

# Transport mechanism in anionic conductive ionomers from temperature and pressure conductivity measurements

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## Abstract

Anionic ionomers exclusively conducting by  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BF_4^-$ ,  $(CF_3SO_2)_2N^-$ , anions are synthesised by grafting a quaternary ammonium salt into an unsaturated poly(oxyethylene) matrix. An experimental set up allows accurate measurements of their conductivity versus pressure,  $P$  (1–5000 bars) as well as versus temperature,  $T$  (290–390 K). Experimental data give access to an “apparent activation volume” decreasing with increasing temperature and currently between 10 and 30 cm<sup>3</sup>/mol in the temperature range 390–300 K.

A microscopic approach is developed assuming an activated mechanism for charge carrier formation and a free volume model for their mobility. According to this model the apparent activation volume would result from the contribution of two terms. The first one, negative, would be related to the formation of charge carriers, the second one, positive, to their migration. The negative value associated to charge carriers formation can be explained by a volumic contraction induced by the dissociation phenomena. The free volume values necessary to the anionic migration are close to the anion volume at room temperature. This result is in agreement with a weak interaction between polyethers and anions.

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## 1. Introduction

The present study is an attempt to elucidate the mechanisms involved in ionic migration for salt polymer complexes. Such polymers are extensively studied for potential applications as electrolytes in lithium batteries. The so-called “dry salt polymer complexes” associate a polymer matrix as single solvent of a lithium salt. The polymer matrix can be poly(oxyethylene) (POE), comb poly(oxyethylene), and the lithium salts are currently lithium perchlorate  $LiClO_4$ , lithium triflate  $LiCF_3SO_3$  or lithium bis(trifluoromethanesulfonyl)amide  $LiN(CF_3SO_2)_2$ , (LiTFSI). In such a polymer electrolyte, the anion and the

cation are simultaneously mobile and make difficult the understanding of their respective ionic displacement mechanisms.

To discriminate between anion and cation and to compare their migration, we have synthesised purely cationic and anionic conductive ionomers in which the counter ions are grafted and then immobilised on the macromolecular chains. A previous work was devoted to cationic ionomers [1]. Present results concern the effect of temperature and pressure on the anionic ionomers.

In order to simplify the system, single-ion conducting polymers were prepared, in order to get ionomers with either anion or cation mobility. The polymer electrolyte was designed in such a way (i) to avoid creeping; (ii) to be amorphous in a wide temperature range; (iii) to have high solvating ability. Thus, we selected unsaturated polyethers

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which can be easily cross-linked by UV or thermal free-radical initiation. Prepolymers with the same length of oligoether blocks between two unsaturated sites were selected, to keep the same solvating ability and the same cross-link density. A diallylamine is chased to simultaneously fixing the cation and cross-linking the polymer chains. The latter undergoes a cyclization during the cross-linking step providing a five-membered cycle. Therefore, except the nature of the ion-pair, single cation and anion conducting polymers are identical.

## 2. Experimental

### 2.1. Anionic ionomer preparation and characterisations

The synthesis procedure is described in details elsewhere [2]. The ionomers are prepared by cross-linking a quaternary ammonium salt with an unsaturated pre-polymer. This pre-polymer matrix is formed by macromolecular chains, containing solvating oxygen atoms and double C=C bonds. It is prepared by the polycondensation reaction between  $\alpha,\omega$ dihydroxyoligopolyoxyethylene (PEG) ( $\overline{M}_W = 1000$ ) and an unsaturated dihalide isobutenyl compound, 3-chloro-2-chloromethyl-1-propene [3] (Fig. 1a).

