

# Effect of Cation and Salt Concentration on Conductivity and Microstructure Characteristics of Polyether Electrolytes Doped with Alkali Metal Perchlorates

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The effect of the type of alkali metal cation on the conductivity and ion transport mechanism is analyzed for PEGME–MClO<sub>4</sub> electrolytes (where M = Li, Na, K, Rb, Cs). The data are obtained in the wide alkali metal perchlorate concentration (from 10<sup>−5</sup> to 5 mol/kg PEGME) range. The obtained results evidenced that at salt concentrations less than 10<sup>−3</sup> mol/kg higher conductivities are obtained for Li, Na, and K perchlorates, whereas at salt concentrations greater than 1 mol/kg conductivities measured for Cs and Rb perchlorates are higher. At intermediate salt concentration ranges, conductivities measured for all systems are similar. The observed trends are supported by the viscosity and IR results describing the ion–ion and ion–polymer interactions. The formation of ionic associates is additionally monitored by the application of the Fuoss–Kraus formalism to the salt concentration dependence of the molar conductivity.

## Introduction

The interest in the studies of polymer electrolytes arises from the possibility of their applications in a variety of electrochemical devices working from subambient to moderate temperatures.<sup>1–3</sup> The use of polymer electrolytes in lithium or (and) lithium ion batteries are of particular importance. So far, mainly polymer gels have been used in ambient temperature devices due to the insufficient conductivity and low cation transference number of solid polymer electrolytes mainly based on polyethers.<sup>4</sup> Several methods of modification of the structure of polyether electrolytes were suggested and studied to enhance ionic conductivity and cation transference number.<sup>1–3,5</sup> Although some of those modifications were very successful, the electrolytes obtained still exhibit properties not suitable for applications at ambient or subambient temperature lithium or lithium ion batteries.<sup>1,3</sup>

Another important group of studies devoted to polyether electrolytes was to find out the ionic transport mechanism in these systems and its relation to temperature, ionic dopant type, and its concentration. These studies were often performed for low molecular weight analogues of polyethers.<sup>6,7</sup> The effect of the type of end polymer chain group and anion structure on ionic association, lithium ion transport, and electrolyte microstructure was analyzed.<sup>8–16</sup> Most of these studies were, however, performed within the limited salt concentrations and temperature ranges.<sup>8–16</sup>

In the present work the effect of the type of alkali metal cation on the conductivity and cation transport mechanism is analyzed for poly(ethylene glycol) methyl ether (PEGME)–MClO<sub>4</sub> electrolytes (where M = Li, Na, K, Rb, Cs). The discussion is supported by the data obtained from impedance spectroscopy, viscosity, FT-IR, and DSC experiments. The data are obtained in the wide alkali metal perchlorate concentration (from 10<sup>−5</sup> to 5 mol/kg PEGME) range.

Changes in the ionic conductivity as a function of the type of alkali metal perchlorate and its concentration are analyzed on the basis of impedance spectroscopy experiments. The changes in the molar conductivity as a function of salt concentration are analyzed according to the Fuoss–Kraus formalism to calculate fractions of free ions, ion pairs, and higher aggregates. Ion–ion and ion–polymer interactions are analyzed on the basis of FT-IR experiments. IR data are supported by the studies of the electrolyte viscosity and polymer chain flexibility performed by rheological and DSC techniques.

## Experimental Section

**Sample Preparation.** PEGME (*M*<sub>w</sub> = 350, Aldrich, mono-methyl-capped, melting temperature equal to −8 °C) was filtered, dried on a vacuum line at ~60 °C for 72 h, and then, under a vacuum of 10<sup>−5</sup> Torr, stringently freeze-dried using freeze–pump–thaw cycles. While still under vacuum, the polymer was transferred to an argon-filled drybox (moisture content lower than 2 ppm), where the salt was dissolved into the polymer using a magnetic stirrer. The salt concentration varied from 10<sup>−5</sup> to 5 mol/kg of polymer. Samples with the salt concentration from 5 down to 0.5 mol/kg were prepared by the direct dissolution of the salt in a polymer. Samples of the highest salt concentrations were heated to 50 °C to facilitate the dissolution process. Samples of lower salt concentrations were prepared by the successive dilution of a batch containing the electrolyte with 0.5 mol/kg of alkali metal salt. LiClO<sub>4</sub>, NaClO<sub>4</sub>, KClO<sub>4</sub>, RbClO<sub>4</sub>, and CsClO<sub>4</sub> (Aldrich, reagent grades) were dried under vacuum at 10<sup>−5</sup> Torr at 120 °C prior to the dissolution. All samples were equilibrated at ambient temperature for at least 1 month before undertaking any experiments. (The compositions of all synthesized electrolytes are described in Table A (Supporting Information).)

