TRGDMA] = 2.00$. Films prepared at this composition showed the highest values of conductivity reaching $6.3 \cdot 10^{-5}$ S/cm at ambient temperature. In comparison to the copolymer films the complexes prepared without acrylonitrile exhibit somewhat lower conductivities. It should be added that these materials are expected to show the highest degree of crosslinking because of the absence of acrylonitrile which decreases the crosslinking density.

The temperature-dependence of the conductivity has been considered using the classical Arrhenius plot, where

$$\sigma = A \exp(-E_a/kT)$$

Fig.2 presents related curves for the films of experiment c at three selected salt contents. A typical Arrhenius-type behaviour ($E_a = 30.6$ kJ/mol) can only be ascertained at the highest salt concentration ($[EO]/[Li^+] = 19.3$). It may be attributable to a crystalline phase structure (15), probably due to increased interionic interactions.

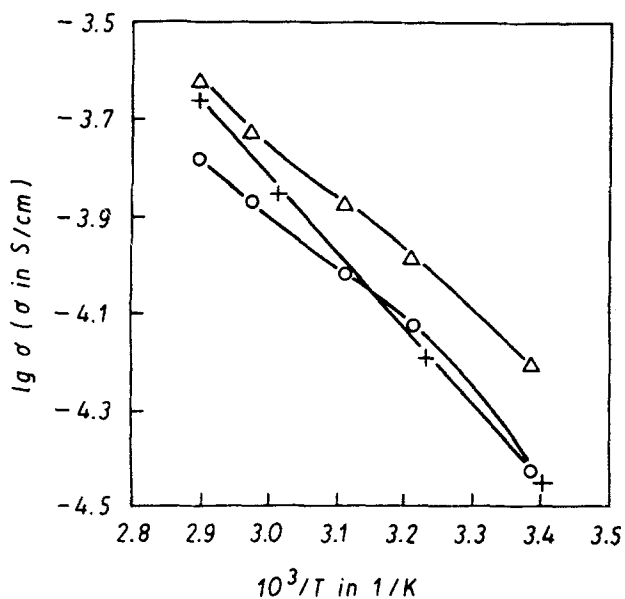


Fig.2 Temperature-dependence of the conductivity, σ , for cross-linked complexes of $[\text{AN}]:[\text{TRGDMA}] = 2.00$ and LiCF_3SO_3 at $[\text{EO}]/[\text{Li}^+] = 19.3$ (+) 25.8 (Δ) and 30.5 (o)

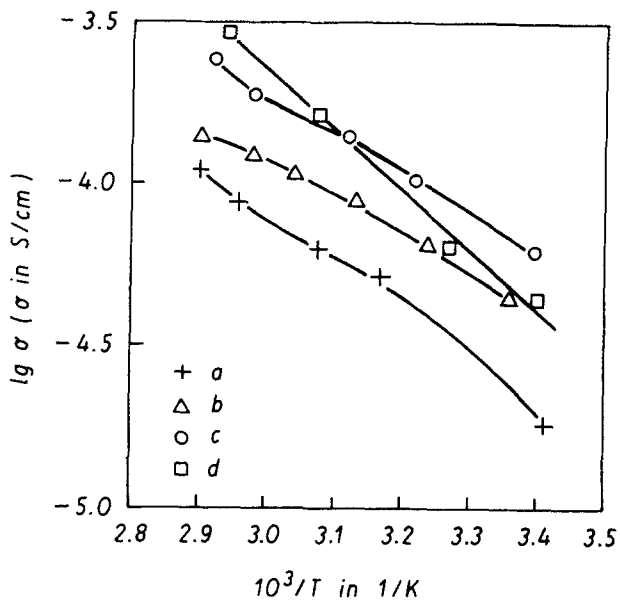


Fig.3 Temperature-dependence of the conductivity, σ , for cross-linked complexes of $[\text{AN}]/[\text{TRGDMA}] = 0; 0.67; 2.00; \text{ and } 4.00$ and LiCF_3SO_3 at optimum salt concentration

A similar feature is given in Fig.3 depicting the temperature-dependence of all complexes studied at the optimum composition in relation to conductivity. Crosslinked copolymer films with the highest content of acrylonitrile show a nearly Arrhenius-type relationship ($E_a = 21-35$ kJ/mol) which can be derived over the complete range of salt concentration considered. That seems to be connected with their most probable tendency to form microcrystalline domains by a favoured association with the salt caused by the nitrile groups. Studies about the structure of the networks and the glass transition of the complexes are in preparation.

Conclusions

The insertion of the highly polar acrylonitrile into polyether-based network structures plasticized with PEGDME was found to enhance the conductivities of their complexes with LiCF_3SO_3 depending on the molar ratio of crosslinker to comonomer. However, one can imagine that the external plasticizer providing a liquid-like phase behaviour plays the main part in solvating the salt in the systems described in this paper. For this reason it should be interesting to investigate systems with a more dominant influence of a highly polar co-component. Work is still in progress to clarify this point.

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