A diallyldimethylammonium salt  $R_N^+X^-$  is further grafted under UV reaction to this pre polymer using a photo initiator (IRGACURE<sup>®</sup> 2959, CIBA) (Fig. 1b).  $R_N^+$  represents the  $(CH_2=CH-CH_2)_2N^+(CH_3)_2$  cation associated to various  $X^-$  anions. The  $R_N^+X^-$  salts are prepared by ionic exchange [2] from the diallyldimethylammoniumchloride

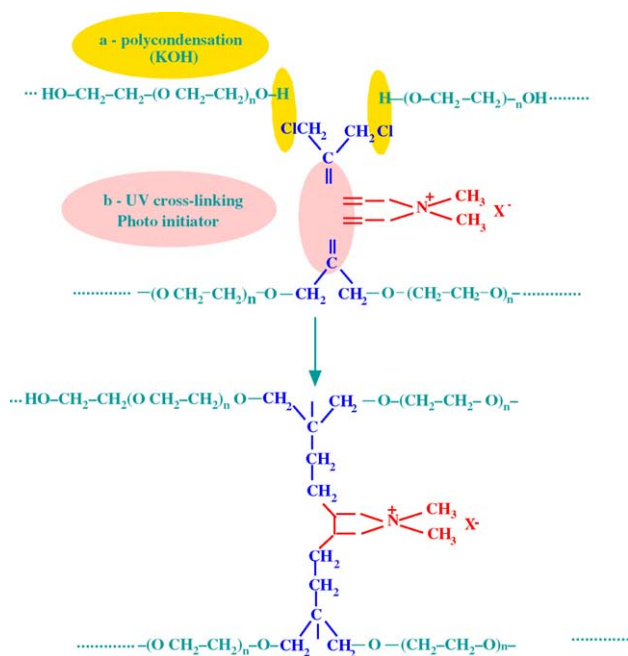


Fig. 1. Preparation of the anionic ionomers. (a) First step preparation of the pre-polymer by polycondensation. (b) Salt grafting to the polymer.

salt  $R_N^+Cl^-$ , commercially available (Aldrich, 65 wt% solution in water). This salt polymerizes quite rapidly. The mechanism leads to intramolecular cyclization with five membered pyrrolidine ring formation [4].

Gel permeation chromatography (GPC) allows to identify the nature and the quantity of unreacted species. In most cases, it reveals the absence of initial pre-polymer and photo initiator. The amount of bonded  $R_N^+X^-$  is calculated taking into account GPC results and weight difference of the polymer film, before and after washing and drying. Concentration in anion  $X^-$  is expressed as the molar ratio O/X of oxygen atoms belonging to polycondensate.

For the ionic conductivity measurements as a function of pressure and temperature we have selected ionomers with different anions,  $X = Cl, Br, I, BF_4, N(CF_3SO_2)_2, (TFSI)$  and with similar anionic concentration (O/X #30).

Differential scanning calorimeter (DSC) measurements are used for thermal characterisation of the ionomers. Melting temperatures,  $T_m$ , of the crystalline phase are between 257 K and 278 K. They are semi crystalline below room temperature.  $T_g$  values of the glassy phase are almost constant ( $217 \pm 2$  K) and independent of the anion. When the pre polymer is reticulated through the unsaturated C=C bonds, without  $R_N^+X^-$  salts,  $T_g$  is also found to 218 K which means that the grafted salt weakly interacts with the polyether chains. Same results and conclusion were drawn from the previous study on cationic ionomers [1].

### 2.2. Conductivity measurements as function of temperature and pressure

The polymer electrolyte samples are circular membranes of about 13 mm in diameter and of 0.1–0.4 mm thickness. Electrodes are platinum foils stuck to platinum leads with a platinum paint. The electrolyte and the electrodes are then coated with an electrically insulating silicon polymer allowing the pressure transfer to the sample. The coated samples are introduced in the chamber of an isostatic press. A silicon oil is used as the pressure fluid in the range 1–5000 bars. A heating element immersed in the silicon oil allows to adjust the temperature between the room one and 120 °C. A piezo-electric pressure sensor and a Fe-constantan thermocouple determine the pressure and the temperature inside the chamber, respectively.

The conductance,  $G$ , of the sample is measured by the impedance technique in the frequency range 5 Hz–13 MHz. The experimental set up and experimental procedures have been described in previous paper [5]. Because of the negligible values of the thermal expansion and the volumic compressibility coefficients of the polymers, the conductivity values,  $\sigma$ , are directly deduced from the conductance values ( $\sigma = G\ell/S$ ) using the geometric parameters,  $\ell$  (thickness) and  $S$  (electrode surface), of the samples measured at room temperature under atmospheric pressure.

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