## Experimental Techniques

**DSC Studies.** DSC data were obtained between −110 and +150 °C using the UNIPAN 605 M scanning calorimeter with

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a low-temperature measuring head and liquid nitrogen cooled heating element. The samples were equilibrated by slow cooling to  $-110\text{ }^{\circ}\text{C}$  and then heated at  $10\text{ }^{\circ}\text{C}/\text{min}$  to  $150\text{ }^{\circ}\text{C}$ . An empty aluminum pan was used as the reference. The estimated experimental error of the determination of the glass transition temperature ( $T_g$ ) is  $\pm 2\text{ }^{\circ}\text{C}$ .

**Conductivity Measurements.** The impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range of 1 Hz to 100 kHz. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature controlled oven. The experiments were performed in a constant volume cylindrical cell with electrode diameter equal to 7.8 mm and fixed electrolyte thickness equal to 1.6 mm. The reproducibility of impedance spectroscopy results was checked by the multiple experiments performed at room temperature. All results obtained for samples of the same composition did not differ by more than 10%. To check the effect of the residual catalyst, possibly included in the PEGME, on the ionic conductivity of the studied electrolytes, the room-temperature conductivity of PEGME was also measured and was equal to  $\sim 10^{-9}\text{ S/cm}$ . This value is roughly 2 orders of magnitude lower than the lowest conductivity measured for the electrolyte sample. Therefore we have concluded that the effect of the presence of residual traces of catalysts and other impurities on the conductivity of the electrolytes studied can be neglected.

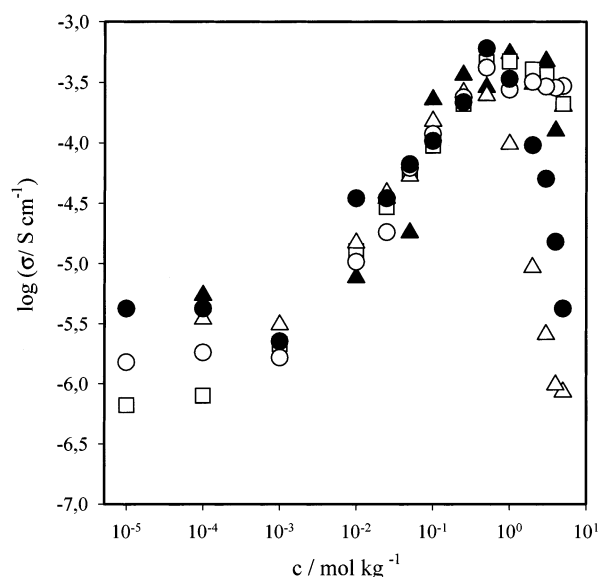
**FT-IR.** Infrared absorption spectra were recorded on a computer-interfaced Perkin-Elmer 2000 FT-IR system with a wavenumber resolution of  $2\text{ cm}^{-1}$ . FT-IR studies were performed at  $25\text{ }^{\circ}\text{C}$ . Electrolytes were sandwiched between two NaCl plates and placed in the FT-IR temperature controlled cell; the accuracy of the temperature was estimated to be  $\pm 1\text{ }^{\circ}\text{C}$ .

**Rheological Experiments.** Rheological experiments were conducted at  $25\text{ }^{\circ}\text{C}$  using the Bohlin Visco 88BV viscometer in two coaxial cylinders geometry. The measurements were performed within a shear rate of  $24\text{--}1200\text{ cm}^{-1}$ . The estimated error of the rheological experiments is 10%.

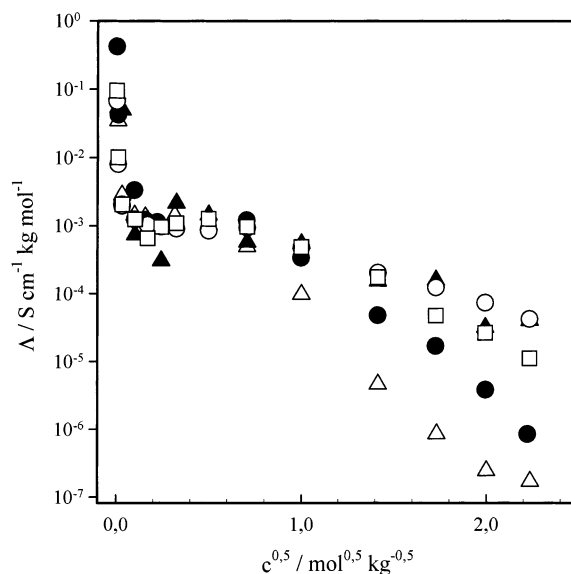
## Results

Figure 1 presents changes of the ionic conductivity as a function of perchlorate concentration obtained for PEGME- $\text{MClO}_4$  electrolytes. At low salt concentrations up to  $10^{-3}\text{ mol/kg}$  conductivities measured for Li, Na, and K perchlorate doped electrolytes are higher than the conductivities measured for systems doped with Rb and Cs perchlorates. The latter ones are about 1 order of magnitude lower. In the salt concentration range from  $10^{-3}$  to approximately  $1\text{ mol/kg}$  electrolyte conductivities do not depend on the type of alkali metal cation and do not differ from each other by more than the experimental error of the impedance spectroscopy experiments. Small differences in the conductivity measured for samples assigned to the same composition may also result from in fact slight variation in the sample composition (see Table A in the Supporting Information). At salt concentrations higher than  $1\text{ mol/kg}$  conductivities obtained for electrolytes doped with Li and Na perchlorates are considerably lower than for the other systems studied.

The same trends (especially at high salt concentrations) can easily be observed in Figure 2 where the molar conductivity as a function of the square root of salt concentration is presented. The differences in conductivities of the electrolytes studied correspond to the regions in which the formation of ion pairs takes place (low salt concentrations) and in which the effect of



**Figure 1.** Changes in ionic conductivity as a function of salt concentration measured at  $25\text{ }^{\circ}\text{C}$  for (●) PEGME- $\text{NaClO}_4$ , (□) PEGME- $\text{CsClO}_4$ , (△) PEGME- $\text{LiClO}_4$ , (▲) PEGME- $\text{KClO}_4$ , and (○) PEGME- $\text{RbClO}_4$  electrolytes. Error bars are within the size of the experimental points.



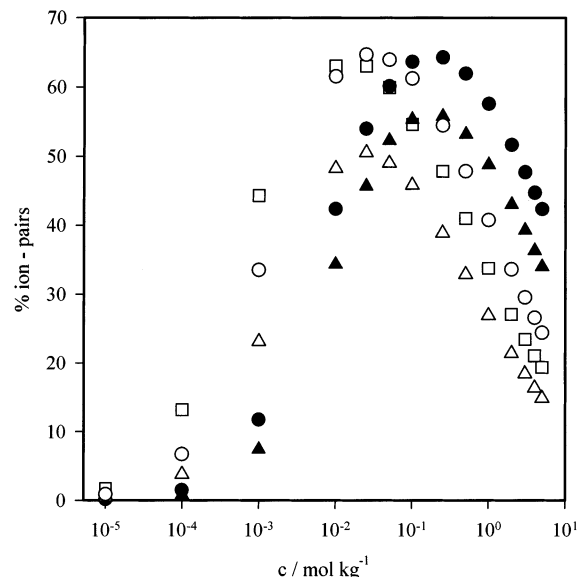
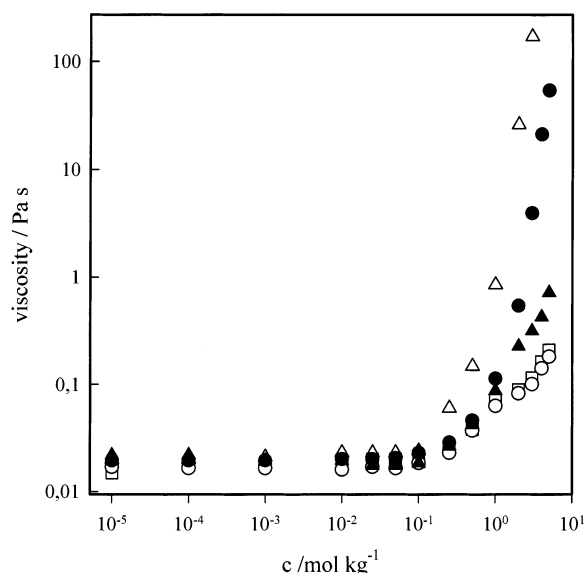
**Figure 2.** Changes in molar conductivity as a function of square root of molar concentration measured at  $25\text{ }^{\circ}\text{C}$  for (●) PEGME- $\text{NaClO}_4$ , (□) PEGME- $\text{CsClO}_4$ , (△) PEGME- $\text{LiClO}_4$ , (▲) PEGME- $\text{KClO}_4$ , and (○) PEGME- $\text{RbClO}_4$  electrolytes. Error bars are within the size of the experimental points.

the increase in the electrolyte viscosity with an increase in the salt concentration (high salt concentrations) has a dominant effect on ionic conductivity according to the original Fuoss-Krauss assumptions.<sup>17,18</sup>

In Figure 3 changes in the concentration of ion pairs as a function of salt concentration are depicted. The fraction of ion pairs was calculated on the basis of the Fuoss-Krauss formalism, as described previously by several authors.<sup>8,17,19,20</sup> Data used in calculations of the fraction of ion pairs are included in Table 1. At low salt concentrations the fraction of ion pairs for Rb and Cs perchlorates is higher than that for systems doped with other alkali metal perchlorates. The maximum in the fraction of ion pairs occurs at lower salt concentration for Li, Rb, and Cs perchlorate based electrolytes than for  $\text{NaClO}_4$  and

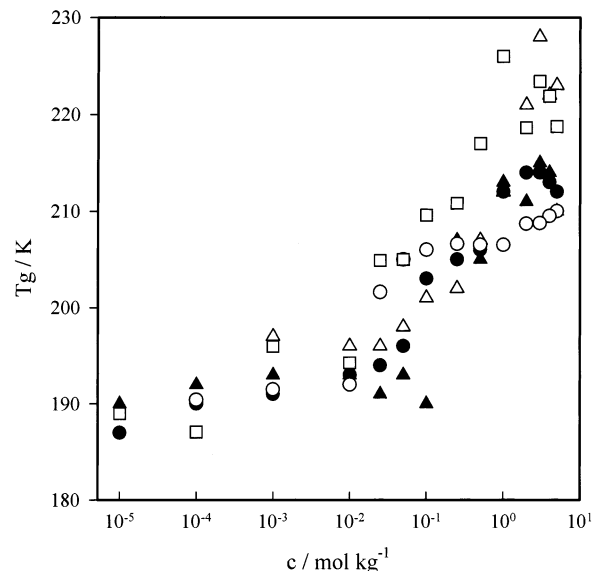
**TABLE 1: Physicochemical Data Used for the Calculation of Ionic Association on the Basis of the Fuoss–Kraus Formalism**

data	PEGME–LiClO <sub>4</sub>	PEGME–NaClO <sub>4</sub>	PEGME–KClO <sub>4</sub>	PEGME–RbClO <sub>4</sub>	PEGME–CsClO <sub>4</sub>
av Walden ( $\Lambda_o\eta$ )	0.614	0.681	0.816	0.841	0.838
$\Lambda_o/S$ cm <sup>-1</sup> mol <sup>-1</sup> kg	$3.35 \times 10^{-3}$	$3.72 \times 10^{-3}$	$4.46 \times 10^{-3}$	$4.60 \times 10^{-3}$	$4.58 \times 10^{-3}$
$\lambda_o/S$ cm <sup>-1</sup> mol <sup>-1</sup> kg	$2.23 \times 10^{-3}$	$2.48 \times 10^{-3}$	$2.97 \times 10^{-3}$	$3.06 \times 10^{-3}$	$3.05 \times 10^{-3}$
$\gamma/g$ cm <sup>-3</sup>	1.094	1.094	1.094	1.094	1.094
$\eta/Pa$ s	0.020	0.020	0.020	0.020	0.020
$K_I/mol^{-1}$ kg	501	154	98	941	1459
$K_T/mol^{-1}$ kg	54.0	6.7	7.5	40.5	69.4

**Figure 3.** Changes in the concentration of ion pairs as a function of salt concentration calculated on the basis of the Fuoss – Kraus formalism at 25 °C for (●) PEGME–NaClO<sub>4</sub>, (□) PEGME–CsClO<sub>4</sub>, (△) PEGME–LiClO<sub>4</sub>, (▲) PEGME–KClO<sub>4</sub>, and (○) PEGME–RbClO<sub>4</sub> electrolytes.**Figure 4.** Changes in the electrolyte viscosity as a function of salt concentration. Data obtained at 25 °C for (●) PEGME–NaClO<sub>4</sub>, (□) PEGME–CsClO<sub>4</sub>, (△) PEGME–LiClO<sub>4</sub>, (▲) PEGME–KClO<sub>4</sub>, and (○) PEGME–RbClO<sub>4</sub> electrolytes.

KClO<sub>4</sub> doped systems. At high salt concentrations the fraction of ion pairs for Na and K perchlorates doped electrolytes is the highest.

Figure 4 presents the changes in the electrolyte viscosity as a function of MClO<sub>4</sub> concentration for PEGME–MClO<sub>4</sub> electrolytes at 25 °C. Up to the salt concentration equal to 0.25

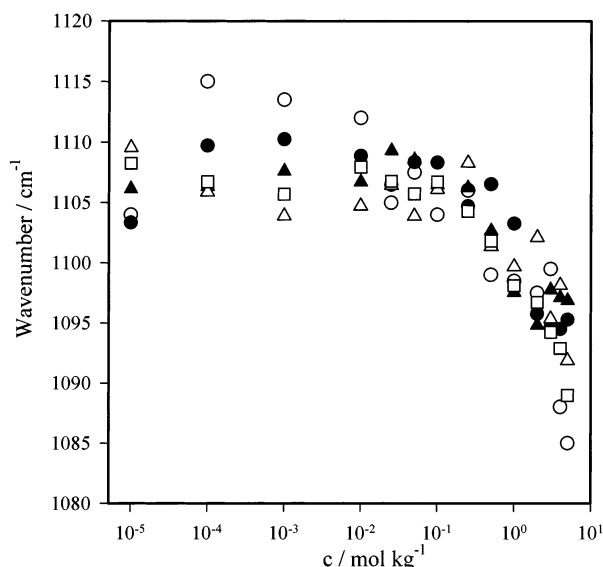
**Figure 5.** Changes in the  $T_g$  as a function of salt concentration. Data for (●) PEGME–NaClO<sub>4</sub>, (□) PEGME–CsClO<sub>4</sub>, (△) PEGME–LiClO<sub>4</sub>, (▲) PEGME–KClO<sub>4</sub>, and (○) PEGME–RbClO<sub>4</sub> electrolytes.

mol/kg viscosities are roughly independent of the type of alkali metal cation. At higher salt concentrations viscosity increases with a decrease in the size of alkali metal cation and is the highest for LiClO<sub>4</sub> and NaClO<sub>4</sub> doped electrolytes.

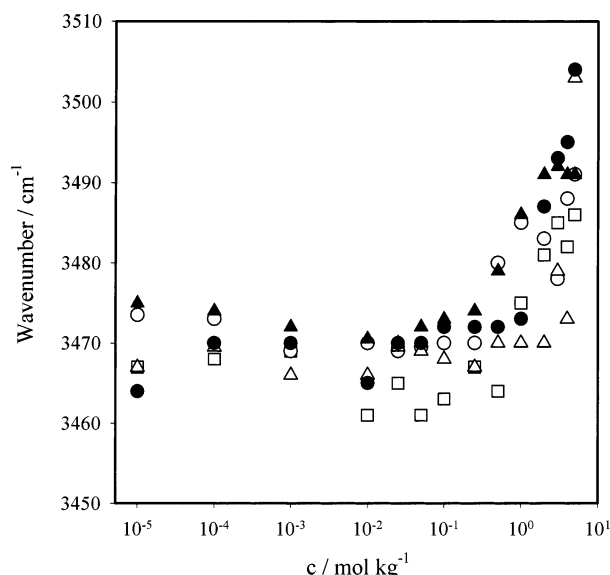
In Figure 5 changes in the glass transition temperature as a function of MClO<sub>4</sub> concentration are shown. In the entire salt concentration range  $T_g$  varied rather randomly as a function of the type of alkali metal cation and generally increases with an increase in the MClO<sub>4</sub> concentration. At MClO<sub>4</sub> concentrations higher than 1 mol/kg glass transition temperatures measured for electrolytes doped with LiClO<sub>4</sub> and CsClO<sub>4</sub> are higher than for electrolytes doped with other alkali metal perchlorates.

Figure 6 shows changes in the maximum of the C–O–C stretch as a function of MClO<sub>4</sub> concentration. Up to the salt concentration equal to ~1 mol/kg the position of the C–O–C maximum is between 1100 and 1110 cm<sup>-1</sup> for all electrolytes studied. For higher salt concentrations the position of the C–O–C peak shifts to lower wavenumbers and for the salt concentrations greater than 3 mol/kg the position of C–O–C stretch for RbClO<sub>4</sub> and CsClO<sub>4</sub> doped electrolytes occurs roughly at 10 cm<sup>-1</sup> lower wavenumbers than for other electrolytes studied.

Figure 7 presents the position of the maximum of IR O–H vibrations as a function of salt concentration for PEGME – MClO<sub>4</sub> electrolytes. Up to the salt concentration of ~1 mol/kg the position of O–H maximum is between 3460 and 3480 cm<sup>-1</sup> for all electrolytes studied and changes rather randomly with the salt concentration and type of alkali metal cation. At higher salt concentrations the upshift of the O–H maximum is observed. The position of the O–H maximum in this salt concentration range depends on the type of alkali metal cation



**Figure 6.** Changes in the maximum of the C–O–C stretching mode as a function of salt concentration for (●) PEGME–NaClO<sub>4</sub>, (□) PEGME–CsClO<sub>4</sub>, (△) PEGME–LiClO<sub>4</sub>, (▲) PEGME–KClO<sub>4</sub>, and (○) PEGME–RbClO<sub>4</sub> electrolytes.



**Figure 7.** Position of maximum of IR O–H vibrations as a function of salt concentration for (●) PEGME–NaClO<sub>4</sub>, (□) PEGME–CsClO<sub>4</sub>, (△) PEGME–LiClO<sub>4</sub>, (▲) PEGME–KClO<sub>4</sub>, and (○) PEGME–RbClO<sub>4</sub> electrolytes.

and is higher for electrolytes doped with Li, Na, and K perchlorates.

## Discussion

On the basis of the analysis of the changes in the molar conductivity as a function of salt concentration, three characteristic regions describing the conductivity behavior can be distinguished. At salt concentrations below  $10^{-3}$  mol/kg PEGME molar conductivity decreases with an increase in salt concentration most probably due to the formation of solvent separated ion pairs. At intermediate salt concentration range ( $10^{-3} < c < 1$  mol/kg PEGME) there is a slight increase in the conductivity due either to the redissociation of ion pairs or to the formation of positively or negatively charged triplets. According to the literature data<sup>9,10</sup> the former effect seems to be more probable. If the formation of ionic triplets occurs, the positive ones are

easier to form according to the quantum mechanical calculations.<sup>21</sup> At salt concentrations higher than 1 mol/kg PEGME the increase in the viscosity is observed (see Figure 4), which results in the decrease in the molar conductivity. This increase in the viscosity can be associated with the formation of intermolecular transient cross-links via positively charged triplets, as described extensively in the former papers.<sup>9,10,21,23</sup> At low and intermediate salt concentrations intramolecular cross-links formed by alkali metal cations coupled to ether oxygens or end polymer chain OH groups are predominant.

By analyzing changes in the conductivity as a function of the type of alkali metal perchlorate, one can postulate different ion conduction behaviors corresponding to the above-mentioned salt concentration regions. At salt concentrations up to  $\sim 10^{-3}$  mol/kg PEGME the conductivities of Li, Na, and K electrolytes are higher than those for Rb and Cs salts. These might be due to the lower fraction of ion pairs for systems with smaller cations, as shown in Figure 3 on the basis of Fuoss–Krauss calculations. At low salt concentrations the electrolyte's viscosity and flexibility of polyether segments are similar, as shown from viscosity and DSC studies (see Figures 4 and 5).

At the intermediate salt concentration range (from  $\sim 10^{-3}$  to  $\sim 1$  mol/kg) the formation of intramolecular transient cross-links dominates, which results in similar viscosity and  $T_g$  values for all electrolytes studied. The latter increases for all electrolytes studied compared with the values obtained at lower salt concentrations. The ion pair fraction increases and reaches the maximum. The differences between the fraction of ion pairs as a function of type of alkali metal cation are small. In this salt concentration range the conductivities obtained for all electrolytes are very similar. According to previous microstructural findings<sup>9,21,23</sup> it seems that in this salt concentration range cations are trapped in the cages formed by polyether and OH oxygens. Therefore the possibility of their movement is reduced. It seems that in this salt concentration range anions, which do not form contact ion pairs with cations and reside outside cation's cages, are dominant charge carriers. This results in comparable conductivity values for all electrolytes studied despite the type of cation used. It is interesting to note that similar trends were previously found by us and Ingram's group for polyether electrolytes doped with alkali metal thiocyanates in a similar salt concentration range.<sup>9–10,15</sup>

At salt concentrations greater than 1 mol/kg of MClO<sub>4</sub> the viscosity of the electrolyte has a dominant effect on ionic conductivity. The increase in the viscosity is due to the formation of intermolecular transient cross-links.<sup>1–3</sup> The cross-links are preferentially formed via positively charged triplets.<sup>22</sup> For the electrolytes studied the cross-links can be coupled either to ether oxygens or to the end chain OH groups. Because perchlorate anions are involved in the formation of transient cross-links, their conductivity is reduced, which results in the overall reduction in conductivity observed in this salt concentration range. This behavior is additionally coupled with an increase in the viscosity due to the formation of transient cross-links. Due to the higher polarizability of smaller alkali metal cations they should have a stronger tendency to cross-link formation, which is confirmed by conductivity and viscosity data (see Figures 1, 2, and 4).

Hereby, we would like to point out the qualitative difference between description of flexibility by viscosity and  $T_g$  data. Both parameters show a decrease in the flexibility at the salt concentration range above  $\sim 0.25$  mol/kg. However, viscosity data obtained for different cations are clearly distinguishable (differences are of orders of magnitude) whereas  $T_g$ 's differ from



each other only slightly more than the experimental error of DSC experiments. This behavior is similar to that described by McLin and Angell in their excellent paper.<sup>16</sup> According to their assumptions in low molecular weight unentangled polymers “viscosity can be expected to serve as a useful guide to the forces impeding the motion of ions present in the solution”. For high molecular weight polymers microviscosity described by the  $T_g$  is a parameter to be used. Similar trends in the viscosity versus  $T_g$  behavior are seen in the present work. We also draw the readers attention to the fact that the related viscosity and conductivity measurements (which are nicely coupled to each other) are obtained at the same temperature, therefore for the same structure of the polymers matrix. Contrary to this,  $T_g$  values are related to different temperature ranges at which structure of the polymer matrix is more complicated due to the presence of the crystalline phase.

On the basis of the IR observations (Figures 6 and 7) these cross-linking triplets are preferentially coupled to the end chain O—H groups for the Li and Na systems and to the polyether oxygens for K, Cs, and Rb salts. Such behavior can be explained on the basis of the hard—soft acid—base concept developed by Pearson.<sup>24</sup> Li and Na cations are harder acids than K, Rb, and Cs cations and therefore preferentially interact with hard OH base, which is evidenced by the upshift of the OH mode.<sup>7</sup> Softer cations on the other hand interact with softer base centers on polyether oxygens. For the first case the formation of cross-links results in the abrupt increase in the viscosity (see Figure 4) and therefore in the reduction in the conductivity. For K, Rb, and Cs salts the increase in the viscosity is smaller most probably due to the higher liability of cross-links formed via polyether oxygens.

## Conclusions

The conductivity of the set of PEGME based electrolytes doped with alkali metal perchlorates has been studied as a function of alkali metal cation and salt concentration. It has been found that at salt concentrations less than  $10^{-2}$  mol/kg higher conductivities are obtained for Li, Na, and K perchlorates, whereas at salt concentrations greater than 1 mol/kg conductivities measured for Cs and Rb perchlorates are higher. At intermediate salt concentration ranges, conductivities measured for all systems are similar. The observed trends are explained by the formation of various cross-links involving alkali metal cations and positively charged triplets. The effect of these interactions on the ionic conduction was monitored by the viscosity and IR studies describing the ion—ion and ion—polymer interactions. The formation of ionic associates is additionally monitored by application of the Fuoss—Kraus formalism to the salt concentration dependence of the molar conductivity.

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**Supporting Information Available:** Compositions of the electrolytes studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Note Added after ASAP Posting

This article was released ASAP on 3/16/2004. In the Results section, paragraph 4, 20 °C was changed to 25 °C. In the Discussion section, last sentence of paragraph 3, footnote 9—12 was changed to 9—10,15. The correct version was posted on 3/18/2004.

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